

# Synthesis of New Materials for Light-Emitting Electrochemical Cells

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### Synthesis of New Materials Light-Emitting Electrochemical Cells

### Abstract

The thesis consists of three main parts. In the first chapter, the historical development of emitting materials used in light emitting electrochemical cells is summarized. In the second part, experimental studies are presented. In the experimental section; two new ionic organic small molecules and three new iridium complexes were synthesized. In the third chapter, structural, electrochemical and photophysical characterization of synthesized molecules and computational studies of small organic molecules are presented.

In this thesis, MR-TADF type molecules with DiKTa core structure, which were previously used in OLED applications in the literature, were modified for use in LEC applications. It is aimed to bring innovation to the literature on LEC device applications with two DiKTa type ionic molecules. The device with DiKTa-DPA-OBuIm shows a steeper injection, reaching values of 10,000 A m<sup>-2</sup> at 8 V when compared to the device with DiKTa-OBuIm, which shows a current density of 1000 A m<sup>-2</sup> at the same voltage value. Light emission was detected at around ~5 V, with values of 15 cd m<sup>-2</sup> for the device with DiKTa-DPA-OBuIm and around 2 cd m<sup>-2</sup> for the devices with DiKTa-OBuIm and the host-guest system, each at 8 V.

LEC devices were fabricated with two new iridium complexes synthesized within the scope of the thesis. Devices emitting green-blue emission have been brought to the literature. The LEC device fabricated with **2a** performed better results with maximum current density, luminance, and luminous power efficiency of 1529 mA cm<sup>-2</sup>, 30.95 cd cm<sup>-2</sup>, and  $7.77 \times 10^{-4}$  lm W<sup>-1</sup>, respectively.

**Keywords:** Light-Emitting Electrochemical Cell (LEC), small organic molecule, iridium complexes, Thermally Activated Delayed Phosphorescence, Density-functional theory (DFT)

### Işık Yayan Elektrokimyasal Hücreler için Yeni Malzeme Sentezi

# Öz

Bu doktora tezi üç temel bölümden oluşmaktadır. Birinci bölümde ışık yayan elektrokimyasal hücrelerde kullanılan emisyon veren malzemelerin tarihsel gelişimi özetlenmiştir. İkinci bölümde deneysel çalışmalar sunulmuştur. Deneysel bölümde; iki yeni iyonik yapılı organik küçük molekül ve üç yeni iridium kompleksi sentezlenmiştir. Üçüncü bölümde sentezlenen moleküllerin yapısal, elektrokimyasal ve fotofiziksel karakterizasyonu ve küçük organik moleküllerin hesapsal çalışmaları sunulmuştur.

Bu çalışmada, literatürde daha önce OLED uygulamalarında kullanılan DiKTa çekirdek yapısına sahip MR-TADF tipi moleküller, LEC uygulamalarında kullanılmak üzere modifiye edilmiştir. DiKTa tipi iki iyonik molekül ile LEC cihaz uygulamaları literature yenilik kazandırılması amaçlanmıştır. DiKTa-DPA-OBuIm ile üretilen cihaz, aynı voltaj değerinde 1000 A m<sup>-2</sup> akım yoğunluğu gösteren DiKTa-OBuIm ile üretilen cihaza kıyasla 8 V'ta 10.000 A m<sup>-2</sup> değerlerine ulaşan daha dik bir enjeksiyon gösterir. DiKTa-DPA-OBuIm'li LEC cihaz için 15 cd m<sup>-2</sup> ve DiKTa-OBuIm'li cihazlar ve host-guest sistemi için yaklaşık 2 cd m<sup>-2</sup> değerleriyle, her biri 8 V'ta olmak üzere ~5 V civarında ışık emisyonu tespit edildi.

Tez kapsamında sentezlenen üç yeni iridyum kompleksi ile LEC cihazı yapılmışır. Yeşil-mavi emisyon veren cihazlar literature kazandırılmıştır. 2a kompleksi ile üretilen LEC cihazının, sırasıyla 1529 mA cm<sup>-2</sup>, 30.95 cd cm<sup>-2</sup> ve 7.77x10<sup>-4</sup> lm W<sup>-1</sup> maksimum akım yoğunluğu, parlaklık ve ışık gücü verimliliği ile daha iyi sonuçlar verdiği anlaşıldı.

Anahtar Kelimeler: Işık Yayan Elektrokimyasal Hücre (LEC), Küçük Organic Molekül, İridiyum Kompleksleri, Termal Olarak Aktive Gecikmeli Fosforesans, Yoğunluk Fonksiyonel Teorisi

To my dear daughter, Zeynep Yağmur

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### List of Abbreviations

А	Acceptor
B <sub>3</sub> PYMPM	4,6-Bis(3,5-di(pyridin3-yl)phenyl)-2-methylpyrimidine)
CE	Current Efficiency
Cat	Catalyst
СТ	Charge Transfer
CIE	Commission Internationale d'Éclairage
BCzPh	9,9'-Diphenyl-9H,9'H-3,3'-bicarbazole
BAlq	Bis(8-hydroxy-2-methylquinolinato)-(4-phenylphenoxy)aluminum
Liq	8-Quinolinolato lithium
D	Donor
DCM	Dichloromethane
DPEPO	Bis[2-(diphenylphosphino)phenyl]ether oxide
DPS	Diphenyl sulfone
DPPS	Diphenylbis(4-(pyridin-3-yl)phenyl)silane)
EL	Electroluminescence
EML	Emission Layer
EQE	External Quantum Efficiency
GC	Gas Chromatography
M.p	Melting point
d	Doublet
FBE	Fen Bilimleri Enstitüsü
FMOE	Frontier Molecular Orbital Engineering
FWHM	Full-Width at Half-Maximum
Hz	Hertz

НОМО	Highest Occupied Molecular Orbital
HATCN	1,4,5,8,9,11-Hexaazatriphenylene hexacarbonitrile
HIL	Hole Injection Layer
IQE	Internal Quantum Efficiency
ITO	Indium doped tin oxide
İKÇÜ	İzmir Kâtip Çelebi University
LEC	Light-Emitting Electrochemical Cell
LED	Light-emitting diode
LUMO	Lowest Unoccupied Molecular Orbital
m	Multiplet
mCP	1,3-Bis(N-carbazolyl)benzene
m-MTDATA	4,4',4"-tris[(3-Methylphenyl)-phenylamino]triphenylamine
mCBP	3,3'-Di(9H-carbazol-9-yl)-1,1'-biphenyl
NMR	Nuclear Magnetic Rezonance
ORCID	Open Researcher and Contributor ID
OLED	Organic Light-Emitting Diodes
PE	Power Efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PMMA	Poly(methyl methylacrylate)
PLQY	Photoluminescence Quantum Yield
PO-15	Poly[N, N'-bis(4-butylphenyl)-N, N'-bisphenylbenzidine]
РРТ	2,8-Bis(diphenylphosphoryl)dibenzo-[b,d]thiophene
PVK	Poly(N-vinylcarbazole)
PXZ	Phenoxazine
PTZ	Phenothiazine
RISC	Reverse Intersystem Crossing
$\mathbf{S}_1$	Singlet Excited State

SiCz	Diphenyldi(4-(9-carbazolyl)phenyl)silane
SPP	Surface Plasmon Polaritons
SOMO	Singly occupied molecular orbital
TÜBİTAK	Türkiye Bilimsel ve Teknolojik Araştırma Kurumu
TADF	Thermally Activated Delayed Fluorescence
TAPC	4,4'-Cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine
TBBD	N4,N4,N4',N4'-Tetra([1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4,4'- diamine
TCTA	Tris(4-carbazoyl-9-ylphenyl)amine
TPSi-F	Triphenyl-(4-(9-phenyl-9H-fluoren-9-yl)phenyl)silane
CzPhPy	4,6-Bis(3-(9H-carbazol-9-yl)phenyl)pyrimidine
DPPyA	9,10-Bis(6-phenylpyridin-3-yl)anthracene
TPBI	2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole
TTA	Triplet-triplet annihilation
TmPyPb	1,3,5-Tri(m-pyridin-3-ylphenyl)benzene
t	Triplet
$T_1$	Triplet Excited State
3TPYMB	Tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane

# List of Symbols

$\Delta E_{ m ST}$	Energy difference between T1 and S1 [eV]
$\tau_d$	The delayed component of the emission lifetime $[\mu s]$
λ	Wavelength [nm]
mg	Mass
$\Phi_{d}$	The delayed component of the PLQY
$\Phi_{\mathrm{T}}$	Triplet formation yield
$\Theta_{\parallel}$	Horizontal dipole ratio

### Chapter 1

### Introduction

Solid-State Lighting (SSL) has enormous energy savings potential worldwide and lighting accounts for 15-22% of electricity consumption depending on the country. SSL technology generates less heat (low energy-heat conversion) and shows more stability than filament lamps. SSL devices are divided into three main groups: lightemitting diodes (LEDs), light-emitting organic diodes (OLEDs), and light-emitting electrochemical cells (LECs). LED technology is generally a point light source consisting of a combination of several elements such as In, Ga, P, and N [1]. OLEDs have been investigated since the first discovery by C. W. Tang and Van Slyke, because OLEDs ensure better image clarity and contrast, faster reaction time rates, can be viewed from a broader range of angles, and are smaller and lighter (Figure 1.1) [2]. Even more astounding is the fabricating these devices on flexible substrates, allowing OLEDs to be rolled up, a feature unimaginable in previous generations of displays. Because they do not need the usage of a backlighting system, OLEDs are also more effective in terms of energy. Given that lighting accounts for over 20% of worldwide power usage, widespread adoption of OLEDs as a lighting technology has the potential to save a large amount of energy[3]. OLEDs generally have several layers of organic semiconductors.

### 1.1 Working Principle of Organic Light-Emitting Diodes (OLEDs)

OLEDs are thin multilayer devices typically contain several organic semiconductor layers [4]. By applying an external voltage, the electrons and holes (charge carriers) are generated at the cathode and anode, respectively. The charge carriers are then injected into the electron injection and hole injection layers. The electrons and holes next travel into the emissive layer (EML) through the electron transport and hole transport layers, respectively, where charge carrier recombination and excitons are formed. When the excitons relax radiatively from the excited state to the ground state, electroluminescence (EL) occurs. The emissive layer design is the most crucial component in obtaining high efficiency in OLED devices [5].



Figure 1.1: The structure of first OLEDs a) single-layered and b) double-layered

In order to reduce the production cost of OLEDs and make them commercially available for lighting applications, there are certain characteristics that the emitter must have. Organic emitters must have high photoluminescence quantum efficiencies (PLQYs) that directly effects the device efficiency. The energy levels of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) (i.e., frontier molecular orbitals) of each material in the device must be ideally approximately aligned to: I) reduce the barrier to charge injection, and II) manage the recombination area within the device, which has a strong influence on both efficiency and lifetime of the device[6]. To produce thin films with optimum morphology, organic emitters must be thermally stable enough to be suitable with vacuum deposition during device building or spin-coated during solution processing. Irrespective of the fabrication technique used, the emitters must remain morphologically stable throughout device operation when Joule heat is created[7], [8]. Aside from the above listed requirements, another critical challenge to handle is the control of hole and electron recombination within the device, each with its own spin.

# 1.2 Emitter Development and Industry Milestones of OLEDs

When the emitter is electrically excited, hole and electron recombination leads in a 75% to 25% of triplet to singlet excited states, according to spin statistics[9]. The research and design of emitters for OLEDs that can completely collect both singlet and triplet excitons are crucial for achieving satisfactory device performances with high EQEs. Three generations of emitters have been extensively investigated and designed to reach this aim, with the next generation of emitters presently being constructed in tandem.

The OLED emitter 'generations' is according to the type of emission utilized to emit light. The first generation of OLEDs is based on fluorescent emitters. The second one is based on phosphorescence and the third generation is based on thermally activated delayed fluorescence (TADF) as the light-emitting process.

### 1.2.1 First Generation Emitters

Fluorescent OLEDs, which contain organic dyes as an emitter, are known as firstgeneration OLEDs. Because the intersystem crossing (ISC) transition between states with different electronic spin multiplicities is non-radiative, only the passage of singlet excitons to the singlet ground state  $(S_1 \rightarrow S_0)$  is theoretically permitted for fluorescence. As a result, only around 25% of the singlet excitons can be utilized to generate light. The highest limit of the EQE of OLEDs using standard fluorescent emitters without extra optical outcoupling is 5%. The structure of first-generation emitters mentioned below are given in Figure 1.2.



Figure 1.2: Structure of first-generation emitters

#### 1.2.1.1 First Generation Green Emitters

Tang and VanSlyke's first OLED device, introduced in 1987, contained the fluorescent emitter 8-hydroxyquinoline aluminum (Alq<sub>3</sub>; Fig1.2)[2]. The green OLED device showed an EQE of 1% with a brightness of above 1000 cd m<sup>-2</sup> and an  $\lambda_{EL}$  = 550 nm at a driving voltage of lower than 10 V. After this report, OLEDs have continuously got attention ever since.

#### 1.2.1.2 First Generation Orange-Red Emitters

Chen and co-workers reported the first report of red-dopant-based red OLED in 1989[10]. In this report, two orange-red OLED devices fabricated with 4- (dicyanomethylene)-2-methyl-6-[4(dimethylaminostyryl)-4H-pyran] (DCM) emitters DCM1 and DCM2 performed an EQEs of 2.3% with a  $\lambda_{EL} = 570-620$  nm for DCM1 and  $\lambda_{EL} = 610-650$  nm, based on the changing doping concentration (Figure 1.2). Because of quenching caused by concentration-dependent aggregation, red fluorescent materials were mainly limited to additive use as emitters in the fabrication of red OLEDs rather than being used in non-doped devices. Emitters with wavelengths higher than 610 nm were often developed using polar or  $\pi$ -conjugated structures[11]. Owing

to dipole-dipole interactions or significant intermolecular  $\pi$ -stacking, this design resulted in solid state aggregation. As a result, quenching caused solid state fluorophores that were weakly emissive or even non-emitting. Furthermore, it was understood that additive-based red OLEDs required additional improvement since the efficient and bright additives were insufficiently red, and the red enough additives were insufficiently efficient and brilliant[11].

Later, Usuki and colleagues devised a strategy to overcome the problem of concentration quenching of red dopants by introducing an emitting assist dopant like rubrene that supplied the energy gap between the host and the red dopant[12]. In addition to doped red OLEDs, Hasegawa and co-workers presented the first host-emitting non-doped red OLED in 2000[13].

#### 1.2.1.3 First Generation Blue Emitters

Anthracene derivatives are frequently used to make blue fluorescent emitters. These derivatives have a broad bandgap, a robust chemical structure, high thermal stability, and outstanding charge-transporting characteristics[14].

By adding bulky substituents to the 9- or 10-position, the color of the emission may be varied from blue to deep blue. A non-doped device containing of the fluorescent emitter **2PAn** performed an EQE of 2.82%, with a  $\lambda_{EL}$  at 452 nm (CIE: 0.71, 0.21), (Figure 1.2)[15]. The CIE coordinates are not optimal due to molecule aggregation in the thin film, which quenches fluorescence and red-shifts the emission spectrum. In comparison, emitter **'Bu2NapAn** emitted outstanding deep blue light with CIE coordinates (0.149, 0.086) and higher efficiency with an EQE of 5.17% ( $\lambda_{EL}$  = 444 nm) thanks to the inhibition of aggregation by the *tert*-butyl group (Figure 1.2)[16].

#### 1.2.2 Second Generation Emitters

In the second generation OLEDs, phosphorescent heavy-metal complexes have been researched and designed as emitters to obtain the remaining 75% of excitons in triplet states[17]. Due to improved spin-orbit coupling produced by heavy-metal atoms like iridium or platinum, the resultant complexes can speed up radiative deactivation through phosphorescence from the lowest-lying triplet state  $T_1$  to the ground state  $S_0$ 

and enable ISC from the lowest-lying singlet state  $S_1$  to  $T_1$ . This triplet-based approach and relaxation procedure enables phosphorescent heavy-metal-based emitters to achieve internal quantum efficiency (IQE) of up to 100%, which is critical for achieving high EQE OLED devices. The structure of second-generation green emitters, orange-red emitters and blue emitters mentioned below are given in Figure 1.3, Figure 1.4 and Figure 1.5, respectively.

#### 1.2.2.1 Second Generation Green Emitters

Watts's group reported *fac*-tris(2phenylpyridine)iridium (*fac*-Ir(ppy)<sub>3</sub>) emitter which has been often used as a green emitting dopant in OLEDs thanks to its stability and good electroluminescence efficiency[18].

Forrest et al. published a green phosphorescent OLED (PhOLED) with an  $\lambda_{EL}$  at 510 nm and a EQE of 8% in 1999[19]. They investigated the photochemical isomerization of facial (*fac-*) and meridonal (*mer-*) tri-cyclometallated Ir(III) complexes in terms of electrochemical and photophysical properties[20]. In principle, the energetically favorable facial isomers have same bond lengths to *mer-Ir(CN)*<sub>3</sub> complexes. These type of complexes almost certainly inhibits the quenching pathway, resulting in enhanced quantum efficiencies. Many functional auxiliary ligands with varying ligand field strengths have also been used in the bis- or tris-cyclometalated Ir(III) complexes for color-tunable OLEDs[21].



Figure 1.3: Second Generation green emitters

Thomson and his group produced vapor-deposited PhOLEDs using heteroleptic  $(CN)_2Ir(acac)$  complexes (acac = acetylacetonate, CN = cyclometalated bidentate ligand) as dopants in emissive layer in 2001 (Figure 1.3)[22]. The emission color of these  $(CN)_2Ir(acac)$ -doped PhOLEDs ranged from green to red. The OLED device based on  $Ir(ppy)_2acac$  performed the highest efficiency of EQE = 12.3% with a  $\lambda_{EL}$  = 525 nm among doped emitters.

Another alternative approach to change color of Ir(III)-based triplet emitters is the addition of different functional groups such as Ph<sub>3</sub>Si–, Ph<sub>2</sub>N–, B(Mes)<sub>2</sub>–, PhO– and, PhS– to the phenyl ring of ppy in [Ir(ppy-X)<sub>2</sub>(acac)] complexes[23]. The OLEDs based on ppy-kind cyclometalated Ir(III) complexes as emitters showed modest EQE values between 4% and 16% with  $\lambda_{EL}$ = 505-609 nm.

Wang et al. integrated the rigid carbazole dendron to the  $Ir(CN)_3$  complexes, yielding the **G2** dendrimer with an 87% PLQY in solution (Figure 1.3)[24]. The PhOLED performed a higher brightness than 20 000 cdm<sup>-2</sup> with a high EQE of 16.6% ( $\lambda_{EL}$ = 528 nm) with doping **G2** into a carbazole-based host.

Kim's group investigated the impact of the orientation on the well-designed  $Ir(ppy)_3$ ,  $Ir(ppy)_2acac$ , and  $Ir(ppy)_2tmd$  (ppy = 2-phenylpyridine, tmd = 2,2,6,6-tetramethylheptane-3,5-diketonate) in 2014[25].  $Ir(ppy)_2tmd$  has a high horizontal dipole ratio ( $\Theta_1$ ) of 78% showed a high PLQY of 96%. Using the  $Ir(ppy)_2tmd$  as an emitter, one of the best green OLEDs was achieved with a remarkable EQE of 32.3%.

Forrest and co-workers presented the first attempts to utilize the  $[Pt(C^N)(O^O)]$ (O^O =  $\beta$ -diketonate ligand) monomer and excimer as OLED dopants in 2002[26]. The complexes of conjugated aryl-substituted diphenylpyridines (NNC- or NNCunits) with tridentate cyclometalated Pt(II) exhibit high triplet metal-to-ligand charge transfer (MLCT) emission as well as good film-forming efficiencies, and they have subsequently been employed in OLEDs[21].

In 2015, Che et al. synthesized a series of pincer Pt(II) complexes based on C-deprotonated C^N^N ligands with various extended  $\pi$ -conjugation[54]. The best EQE of 22.8% was achieved with the device based on the phosphorescent [Pt(t BuPh-C^N^N-Qu)][C=CC\_6F\_5] emitter with a green emission (CIE coordinates = 0.368, 0.598).

Yam's group published a solution-processed PhOLEDs containing the highly luminous Au(III) complex [Au(2,5-F<sub>2</sub>C<sub>6</sub>H<sub>3</sub>—C^N^C) (C=C-C<sub>6</sub>H<sub>4</sub>N(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-*p*] in 2010[27]. EQE was reported as 11.5% with a  $\lambda_{EL} = 528$  nm. In recent years, researcher have been done to develop a new family of d<sup>10</sup> metal complexes with excellent optical characteristics for use in PhOLEDs.

#### 1.2.2.2 Second Generation Orange-Red Emitters

The first efficient PhOLED reported by Forrest's group in 1998. The PhOLED based on 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum (II) (**PtOEP**) emitter exhibited EQE of 4%[28].



Figure 1.4: Second Generation orange-red emitters

During the following decades, tremendous progress was achieved in the PhOLED field, with phosphorescent compounds for multicolor displays being used to increase device performance. Due to the difficulties in limiting triplet-triplet annihilation and obtaining efficient radiative decay of MLCT states, red phosphorescent emitters are rare. From a basic approach, per-deuterated and per-fluorinated techniques, which have been used to inhibit the quenching process and minimize vibrational overlap by reducing the amount of high-frequency vibrations related to C—H, O—H, and N—H stretching, are two viable process[29].

Although some metal complexes including Re(I), Eu(III), or Zn(II) are well-known monochromatic red emitters, the utilize of these complexes for device fabrication is still limited due to their low solubility and luminescence efficiency. The cyclometalated neutral Ir(III) complexes are typically recognized as potential alternatives for red PhOLEDs with high efficiency. Most of the reported neutral red phosphors derived from the 1-phenylisoquinoline, 2-phenylquinoline, or

acetylacetonate ligands are the  $\beta$ -diketonate derivative complexes or homoleptic complexes[30]. Thompson's group synthesized red emitter, bis(2-(2'-benzo[4,5-a]thienyl)pyridinato-N,C<sup>3'</sup>) iridium(acetylacetonate) **Btp2Ir(acac)**. The OLED device showed EQE of 7% with emission wavelengths of 616 nm (Figure 1.4)[22].

In 2003, Hoshino and co-workers discovered that another known red emitter tris[1phenylisoquinoline-C2,N]iridium(III), **Ir(piq)**<sub>3</sub>, has a k<sub>r</sub> value that is around one order of magnitude higher than other members of the Ir(C^N)<sub>3</sub> types. The OLED device with **Ir(piq)**<sub>3</sub> performed an EQE of 12.3% (Figure 1.4) ( $\lambda_{EL}$ =620 nm)[31].

The introducing aromatic ligands with electron donating groups, such as methoxy and amine groups, generally results in red-shifted emission due to the competing  $\sigma$ -withdrawing character of ligands, leading to a destabilization of the HOMO level[30]. Wang and co-workers presented one of these methods by adding aromatic amines to C^N ligands of Ir(C^N)<sub>3</sub> complexes for red-shifted emission[62]. The pure red-emitter, **Ir-G1** (Figure 1.4), has a higher HOMO energy level and high morphological stability. The OLED device showed an EQE of 11.65% with CIE color coordinates of (0.70, 0.30). the isoquinoline ring that has larger  $\pi$ -electronic conjugation adjusted the emission of Ir(III) complexes to the deep red spectral region (>620 nm).

In 2011, Kwon and colleagues also employed methyl moiety and sterically bulky tertbutyl moieties to reduce the self-quenching effect of  $[(phq)_2Ir(acac)]$  (phq = 2phenylquinoline) complexes, as reported in 2011. An EQE of 24.6% and an emission wavelength of 610 nm were achieved by a high efficiency red PhOLED based on the  $Ir(mphmq)_2(tmd)$  phosphor[32].

Wong and colleagues added the diarylboron unit to heteroleptic Ir(III) complexes using ancillary acac ligands in 2018. Until now, maximum EQE value for Ir(III)-based red PhOLEDs employing **PyThIr** of over 28% with  $\lambda_{EL} = 604$  nm was achieved with the incorporation of a strong electron-deficient effect and the significant electron-transporting ability of the diarylboron group[33].

#### 1.2.2.3 Second Generation Blue Emitters

Ionic transition metal complexes (iTMCs) are also used as an emitter in OLED devices due to high SOC. Especially, iridium and platinum complexes are used to achieve blue

emission. Forrest and co-workers fabricated blue phosphorescent OLED with **FIrpic** emitter in 2001. The reported EQE was 5.7% with  $EL_{max}$  at 475nm (CIE = 0.16, 0.29)[34]. Although several iridium complexes based on C^N ligands have exhibited remarkable emission efficiency in the sky-blue region, it is preferable to obtain deepblue Ir(III) phosphors with a lower HOMO energy[35, 36]. The triplet energies must be minimum 2.8 eV to obtain a blue shift in the emission [37]. By inserting electronwithdrawing units, the triplet energy can be enhanced. In the OLED device, the linked nitrile group in **FCNIrpic** enhances the triplet energy to 2.74 eV with an EQE of 22.1 % and  $\lambda_{EL} = 466$  nm (Figure 1.5)[38].



Figure 1.5: Second Generation Blue Emitters

To increase the color intensity of blue PhOLEDs, a variety of modified arylpyridinetype analogs with various substituents and ancillary ligands have been developed[37]. In 2016, Forrest and colleagues reported the production of effective blue PhOLEDs generated from (*fac-*) and (*mer-*)Ir(pmp)<sub>3</sub> complexes, given in Figure 1.5 [39]. These complexes exhibit deep blue emission ( $\lambda_{PL} = 418$  nm) with less conjugation of the ligand scaffold by using the  $\sigma$ -donating capabilities of N-heterocyclic carbene (NHC) ligands. Device based on **fac-Ir(pmp)**<sub>3</sub> exhibited deep blue emission with color coordinates of (0.16, 0.09) and the highest brightness (>7800 cd  $m^{-2}$ ) among the PhOLEDs recorded to date (Figure 1.5).

The meridional homoleptic Ir(III) complex *mer-2* carrying the CF<sub>3</sub>— substituted NHC ligands was described by Zysman-Colman and co-workers presented in 2018 [40]. The *mer-2* complex had a deep blue emission at 412 nm with a PLQY of 72% in solution, due to the strong electron-withdrawing impact of the *meta*-CF<sub>3</sub>— group. At a brightness of 100 cd m<sup>-2</sup>, the device employing **mer-2** complex achieved a high EQE of 12.5%. Furthermore, the stable vacuum-deposited OLED has a very small CIE y-coordinate (0.1).

Recently, a novel series of dfpysipy-type Ir(III) complexes with an excellent bright blue PL emission at 445-450 nm and a narrow wavelength presented by Kim and his group[41]. In this report the highest EQE was 31.9% of a deep blue device doped with Ir-2 among the fabricated PhOLEDs with a CIE y-coordinate smaller than 0.20.

### 1.2.3 Third Generation Emitters

Despite the fact that emitters derived from phosphorescent heavy-metal complexes have shown promise and have been used in commercial electroluminescent goods, the usage of heavy-metal atoms restricts their marketing due to environmental concerns and cost considerations[42]. As a result, the development of emitters that do not use high-cost and ecologically hazardous chemicals while providing high IQEs has become a higher priority. One approach is the extremely promising thermally activated delayed florescence (TADF) mechanism, which is being researched and used with growing interest both in academia and industry.

The energy gap ( $\Delta E_{ST}$ ) between the lowest-lying singlet state (S<sub>1</sub>) and the lowest-lying triplet state (T<sub>3</sub>) in TADF molecules is typically modest (T<sub>1</sub>). The theoretically spin-forbidden reverse intersystem crossing (RISC) process is thermally triggered when the T<sub>1</sub> excitons have a sufficiently long lifespan, allowing the triplet excitons to upconvert into the S<sub>1</sub> state and radiatively relax to the ground state, resulting in a theoretical IQE of 100%[43].

Perrin et al. [44] reported delayed florescence (DF) first time in solid uranyl salts. The latter study gave rise to the term "E-type delayed fluorescence." In 2011, Adachi et al. reported the first purely organic TADF emitter, **PIC-TRZ** is depicted in Figure 1.6[45]. Because the EQE of the OLED was 5.3%, which is comparable to the traditional fluorescent emitters, it was not the proof that the TADF mechanism of emission in the device. In 2012, same group reported a series of pure organic TADF emitters (**CDCBs**) which use the rISC mechanism of DF and named it "thermally activated delayed fluorescence (TADF)" to utilize the triplet states of molecules generated under electric excitation within OLEDs and proved high efficiency electroluminescence for the first time [43]. The molecular structure of **CDCBs** are given in Fig. 1.6. This study has been the main motivation for research interest of designing novel emitters and exploring the photophysics of the TADF process[46].



First purely organic TADF emitter: PIC-TRZ



4CzPN: R= carbazolyl 2CzPN: R= H



4CzTPN: R= H 4CzTPN-Me: R= Me 4CzTPN-Ph: R= Ph

#### Figure 1.6: Structure of PIC-TRZ and CDCBs emitters

4CzIPN

The literature on TADF emitters until now demonstrates that the design of novel TADF molecules has mostly focused on large-scale synthetic programs aiming at discovering and then using structure-property relationships. However, while these can

provide to continuous progress and simple design rules that can be used to manage a specific feature, such as the emission or absorption wavelength, it is usually ineffective in simultaneously controlling all of the needed photophysical properties.

In the first design, TADF emitters are built on charge-transfer (CT) principles, with electron donor and electron acceptor groups separated by a large dihedral angle. Donors and acceptors can be linked in various ways and placed to obtain the photophysical qualities required for the light-emitting performances of the devices. This class of structure can be donor-acceptor (D-A), donor- $\pi$  linker-acceptor (D- $\pi$ -A), donor-acceptor-donor (D-A-D) or donor- $\pi$  linker-acceptor- $\pi$  linker-donor (D- $\pi$ -A- $\pi$ -D).

Two strategies are needed to optimize the basic RISC process: decrease the singlettriplet energy gap ( $\Delta E_{ST}$ ) and maximize spin-orbit coupling (SOC) constant. It is possible to obtain small  $\Delta E_{ST}$  with the separation HOMO and LUMO using strong donor and acceptor units. The up-conversion process is prohibited if there is a large energy barrier between singlet and triplet excited states. The small  $\Delta E_{ST}$  would activate the RISC process, minimize the delayed fluorescence, and enhance the up conversion. Another driving force for the RISC process is spin–orbit coupling that is associated with the El–Sayed rule[47]. The ISC between charge transfer (CT) excited states is forbidden. That means up-conversion from CT triplet state (CT<sub>3</sub>) to CT singlet state (CT<sub>1</sub>) state is not possible. Due to the origin of the singlet excited state of the donoracceptor type TADF emitter is CT<sub>1</sub>, the El–Sayed rule indicates that the triplet excited state must originate from the local triplet excited state (LE<sub>3</sub>) or hybrid state of LE<sub>3</sub> and CT3 [48,49]. As a result, the control strategy of small  $\Delta E_{ST}$  and LE<sub>3</sub> including triplet excited state is essential in up-converting triplet excitons into singlet excitons.

Aside than the RISC mechanism, the fluorescence mechanism in TADF emitters must be improved for high photoluminescence quantum yield. To achieve high PLQY, high HOMO and LUMO overlap is needed, which is associated with large oscillator strength of the radiative transition from the S<sub>1</sub> state[50]. As mentioned before, the wave functions of the HOMO and LUMO must be spatially well separated to obtain small  $\Delta E_{ST}$ . Consequently, the conditions of the two requirements contradict each other. In most situations, two requirements can be met by introducing a  $\pi$  linker the molecular structure.

#### 1.2.3.1 Third Generation Green-Yellow Emitters

The green-yellow TADF emitters which have electroluminescence between 500-580 nm were summarized in this section. The structural variety of TADF emitters is restricted by their stringent design criteria. Green TADF emitters usually contain sulphone, cyano, ketone and triazine as an electron-accepting unit. The synthetic versatility of organic materials motivates us to investigate the electron-acceptor units to design efficient TADF emitters to enhance their versatility and applicability.

Adachi et al. presented TADF emitters that contain carbazole as a donor and a dicyanobenzene (phthalonitrile) as an acceptor in their pioneering report[43]. The donor carbazoles have twisted confirmation in the phthalonitrile plane, which is the keystone for the molecular design. The regiochemistry of the carbazole donors and nitrile acceptor around the core benzene ring allows these family of emitters to emit various colors from the visible spectrum. The best green device (ITO/ $\alpha$ -NPD/5wt%emitter:CBP/TPBi/LiF/Al) in this report was obtained based on **4CzIPN** ( $\lambda_{max}$ :  $\approx$ 510 nm; PLQY: 82%;  $\tau_d$ : 3370 µs in 6wt%CBP;  $\Delta E_{ST}$ : 0.08 eV) with an EQE<sub>max</sub> 19.3% and EL<sub>max</sub> at  $\approx$ 510 nm.

Cyano-based acceptors are used in many green-to-yellow TADF emitters. Molecular structure of green-yellow TADF emitters based on cyano-based acceptors are given in Figure 1.7.



Figure 1.7: Molecular structure of green-yellow TADF emitters based on cyano acceptors

Lee et al. altered **4CzIPN** with *tert*-butyl groups to increase solubility in **t4CzIPN** ( $\lambda_{max}$ :  $\approx$ 520 nm; PLQY: 78%;  $\tau_d$ : 2.9 µs in 3wt%SiCz)[51]. The *tert*-butyl group hinders intermolecular interactions and aggregation. Furthermore, this group stabilizes the morphology of thin films which is needed for achieving the fabrication of solutionprocessed TADF devices. The solution-processed device (ITO/PEDOT:PSS/PVK/1wt%emitter:SiCz/TSPO1/LiF/Al) based on **t4CzIPN** (EQE<sub>max</sub>: 18.3%) showed better performance compared to **4CzIPN** (EQE<sub>max</sub>: 8.1%).

Taneda et al. synthesized **3DPA3CN** ( $\lambda_{max}$ : 533 nm; PLQY: 100%;  $\tau_d$ : 550 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.10 eV), a highly efficient TADF material that exhibits both 100% PLQY and 100% efficiency of triplet utilization through RISC[52]. In the DPEPO host, **3DPA3CN** has an ideal horizontal orientation, resulting in increased light outcoupling. The green OLED device (ITO/ $\alpha$ -NPD/mCBP/6wt%emitter: DPEPO/TPBI/LiF/Al) exhibited a high EQE<sub>max</sub> of 21.4% with EL<sub>max</sub> at  $\approx$ 540 nm.

Nakagawa et al. presented a yellow TADF emitter **spiroCN** ( $\lambda_{max}$ :  $\approx$ 540 nm; PLQY: 27%;  $\tau_d$ : 14 µs in 6wt%mCP;  $\Delta E_{ST}$ : 0.06 eV) comprises electron donating diphenylamine and electron accepting cyano groups on the two different

spirobifluorene units. Spirobifluorene was preferred due to its good thermal and color stability[53]. Although its excellent RISC, poor PLQY (27%) in doped film in mCP of the emitter restricts the device's efficiency (ITO/ $\alpha$ -NPD/6wt%emitter:mCP/Bphen/MgAg/Ag), resulting in a low EQE<sub>max</sub> of 4.4 % and an EL<sub>max</sub> of  $\approx$ 550 nm.

Following the report, the group demonstrated another green TADF emitter namely **ACRFLCN** ( $\lambda_{max}$ : 485 nm; PLQY: 67%;  $\tau_d$ : 160, 940, 3900 µs in 6wt% triphenyl-(4-(9-phenyl-9H-fluoren-9-yl)phenyl)silane (TPSi-F);  $\Delta E_{ST}$ : 0.10 eV)[54]. Spiro acridine group was chosen to separate donor (amine) and acceptor units (nitrile) moieties. The PLQY of the emitter is 67%, resulting in a higher EQE of 10.1% with EL<sub>max</sub> at ≈500 nm (ITO/TAPC/mCP/6wt% emitter:TPSi-F/TmPyPB/LiF/Al).

Tang et al. reported a solution-processed device based on the green emitter **4CzCNPy** ( $\lambda_{max}$ : 560 nm; PLQY: 55%;  $\tau_d$ : 8.4 µs in toluene;  $\Delta E_{ST}$ : 0.07 eV) contains 4cyanopyridine acceptor[55]. The cyano group is significant because it gives the molecule the TADF feature. Furthermore, it enhances the PLQY compared parent **4CzPy** whose n– $\pi^*$  state quenches the emission, while **4CzCNPy** emits from intramolecular charge-transfer (ICT) states. The device (ITO/PEDOT:PSS/8wt%emitter:mCP/TmPyPB/LiF/Al) exhibited EQE<sub>max</sub> of 11.3% and CIE coordinates of (0.34, 0.59).

Cho et al. put forward a novel emitter design strategy namely "dual emitting core"[56]. This is a method wherein two emitting chromophores are linked together to boost both molar absorptivity and emission efficiency owing to an enhanced transition dipole moment. They supported this strategy with comparing the PLQYs and device performance between **DDCzIPN** (dual-core) ( $\lambda_{max}$ : 477 nm; PLQY: 91%;  $\tau_d$ : 2.8 µs in toluene;  $\Delta E_{ST}$ : 0.13 eV) and **DCzIPN**[56](ordinary single-core) ( $\lambda_{max}$ : 447 nm; PLQY: 87%;  $\tau_d$ : 1.2 µs in 15wt%mCP;  $\Delta E_{ST}$ : 0.05 eV). In degassed toluene, the PLQYs of the dual-core and single-core emitters are 91% and 67%, respectively, in accordance with the former's increased EQE (18.9% at CIE coordinates of (0.22, 0.46); ITO/PEDOT:PSS/TAPC/mCP/emitter:mCP:BmPyPb/TSPO1/TPBI/LiF/AI)

(BmPyPb = 1,3-bis(3,5-dipyrid-3-ylphenyl)benzene) compared with that of the latter (16.4% at CIE coordinates of (0.17, 0.19); ITO/PEDOT:PSS/TAPC/mCP/15wt%

emitter:mCP/TSPO1/LiF/Al). Nevertheless, connecting two chromophores leads in prolonged conjugation and undesirable red shifting of the emission.

Later, the same group published a variety emitters with twin cores of dual-core TADF emitters called **33TCzPN** ( $\lambda_{max}$ : 470 nm; PLQY: 87%;  $\tau_d$ : 2.35 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.11 eV), **34TCzPN** ( $\lambda_{max}$ : 448 nm; PLQY: 66%;  $\tau_d$ : 2.96 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.16 eV), and 44TCzPN ( $\lambda_{max}$ : 444 nm; PLQY: 61%;  $\tau_d$ : 4.21 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.21 eV)[57]. Their structures differ depending on the interconnection pattern's regiochemistry. According to density functional theory (DFT) calculations, the dihedral angles between the central two carbazoles for 33TCzPN, 34TCzPN, and 44TCzPN are 40°, 56°, and 87°, respectively, and so, whereas the two emitter units in **33TCzPN** are conjugated, they are not in **34TCzPN** and 44TCzPN. The emission maxima of 33TCzPN ( $\lambda_{max}$ : 470 nm) are red-shifted, but the emission maxima ( $\lambda_{max}$ : 444–448 nm) of **34TCzPN** and **44TCzPN** are comparable isolated DCzIPN chromophores. The OLED device to two green (ITO/PEDOT:PSS/TAPC/mCP/20wt%emitter:DPEPO/TSPO1/TPBI/LiF/Al) fabricated with 33TCzPN exhibited an EQE of 17.9% at CIE coordinates of (0.29, 0.52), whereas the OLEDs with 34TCzPN and 44TCzPN were sky-blue with outstanding EQEs of 21.8% with a CIE coordinates of (0.17, 0.29)

(ITO/PEDOT:PSS/TAPC/TCTA/mCP/10wt%emitter:DPEPO/TSPO1/TBi/LiF/Al) and 19.5% with a CIE coordinates of (0.16, 0.23) (ITO/PEDOT:PSS/TAPC/mCP/10wt%emitter:DPEPO/TSPO1/TPBI/LiF/Al), respectively.

Chen et al. reported two TADF emitters namely **oPTC** ( $\lambda_{max}$ : 511 nm; PLQY: 46.6%;  $\tau_d$ : 57.9 µs in 6.5wt%mCP;  $\Delta E_{ST}$ : 0.02 eV) and **mPTC** ( $\lambda_{max}$ : 498 nm; PLQY: 54.9%;  $\tau_d$ : 12.9 µs in 6.5wt%mCP;  $\Delta E_{ST}$ : 0.01 eV) which were isomer[58]. Although their photophysical and electrochemical properties were very similar, **mPTC** which have more sterically restricted conformation showed higher color purity (FWHM: 86 nm for **mPTC** and FWHM: 97 nm for **oPTC**) in the device. Therefore, the most effective device (ITO/TAPC/TCTA/6.5wt%emitter:mCP/TmPyPb/LiF/Al) was fabricated based on **oPTC** given an EQE of 19.9% with CIE coordinates of (0.22, 0.40).

Green TADF emitters depending on cyano can be grouped into three types:
A monomeric derivative with *ortho* streric hindrance (4CzIPN, t4CzIPN and 3DPA3CN);

II) a homoconjugation derivatives that depends on through-space interactions to separate HOMO and LUMO (**Spiro-CN** and **ACRFLCN**);

III) dimeric emitters with orthosteric hindrance to separate HOMO and LUMO (DDCzIPN).

Monomeric emitters have a low  $\Delta E_{ST}$  (<0.1 eV) and high solid-state PLQYs (81.8– 100%), making them ideal for developing green TADF emitters. Especially, **4CzIPN** is regularly used to test novel specialized host components and is likely the most extensively researched TADF emitter, with the highest reported EQE of 31.2%. Homoconjugation, on the other hand, may be used to provide perfect HOMO and LUMO separation, although these emitters have lower PLQYs than monomeric and dimeric emitters. This is due to the fact that homoconjugation restricts orbital overlap too much, causing the transition dipole moment to be drastically decreased, resulting in lower emission efficiency. This situation is particularly acceptable for **Spiro-CN**, which has a solid-state PLQY of just 26%, severely limiting device performance. The dimeric emitters have a relatively larger  $\Delta E_{ST}$  (0.11-0.21 eV) than the other two groups of emitter types. It is notable that the PLQYs in toluene (61–87%) of these dimeric emitters are lower than those of their monomeric counterparts (e.g., 93% for **4CzIPN**), which contradicts the design paradigm of these emitters (i.e., an enhance in molar absorptivity to maximize the PLQY).

Another acceptor, 1,3,5-triazine (TRZ), is found in a large number of green TADF emitters. The structure of triazine based green emitters are given in Figure 1.8.



Figure 1.8: Chemical structures of triazine-based green TADF emitters; PXZ-TRZ, PTZ-TRZ, DPA-TRZ, DAC-II, bis-PXZ-TRZ, tri-PXZ-TRZ, 3ACR-TRZ, 23aICTRZ, 23bICTRZ and 32bICTRZ

**PXZ-TRZ** ( $\lambda_{max}$ :  $\approx$ 540 nm; PLQY: 66%;  $\tau_d$ : 0.68 µs in 6wt%CBP;  $\Delta E_{ST}$ : 0.07 eV) is a phenoxazine donor-based green TADF emitter (Figure 1.8)[59]. Even though the molecule seems to be mostly planar at firstly, the crystal structure shows that the dihedral angle between the donor and acceptor is 74.9°, which significantly localizes the HOMO **OLED** device and LUMO. The (ITO/α-NPD/6wt%emitter:CBP/TPBi/LiF/Al) with **PXZ-TRZ** performed an EQE of 12.5% with ELmax at 529 nm. When phenoxazine (PXZ) is replaced with phenothiazine (PTZ), a new TADF emitter called **PTZ-TRZ** ( $\lambda_{max}$ : 562 nm; PLQY: 66%;  $\tau_d$ : 0.3–0.5  $\mu$ s in 2wt%mCBP;  $\Delta E_{ST}$ : 0.18 eV) emerges, which shows a dual ICT emission owing to two distinct conformations of the phenothiazine in the ground state: quasi-axial and quasi-equatorial[60]. Only the latter conformation yields TADF because the former has a big  $\Delta E_{ST}$  of 1.14 eV while the latter has a considerably lower  $\Delta E_{ST}$  of 0.18 eV. The device (ITO/α-NPD/2wt%emitter:mCBP/TPBi/LiF/Al) with **PTZ-TRZ** emitter exhibits a green emission with an EQE of 10.8% and  $EL_{max}$  at 532 nm. The emitter **DPA-TRZ** ( $\lambda_{max}$ : 540 nm; PLQY: 100%;  $\tau_d$ : 160µs in 6wt%mCBP;  $\Delta E_{ST}$ : 0.11 eV) is made by altering phenoxazine with 4,4'-bis(diphenylamino)phenylamine, whose nonradiative decay is entirely inhibited in doped film (6wt% in mCBP), resulting in 100% PLQY[61]. **DPA-TRZ** has a higher PLQY than **PXZ-TRZ** due to preferable orbital overlap between the donor and acceptor units, resulting in a larger transition dipole The moment and hence а higher k<sub>r</sub>. device (ITO/α-NPD/6wt%emitter:mCBP/TPBI/LiF/Al) based on DPA-TRZ shows an EQE of 13.8% and EL<sub>max</sub> at 548 nm in green region. **DACT-II** ( $\lambda_{max}$ :  $\approx$ 520 nm; PLQY: 100% in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.01 eV), a near analog, achieves 100% emission and RISC resulting efficiency at the same time, in а green device (ITO/TAPC/9wt%emitter:CBP/BAlq/Liq/Al) (BAlq bis(8-hydroxy-2-= methylquinolinato)- (4-phenylphenoxy)aluminum; Liq = 8-quinolinolato lithium) with an outstanding EQE of 29.6% and  $EL_{max}$  of  $\approx$ 520 nm[62]. The superior photophysical characteristics of **DACT-II** are the result of fine-tunable the dihedral angle ( $\alpha$ ) between the core carbazole and the linking phenyl ring, which allows the oscillator strength (f) and the  $\Delta E_{ST}$  to be tuned (f and  $\Delta E_{ST}$  both rise with ascending conjugation). The former is tied to the effectiveness of the RISC process and hence increases the PLQY, whilst the latter is linked to the large radiative decay rate  $(k_r)$ . As a result, although **PXZ-TRZ** has a PLQY of 66 percent due to the 74.9° dihedral angle between the donor and the bridge, **DACT-II** has a PLQY of unity.

Due to its greater  $\Delta E_{ST}$ , **DAC-BTZ** ( $\lambda_{max}$ : 496 nm; PLQY: 82%;  $\tau_d$ : 52 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.18–0.22 eV), a near analog of **DACT-II** in which the triazine is replaced to benzothiazole, results in a blue OLED device (EL<sub>max</sub> at 493 nm) with a significantly lower EQE of 10.3% (0.009 eV)[63]. This shows that in the constructing of high effective TADF emitters, acceptor selection is critical.

Tanaka et al. used this design to obtain the di and tri substituted derivatives **bis-PXZ-TRZ** ( $\lambda_{max}$ : 560 nm; PLQY: 64%;  $\tau_d$ : 1.3 µs in 6wt%mCP;  $\Delta E_{ST}$ : 0.05 eV) and **tri-PXZ-TRZ** ( $\lambda_{max}$ : 568 nm; PLQY: 58%;  $\tau_d$ : 1.1 µs in 6wt%mCP;  $\Delta E_{ST}$ : 0.07 eV), respectively, to adjust the emission color[64]. Even though there is a considerable redshift in emission when compared to its analog **PXZ-TRZ**, the PL and EL spectra of **bis-PXZ-TRZ** and **tri-PXZ-TRZ** are extremely comparable. This is because the extra PXZ arms are metadisposed in a way that does not significantly influence conjugation length. Nonetheless, employing **tri-PXZ-TRZ**, the device (ITO/ $\alpha$ -NPD/6wt%emitter:mCBP/TPBi/LiF/Al) exhibits an EQE of 13.3% and EL<sub>max</sub> at 553 nm in green color region.

Adachi's group reported a green emitter, **3ACR-TRZ** ( $\lambda_{max}$ : 504 nm; PLQY: 98%;  $\tau_d$ : 6.7 µs in 16wt%CBP;  $\Delta E_{ST}$ : 0.02 eV), which exhibits a highly efficient triplet

utilization of 96% together with a PLQY close to unity in doped CBP [65]. Even though the dihedral angle between the acridan and the phenyl bridge is approximately 90°, the emitter's PLQY remains quite high. This discovery appears to contradict the design paradigms of **PXZ-TRZ** and **DACT-II**, in which the torsional angle between the donor and the phenyl bridge is critical for the balance of PLQY and  $\Delta E_{ST}$ . The solution-processed OLED device (ITO/PEDOT:PSS/16wt%emitter:CBP/BmPyPhB/Liq/Al) (BmPyPhB = 1,3-bis[3,5di(pyridin-3-yl)phenyl]benzene) exhibited a very high EQE of 18.6% with a EL<sub>max</sub> at  $\approx$ 520 nm.

In 2018, Duan's group reported three TADF emitters (**23aICTRZ**, **23bICTRZ** and **32aICTRZ**) derived from the indolocarbazole isomers (Figure 1.8)[66]. Among all emitters, OLED device with **32aICTRZ** ( $\lambda_{max}$ : 477 nm; PLQY: 93%;  $\tau_d$ : 3.3 µs in toluene;  $\Delta E_{ST}$ : 0.15 eV) emitter demonstrated outstanding TADF performances with an EQE of 25.1%. The EQEs of devices with **23aICTRZ** ( $\lambda_{max}$ : 474 nm; PLQY: 96%;  $\tau_d$ : 15.5 µs in toluene;  $\Delta E_{ST}$ : 0.25 eV) and **23bICTRZ** ( $\lambda_{max}$ : 457 nm; PLQY: 92%;  $\tau_d$ : 16.4 µs in toluene;  $\Delta E_{ST}$ : 0.27 eV) were reported to be 18.9% and 18.1% respectively.

The acceptors based on sulfone are also utilized for green TADF emitter design, although, unlike blue TADF analogs, diphenyl sulfone isn't any longer practical due to its extremely poor acceptor strength (LUMO:  $\approx 2.5-2.6$  eV). The structures of sulfone-based green TADF emitters are depicted in Figure 1.9.



Figure 1.9: Chemical structures of sulfone-based green TADF emitters; DTAO, TXO-TPA, TXO-PhCz, PXZDSO2 and ACRDSO2

Kim et al. published a comparable green emitter namely **DTAO** ( $\Delta E_{ST}$ : 0.19 eV) in which di-*tert*-butylcarbazole was substituted based on dimethylacridan donor (Figure 1.9)[67]. The OLED device (ITO/PEDOT:PSS/TAPC/mCP/10wt% emitter:mCP:TPBi/TSP01/TPBi/LiF/Al) performed an EQE of 14.3% and CIE coordinates of (0.32, 0.56).

Wang et al. synthesized two green TADF emitters namely **TXO-PhCz** ( $\lambda_{max}$ : 520 nm; PLQY: 90% in 5wt%mCP;  $\Delta E_{ST}$ : 0.07 eV) and **TXO-TPA** ( $\lambda_{max}$ : 580 nm; PLQY: 83% in 5wt%mCP;  $\Delta E_{ST}$ : 0.05 eV) contain thioxanthone acceptors[68]. The structures of TXO-PhCz TXO-TPA and are given in Figure 1.9. The devices (ITO/PEDOT/TAPC/5wt%emitter:mCP/TmPyPB/LiF/Al) fabricated with these two emitters showed an EQEs of 21.5% and 18.5% with a CIE coordinates of (0.31, 0.56) and (0.45, 0.53), respectively. The TPA analog has a significantly redshifted emission by 60 nm (1990 cm<sup>-1</sup>) when compared to the PhCz derivative, owing to the former's considerably more powerful donor (HOMO: 5.37 eV) than the latter's (HOMO: 5.78 eV). Other photophysical properties, such as PLQY and  $\Delta E_{ST}$ , are likely to be unaffected by donor selection. Later, for better charge and exciton confinement, the researcher created an emitting layer with a multi-quantum-well structure made of replacing nanolayers of mCP and TXO-PhCz. The OLED device (ITO/PEDOT:PSS/TAPC/TXO-PhCz:mCP(multi-quantum-well)/TmPyPB/LiF/Al)

with this upgraded design had a higher EQE of 22.6% compared to the first device design 21.5% EQE (ITO/ PEDOT/TAPC/5wt%emitter:mCP/TmPyPB/LiF/Al)[69].

Xie et al. presented two emitters called **ACRDSO2** ( $\lambda_{max}$ : 575 nm; PLQY: 71%;  $\tau_d$ : 8.3 µs in 6wt%CBP;  $\Delta E_{ST}$ : 0.06 eV) and **PXZDSO2** ( $\lambda_{max}$ : 540 nm; PLQY: 62%;  $\tau_d$ : 5.0 µs in 6wt%CBP;  $\Delta E_{ST}$ : 0.05 eV) contain a thianthrene-9,9',10,10'-tetraoxide unit as an acceptor[70]. Similar with the **TXO-PhCz** and **TXO-TPA** emitters, the donor choice mostly influences the emission energy while leaving other photophysical characteristics largely unchanged. The phenyl link between the electron donor and electron acceptor, according to the authors, reduces nonradiative internal conversion channels while boosting the radiative rate constant (kr), resulting in a high PLQY. These two emitters could be vacuum deposited or solution-processed for fabrication. Surprisingly, regardless of fabrication method, they demonstrated equal device (ITO/HAT-CN6/TAPC/6wt%emitter:CBP/TmPyPB/LiF/Al) performance (EQEs: 15.2–19.2%). **ACRDSO2** and **PXZDSO2** showed green (CIE coordinates of (0.34, 0.57)) and yellow (CIE coordinates of (0.44, 0.54)) emission, respectively.

1,3,4-Oxadiazole and its analogues are also frequently contained in green TADF emitters. Molecular structure of green TADF emitters based on 1,3,4-oxadiazole and its derivatives are given in Figure 1.10.

Lee et al. synthesized a variety emitters (**PXZ-OXD**, **PXZ-TAZ**, **2PXZ-OXD**, and **2PXZ-TAZ**) containing phenoxazine as an electron donating group and 1,3,4oxadiazole and 1,2,4-triazole as an electron accepting group[71]. In their work, they discovered that D–A–D kind compounds (**2PXZ-OXD** and **2PXZ-TAZ**) have better PLQYs as well as a more effective RISC process than D–A kind derivative (**PXZ-OXD** and **PXZ-TAZ**). Based on **2PXZ-OXD** as a green emitter, the best device performance was obtained ( $\lambda_{max}$ : 517 nm; PLQY: 87%;  $\tau_d$ : 520 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.15 eV), which exhibited an EQE of 14.9% with CIE coordinates of (0.25, 0.45) (ITO/ $\alpha$ -NPD/mCP/6wt%emitter:DPEPO/DPEPO/TPBi/LiF/AI).



Figure 1.10: Molecular structure of green TADF emitters based on 1,3,4-Oxadiazole and its derivatives

Tanaka et al. investigated the impact of atom substitution on TADF by comparing **2PXZOXD** (a.k.a. **bis-PXZ-OXD**) and **bis-PXZ-TDZ** ( $\lambda_{max}$ :  $\approx$ 540 nm; PLQY: 69%;  $\tau_d$ : 7, 56, 311 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.11 eV). The type of chalcogen in the acceptor is the only difference between the two emitters[72]. Owing to the existence of unoccupied 3d orbitals on the sulfur atom, it was determined that sulfur substitution leads to increased acceptor strength and greater intersystem crossing, resulting in a lower  $\Delta E_{ST}$  and higher kRISC. Therefore, **bis-PXZ-TDZ** contributes a greater proportion of EQE from the delayed component (n<sub>delayed</sub>: 78.0%) than **2PXZ-OXD** ( $\eta_{delaved}$ : 65.1%). However, it is crucial to note that a high delayed does not always transfer into a better TADF emitter since the emission efficiency from the singlet state is The device (ITO/a-NPD/mCP/6wt%emitter:DPEPO/DPEPO/ critical. TPBi/LiF/Al) EQEs and ELmax of **2PXZ-OXD** and **bis-PXZ-TDZ** were reported to be 14.9% and 10.0% and 508 and 537 nm, respectively.

Sagara et al. reported a variety of green TADF emitters (**BT**, **BT2**, **BOX**, **cis-BOX2**, and **trans-BOX2**) built on phenoxazine donors and benzoxazole or benzothiazole accepters to compare the characteristics and device performance of D-A and D-A-D molecular architecture[73]. It was found that D-A-D type compounds have faster radiative rate constants (kr), enhanced PLQYs, and smaller  $\Delta E_{ST}$ . All emitters showed acceptable device performance ranging between EQEs of 9.1% and 16.6%. The best

device (ITO/ $\alpha$ -NPD/6wt%emitter:mCBP/TPBi/LiF/Al) performance was obtained with OLED fabricated with **cis-BOX2** ( $\lambda_{max}$ :  $\approx$ 510 nm; PLQY: 98% in 6wt%mCBP;  $\Delta E_{ST}$ : 0.03 eV) as the emitter. According to the results, it is clear that D-A-D type compounds showed better performance compared with their D-A parents as OLED emitters.

In 2016, Adachi's group reported that **cis-BOX2** showed a totally horizontal orientation when doped into a CBP matrix. Deposition temperature must be kept under the glass-transition temperature of the CBP matrix; otherwise, the horizontal orientation would be lost. The device (ITO/TAPC/15wt%cis-BOX2:CBP/6wt%cis-BOX2:CBP)/PPT/LiF/Al) has an EQE of 33.4% thanks to the considerably improved light-outcoupling[74]. It is expected that **trans-BOX2** should have a very comparable molecular length, planarity, and shape to **cis-BOX2**, and so it would be predicted that **trans-BOX2** would offer a preference horizontal arrangement, as **cis-BOX2** does.

Another green emitter, **PXZ-POB** ( $\lambda_{max}$ : 492 nm; PLQY: 92%;  $\tau_d$ : 2.69 µs in 1wt%PMMA;  $\Delta E_{ST}$ : 0.06 eV) contains phenoxazine as a donor and a 1,3diaryloxybenzene borane as an acceptor was reported by Hirai et al[75]. Molecular structure of **PXZ-POB** is given in Figure 1.11. The device (ITO/HAT-CN/TBBD/TCTA/20wt%emitter:2c/TPBI/LiF/Al) (TBBD = N4,N4,N4', N4' tetra([1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4,4'-diamine) based on **PXZ-POB** achieved a high EQE of 15.2% with EL<sub>max</sub> at 528 nm. But the operational stability of the device is poor with an LT80 of less than 1 h.



Figure 1.11: Molecular structure of TB-1PXZ, TB-2PXZ, TB-3PXZ, PXZ-POB, CzDBA and tBuCzDBA emitters

Liu et al. also reported several TADF emitters (**TB-1PXZ**, **TB-2PXZ**, and **TB-3PXZ**) derived from phenoxazine donor and tridurylborane acceptor (Fig. 1.11) [76]. Increasing phenoxazine substitution across the series resulted in lower  $\Delta E_{ST}$  (0.12, 0.05, and 0.01 eV) and higher PLQY (12%, 47%, and 95%), which is analogous to the observed behavior in related phosphine oxides systems (PXZPOs). The best solution-processed device (ITO/PEDOT:PSS/10wt%emitter:CzSi/TmPyPB/Liq/Al) was achieved based on **TB-3PXZ** ( $\lambda_{max}$ : 509 nm; PLQY: 95%;  $\tau_d$ : 1.3 µs in 10wt%CzSi;  $\Delta E_{ST}$ : 0.01 eV) with an EQE<sub>max</sub> of 13.9%.

In 2018, Cheng et al. published two rod-like emitters, **CzDBA** ( $\lambda_{max}$ :  $\approx$ 550 nm; PLQY: 100%;  $\tau_d$ : 1.0 µs in 1wt%CBP;  $\Delta E_{ST}$ : 0.22 eV) and **tBuCzDBA** ( $\lambda_{max}$ 550 nm; PLQY: 86%;  $\tau_d$ : 1.2 µs in 1wt%CBP;  $\Delta E_{ST}$ : 0.11 eV), both of which are D-A-D type TADF molecules with 9,10-dihydro-9,10-diboraanthracene and carbazole groups (seen in Figure 1.11)[77]. These emitters have a low  $\Delta E_{ST}$  and outstanding PLQYs due to their high horizontal emission dipole orientations and high horizontal emission dipole orientations and high horizontal emission dipole orientations. The use of **CzDBA** as an emitter resulted in a green OLED with a record-high EQE of 37.8%, indicating a new research route for highly efficient TADF-based OLEDs.

Adachi's group presented the **HAP-3MF** ( $\lambda_{max}$ : 520 nm; PLQY: 26% in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.17 eV) emitter, which uses a fascinating heptaazaphenalene[78]. Structure of **HAP-3MF** is depicted in Figure 1.12. This emitter comes out among all the TADF

emitters published so far for two reasons: To begin the lowest singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) associated in the RISC process are all highly  $n-\pi^*$  excited states, which is rare. Second, **HAP-3MF** is perhaps the only TADF emitter for OLED applications that do not use a nitrogen-based donor, with heptaazaphenalene acting as the acceptor. Unfortunately, because emission arises from an  $n-\pi^*$  excited state,  $k_r$  is modest ( $10^{-6}$  s<sup>-1</sup>), resulting in a comparatively low PLQY of 26% in degassed toluene. OLED device with **HAP-3MF** (ITO/NPD/mCP/6wt%emitter:DPEPO/DPEPO/TPBI/LiF/AI) showed green emission with an EQE<sub>max</sub> of 6.0% and an EL<sub>max</sub> at  $\approx$ 520 nm.



Figure 1.12: Molecular structure of TPXZ-as-TAZ, DPXZ-as-TAZ, PXZPM, PXZMePM, PXZPhPM and HAP-3MF emitters

In 2016, three green TADF emitters namely **PXZPM** ( $\lambda_{max}$ : 535 nm; PLQY: 88%;  $\tau_d$ : 3.14 µs in 6wt%CBP;  $\Delta E_{ST}$ : 0.08 eV), **PXZMePM** ( $\lambda_{max}$ : 524 nm; PLQY: 89%;  $\tau_d$ : 1.80 µs in 6wt%CBP;  $\Delta E_{ST}$ :  $\approx 0.10 \text{ eV}$ ), and **PXZPhPM** ( $\lambda_{max}$ : 528 nm; PLQY: 91%;  $\tau_d$ : 1.82 µs in 6wt%CBP;  $\Delta E_{ST}$ : 0.03 eV) containing pyrimidine were reported by Wu et al (Fig. 1.12)[79]. Pyrimidine is weaker acceptor due to having two nitrogen atoms compared to triazine analog, therefore, these emitters showed blue shifted of  $\approx 20$  nm in emission spectra. Pyrimidine and triazine classes of emitters show extremely similar  $\Delta E_{\rm ST}$  ( $\approx 0.05$  eV), whereas the triazine emitters have lower PLQY (64%) than the pyrimidine All of the OLED ones (88-91%). devices (ITO/TAPC/TCTA/6wt%emitter:CBP/Tm3PyPB/LiF/Al) showed the same turn-on voltage (3.4 V) and similar ELmax (527-531 nm). Although their EQEs were comparable similar (19.9-24.6%), the highest EQE (EQE<sub>max</sub>: 24.6%) was obtained with **PXZPhPM** emitter.

Xiang et al. introduced two yellow emitters namely **TPXZ-as-TAZ** ( $\lambda_{max}$ : 555 nm; PLQY: 53%;  $\tau_d$ : 1.10 µs in 1.5wt%CBP;  $\Delta E_{ST}$ : 0.03 eV) and **DPXZ-as-TAZ** ( $\lambda_{max}$ : 553 nm; PLQY: 43%;  $\tau_d$ : 0.98 µs in 1.5wt%CBP;  $\Delta E_{ST}$ : 0.08 eV) contain an asymmetric 1,2,4-triazine as an acceptor and phenoxazine as a donor [80]. The most effective device (ITO/TAPC/TCTA/1.5wt%emitter:CBP/TmPyPB/LiF/Al) fabricated with **TPXZ-as-TAZ** performed an EQE of 13.0% and yellow emission at CIE coordinates of (0.45, 0.52). Surprisingly, at a high brightness of 1000 cdm<sup>-2</sup>, the device had a moderate efficiency roll-off of 11.5%, attributed to a short decay lifespan of the delayed component (1.10 µs) that helps to minimize triplet quenching mechanism.

In 2016, Adachi et al. reported two emitters called **AcPmBPX** ( $\lambda_{max}$ : 492 nm; PLQY: 46%;  $\tau_d$ : 925 µs in 6wt%mCP;  $\Delta E_{ST}$ : 0.05 eV) and **PxPmBPX** ( $\lambda_{max}$ : 530 nm; PLQY: 57%;  $\tau_d$ : 314 µs in 6wt%mCP;  $\Delta E_{ST}$ : 0.02 eV), derived from an X-shaped benzoylbenzophenone unit are given in Figure 1.13[81]. A high dihedral angle exists between the peripheral donor and the central benzoylbenzophenone acceptor in this molecular design, resulting in enhanced separation between HOMO and LUMO. **PxPmBPX**, for instance, achieved an extremely low  $\Delta E_{ST}$  of 0.02 eV. With EQEs of 10.0% and 11.3%, devices (ITO/-NPD/mCP/6wt%emitter:mCBP/PPF/TPBi/LiF/Al) employing **AcPmBPX** and **PxPmBPX** showed green (EL<sub>max</sub> at 504 nm) and yellow (EL<sub>max</sub> at 541 nm) emission, respectively.

In 2017, Chen et al. reported two TADF emitters **AI-Cz** ( $\lambda_{max}$ : 510 nm; PLQY: 72%;  $\tau_d$ : 81 µs in 1wt%mCBP;  $\Delta E_{ST}$ : 0.06 eV) and **AI-TBCz** ( $\lambda_{max}$ : 545 nm; PLQY: 67%;  $\tau_d$ : 64 µs in 1wt%mCBP;  $\Delta E_{ST}$ : 0.03 eV) containing an aromatic-imide, which exhibited delayed emission thanks to the small  $\Delta E_{ST}$  (< 0.1 eV). The green OLED device with the **AI-Cz** emitter showed a high EQE of 23.2% with EL<sub>max</sub> at 510 nm[82].



Figure 1.13: Molecular structure of green TADF emitters; AI-Cz, AI-TBCz, PxPmBPC and AcPmBPC

#### 1.2.3.2 Third Generation Orange-Red Emitters

CT emission is originated from the singlet emission in the donor and acceptor type molecules so that the degree of CT character determined the emission energy. The red TADF emitters need small singlet energy, which is usually obtained by enhancing CT character tuned by donor and acceptor strength of the molecules. The higher CT character can be obtained by using strong donors and acceptors or rising the quantity of donors and acceptors. In general, strong donors have shallow HOMO and strong acceptors have deep LUMO, resulting in a small HOMO-LUMO gap and low singlet emission energy[83]. Because low singlet energy is required to generate red emission in the TADF emitters, both strong donors and acceptors are employed to construct the red TADF emitters.

While triphenylamine, *t*-butylated triphenylamine, dimethylacridane, and diphenylacridane are usually used as an donor moiety, diphenyltriazine, quinoxaline, dibenzophenazine, heptazine, cyanobenzene, dicyanobenzene, dicyanopyrazine, dicyanopyrazino phenanthrene, quinoxaline-6,7-dicarbonitrile, 11,12dicyanodibenzo[a,c]phenazine (CNBPz), benzophenone, anthraquinone, naphthalimide, benzothiadiazole, benzothiazole, and acenaphtho[1,2-b]pyrazine-8,9dicarbonitrile are used as an acceptor moiety in red TADF emitters.

From the first report of pure organic orange-red TADF emitter **4CzTPN-Ph**[43], considerable progress in this field has in recent years. Nowadays, EQEs have reached up to  $\approx 30\%$  with the luminescence ranging between 580 and 700 nm with the developments.

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Adachi's group reported the first TADF orange-red emitter, **4CzTPN-Ph** ( $\lambda_{max}$ : 577 nm; PLQY: 26%;  $\tau_d$ : 1.1 µs in toluene) derived from 1,4-dicyanobenzene acceptors and carbazole-derived donors in 2012. A main strategy was to link strong electron-deficient 1,4-dicyanobenzone acceptor and four carbazole-derived donors for strong donor character. The EQE<sub>max</sub> was reported as 11.9% ( $\lambda_{EL} = 580$  nm). In 2013, the same group introduced an OLED with a red-shifted emission ( $\lambda_{EL} > 600$  nm) with an EQE of 17.5% and CIE coordinates of (0.60, 0.40) derived from the heptazine-based emitter molecule **HAP-3TPA** ( $\lambda_{max}$ : 560 nm; PLQY: 95%;  $\tau_d$ : 48 µs in 1wt%:2,6-dicarbazolo-1,5-pyridine (26mCPy);  $\Delta E_{ST}$ : 0.17 eV) and a larger amount of heteroatoms in the acceptor unit[84].

In 2015, Wang and coworkers presented one of the deep-red OLED devices with an EQE<sub>max</sub> of 9.8% fabricated with a **TPA-DCPP** ( $\lambda_{max}$ : 645 nm; PLQY: 50%;  $\tau_d$ : 86.2 µs in 10wt%TPBI;  $\Delta E_{ST}$ : 0.13 eV) emitter derived from phenanthrene[85].

In 2018, Yang et al. introduced two emitters namely **NAI-DMAC** ( $\lambda_{max}$ : 582 nm; PLQY: 59.9 %;  $\tau_d$ : 14.7 µs in 1.5wt%mCPC;  $\Delta E_{ST}$ : 0.09 eV) and **NAI-DPAC** ( $\lambda_{max}$ : 570 nm; PLQY: 78.9%;  $\tau_d$ : 48.7 µs in 1.5wt%mCPC;  $\Delta E_{ST}$ : 0.17 eV)[86]. An OLED device fabricated with **NAI-DMAC** and **NAI-DPAC** emitters showed an EQE of 29.2% with an  $\lambda_{EL} = 584$  nm and an EQE of 23.4% with an  $\lambda_{EL} = 597$  nm, respectively. The obtained EQE of 29.2% is the highest yield among all orange-red TADF emitters. The strategy of Yang's group was based on enhancing the rigidity of the molecular structure and also charge transfer (CT) state, in combination with the optical microcavity effect that has provided high EQEs for orange-red OLEDs.

In 2019, the same group reported orange-red emitter, **NAI-R3** ( $\lambda_{max}$ : 593 nm; PLQY: 66%;  $\tau_d$ : 3.14 µs in 1.5wt%mCP;  $\Delta E_{ST}$ : 0.58 eV) which was with extended donor units with tert-butylbenzene groups. Solution-processed OLED device exhibited an EQE of 22.5% with an  $\lambda_{EL} = 622$  nm[87]. The same year, a novel red TADF emitter, **TPA-PZCN** ( $\lambda_{max}$ :  $\approx$ 610nm; PLQY: 97%;  $\tau_d$ : 132.98 µs in 15wt%CBP;  $\Delta E_{ST}$ : 0.13 eV), containing dibenzo[a,c]phenazine-3,6-dicarbonitrile as a new acceptor unit was reported by Liao et al. They used a strategy based on increasing structural rigidity and the acceptor strength by limiting the nonradiative transition with a using large planar backbone[88]. The OLED with **TPA-PZCN** exhibited a high EQE of 27.4% with  $\lambda_{EL} = 622$  nm thanks to this strategy. Recently, Cheng et al. presented an orange-red device

with the 9,10 diboraanthracene (DBA)-based, **dmAcDbA** emitter with an EQE of 24.9% and  $\lambda_{EL} = 583$  nm[89].

In 2016, Monkman's group reported an OLED device based on dibenzo[a,j]phenazinebased emitter belonging to U-shaped D-A-D TADF systems namely **POZ-DBPHZ** ( $\lambda_{max}$ : 595 nm; PLQY: 79% in 10wt%CBP;  $\Delta E_{ST}$ : 0.02 eV) with an EL wavelength of 610 nm and EQE of 16%[90]. Since then, third-generation orange-red emitters have made significant progress, resulting to the introduction of TADF emitters with luminescence in the area between 580 and 700 nm and EQEs of up to 30%.

Chen et al. published a solution-processed red TADF OLED with **red-1b** ( $\lambda_{max}$ : 622 nm; PLQY: 28%;  $\tau_d$ : 82.8 µs as neat;  $\Delta E_{ST}$ : 0.40 eV) without doping[91]. Magnetoelectroluminescence studies show that the material can undergo both TADF and triplet–triplet annihilation (TTA) processes, based on the current density in the device. The EQE was reported to be 1.75% (ITO/PEDOT:PSS/PVK/emitter/TPBi/CsF/Al) with CIE coordinates of (0.65, 0.33).

Data et al. synthesized a series of three TADF emitters contain dibenzo-[a,j]phenazine acceptors, **t-BuCz-DBPHZ** ( $\lambda_{max}$ : 509 nm; PLQY: 31%;  $\tau_d$  not observed in 10wt%CBP;  $\Delta E_{ST}$ : 0.33 eV), **MeODP-DBPHZ** ( $\lambda_{max}$ : 592 nm; PLQY: 58%;  $\tau_d$ : 16, 6440 µs in 10wt%CBP;  $\Delta E_{ST}$ : 0.19 eV), and **POZDBPHZ** ( $\lambda_{max}$ : 595 nm; PLQY: 79%;  $\tau_d$ : 1.84, 26.4 µs in 10wt%CBP;  $\Delta E_{ST}$ : 0.02 eV)[92]. **t-BuCz-DBPHZ** exhibited bluer emission than **MeODP-DBPHZ** and **POZDBPHZ** due to the tert-butyl carbazole's substantially lower donating capacity, as well as the greatest  $\Delta E_{ST}$  due to the weaker ICT character. While the OLED (ITO/NPB/10wt%emitter:CBP/TPBi/BCP/LiF/Al) with **t-BuCz-DBPHZ** (EQE:  $\approx$ 7%) was green-emitting, those using **MeODP-DBPHZ** (EQE:  $\approx$ 10%) and POZ-DBPHZ (EQE:  $\approx$ 16%) emitted red light due to the stronger donors. Surprisingly, when 10wt%POZDBPHZ was doped in the m-MTDATA host (m-MTDATA = 4,4',4''-tris[(3-methylphenyl)-phenylamino]triphenylamine) as the emissive layer, strongly exciplex-driven NIR emission at 741 nm was observed with an excellent EQE of about 5%. No corroborating evidence was provided to support the TADF mechanism of this exciplex system.

#### 1.2.3.3 Third Generation Blue Emitters

The synthesis of novel blue emitters for OLED applications has developed rapidly in recent decades. To use blue TADF emitter in OLED device must be capable of achieving high EQE, low-efficiency roll-off, high color purity, and long lifetime. For OLED including these properties, the blue emitter has a high PLQY, a large energy gap between the HOMO and the LUMO, and a small  $\Delta E_{ST}$ , triple-to-single fast inverse crossover (RISC), and high horizontal dipole orientation in thin film[93].

While diazatriphenylene, triazine, benzoylpyridine, diphenylsulfone, thioxanthene, cyano, and their derivatives have mostly used as an acceptor unit, carbazole, acridone, benzophenone, acridine, indolocarbazole, diazafluorene, and their derivatives have been used as a donor unit for designing blue TADF emitter. The problem with the blue OLEDs is not only the operation lifetime and degradation of the material because of having higher energy but also the device efficiency roll-off at high brightness. Therefore, the most challenging duty is obtaining stable deep-blue emitters and OLEDs in this field. However, development toward a deep-blue or blue hyperfluorescence OLED ( $\lambda_{EL}$ < 450 nm) remains limited, owing to the scarcity of deep-blue or ultraviolet TADF materials with short  $\tau_d$ . The highest reported EQEs is 27% until now.

In 2012, Adachi et al. published the very first class of deep-blue TADF emitters containing diphenylsulfone as an acceptor. The OLED device (ITO/ $\alpha$ -NPD/TCTA/CzSi/10wt%emitter:DPEPO/DPEPO/TPBI/LiF/Al) (TCTA = tris(4-carbazoyl-9-ylphenyl) amine; DPEPO = bis[2-(diphenylphosphino)phenyl] ether oxide; TPBI = 2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) based on **3 (DTC-DPS)** ( $\lambda_{max}$ : 423 nm; PLQY: 80%;  $\tau_d$ : 540 µs, 2600 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.32 eV) showed an EQE of 9.9% ( $\lambda_{EL}$  =423 nm) with a CIE coordinates of (0.15, 0.07). The authors put forward that if the energy difference between the lower energy triplet donor-centered locally excited  $\pi$ - $\pi^*$  state (3LE) and the higher energy triplet charge-transfer state (3CT) is small, a small  $\Delta E_{ST}$  can be achieved. This hypothesis was confirmed by the existence of delayed fluorescence when the solvent of the emitter was altered from nonpolar hexane to polar methanol, where the 3CT is stabilized, evidenced by the positive solvatochromism. Under this situation, followed by efficient RISC to 1CT, reverse internal conversion (RIC) happens from 3LE to 3CT.

Emitter 1 and 2, although having a similar energy 1CT state similar to 3 (DTC-DPS), they have larger  $\Delta E_{ST}$  of 0.54 eV and 0.45 eV, respectively, because of having diphenylamine group that 3LE state energy is lower than carbazole one. Furthermore, due to the high intrinsic energies of charge-transfer singlet and triplet states, obtaining deep-blue TADF emitters that adhere to this ordering of excited states is quite difficult. Therefore, it is important to control the conjugation length (e.g., through steric or substitution pattern) and the choice of the donor in molecular design.

Adachi's group presented a sky-blue emitter **2CzPN** ( $\lambda_{max}$ :  $\approx$ 473 nm; PLQY: 47%;  $\tau_d$ : 166 μs in toluene). The sky-blue OLED device (ITO/α-NPD/mCP/5wt%emitter:PPT/PPT/LiF/Al) with 2CzPN exhibited an EQE of 8.0% with an EL wavelength of 473 nm[43]. Some of the most common structural systems for blue TADF emitters are cyano-based acceptor units. The same group achieved a higher EQE of 13.6% (ITO/a-NPD/mCP/6wt%emitter:mCP/PPT/TPBi/LiF/Al) by doping the emitter in a p-type host (mCP) to avoid exciplex formation between the hole-transporting layer and the emitting layer [94]. The highest EQE (21.8%) with the same emitter was reported by Sun and coworkers with the device configuration of  $ITO/4wt\%ReO_3:mCP/5wt\%emitter:mCP:PO15/4wt\%Rb_2CO_3:PO-15/Al$  (PO-15 = poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine]) for maximum charge balance and minimize electrical loss[95]. Nonetheless, with higher current densities, the device's efficiency dropped dramatically, and the best 21.8% EQE was only obtained at 0.01 mA cm<sup>-2</sup>. The development of blue TADF emitters has accelerated then.

Lee et al. reported two derivatives of **2CzPN** by replacing carbazole donor with benzofurocarbazole and benzothienocarbazole (**BFCz-2CN** ( $\lambda_{max}$ : ~480 nm; PLQY: 85%;  $\tau_d$ : 2.6 µs in 1wt%mCP;  $\Delta E_{ST}$ : 0.13 eV) and **BTCz-2CN** ( $\lambda_{max}$ : ~480 nm; PLQY: 85%;  $\tau_d$ : 1.98 µs in 1wt%mCP;  $\Delta E_{ST}$ : 0.17 eV)[96]. Benzofurocarbazole and benzothienocarbazole donors have a more rigid structure, resulting similar emission energies and more efficient RISC processes. However, **BFCz-2CN** and **BTCz-2CN** showed higher PLQYs (94.6% and 94.0%, respectively in degassed toluene) compared with **2CzPN** (47% in degassed toluene). Despite the higher conjugation of the donor's fused structure and the presence of electron-donating oxygen and sulfur atoms, all of which increase the HOMO level (from 6.17 to 6.19 eV), sky-blue emission was still

produced in a doped thin film and device. The authors achieved an EQE of 5.0% for the OLED using the parent emitter **2CzPN**, the devices (ITO/PEDOT: PSS/TAPC/mCP/1wt%emitter:mCP/TSPO1/LiF/Al) based on **BFCz-2CN** and **BTCz-2CN** exhibited higher EQEs of 12.1% and 11.8%, respectively at the same wavelength (EL<sub>max</sub>: 486 nm).

Another possible RISC mechanism for TADF emitters was hypothesized by Dias et al[97]. They conducted a comprehensive photophysical investigation on a variety of emitters and discovered that RISC is still achievable and may even be very efficient for emitters with  $\Delta E_{ST}$  greater than 0.3 eV. For example, although the emitter **DTC-DBT**[98] possesses a high  $\Delta E_{ST}$  of 0.35 eV, 100% of the triplet excitons can be harvested by the RISC mechanism. In the presence of heteroatom lone pairs compose a "hidden"  $3n-\pi^*$  state between the higher 3CT and the lower 3LE states. As a result, up-conversion occurs in a more complicated cascade:  $3LE \rightarrow 3n\pi^* \rightarrow 3CT \rightarrow 1CT$ ; the energy gap between the higher 3CT and the  $3n-\pi^*$  represented in their work was approximately 0.38 eV, which is believed likely too large for an efficient up-conversion. Chen et al. demonstrated that the lowest 3LE state of the same molecule, **DTC-DBT**, already contains some mixing with the  $3n-\pi^*$  state.

As a follow up to their pioneering blue TADF emitter **DTC-DPS**, Adachi et al. modified **DTC-DPS** by altering di-tert-butylcarbazol with dimethoxycarbazole to obtain deep-blue emitter **DMOC-DPS** ( $\lambda_{max}$ : 455 nm; PLQY: 80%;  $\tau_d$ : 114 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.21 eV)[99]. The addition of the stronger electron-donating methoxy groups decreases the S1 state while maintaining the energy of T<sub>1</sub>. The smaller  $\Delta E_{ST}$  was obtained with **DMOC-DPS** (0.21 eV) compared to the **DTC-DPS** (0.32 eV), resulting in a shorter component lifetime (114 µs for **DMOC-DPS**, 540 and 2600 µs for **DTC-DPS**). The deep blue OLED device (ITO/ $\alpha$ -NPD/TCTA/CzSi/10wt% emitter:DPEPO/DPEPO/TPBI/LiF/AI) with **DMOC-DPS** showed lower efficiency roll-off with an EQE of 14.5%. The same group published another blue emitter named **DMAC-DPS** ( $\lambda_{max}$ : 464 nm; PLQY: 80%;  $\tau_d$ : 3.1 µs in 10wt%mCP;  $\Delta E_{ST}$ : 0.08 eV) which is the most promising due to its smallest  $\Delta E_{ST}$  and high solid-state PLQY among the diphenylsulfone-based deep-blue TADF emitters[75]. The acridone donor is an electron-rich donor which enhances the HOMO/LUMO separation due to its highly rigid structure, resulting increasing nonradiative decay paths from the excited state and a small  $\Delta E_{ST}$ . OLED device (ITO/ $\alpha$ -NPD/TCTA/CzSi/10wt%emitter:DPEPO/DPEPO/TPBI/LiF/Al) demonstra-ted an EQE of 19.5% with an EL wavelength of 470 nm (CIE=0.16, 0.20). The **DMAC-DPS** has also been used in nondoped device configuration, which showed higher device reliability[100]. OLED device, which was nondoped configuration based on the similar emitter, **DMAC-BP** ( $\lambda_{max}$ : 506 nm; PLQY: 85%;  $\tau_d$ : 2.7 µs as neat emitter;  $\Delta E_{ST}$ : 0.07 eV), also showed a high EQE of 18.9%.

Another deep blue emitter **DMTDAc** containing acridone as a donor and 9,9-dimethyl-9H-thioxanthene-10,10-dioxide as an acceptor was reported by Lee, Song, and Lee in 2016[97]. In the **DMTDAc** molecule, the additional methylene group linked to the phenyl rings of the thioxanthene-dioxide moiety decreases vibrational motion, leading narrows the emission spectrum. The device fabricated with **DMTDAc** (ITO/PEDOT:PSS/TAPC/mCP/30wt%emitter:UGH3:TSPO1/TSPO1/TPBI/LiF/Al) (PEDOT:PSS = poly(3,4-ethylenedioxythiophene)-poly(styrene-sulfonate); TAPC = 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine]) exhibited a deepblue emission with an EQE of 19.8% and CIE coordinates of (0.15, 0.13).

The examples of D-A-A-D (donor-acceptor-acceptor-donor) emitter system, DTC**pBPSB** ( $\lambda_{max}$ : 461 nm; PLQY: 67%;  $\tau_d$ : 1.23 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.05 eV) and **DTC-mBPSB** ( $\lambda_{max}$ : 434 nm; PLQY: 71%;  $\tau_d$ : 1.16 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.24 eV) obtained by changing diphenylsulfone acceptor was with a pbis(phenylsulfonyl)benzene moiety by Kido et al.[101]. DTC-pBPSB exhibited redshifted emission compared to **DTC-mBPSB** due to the longer effective conjugation. The smaller  $\Delta E_{ST}$  was attributed to its lower 1CT state and therefore a smaller gap concerning the lowest localized triplet state. As a result, the connection mode of the emitter has a significant impact on its photophysical properties. The sky-blue and OLED (ITO/NPB/TCTA/CzSi/10wt%emitter: deep-blue devices DPEPO/DPEPO/TPBI/LiF/A1) (NPB = N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'biphenyl)-4,4'-diamine) based on DTC-pBPSB and DTC-mBPSB performed EQEs of 11.7% and 5.5% with CIE coordinates of (0.18, 0.19) and (0.15, 0.08), respectively.

Lee and co-workers presented novel two emitters **Cz2BP** ( $\lambda_{max}$ : 444 nm; PLQY: 55%;  $\tau_d$ : 710 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.21 eV) and **CC2BP** ( $\lambda_{max}$ : 475 nm; PLQY: 73%;  $\tau_d$ : 460 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.14 eV) containing benzophenone as an electron donor unit[97] . **CC2BP** has not only smaller  $\Delta E_{ST}$  but also higher donor strength compared to **Cz2BP** due to its extended donor system with carbazole. The fabricated two blue OLED devices (ITO/ $\alpha$ -NPD/mCP/6wt%emitter: DPEPO/DPEPO/TPBi/LiF/Al) with **Cz2BP** and **CC2BP** showed EQEs of 8.1% and 14.3% with CIE coordinates of (0.16, 0.14) and (0.17, 0.27), respectively.

Rajamalli and co-workers presented two new emitters **DCBPy** ( $\lambda_{max}$ : 514 nm; PLQY: 88%; τ<sub>d</sub>: 0.6 μs in 5wt% 9,9'-(sulfonylbis(4,1-phenylene))bis(9H-carbazole) (CzPS);  $\Delta E_{ST}$ : 0.07 eV) and **DTCBPy** ( $\lambda_{max}$ : 518 nm; PLQY: 91%;  $\tau_d$ : 1.0 µs in 5wt% 4,4'bis(N-carbazolyl)-1,1'-biphenyl (CBP);  $\Delta E_{ST}$ : 0.08 eV) containing a benzoylpyridine as an acceptor unit[93]. DTCBPy showed a small redshifted of 4 nm in emission spectrum due to having tert-butyl groups. Intramolecular interaction between the ortho carbazole donor and the benzoylpyridine acceptor was thought both to induce efficient TADF and also prevent intermolecular aggregation in the solid state. Hence, the higher PLQY was achieved in the solid state (up to 91.4%) compared with solution (14–36%). (ITO/NPB/mCP/5wt%emitter:CzPS/DPEPO/TmPyPb/ **DCBPy** LiF/Al) and **DTCBPy** (ITO/NPB/TAPC/5wt%emitter:CBP/PPT/TmPyPb/LiF/Al) (TmPyPb = 1,3,5-tri(m-pyridin-3-ylphenyl)benzene; PPT = 2,8-bis(diphenylphosphoryl)dibenzo-[b,d]thiophene) gave sky-blue and green OLED devices with EQEs of 24.0% and 27.2% with CIE coordinates of (0.17, 0.36) and (0.30, 0.64), respectively.

1,3,5-triazine is another common acceptor unit that is used for obtaining blue TADF emitters. Adachi and co-workers published a blue-greenish emitter CzT ( $\lambda_{max}$ : 502 nm; PLQY: 40%;  $\tau_d$ : 42.6 µs in 3wt%DPEPO;  $\Delta E_{ST}$ : 0.09 eV) in 2013[100]. OLED device (ITO/a-NPD/TCTA/CzSi/3wt%emitter:DPEPO/DPEPO/ fabricated with CzT TPBi/LiF/Al) exhibited an EQE of 6% at CIE coordinates of (0.23, 0.40). Although **PhCzTAZ** (PhCzTAZ = 3-(2'-(4,6-diphenyl-1,3,5-triazine-2-yl)-[1,1'-biphenyl]-2yl)-9-phenyl-9H-carbazole) is a structurally similar emitter did not show TADF properties because of the absence of charge-transfer emission, most likely owing to steric effect around the biphenyl bridge, which limits HOMO and LUMO communication. The same group reported **BCzT** ( $\lambda_{max}$ : 483 nm; PLQY: 96%;  $\tau_d$ : 33  $\mu$ s in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.29-0.33 eV) to enhance of the PLQY with the adding phenyl-ring between triazine and bicarbazole units[100]. An additional phenyl as a bridge enhances the overlap between the HOMO and the LUMO because it increases

conjugation. Consequently, the additional phenyl-ring bridge increases the overlap density between the excited state and the ground state ( $\rho 10$ ), resulting in a higher dipole moment and radiative rate constant (kr). High RISC rate (kRISC) and high radiative rate constants (kr) are required for efficient TADF. Triplet-to-light efficiency is defined as the ratio of PLQY contribution by delayed component ( $\Phi_d$ ) to triplet formation yield ( $\Phi_{\rm T}$ ). Although **BCzT** has higher  $\Delta E_{\rm ST}$ , the triplet-to-light efficiency in BCzT (76.2%) is much higher than in CzT (25%). It is believed that because BCzT has a much higher kr, it reduces cycling between singlet and triplet states, thereby eliminating the possibility of nonradiative decay in both singlet and triplet states. The device-based BCzT resulted in a sky-blue emission (ITO/α-NPD/mCBP/6wt%emitter:DPEPO/TPBi/LiF/Al) with an EQE of 21.7% and ELmax at 492 nm, which was significantly improved compared to the 6%  $EQE_{max}$  obtained by the OLED based on CzT.

In 2015, Kim et al. published two blue TADF emitters **DCzTrz** ( $\lambda_{max}$ :  $\approx$ 420 nm; PLQY: 43%;  $\tau_d$ : 3.1 µs in toluene;  $\Delta E_{ST}$ : 0.25 eV) and **DDCzTrz** ( $\lambda_{max}$ :  $\approx$ 430 nm; PLQY: 66%;  $\tau_d$ : 2.8 µs in toluene;  $\Delta E_{ST}$ : 0.27 eV). The only difference between them was two additional carbazole moieties attached to the phenyl ring in a meta-position in **DDCzTrz**[102]. The two emitters have almost same emission energy and  $\Delta E_{ST}$ because "meta connections" limit conjugation length. The OLED (ITO/PEDOT:PSS/TAPC/mCP/25wt%emitter:DPEPO/TSPO1/TPBI/LiF/Al) devices with DCzTrz and DDCzTrz performed EQE<sub>max</sub> of 17.8% and 18.9% at CIE coordinates of (0.15,0.15) and (0.16, 0.22), respectively.

Adachi's group published a highly planar sky-blue TADF emitter named **CC2TA**  $(\lambda_{max}: \approx 490 \text{ nm}; \text{PLQY}: 62\%; \tau_d: 22 \ \mu \text{s} in 6wt\%\text{DPEPO}; \Delta E_{ST}: 0.06 \ eV)$  containing carbazolyl units as a donor unit and triazine as an acceptor unit[103]. The outcoupling efficiency of the **CC2TA** was reported to be 31.3% and the device (ITO/ $\alpha$ -NPD/mCP/6wt%emitter:DPEPO/DPEPO/TPBi/LiF/Al) showed an EQE<sub>max</sub> of 11% with EL<sub>max</sub> at 490 nm.

Tsai et al. presented a novel sky-blue TADF emitter **DMAC-TRZ** ( $\lambda_{max}$ : 495 nm; PLQY: 90%;  $\tau_d$ : 1.9 µs in 8wt%mCPCN;  $\Delta E_{ST}$ : 0.05 eV), which, when doped in mCPCN, performed a highly efficient device (ITO/PEDOT:PSS/TAPC/mCP/8wt% emitter:mCPCN/DPPS/3TPYMB/LiF/Al) (3TPYMB = tris(2,4,6-trimethyl-3-

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(pyridin-3-yl)phenyl)borane; DPPS = diphenylbis(4- (pyridin-3-yl)phenyl)silane) with an EQE of 26.5% ( $\lambda_{EL}$  = 490 nm) with a of CIE coordinates of (0.21, 0.50)[104]. Acridan is a stronger donor than carbazole, resulting redshifted emission compared to carbazole-based triazine TADF emitters. Surprisingly, the emitter also showed an a high EQE of 20% without using a host.

The TADF emitter **spiroAC-TRZ** ( $\lambda_{max}$ : 483 nm; PLQY: 100%;  $\tau_d$ : 2.1 µs in 12wt%mCPCN;  $\Delta E_{ST}$ : 0.07 eV) contains triazine acceptor and an acridine derivative donor[105]. The phenyl rings on the acridine unit in **spiroAC-TRZ** decrease the electron-donating capacity of the donor, resulting in a favorable hypsochromic shift in the emission compared to **DMAC-TRZ**. The OLED device fabricated with **spiroAC-TRZ** showed an EQE<sub>max</sub> of 36.7% with EL<sub>max</sub> at 480 nm and CIE coordinates of (0.18, 0.43). With this high EQE, the OLED fabricated with **spiroAC-TRZ** is the best value among the blue TADF device reported until now.

Silicon has a rigid tetrahedral structure and also owing to its size, efficiently limits nonradiative decay pathways and promotes the morphological stability of the molecule. Sun and co-workers published reported a potential deep-blue TADF emitter named **DTPDDA** ( $\lambda_{max}$ : 444 nm; PLQY: 74%;  $\tau_d$ : 0.1, 2.3, 25.4 µs in 16wt% mCP:TSPO1;  $\Delta E_{ST}$ : 0.14 eV) containing the acceptor of triazine[106]. OLED device fabricated with **DTPDDA** (ITO/4wt%ReO<sub>3</sub>:mCP/mCP/16wt%emitter:mCP:TSPO1/ TSPO1/4wt%Rb<sub>2</sub>CO<sub>3</sub>:TSPO1/Al) showed deep blue emission according to CIE coordinates of (0.149, 0.197). Moreover, the highest value ever reported external quantum efficiency (EQE) of 22.3% for blue OLED with fluorescent emitter was achieved at that time.

Because of the longer Si–C bond, which reduces antibonding interactions between the two azasiline carbons linked to the silicon atom, the HOMO of the azasiline (5.57 eV) is lower than that of the carbon analog **DMAC-TRZ** (HOMO: 5.30 eV). The bandgap is increased by reducing the HOMO energy level, which leads to deep-blue emission[107].

In OLEDs, the external quantum efficiency (EQE) is a function of both IQE and the light out-coupling efficiency. Molecules emit generally the light in a perpendicular direction to their transition dipole moment (TDM). The light emitted from the device

can be reduced by up to 25% of the amount of light emitted from the emitter due to total internal reflection at the interface between the two electrodes and binding to surface plasmon polaritons (SPP) at the interface with the cathode. For this reason, designing horizontal orientation of the TDM of an emitter in a thin-film layer is an important strategy to enhance the amount of light exiting the device. Based on the these information, Lyn et al. investigated the relationship between structure and the tendency for the emitter to be horizontally oriented in a series of acridine-triazine derivatives [105]. Doped films of **DMAC-TRZ** ( $\lambda_{max}$ : 504 nm; PLQY:90 %;  $\tau_d$ : 1.9 µs in 12wt%mCPCN;  $\Delta E_{ST}$ : 0.06 eV), **DPAC-TRZ** ( $\lambda_{max}$ : 482 nm; PLQY: 82%;  $\tau_d$ : 2.9  $\mu$ s in 12wt%mCPCN;  $\Delta E_{ST}$ : 0.01 eV), and **SpiroAC-TRZ** ( $\lambda_{max}$ : 483 nm; PLQY: 100%;  $\tau_d$ : 2.1 µs in 12wt%mCPCN;  $\Delta E_{ST}$ : 0.07 eV) in mCPCN show orientations from isotropic to horizontal with anisotropy factor values of 0.28, 0.22, and 0.17, respectively. These results can be attributed to the positive effect that bulkier groups at the terminus of the molecule have on the orientation of the emitter. The OLED device fabricated with these emitters exhibited an EQE of 27.4% for DMAC-TRZ, 25.8% for DPAC-TRZ, and 36.7% for SpiroAC-TRZ with an of CIE coordinates of (0.21, 0.50), (0.17, 0.38), and (0.18, 0.43), respectively. Beyon's group and Kaji's group presented four carbazole-based emitters named CzTRZ, BCzTRZ, TCzTRZ[108], and DACT-II[100] by also using this strategy. Results showed that increasing the number of carbazoles made orientation more horizontal. DACT-II, which has the most carbazole units, aligned horizontally, and the OLED based on this emitter showed an EQE<sub>max</sub> of 29.6%. The indolocarbazole (ICz) is a donor unit that has a planar and rigid structure. It is easy to functionalize the two nitrogen atoms in the unit to have a horizontal orientation. Xiang et al. and Maeng et al. reported Ind-CzpTr1 and IndCzpTr2[109], and TRZ-TPDICz[97], respectively, containing ICz units because of its properties mentioned . These emitters showed high EQE<sub>max</sub> values of 14.5%, 30%, and 30.3%, due in part to their horizontal orientation. Zysman-Colman and co-workers presented the first example of a di-functionalized ICz-based A-D-A type TADF emitter, ICzTRZ. Addition of a second ICz unit leaded to an increased energy gap between HOMO and LUMO with a blue-shifted in the emission spectra. The sky-blue emitting OLED device showed a high-performance EQE<sub>max</sub> of 22.1%, and a luminance level reaching 7800  $cdm^{-2}$  (CIE = 0.17, 0.32)[110].

Komatsu and coworkers published three sky-blue emitters called **Ac–MPM** ( $\lambda_{max}$ : 489 nm; PLQY: 80%;  $\tau_d$ : 26.2 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.19 eV), **Ac–PPM** and **Ac–HPM** by altering the triazine acceptor with pyrimidine[111]. Devices with these three emitters were performed by small turn-on voltage (< 3.0V) among which **Ac-MPM** showed the most efficient double-emission-layer (DEML) device (ITO/TAPC/10wt%emitter:mCP/10wt%emitter:DPEPO/B3PyPB/LiF/Al) (B<sub>3</sub>PyPB = 1,3-bis(3,5-dipyrid-3-ylphenyl)benzene) with an EQE of 24.5% and CIE coordinates of (0.19, 0.37).

Diazatriphenylene (ATP) is an electron donor, has a high triplet energy level ( $E_T$ : 2.9 eV) which is essential for the design of blue TADF emitters. Adachi's group published D-A-D type TADF emitters **ATP-ACR** ( $\lambda_{max}$ : 492 nm; PLQY: 49% in 6wt%mCP;  $\Delta E_{ST}$ : 0.16 eV), **m-ATP-ACR** ( $\lambda_{max}$ : 483 nm; PLQY: 52% in 6wt%mCBP;  $\Delta E_{ST}$ : 0.13 eV), **m-ATP-CDP** ( $\lambda_{max}$ : 499 nm; PLQY: 77% in 6wt%mCP;  $\Delta E_{ST}$ : 0.13 eV), **m**-**ATP-PXZ** ( $\lambda_{max}$ : 524 nm; PLQY: 81% in 6 wt%mCP;  $\Delta E_{ST}$ : 0.04 eV), and **ATP-PXZ**  $(\lambda_{max}: 529 \text{ nm}; \text{PLQY}: 63\% \text{ in } 6 \text{ wt}\%\text{mCP}; \Delta E_{\text{ST}}: 0.09 \text{ eV})$ , containing various donor substituents such as phenoxazine (PXZ), 9,9-dimethylacridane (ACR), and 3-(diphenylamino)carbazole (CDP) at 6, 11- and 7,10-positions on ATP core[112]. The steric hindrance introduces twisting between the donor and acceptor units successfully separates with HOMO and LUMO, resulting in small  $\Delta E_{ST}$ . The lowest  $\Delta E_{ST}$  values were obtained with m-ATP-PXZ, and ATP-PXZ, due to the large dihedral angles (ca. 80-90°) between the ATP core and PXZ units. The device is based on m-ATP-ACR and **ATP-ACR** (ITO/α-NPD/mCP/6wt%emitter:mCPB/PPT/TPBi/LiF/Al) exhibited sky-blue emission with an EQE<sub>max</sub> of 8.7% and 7.5% and EL<sub>max</sub> at 486 nm and 496 nm, respectively. On the other hand, the device fabricated with m-ATP-PXZ and **ATP-PXZ** (ITO/α-NPD/mCP/6wt%emitter:CPB/TPBi/LiF/Al), where ACR (HOMO: -5.9 eV) is altered by the stronger donor PXZ (HOMO: -5.7 eV), showed green emission with an EQE<sub>max</sub> of 12.6% and 11.7% and EL<sub>max</sub> at 516 and 529 nm, respectively.

Liu et al. presented a novel TADF emitter namely **CPC** ( $\lambda$ max:  $\approx$ 500 nm; PLQY: 50%;  $\tau_d$ : 46.6 µs in 13wt%mCP;  $\Delta E_{ST}$ : 0.04 eV) by linking carbazole donor and pyridine-3,5-dicarbonitrile acceptor directly[113]. Sky-blue OLED device (ITO/TAPC/TCTA/13wt%emitter:mCP/TmPyPB/LiF/Al) showed a highly efficient EQE of 21.2% at CIE coordinates of (0.20, 0.35).

Aside from developing emitters with 100% IQE, the efficiency of the device may be increased by raising the light-outcoupling efficiency, which is commonly about 20% for conventional emitters. Mayr's group developed **CC2TA**, ( $\lambda_{max}$ : ~490 nm; PLQY: 62%;  $\tau_d$ : 22 µs in 6wt%DPEPO;  $\Delta E_{ST}$ : 0.06 eV)[103]. It has previously been proven that planar, long, linear molecules have favored horizontal orientations on the substrate owing to favorable intermolecular interactions with the host during film deposition. The horizontal positioning of emitters in the film optimizes the orientation of their transition dipole, improving light outcoupling[114]. The outcoupling efficiency of the CC2TA emitting layer was determined to be 31.3% and the device (ITO/ $\alpha$ -NPD/mCP/6wt%emitter:DPEPO/DPEPO/TPBi/LiF/Al) showed an EQE of 11% with EL<sub>max</sub> at 490 nm.

Li and his group evaluated two TADF emitters **26IPNDCz** ( $\lambda_{max}$ :  $\approx$ 490 nm; PLQY: 72%;  $\tau_d$ : 9.2 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.06 eV) and **35IPNDCz** ( $\lambda_{max}$ :  $\approx$ 500 nm; PLQY: 58%;  $\tau_d$ : 145 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.14 eV) to investigate the influence of the nitrile substituent location on the photophysical characteristics and device performance[115]. Because of the steric hindrance between the nitriles and the donor unit, the dihedral angle between the dicyanobenzene acceptor and the 3,3'-bicarbazolyl donor in **26IPNDCz** (69°) is higher than in **35IPNDCz** (50°) with ortho substitution. Therefore, a decreased exchange integral between the HOMO and the LUMO is realized in **26IPNDCz**, leading to lower  $\Delta E_{ST}$ , indicated by the significantly shorter delayed component lifetime (9.2 µs) than that of **35IPNDCz** (145 µs). In comparison to 35IPNDCz, the greater dihedral angle in 26IPNDCz reduces the conjugation length, resulting in a somewhat blue shifted emission. The devices (ITO/a-NPD/mCP/10wt%emitter:DPEPO/TPBi/LiF/Al) based on these two emitters showed blue-greenish emission (ELmax: 487 nm for 35IPNDCz and 501 nm for 26IPNDCz) with similar EQEs (9.2% for 35IPNDCz and 9.6% for 26IPNDCz). According to the authors, the significant identifying characteristic was the decreased efficiency roll-off observed in the device with 26IPNDCz because to its shorter triplet lifetime as a result of the faster RISC rate.

Park et al. proposed three potential TADF emitters (**DCN1–3**) for OLED applications[116]. Whereas TADF was observed in **DCN3** ( $\lambda_{max}$ : 482 nm; PLQY: 49%;  $\tau_d$ : 3.26 µs in toluene;  $\Delta E_{ST}$ : 0.13 eV), **DCN1** and **DCN2** did not show any TADF properties. This was explained by the larger  $\Delta E_{ST}$  values of **DCN1** and **DCN2**. Although a plausible assertion, no experimental  $\Delta E_{ST}$  values were given in the report. Because the molecular scaffolds of both compounds are nearly identical, the occur of TADF should be due to the larger spacing of the HOMO to the peripheral carbazoles in **DCN3** compared to the isophthalonitrile-localized LUMO.

Two solution-processable blue emitters **3CzFCN** ( $\lambda_{max}$ :  $\approx$ 440 nm; PLQY: 74%;  $\tau_d$ : 28 µs in 10wt%diphenyldi(4-(9-carbazolyl)phenyl)silane (**SiCz**);  $\Delta E_{ST}$ : 0.06 eV) and **4CzFCN** ( $\lambda_{max}$ :  $\approx$ 460 nm; PLQY: 100%;  $\tau_d$ : 17 µs in 10wt%SiCz;  $\Delta E_{ST}$ : 0.06 eV) were reported by Cho et al.[117]. The introduction of fluorine atoms in these emitters enhanced hydrophobicity and solubility in aromatic solvents such as toluene. Furthermore, blueshift emission was observed due to the weaker electron-withdrawing ability of fluorine compared to nitrile. The solution-processed OLED (ITO/PEDOT:PSS/PVK/15wt%emitter:SiCz/TPBI/LiF/Al) based on **4CzFCN** as an emitter showed a particularly high EQE of 20.0% with CIE coordinates of (0.16, 0.26).

Phosphine oxides can behave as weak acceptors for achieving blue TADF emitters, according to Duan et al. the three emitters' photophysical and electrochemical characteristics were found to be nearly identical[118]. However, as compared to the mono- and disubstituted analogs ( $\Delta E_{ST}$ : 0.26 eV and 0.19 eV, respectively), the triply substituted **TPXZPO** maximizes the ICT character and so has the shortest  $\Delta E_{ST}$  ( $\Delta E_{ST}$ : 0.26 eV). OLED (ITO/MoO<sub>3</sub>/NPB/mCP/10wt%emitter:DPEPO/DPEPO/Bphen/LiF/Al) (Bphen = 4,7-diphenyl-1,10-phenanthroline) fabricated with **TPXZPO** as the emitter exhibited slightly blueshifted  $\lambda_{EL}$  at 464 nm, 100% exciton utilization efficiency, and an EQE of 15.3% with CIE coordinates of (0.17, 0.20).

Using spiro structures for designing TADF emitters would be promising owing to its orthogonally connected  $\pi$ -conjugated system. Two TADF emitters, **A-AF** and **DPAA-AF** ( $\lambda_{max}$ :  $\approx$ 500 nm; PLQY: 70%;  $\tau_d$ : 4.3 µs in 6wt%mCP;  $\Delta E_{ST}$ : 0.02 eV) contains acridane or bis(diphenylamino)acridane as a donor and diazafluorene unit as an acceptor were reported by Adachi's group in 2014[119]. Whereas **A-AF** containing

acridane did TADF not show properties, **DPAA-AF** with bis(diphenylamino)acridaneas the donor showed TADF because of small overlap between the HOMO and LUMO thanks to additional peripheral diphenylamine units. A blue-green OLED device fabricated with **DPAA-AF** as the emitter (ITO/ $\alpha$ -NPD/mCP/6wt%emitter:mCP/PPT/TPBi/LiF/Al) showed an EQE of 9.6% with  $\lambda_{EL}$  at 499 nm. The same group published another TADF emitter **ACRSA** ( $\lambda_{max}$ :  $\approx$ 500 nm; PLQY: 81%;  $\tau_d$ : 5.3 µs in 20wt%DPEPO;  $\Delta E_{ST}$ : 0.03 eV), based on the spiroanthracenone. OLED device performed a blue-greenish device (ITO/a-NPD/mCP/20wt%emitter:DPEPO/ DPEPO/TPBi/LiF/Al) with an EQE of 16.5% and EL<sub>max</sub> at  $\approx$ 500 nm[120].

In 2018, Adachi et al. published a series of novel TADF emitters containing substituted carbazoles as donor and benzonitrile as acceptor named **DCzBN1** ( $\lambda_{max}$ : 403 nm; PLQY: 28%;  $\tau_d$ : 18 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.31 eV), **DCzBN2** ( $\lambda_{max}$ : 417 nm; PLQY: 66%;  $\tau_d$ : 11.2 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.22 eV), **DCzBN3** ( $\lambda_{max}$ : 414 nm; PLQY: 76%;  $\tau_d$ : 13.5 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.26 eV), **DCzBN4** ( $\lambda_{max}$ : 460 nm; PLQY: 86%;  $\tau_d$ : 5.5 µs in 10wt%DPEPO;  $\Delta E_{ST}$ : 0.14 eV)[121]. The highest EQE was achieved, without sacrificing the color purity, with the OLED fabricated with **DCzBN3**, having di-*tert*-butylcarbazo units, which was the first deep-blue TADF OLED with a y-coordinate below (0.07) with an EQE of 10.3% and EL<sub>max</sub> at 428 nm with CIE coordinates of (0.16, 0.06).

In 2019, Cheng's group published two novel sky-blue TADF emitters **246tCzPPC**, **26tCzPPC**, and **35tCzPPC**. OLED device based on **246tCzPPC** exhibited an EQE of 29.6% and EL<sub>max</sub> at 491 nm with CIE coordinates of (0.18, 0.40)[122].

The same year, Kido et al. presented a series of imidazole-based TADF emitters named **Ac-BIP**, **PXZ-BIP**, and **PXZ-IP** containing acridine and phenoxsazine as a donor moiety. OLED device (ITO/triphenylamine-containing polymer: PPBI/TAPC/10wt% emitter:mCP/10wt% PXZ-BIP-dopedDPEPO/B3PyPB/LiF/Al) based on **PXZ-BIP** performed with an EQE<sub>max</sub> of 20.1%, and EL<sub>max</sub> at 497 nm, with CIE coordinates of (0.22, 0.42)[123] . Unfortunately, the PXZ-BIP-based device showed greenish-blue emission. To obtain blue emission, a double emission layer (DEML) device was fabricated using mCP and DPEPO as a host material. The DEML device exhibited sky-blue emission with an EQE<sub>max</sub> of 21.0% with CIE coordinates of

(0.21, 0.37). OLED devices fabricated with **Ac-BIP** and **PXZ-IP** exhibited deep-blue emission with the CIE coordinates of (0.16, 0.10) and (0.19, 0.30) and an EQE<sub>max</sub> of 2.6% and 5.9%, respectively. The high-efficiency roll-off was observed at the high brightness owing to the long-delayed fluorescent lifetime ( $\approx$ 140 µs) leading to triplet-triplet annihilation (TTA). The authors showed that imidazole has great potential for designing blue TADF emitters.

 $\Phi_{out}$ , which is an optical out-coupling efficiency is one of the factors affecting EQE. Although this value is usually lower than 25% for traditional planar OLEDs with isotropically oriented emitters, it is possible to be upgraded to over 45% with an entirely horizontal emitting dipole orientation. Yang et al. published the blue TADF emitters **SBA2DPS**  $\lambda_{max}$ : 459 nm; PLQY: 60%;  $\tau_d$ : 4.3 µs in 30wt%DPEPO;  $\Delta E_{ST}$ : 0.09 eV), and **DMAC-1DPS** ( $\lambda_{max}$ : 468 nm; PLQY: 61%;  $\tau_d$ : 4.2 µs in 30wt%DPEPO;  $\Delta E_{\rm ST}$ : 0.07 eV), contain diphenyl sulfone (DPS) as an electron acceptor unit and spirobiacridine (SBA) as an electron donor. which performed in the respective OLED with an EQE of 25.5%, and EL wavelength of 467 nm, and CIE coordinates of (0.15, 0.20)[124]. They introduced a spiro-linked double D–A molecular architecture for TADF emitters. It was demonstrated that the molecular length of **SBA2DPS**  $(\Theta_1$ : 59%) was remarkably elongated without extending the  $\pi$ -conjugation compared to **DMAC-1DPS (Θ⊨** 87%). Consequently, **OLEDs** (ITO/MoO3/TAPC/mCP/DPEPO:30wt%SBA-2DPS/3TPYMB/LiF/Al) based on SBA2DPS and DMAC-1DPS emitters exhibited blue emission with CIE coordinates of (0.15, 0.20) and (0.16, 0.26), and a high EQE<sub>max</sub> of 25.5% ( $\lambda_{EL}$ : 467) and EQE<sub>max</sub> of 17.4% (λ<sub>EL</sub>: 477).

In 2020, Tang and co-workers published two pairs of blue TADF isomer emitters based on benzonitrile derivatives[125]. These emitters contain both 3,6-di-*tert*butylcarbazole and carbazole as donor units however arranged differently. Solutionprocessed non-doped OLEDs based on blue TADF emitters, exhibiting the external quantum efficiencies (EQEs) of 25.8%, 24.5%, 19.5%, and 19.1% for 2Cz2tCzBn, 2tCz2CzBn, 2PhCz2tCzBn, and 2tCz2PhCzBn, respectively. The OLED device with 2tCZ<sub>2</sub>CzBn showed a high EQE of 24.5%, and EL<sub>max</sub> at 472 nm, with CIE coordinates of (0.16, 0.24). Recently, Lee et al. published to increase the solubility of the ICz and make it possible for solution process application[126]. *Tert*-butyl and *n*-hexyl were chosen as an alkyl chain to investigate the effect on solubility and materials properties and obtained **tBuICzCz**, **tBuICzPCz** or **HexICzCz** and **HexICzPCz** emitters. Derivatives with hexyl alkyl chains showed better solubility compared to *tert*-butyl. Further, the alkyl chains increased the electrochemical stability by preventing oligomerization. FIrPic was used as a dopant and emitters were used as a host to achieve blue OLED devices. Unfortunately, devices with emitters showed lower brightness and EQE<sub>max</sub> (between 2.26-4.90%) but high-efficiency roll-off, which could be due to the distinct alkyl chains forming different films.

Lee et al. obtained an even higher EQE of 30.4% in an OLED based on the TADF emitter **PhICzDPA**[127]. The device exhibited a sky-blue emission at 482 nm (CIE: 0.13, 0.32) owing to the strong character of the diphenylamine donor.

# Chapter 2

# Thermally Activated Delayed Fluorescence

There are two viable mechanisms for up-conversion from a triplet excited state to a singlet excited state. One possible pathway is up-conversion via triplet-triplet annihilation (TTA) [128]. Although the TTA process is typically unfavorable in phosphorescence-based devices, it can improve EL efficiency in fluorescence-based devices by producing singlet excitons. Depending on the up-conversion process, this extra singlet exciton formation can boost efficiency by 15% to 37.5% [129]. As a result, the maximum internal EL efficiency can be increased by up to  $\Phi_{EL(int)}$  =40% or 62.5%, however this will not result in total EL efficiency. Second possible mechanism is TADF [130], which converts triplet excitons into singlet excited states via reverse intersystem crossing by collecting environmental thermal energy. This eventuates in delayed fluorescence, which could lead to total EL efficiency if the conversion efficiency is 100%. If the conversion efficiency is 100%, this results in delayed fluorescence, which might lead to total EL efficiency.

### 2.1 Thermally Activated Delayed Fluorescence (TADF) Mechanism

Adachi et al. have suggested possible mechanisms to obtain harvesting both singlet and triplet states and prevention triplet annihilation by using thermally activated delayed fluorescence (TADF) as given in Figure 2.1 [131]. For TADF materials, heat increases the reverse intersystem crossing (RISC) from a triplet excited state ( $T_1$ ) to a singlet excited state ( $S_1$ ), thus causing a rise in fluorescence intensity. According to this principle, when TADFs are used in OLEDs, increasing the temperature accelerates reverse ISC, and in this way makes it possible to obtain OLEDs with high EL efficiency, even with a fluorescence decomposition rate.



Figure 2.1: Energy relaxation pathways in an organic system

# 2.2 Multi Resonant Thermally Activated Delayed Fluorescence (MR-TADF) Emitters

In conventional TADF molecular design, while the wave functions of the HOMO and LUMO must be spatially well separated to obtain small  $\Delta E_{ST}$ , high HOMO and LUMO overlap is needed for high PLQY. Although D-A linkage helps to overcome this contradiction, it leads to increased structural relaxation in excited states. Another problem about this type of TADF emitter is having a broad emission with a typical full-width at half-maximum (FWHM) of 80-100 nm because of their charge transfer (CT) characteristic [132], results in poor color purity and increased nonradiative decay rates [133], [134].

Hatakeyama et al. suggested a new design planar boron- and oxygen (or nitrogen)containing polycyclic aromatic structures [75]. This new design, called multiple resonance thermally activated delayed fluorescence (MR-TADF), is an alternative to the traditional donor-acceptor strategy for triplet energy control. Their design included resonance effects of the electron-donating oxygen atom (donor) and electrondeficient boron (acceptor) fragment linked into para position each other. This resonance effect balances the electron density distributions on the HOMO and LUMO orbitals by one atom. The electron-rich moieties are mainly localized on the donor atoms and carbon atoms positioned ortho and para to them, whereas the electrondeficient moieties are localized on the acceptor atoms and the carbon atoms positioned ortho and para to them. The electron-rich moieties are mainly located at the donor atoms and carbon atoms in the ortho and para position to them, whereas the electrondeficient moieties are localized to the acceptor atoms and the carbon atoms are localized to them in the ortho and para positions. In the lowest singlet and triplet excited states, the electron density distribution is delocalized over the area but with alternate electron-rich and electron-poor regions, whereas in the ground state, the electron-density distribution shows the same alternating pattern but with electron-rich and electron-poor areas switched. As a result, the transition from S1 to S0 allows for short-range rearrangement of electron density whereas, more importantly, it provides a high degree of electron-hole overlap. Franck-Condon excitations exhibit high oscillator strength, analogous to locally excited (LE) states, providing both efficient delayed fluorescence and high  $\Phi_{PL}$  in MR-TADF molecules. As a result, the MR-TADF design combines short-range charge density reshuffling, which minimizes singlet-triplet gap, and long-range interactions and delocalization effects, providing high radiative decay rates.

The first MR-TADF molecule reported, **DABOA** (original name is **2a**), was synthesized by the one-step borylation method. **DABOA** has a small  $\Delta E_{ST}$  with 0.15 eV and a high photoluminescence quantum yield,  $\Phi_{PL}$ , with %72 in 1wt % poly(methyl methylacrylate) (PMMA) thin film. There was no device fabrication as the emission maximum value,  $\lambda_{PL}$  is very high in energy at 399 nm in this report[135]. After first report, MR-TADF molecules have got attention.

MR-TADF materials have significant properties that differ from those of traditional TADF materials [43,136]:

- They have a slightly helical and rigid structure, and bathochromic emission caused by aggregation in the pure solid [137].
- They show weak intramolecular charge transfer (CT), with a lowest-lying localized electronic state (LE) of ππ\* character with high radiative rate constants [138]. As a result, their emission shows a high radiative decay time, a small Stokes shift, and a narrow FWHM due to the suppression of vibronic coupling.
- When connected with a strong donor moiety, the core unit has an remarkably short donor (D)/acceptor (A) spatial separation and can convert into an efficient acceptor [138–140].
- Although they possess an optically allowed  $\pi\pi^*$  transition character, the high HOMO–LUMO separation reduces the  $\Delta E_{ST}$ . In contrast to conventional TADF molecules, most MR-TADF molecules, whether in degassed solution or in a solid matrix such as polystyrene, only have a short (nano-second) single-exponential decay component with no TADF property. This property is usually not indicated in the main text of publications but may be seen in the supplemental material [133], [139], [141].
- According to theoretical calculations, all MR-TADF molecules have the same ππ\* character configurations in both S1 and T1 states, with S1→ S0 being an optically permitted process but S1↔ T1 intersystem crossing (ISC) and reverse intersystem crossing (RISC) being inefficient [142].
- Interestingly, when these MR-TADF compounds are doped in an appropriate host film, such as DABNA-1 in mCBP (3,3'-di(9H-carbazol-9-yl)-1,1'-biphenyl)1and QAO in mCP, the TADF properties appear (N,N-dicarbazolyl-3,5-benzene), leading to show good to excellent organic light-emitting diode (OLED) performance [139].

### 2.2.1 Green MR-TADF Emitters

The first green OLEDs containing MR-TADF compounds reported in 2015[135]. In this report MR-TADF molecule **2c** ( $\lambda_{max}$ : 457 nm; PLQY: 60% in ethanol;  $\Delta E_{ST}$ : 0.31 eV) and **2d** ( $\lambda_{max}$ : 459 nm; PLQY: 57% in ethanol;  $\Delta E_{ST}$ : 0.14 eV) used as a host and **2e** ( $\lambda_{max}$ : 477 nm; PLQY: 92% in 1wt%PMMA;  $\Delta E_{ST}$ : 0.06 eV) used a dopant. Despite the short device lifetimes (less than 1 hour) based on dopant **2e**, the EQE<sub>1000</sub> values were 15.2 and 13.9 %, respectively, showing a significant TADF impact. Devices

containing 2c and 2d as a dopant showed superior performance with a EQE<sub>1000</sub> of 20.1% and 20.6% respectively.



Figure 2.2: Molecular structure of 2c, 2d, 2e, OAB-ABP-1, 2PXZBN and 2PTZBN emitters

First series of green MR-TADF emitters, **2F-BN** (λ<sub>max</sub>: 502 nm; PLQY: 88.7%; τ<sub>d</sub>: 25.9 μs in 6wt%mCPBC; Δ*E*<sub>ST</sub>: 0.16 eV), **3F-BN** (λ<sub>max</sub>: 503 nm; PLQY: 83.4%; τ<sub>d</sub>: 16.7 µs in 6wt%mCPBC;  $\Delta E_{ST}$ : 0.08 eV), and **4F-BN** ( $\lambda_{max}$ : 501 nm; PLQY: 91.4%;  $\tau_d$ : 19.0 µs in 6wt%mCPBC;  $\Delta E_{ST}$ : 0.11 eV), with an extended  $\pi$ -conjugation by altering diphenylamine groups with *tert*-butyl carbazole were reported by Duan's group in 2019[143]. The addition of the fluorobenzene units incites a charge transfer character to the HOMO-LUMO transition. The optimized concentration of the emitter for the device fabrication was found to be 9wt% for 2F-BN and 6wt% for 3F-BN and **4F-BN**. The emitters showed great device performances, with  $EQE_{max}$  (PE<sub>max</sub>) values of 22.0 (69.8 lmW<sup>-1</sup>), 22.7 (72.3 lmW<sup>-1</sup>), and 20.9% (51.3 lmW<sup>-1</sup>) for **2F-BN**, **3F-**BN, and 4F-BN, respectively. The OLED device fabricated with 2F-BN showed a fascinating CIE<sub>y</sub> coordinate of 0.60, which is a real development to obtaining MR-TADF compounds which have green emissions. OLEDs based on each of all emitters exhibited low efficiency roll-off. The EQE $_{1000}$  and OLEDs lifetimes at luminescence of 2000 cdm<sup>-2</sup> were presented to be 15.0%, 21.1%, 16.4% and 45.76, 15.53, 10.35 h for 2F-BN, 3FBN, and 4F-BN, respectively.

Hatekayama and co-workers presented a novel MR-TADF emitter namely **OAB-ABP-1** ( $\lambda_{max}$ : 535 nm; PLQY: 90%;  $\tau_d$ : 32 µs in 1wt%PMMA;  $\Delta E_{ST}$ : 0.12 eV) which has extended  $\pi$ -skeleton containing of both ADBNA and DOBNA together (Figure 14)[132]. The solution-processed pure green OLED devices based on **OAB-ABP-1** showed EQE<sub>max</sub> of range between 19.4% and 21.8% ( $\lambda_{EL}$ = 505 nm) depending on the concentration of doping concentration of emitter. These pure green OLEDs represent the first solution-processed OLED combining high color purity and efficiency.



Figure 2.3: Molecular structure of fused borane/amine type green emitters

Duan et al. used a new design strategy namely hybridized multi-resonance and charge transfer (HMCT) which is a promising candidate for narrowband emitters with feasible color tunability [144]. The reported MR-TADF emitter **AZA-BN** ( $\lambda_{max}$ : 522 nm; PLQY: 94%;  $\tau_d$ : 0.16µs in toluene;  $\Delta E_{ST}$ : 0.18 eV) derived from fused aza framework. They used fused aza-aromatics because of having several numbers of fascinating features of  $\pi$ -systems, like easy electron injection, stable electron transport, ability of strong electron accepting, a high triplet state, and facilitated n-type doping. OLED device based on **AZA-BN** exhibited an EQE<sub>max</sub> of 28.2% with CIE coordinates of (0.27, 0.69) which represents the purest green emission ever reported in OLEDs.

Wang et al. proposed another design strategy contains based on frontier molecular orbital engineering (FMOE)[145]. The reported emitter *m*-Cz-BNCz ( $\lambda_{max}$ : 519 nm; PLQY: 97% in toluene;  $\Delta E_{ST}$ : 0.08eV) exhibited both twisted D–A and MR structure properties by introducing an auxiliary donor to a MR core meta position. Ultrapure green OLED devices employing different concentration of *m*-Cz-BNCz showed high EQE<sub>max</sub> range between 26.8% and 31.4% ( $\lambda_{EL} \sim nm 524$ ).

Yasuda et al. reported a series of MR-TADF emitters based on versatile boron- and carbazole-embedded polycyclic aromatic hydrocarbons (PAHs) [146]. The effects of the location and numbers of boron and nitrogen atoms were investigated on the photophysical characteristics. OLED devices based on **BBCz-G** (3) ( $\lambda_{max}$ : 519 nm; PLQY: 99%;  $\tau_d$ : 13µs in 2wt%mCBP;  $\Delta E_{ST}$ : 0.14 eV) and **BBCz-Y** (4) ( $\lambda_{max}$ : 549 nm;

PLQY: 90%;  $\tau_d$ : 11 µs in 2wt%mCBP;  $\Delta E_{ST}$ : 0.14 eV) emitters exhibited green and yellow emission with a EQE<sub>max</sub> of 31.8% and 29.3%, respectively.

Bis(di(t-butyl)carbazolyl)phenylene was used as a parent skeleton to construct B–N consist of a compound **DtBuCzB** ( $\lambda_{max}$ : 481 nm; PLQY: 91%;  $\tau_d$ : 68.8µs in 1 wt% mCBP;  $\Delta E_{ST}$ : 0.13 eV) (another name **BCzBN**) with a large and rigid  $\pi$ -conjugated core skeleton for designing first green MR-TADF emitters. To further red shift the emission to the green region, conjugation was increased through introducing four C<sub>6</sub>H<sub>4</sub> groups to the carbazolyl moieties, and narrowband green emitter **DtBuPhCzB** ( $\lambda_{max}$ : 496 nm; PLQY: 97%;  $\tau_d$ : 61.3µs in 1wt%mCBP;  $\Delta E_{ST}$ : 0.10 eV) was synthesized by Wang's group[147]. OLED devices based on **DtBuCzB** and **DtBuPhCzB** exhibited bluish green and green emission with a EQE<sub>max</sub> of 21.6% ( $\lambda_{EL}$  = 488 nm) and 23.4% ( $\lambda_{EL}$  = 504 nm) with CIE coordinates of (0.10, 0.42) and (0.15, 0.61), respectively.

Yang et al. presented two novel MR-TADF emitters, 2PXZBN and 2PTZBN, containing sulfur atoms to enhance the SOC[148]. 2PXZBN and 2PTZBN exhibited sharp absorption/emission bands at 475/504 and 471/510 nm in diluted toluene solution, respectively. 2PTZBN has a larger stokes shift (29 nm) which can be ascribed to its lower rigid structure because of having a larger size of S atom instead of O atom in its structure compared to **2PXZBN**. The  $\Delta E_{ST}$  values of emitters were calculated from the onset of fluorescence and phosphorescence spectra as 0.19 and 0.15 eV for **2PXZBN** and **2PTZBN**, respectively. The photoluminescence quantum yields (PLQYs) were obtained to be 78.0% for 2PXZBN and 58.0% for 2PTZBN in toluene solutions. The emission maxima of the devices with **2PXZBN** and **2PTZBN** were found to be 522 nm (CIE = 0.28, 0.64) and 527 nm (CIE = 0.28, 0.65), with FWHM of 60 and 58 nm, respectively. The OLED devices with emitters exhibited an EQE<sub>max</sub> of 17.7% for **2PXZBN** and 25.5% for **2PTZBN**. The device with **2PTZBN** showed a 44% improvement of EQE<sub>max</sub> compared to one with **2PXZBN** which was represented one of the highest EQE values in all the green MR-TADF OLEDs. The EQEs at the luminance of 100 cd m<sup>-2</sup> for devices showed 15.3% for 2PXZBN and 21.7% for **2PTZBN** respectively, both having a moderate roll-off of 14%. From the obtained results, it authors deduced that the efficient RISC process that takes advantage of the heavy atom effect (HAE) of sulfur atoms can improve device performance.

Recently, Hatekayama's group reported **CzB2-M/TB** ( $\lambda_{max}$ : 504 nm; PLQY: 87%;  $\tau_d$ : 24 µs in 1wt%PMMA;  $\Delta E_{ST}$ : 0.06 eV) derived from carbazole based DABNA analog[149]. The OLED device employing **CzB2-M/TB** displayed green emission with a high EQE<sub>max</sub> of 26.7%,  $\lambda_{EL}$  at 497 nm and CIE coordinates of (0.12, 0.57).

#### 2.2.2 Orange-Red MR-TADF Emitters

MR-TADF materials are fundamentally challenging to achieve red-shifted emission due to their solid heterocyclic structure, so such materials have developed in blue region emission colors.

In the report of Yasuda's group, MR-TADF emitter **BBCz-R** (5) ( $\lambda_{max}$ : 615 nm; PLQY: 79%;  $\tau_d$ : 53 µs in 2wt%mCBP;  $\Delta E_{ST}$ : 0.19 eV) was obtained by the adding the two para-disposed boron atoms and two nitrogen atoms in the central  $\pi$ -core[146]. Para B- $\pi$ -B and N- $\pi$ -N significantly increase the acceptor and donor strengths, respectively, resulting in large bathochromic shifts both absorption and emission bands. OLED device employing emitter **BBCz-R** (5) showed a high EQE<sub>max</sub> of 22.0%.

Lately, You et al. proposed that functionalization with cyano (CN) provides red-shifted emission while maintaining high color purity in the MR-TADF skeleton[150]. The electron-withdrawing CN group not only restricts structure relaxation with its coplanar conformation, which is needed for a small FWHM required for high color purity but also lowers the LUMO energy level and shifts the emission to red. Based on this strategy, **CNCz-BNCz** and **CN-BCz-BN** molecules were designed from their parent molecules **BCz-BN** and **BBCz-Y**. Introducing the CN group provided red-shifted emission of 15 nm and 32 nm with a small FWHM of 21 nm and 42 nm for **CN-BCz-BN** and **CNCz-BNCz**, respectively. **CNCz-BNCz** is the first example of an orangered MR-TADF emitter which showed a narrowband emission with  $\Phi_{PL}$  of 90%. The OLED fabricated with **CNCz-BNCz** achieved remarkable EQE<sub>max</sub> of 23.0% with CIE coordinates of (0.55, 0.45) and an FWHM of 49 nm.


Figure 2.4: Molecular structure of red MR-TADF emitters; BBCz-R and CNCz-BNCz

#### 2.2.3 Blue MR-TADF Emitters

This part, blue MT-TADF emitters are divided into three categories: I) fused borane/amine (B/N) II) fused borane/oxygen (B/O) III) fused amine/carbonyl

#### 2.2.3.1 Fused Borane/oxygen (B/O) type blue MR-TADF emitters

Wang and co-workers proposed a novel molecular design containing boron and sulfurdoped rigid aromatic framework [151]. S atoms play an important role in reducing the energy band gap to shift the emission from the ultraviolet region to the blue region and improving spin-orbital coupling (SOC) via the heavy atom effect, which supports the RISC process [152]. The reported compounds, **BOO**, **BOS**, and **BSS** exhibited absorption bands at 378, 408, and 431 nm, and emission bands at 396, 434, and 457 nm respectively. three emitters showed narrowband PL spectra, with FWHMs of 30, 29, and 27 nm for **BOO**, **BOS**, and **BSS** respectively. **BOO** showed ultraviolet emission whereas, **BOS** and **BSS** showed red-shifted emission in the blue region. As expected, the emission was blue-shifted thanks to replacing the oxygen atom with a sulfur atom. The  $\Delta E_{STS}$  of the emitters were calculated from their fluorescence and phosphorescence spectra and found to be 0.18, 0.17, and 0.15 eV for **BOO**, **BOS**, and **BSS**, respectively. The OLED device performances presented in this report are derived from the polymers of these emitters. The presented polymer containing emitters and acridan as host exhibited ultrapure blue electroluminescence with FWHM of 31 nm with an EQE<sub>max</sub> of 13%, which was the first ultrapure TADF polymer with narrowband electroluminescence until now.



Figure 2.5: Molecular structure of Fused Borane/oxygen (B/O) type blue MR-TADF emitters

#### 2.2.3.2 Fused Borane/amine (B/N) type blue MR-TADF emitters

Hatakeyama's group altered their design by changing the oxygen atoms for tricoordinate nitrogen atom that is link phenyl to para position to center boron atom in 2016 [133]. The nitrogen atom which is more basic than the oxygen atom led to red-shifted emission in these compounds. Two emitters, **DABNA-1** ( $\lambda_{max}$ : 460 nm; PLQY: 88%;  $\tau_d$ : 8.8 µs in 1wt%mCBP;  $\Delta E_{ST}$ : 0.18 eV) and **DABNA-2** ( $\lambda_{max}$ : 469 nm; PLQY:

90%;  $\tau_d$ : 6.0 µs in 1wt%mCPB;  $\Delta E_{ST}$ : 0.14 eV) were presented in this report. These compounds have a rigid polycyclic structure, which is in the para position concerning each other that can considerably separate the HOMO and LUMO without needing donor or acceptor units. The main differences between these are an additional diphenyl amine group and two phenyl groups. The maximum external quantum efficiencies (EQE<sub>max</sub>) of OLED devices fabricated with these emitters were reported as 13.2% and 20.2%, respectively.



Figure 2.6: Molecular structure of fused borane/amine type blue emitters

Lee and co-workers modified DABNA-1 with tert-butyl groups located para position to the nitrogen atoms and presented *t*-DABNA ( $\lambda_{max}$ : ~470 nm; PLQY: 85%;  $\tau_d$ : 83.3 µs 5wt%DPEPO;  $\Delta E_{ST}$ : 0.17 eV) molecule[153]. With the addition of tert-butyl

groups, it was aimed to decrease intermolecular interactions in the emissive layer and reduce quenching caused by aggregation that is usually observed in thin films at high doping concentrations. The *t*-DABNA showed almost same photophysical properties to DABNA-1, but with an expected redshift of 5 nm at maximum emission. The  $\Delta E_{ST}$  is smaller for *t*-DABNA (0.17 eV) compared to parent DABNA-1 (0.19 eV). The devices were fabricated with *t*-DABNA doped in DPEPO as the host. At 5wt% emitter concentrations, the OLEDs with *t*-DABNA and DABNA-1 showed EQE<sub>max</sub> of 25.1% and 18.7%, respectively. The enhanced performance of *t*-DABNA was attributed to its higher  $\Phi_{PL}$  and decreased intermolecular interactions. Unfortunately, the two devices, both exhibited serious efficiency roll-off and poor device stability, which were ascribed to the long-delayed fluorescence lifetimes.

Hatakeyama and co-workers designed a novel polycyclic structure *v*-DABNA ( $\lambda_{max}$ : 467 nm; PLQY: 90%;  $\tau_d$ : 4.1 µs in 1wt%DOBNA-O-Ar;  $\Delta E_{ST}$ : 0.017 eV; FWHM: 18nm) containing five benzene rings linked to two boron atoms and four nitrogen atoms and two diphenylamino groups[154]. *v*-DABNA exhibited an extremely sharp photoluminescence band in toluene (FWHM = 14 nm) which is the narrowest one among the MR-TADF emitters reported until now. This result was associated with the bonding/anti-bonding character minimizes because of the induces in localization of HOMO and LUMO on different atoms, and the vibronic coupling and vibration relaxation of the resulting non-bonding molecular orbitals (MOs) minimizes. The excellent efficiencies of 34.4% at the maximum (15 cdm<sup>-2</sup>), 32.8% at 100 cdm<sup>-2</sup>, and 26.0% at 1,000 cd m<sup>-2</sup> were achieved with the device fabricated with *v*-DABNA, which were the best performance among the blue OLEDs until now [153-156]. These results have shed light on a new strategy for the development of narrowband organic emitters, as well as significantly improving the performance of displays.

In 2018, Huang et al. changed the structure of **DABNA-1** by introducing a carbazole moiety para position to the boron acceptor (**TBN-TPA**) to enhance the device efficiency[154]. The photoluminescence spectrum of **TBN-TPA** in toluene was redshifted by 20 nm compared to **DABNA-1**, with an FWHM of 26 nm. The high oscillator strength with the low  $\Delta E_{ST}$  gave a high  $\Phi_{PL}$  of 97% in the toluene solution. The  $\Delta E_{ST}$  was found to be 0.14 eV from the onset of the fluorescence and phosphorescence spectra in toluene. The prompt and delayed lifetimes of **TBN-TPA**  doped in 2,6-bis[3-(9H-carbazol-9-yl)phenyl]pyridine) (2,6-DCzPPy) were found to be 6.01 ns and 51.02  $\mu$ s, respectively. At 100 cd m<sup>-2</sup>, the device fabricated with **TBN-TPA** showed effective efficiency values of EQE, CE, and PE of 27.4%, 34.4 cd A<sup>-1</sup>, and 23.5 lmW<sup>-1</sup>, respectively.

Same year, Hatakeyama's group presented three molecules, **B2** ( $\lambda_{max}$ : 455 nm; PLQY: 53%;  $\tau_d$ : 30.4µs in 1wt%PMMA;  $\Delta E_{ST}$ : 0.17 eV), **B3** ( $\lambda_{max}$ : 441 nm; PLQY: 33% in 1wt%PMMA;  $\Delta E_{ST}$ : 0.17 eV), and **B4** ( $\lambda_{max}$ : 450 nm; PLQY: 57% in 1wt%PMMA;  $\Delta E_{\text{ST}}$ : 0.24 eV), which were synthesized by a simplified borylation reaction [156]. The absorption spectra of emitters in 1wt%PMMA showed a maximum of 438 nm, 437 nm, 396 nm, and 440 nm for B2, B2-F, B3, and B4, respectively. All compounds showed narrow blue emission at  $\lambda_{PL}$  of 455, 467, 441, and 450 nm for **B2**, **B2-F**, **B3**, and **B4**, respectively. **B2** emitter showed the smallest FWHM of 32 nm ( $\lambda_{PL} = 455$  nm); by introducing with fluorine atoms, **B2-F**, showed the broadener emission band with an FWHM of 44 nm and redshifted by 17 nm. The bluest emitter, **B3**, showed the lowest  $\Phi_{PL}$  of 33% among them. The  $\Delta E_{ST}$  values were reported ranging from 0.15 to 0.19 eV according to the energy difference between fluorescence (RT) and phosphorescence spectra (at 77K). The CIE coordinates of **B2** and **B3** were (0.14, 0.08) and (0.15, 0.06), respectively. The OLED device fabricated based on a B2 emitter showed deep blue emission (CIE = 0.13, 0.11) with EQE<sub>max</sub> of 18.3% at 1 cd m<sup>-2</sup>. The EL spectrum exhibited a redshifted of 5 nm with an FWHM = 37 nm compared to the PL spectrum. The  $\eta c$  and  $\eta p$  were calculated to be 11.5 cd A<sup>-1</sup> and 7.1 lm W<sup>-1</sup> at 100  $cd m^{-2}$ .

In 2019, Hatakeyama's group presented two novel emitters named **ADBNA-Me-Mes** ( $\lambda_{max}$ : 482 nm; PLQY: 89%;  $\tau_d$ : 165 µs in 1wt% 7-((2'-methyl-[1,1'-biphenyl]-3-yl)oxy)-3,11-di-o-tolyl-5,9-dioxa-13b-boranaphtho[3,2,1-de]- anthracene (DOBNA-OAr);  $\Delta E_{ST}$ : 0.18 eV) and **ADBNA-Me-Tip** ( $\lambda_{max}$ : 479 nm; PLQY: 88%;  $\tau_d$ : 147 µs in 1 wt% (DOBNA-OAr);  $\Delta E_{ST}$ : 0.18 eV)[155]. The fluorescence and phosphorescence spectra of the two emitters showed a maximum at 482 nm and 518 nm for **ADBNA-Me-Me-Mes** and 479 nm and 514 nm for **ADBNA-Me-Tip**, respectively. The small  $\Delta E_{ST}$  values of emitters were found to be 0.19-0.20 eV from these two spectra. The prompt decay and delayed decay lifetimes were reported to be 6.9 ns and 165 µs for **ADBNA-Me-Me-Mes** and 6.0 ns and 147 µs for **ADBNA-Me-Tip**. To investigate the potential of

the emitters OLED devices were fabricated. The device based on emitters showed skyblue emission at 480–481 nm with an FWHM of 32–33 nm. The CIE coordinates of **ADBNA-Me-Mes** and **ADBNA-Me-Tip** were found to be (0.10, 0.27) and (0.11, 0.29), respectively. OLED device fabricated based on **ADBNA-Me-Tip** exhibited an EQE<sub>max</sub> of 21.4% was higher than the one with **ADBNA-Me-Mes** (16.2%).

Many MR-TADF emitters were developed derived from **DABNA-1** with different substituents until now. However, these materials have a small RISC rate constant, which results in efficiency roll-off at high luminance densities. Moreover, the bathochromic shift is seen in all derivatives with increasing  $\pi$ -conjugation, and therefore deep blue emission is difficult to achieve. Considering the results obtained with v-DABNA, the same group presented a new MR-TADF material (v-DABNA-O-Me) with an oxygen atom instead of the same group of nitrogen atoms, which limits the  $\pi$ -conjugation of HOMO due to its lower atomic orbital energy [157]. The fluorescence spectrum of v-DABNA-O-Me exhibited a deep-blue emission band at 464 nm with an FWHM of 24 nm. ΔEST was found to be 29 meV from the emission spectra at 77 K with and without delay. The transient spectrum of the film was examined to investigate TADF properties. The photoluminescence and TADF quantum yield of v-DABNA-O-Me thin films were found to be 0.72 and 0.18, respectively. The lifetimes were found to be 5.1 ns for fluorescence (prompt) and 7.7 µs for TADF (delayed). The higher kRISC values prevent the triplet-triplet and tripletpolaron annihilations in the device[158]. These values are found to be 1.6 x 105 s-1 for *v*-DABNA-O-Me and 2.0 x 105 s<sup>-1</sup> for *v*-DABNA. The device fabricated based on v-DABNA-O-Me showed pure blue emission at 465 nm with an FWHM of 23 nm (CIE = 0.13, 0.10) and EQE<sub>max</sub> of 29.5%. The efficiency roll-off of the OLED device fabricated with **v-DABNA-O-Me** is lower than the one with **v-DABNA**. According to the promising results obtained, this design strategy of changing nitrogen atom with an oxygen atom induces a hypochromic shift in emission spectra and is promising for new MR-TADF emitter design and development.

#### 2.2.3.3 Fused amine/carbonyl type blue MR-TADF emitters

Since replacing nitrogen atoms with oxygen atoms in a polycyclic framework did not activate the TADF phenomenon [135], it paved the way for further investigation of the

versatility of the molecular design of new MR-TADF systems. Lee and co-workers presented a novel design based on rigidified aryl ketones and amine in 2019 [139]. The carbonyl group has been generally used as a functional group for phosphorescence and TADF emitters at room temperature, due to its electron-withdrawing property and small  $\Delta E_{\text{ST}}$  thanks to its electronic transition from the n orbital to  $\pi^*$  orbital that is overlapped orthogonally. Although the small  $\Delta E_{\rm ST}$  of aromatic ketone derivatives is suitable for producing delayed fluorescence, the luminescence efficiency is low due to their flexible structure causing energy losses. The carbon atom in the carbonyl group has sp2 hybridization same as the boron atom and the ability to fuse flexible aryl amine in a six-membered cycle. Quinolino[3,2,1-de]acridine-5,9-dione (QAO) (Figure 2.7) contains one nitrogen atom as a donor moiety in the center and two carbonyl groups that are linked to two phenyl rings at the ortho position relative to nitrogen as an acceptor moiety, ensure opposite resonance effects. And also novel QAO derivative, 3,11-bis(9,9-dimethylacridin-10(9H)-yl)quinolino[3,2,1-de]acridine-7-(*tert*-butyl)-5,9-dione (QAO-DAd) which consisted of 9,9-dimethyl-9,10-dihydroacridine (DMAC) as a donor and and tert-butyl group for increasing solubility was reported in this work (Figure 2.7). The blue OLEDs with QAO showed a good EQE<sub>max</sub> of 19.4% with CIE coordinates of (0.13, 0.18) and an FWHM of 39 nm. The OLED device fabricated with QAO-DAd showed EQE<sub>max</sub> of 23.9% and 19.3% for vacuum-deposited and solution-processed respectively.



Figure 2.7: Molecular structure of DiKTa derivatives

Zhang et al. developed two new TADF compounds, 3-phenylquinolino[3,2,1de]acridine-5,9-dione (3-PhQAD) and 7-phenylquinolino[3,2,1-de]acridine-5,9-dione (7-PhQAD), derived from QAD core (Figure 2.7) [159]. The difference between the two compounds is where the additional phenyl ring is attached. The additional phenyl ring only provides the extension of HOMOs, while the LUMOs are well confined in the QAD core. Both 3-PhQAD and 7-PhQAD exhibit important TADF properties with  $\Delta$ ESTs of 0.18 and 0.19 eV, respectively. Also, structural relaxations were significantly suppressed for the emitters owing to the conjugated rigid molecular structures. 3-PhQAD ( $\lambda_{PL}$  = 466 nm) and 7-PhQAD ( $\lambda_{PL}$  = 464 nm) have  $\Phi_{PL}$  of 73% and 68% in 2wt%mCP, respectively. In OLEDs, 3-PhQAD performs with EQE<sub>max</sub> of 19.1% and a narrow FWHM of 44 nm, while  $EQE_{max}$  of 18.7% and an extremely narrow FWHM of 34 nm for 7-PhQAD. The OLED with 7-PhQAD exhibited a considerable efficiency roll-off with EQE<sub>100</sub> of 5.4% compared to 10.2% for 3-PhQAD. The obtained luminance was 4975 cd m<sup>-2</sup> and 2944 cd m<sup>-2</sup> for 3-PhQAD and 7-PhQAD, respectively. DiKTa derivatives have lower luminance compared to the best boron-based MR-TADF emitters, so, it was needed to develop the performance of this type of MR-TADF emitters.

Zysman-Colman and coworkers reported two novel MR-TADF compounds, DDiKTa[160] and Mes<sub>3</sub>DiKTa[137], containing DiKTa core which has been reported as the name of QAO[139] before. Most MR-TADF compounds are highly planar, so they tend to quench due to aggregation and/or excimer formation. Mes<sub>3</sub>DiKTa was designed to prevent unwanted quenching through aggregation. The mesityl group was chosen because of its orthogonal conformation and preventing to quench caused by aggregation with its steric structure and not affecting the multiple resonance mechanism. Mes<sub>3</sub>DiKTa exhibited  $\Phi_{PL}$  of 80% compared to 75% for the reference DiKTa at 3.5wt% in mCP. The high EQE<sub>max</sub> of 21.1% at a luminance of 25 cdm<sup>-2</sup> was obtained, representing the highest among this type of emitters. Importantly, a higher efficiency roll-off of 31% was also obtained with EQE<sub>100</sub> of 14.5% (FWHM 36 nm) and a remarkably improved maximum luminance of 12 900 cd m-2 for the sky-blue OLED with Mes3DiKTa. DiKTa which is a dimeric compound consisting of two MR-TADF DiKTa core, exhibited blue-green emission with  $\lambda_{EL}$  of 500 nm and EQE<sub>max</sub> of 19% at 9wt% in DPEPO; at 12wt%, the EQE<sub>max</sub> was 18.5%. Four OLED devices were fabricated with different doping concentrations of DPEPO. The best performing OLED showed an EQE<sub>max</sub> of 19% ( $\lambda_{EL}$ : 500 nm) with 9wt%DPEPO doping concentration.

# 2.3 Application of TADF in Light-Emitting Electrochemical Cells

Light-emitting electrochemical cells (LECs) are a form of EL device with a simpler device design than multilayered OLEDs. Thanks to the presence of charged groups, the emitter also functions as a charge transporter in LECs. These groups also promote charge injection from the electrodes, providing charge injection insensitive to electrode work function and allowing the use of an air-stable cathode (e.g., Al). LECs are manufactured using spin-coating processes, and the device performance is largely indifferent to the thickness of the emissive layer[161–163].

So far, three paper published including ionic TADF compounds for LEC applications. The structures of ionic TADF compounds are presented in Figure 2.8.



Figure 2.8: The structures of ionic TADF compounds are reported so far

Zysman-Colman's group published charged organic TADF emitters (1 and 2) for LEC application in 2015 for the first time[164]. MeCN emission is characteristic fluorescence owing to superior stability of the triplet excited state over the singlet excited state, which enhances  $\Delta E_{ST}$  and turns off TADF. Photophysical investigations in both neat and 10% -doped PMMA film, on the other hand, indicate TADF, with considerably improved O<sub>2</sub>-sensitive PLQY. A charged analog of **2CzPN**, **2** emitter ( $\lambda_{max}$ : 536 nm; PLQY: 21%;  $\tau_d$ : 2.73 µs in neat film) in the LEC (ITO/PEDOT:PSS/emitter/Al) showed an EQE of 0.39%. The solution-processed

OLEDs (ITO/PEDOT:PSS/PVK/emitter/B3PYMPM/Ca/Al) (PVK = poly(N-vinylcarbazole);  $B_3PYMPM = 4,6$ -bis(3,5-di(pyridin3-yl)phenyl)-2-methylpyrimidine) based on **2** emitter exhibited EQE of 5.1% with EL<sub>max</sub> at 546 nm and CIE coordinates of (0.41, 0.53), making it one of the best solution-processed, nondoped small-molecule-based TADF OLEDs recorded.

Second contribution for TADF LECs reported in 2017 by Zysman-Colman's group[165]. In this paper, two ionic emitters, **imCzDPS** ( $\lambda_{max}$ : 414 nm, PLQY: 44%;  $\tau_d$ : 48 µs in 5wt%PMMA) and **imDPADPS** ( $\lambda_{max}$ : 409 nm, PLQY: 49%;  $\tau_d$ : 116 µs in 5wt%PMMA), were presented. The LEC device based on **imCzDPS** showed no emission. Although LEC device based on **imDPADPS** showed the modest luminance levels, it is reported that the bluest one among the LECs based on small molecules. LEC device with **imDPADPS** showed  $\lambda_{EL}$  at 423 nm (CIE = 0.15, 0.12) with very poor efficiency (EQE: 1.14%) which was attributed to its electrochemical instability.

In 2021, He and co-workers reported three ionic emitters based on triazin[166]. The donor and triazin acceptor units were orthogonally organized on the central phenyl linkers to separate HOMO and LUMO. The main difference between these three emitters was the substituent of carbazole group; R=H; 1 ( $\lambda_{max}$ : 458 nm; PLQY: 86%;  $\tau_d$ : 5.8 µs in PMMA film); R='Bu; 2 ( $\lambda_{max}$ : 486 nm; PLQY: 90%;  $\tau_d$ : 3.5 µs in PMMA film) and R=Ph; 3 ( $\lambda_{max}$ : 490 nm; PLQY: 87%;  $\tau_d$ : 3.6 µs in PMMA film). A charged emitters in the LEC (ITO/PEDOT:PSS/emitter/Al) showed green emission at 510 nm (CIE = 0.29, 0.52), 530 nm (CIE = 0.34,0.57), and 540 nm (CIE = 0.39,0.55), respectively with an EQE of between 4-6.8%.

Recently, Su and co-workers reported two new ionic TADF emitters namely **Pym-CZ** ( $\lambda_{max}$ : 583 nm; PLQY: 15% in 25wt%BMIM doped film) and **Pym-tBuCZ** ( $\lambda_{max}$ : 593 nm; PLQY: 6% in 25wt%BMIM doped film)[167]. This report is the first orange red LEC fabricated with ionic TADF. The LEC device based on **Pym-CZ** showed the EQE of 1.2%, indicating the promise for a new technique to produce low-cost orange-red LECs.

The LEC device performance metrics of ionic TADF emitters reported are summarized in Table 2.1.

Emitter	$\lambda_{PL}(nm)$	$L_{max}$ (cd/m <sup>2</sup> )	CE (cd/A)	EQE (%)	PE (lm/W)	t <sub>1/2</sub> (h)	CIE (x,y)	Ref
2	538	13	-	0.39	0.70	-	0.35,0.57	[164]
imCzDPS	470	2.1	-	1.14	0.10	-	0.21,0.25	[165]
1	510	225	11.2	4.00	-	6.20	0.29,0.52	
2	530	572	22.6	6.80	-	11.4	0.34,0.57	[166]
3	540	520	19.8	6.20	-	47.8	0.39,0.55	
Pym-CZ	509	2.06	2.48	1.19	2.59	-	0.54,0.46	[167]
Pym-tBuCZ	620	0.39	0.21	0.14	0.22	-	0.58,0.42	[10/]

Table 2.1: The LEC device performance metrics of ionic TADF emitters

TADF emitter with a DiKTa core structure that can be used for LEC applications has not been reported yet. Ionic derivatives of DiKTa have been designed for using in LEC applications.

# 2.4 Application of Iridium (III) complexes in Light-Emitting Electrochemical Cells

No LEC has been found producing blue light and it is nowhere near to the 'ideal deep blue' CIE coordinates (CIE = 0.15, 0.06, as established by the European Broadcast Union, EBU), high efficiency. Additionally, the stability of these sky-blue LECs is clearly inferior to that of their OLED counterparts; device lifetimes are often in the tens of hours at most, compared to thousands of hours recorded for yellow or orange LECs. Given that blue is required to produce white light from a conventional RGB color combination, solving this problem is a top priority.

The introduction of electron-withdrawing groups to the phenyl ring of a cyclometallated ligand may be the most popular approach to obtain blue-shifted emission of cyclometallated Ir(III) complexes. The HOMO is mostly localized at the Ir d-orbital and phenyl moiety, whereas the LUMO is primarily localized at the pyridyl moiety, according to computational study of *fac*-Ir(ppy)<sub>3</sub> complex[168]. As a result, adding electron-withdrawing groups to the phenyl ring allows the HOMO energy level to be stabilized and also adding an electron-donating group to the pyridyl unit can increase the LUMO energy level. The ancillary ligand, bpy (2,2'-bipyridine) and its derivatives are usually used in iridium complexes presented for LEC applications on

which the LUMOs of the complexes are localized. Cationic blue-emitting iridium(III) complexes are symbolized by the formula  $[Ir(C^N)_2(L^L0)]^+$  (L<sup>L</sup>: neutral ancillary ligand).

Significant blue LEC device performance metrics are summarized in Table 2.2.



Figure 2.9: Structure of blue emitting iridium (III) complexes used in LEC devices

Table 2.2: The performance metrics of the LECs e	employing blue-emitting iridium
(III) complexes	

Complex	$\lambda_{PL}(nm)$	PLQY (%)	$L_{max}$ (cd/m <sup>2</sup> )	CE (cd/A)	EQE	PE (lm/W)	t <sub>1/2</sub> (h)	CIE (x,y)	Ref
1	452, 480	(,0)	39	0.65	0.28	-	-	0.20,0.28	[169]
1	$1 452,480^{a}$	20	23	0.51	0.21	-	-	0.33,0.45	
2	492 <sup>a</sup>	100	8	-	14.4	32.1	2.17	0.20,0.36	[170]
2	493 <sup>b</sup>	40	1700	-	4.60	11	-	0.20,0.41	[171]
3	489	24	39	8.4	-	-	-	0.25,0.46	[172]
4	472, 490	54	15	18.3	-	18		0.22,0.41	[173]
5	440	13	113	4.7	-	1.95	0.017	0.24,0.40	[174]
6	472, 501	0.001	15.4	0.2	-	-	24.3	0 / 3 0 53	[175]
								0.43,0.33	[176]
7	477, 500	-	16.1	0.6	-	-	29.8	0.41,0.53	[176]
8	480, 509	-	37	8.7	-	-	15.83	0.26,0.48	[177]

<sup>a</sup>Measured in DCM, <sup>b</sup>Measured in 2-MeTHF

# Chapter 3 Experimental Section

#### 3.1 Materials

All commercially available chemicals and reagent grade solvents were used as received. Solvents used in the reactions were dry and deaerated using a solvent purification system. Air-sensitive reactions are done under a nitrogen atmosphere using Schlenk techniques. Flash column chromatography was carried out using silica gel (Silica-P from Silicycle, 60 Å, 40-63 μm). Analytical thin-layer-chromatography (TLC) was performed with silica plates with aluminum backings (250 µm with F-254 indicator). TLC visualization was accomplished by the use of a 254/365 nm UV lamp. <sup>1</sup>H and <sup>13</sup>C and NMR spectra were recorded on a Bruker Advance spectrometer (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C). The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "dd" for doublet of doublets, "ddd" for doublet of doublet of doublets, "td" for a triplet of doublets and "m" for multiplet. Deuterated chloroform (CDCl<sub>3</sub>) and Deuterated dimethyl sulfoxide (DMSO-d8) were used as the solvents of recording NMR. <sup>1</sup>H NMR spectra were referenced to the corresponding solvent peak. Melting points were measured using open-ended capillaries on an electrothermal melting point apparatus and are uncorrected. High-resolution mass spectrometry (HRMS) was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea.

#### 3.2 Equipment

#### 3.2.1 Electrochemistry measurements

Cyclic Voltammetry (CV) and Differential pulse voltammetry (DPV) measurements were done on an Electrochemical Analyzer potentiostat model 620E and 660B from

CH Instruments at a sweep rate of 100 mV/s. Differential pulse voltammetry (DPV) was performed with an increment potential of 0.004 V and pulse amplitude, width, and period of 50 mV, 0.05, and 0.5 s, respectively. Samples were prepared in electrospectroscopic grade acetonitrile (MeCN) solutions, which were degassed by sparging with MeCN-saturated nitrogen gas for 5 minutes before all measurements. 0.1 M tetra-n-butylammonium hexafluorophosphate, [*n*Bu<sub>4</sub>N]PF<sub>6</sub>, solution in THF was used as a supporting electrolyte. An Ag/Ag<sup>+</sup> electrode was used as the reference electrode; a glassy carbon electrode was used as the working electrode and a platinum wire was used as the counter electrode. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple as the internal standard (0.38 V vs SCE)[178]. The HOMO energy was calculated using the relation  $E_{HOMO} = -(E_{ox} + 4.8) eV[179]$ , where  $E_{ox}$  is the anodic peak potentials of the first oxidation peak of the DPV. LUMO energy was inferred by subtracting the optical energy gap  $E_g$  from the  $E_{HOMO}$  determined from the electrochemical measurements.

#### 3.2.2 Photophysical measurements

Optically dilute solutions of concentrations on the order of  $10^{-4}$  to  $10^{-6}$  M were prepared in spectroelectrochemical grade solvents for absorption and emission analysis. Absorption spectra were recorded at room temperature on a Shimadzu UV-1800 double beam spectrophotometer using a 1 cm quartz cuvette. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least five independent solutions at varying concentrations with absorbance ranging from  $1.06 \times 10^{-5}$  to  $5.06 \times 10^{-7}$  M. Steady-state photoluminescence spectra in solution were recorded at 298 K using Shimadzu RF-6000 Spectro fluorophotometer using homemade Schlenk quartz cuvette. The excitation wavelength for all the steady-state photoluminescence measurements was 325nm. Thin-film FPL measurements were performed using an integrating sphere in a Hamamatsu C9920-02 system.3A xenon lamp coupled to a monochromator enabled excitation selectivity, chosen here to be 378 nm. The output was then fed into the integrating sphere via a fibre, exciting the sample. PL spectra were collected with multimode fibre and detected with a backthinned CCD. The total wt% of this solution was 6%. The solution for spin-coating was prepared by dissolving PMMA in hot chlorobenzene, then mixed with emitter in THF, the resultant solution was filtered using a syringe filter. The  $\Phi_{PL}$  of the films were then measured in air and by purging the integrating sphere with N<sub>2</sub> gas flow. For steady-state and time-resolved PL measurements, thin films of 1wt% emitter in PMMA were spin-cast at 2000 rpm on a quartz substrate from an oxygen-free THF solution that had previously been sonicated for 15 minutes. Solutions used for PL measurements were sonicated for 15 minutes after preparation. The time-resolved PL measurements of the thin films and solutions were carried out using an iCCD camera by exponentially increasing delay and gating times where gating time is kept lower by 10 times compared to the delay time. The samples and cuvettes were kept in a continuous flow He-cryostat with a temperature controller. They were excited at 355 nm by a lamp-pumped Nd: YAG laser (Innolas SpitLight 600). Emission from the samples was focused onto a spectrograph (Oriel MS257) and detected on a gated iCCD camera (iStar A-DH334T-18F-03). The measurements were recorded under He exchange gas unless otherwise stated. Steady-state spectra at RT and 77 K, phosphorescence spectra at 77 K, and RT PLQY measurements were obtained using a Jasco FP-8600 spectrofluorometer for excitation at 325 nm. For the 77K measurements, the sample or cuvette was immersed in liquid nitrogen.

#### 3.3 Synthesis

In this thesis, two organic emitters and three novel iTMC type emitters were synthesized. The structure of the ionic organic small molecules and iridium iTMC molecules which were synthesized are given in Figure 3.1.



Figure 3.1: The structure of the ionic organic small emitters and iTMC emitters which were synthesized

#### 3.3.1 Synthesis of Organic Emitters

3.3.1.1 Synthesis of dimethyl 2,2'-(phenylazanediyl)dibenzoate (1)



A 2-neck flask held under nitrogen was charged with aniline (5.00 mL, 0.05 mol, 1 equiv.), methyl 2-iodobenzoate (24.0 mL, 0.16 mol, 3 equiv.), CuSn (3.00 g, 16 mmol, 0.3 equiv.), copper(I) iodide (0.73 g, 3.8 mmol. 0.07 equiv.), anhydrous potassium carbonate (38.0 g, 0.27 mol, 5 equiv.), and 30 mL anhydrous di-*n*-butyl ether. The resulting reaction mixture was heated to 150 °C and stirred for 5 days. After cooling to room temperature, the reaction mixture was filtered through a pad of celite. The filtrate was mixed with dichloromethane and washed with water (3 x 20 mL). The organic layer was concentrated under reduced pressure. The product was purified by column chromatography (1:4, EtOAc:n-hexane). The product was obtained and dried under vacuum. White solid. **Yield:** 56% (11.01 g). **R**r: 0.54 (2:8 EtOAc : Hexanes on silica gel). **Mp**: 143 - 145 °C. <sup>1</sup>**H NMR (500 MHz, CDCl3) δ (ppm)**: 7.68 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.43 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 2H), 7.23-7.13 (m, 6H), 3.41 (s, 6H). <sup>13</sup>C **NMR (126 MHz, CDCl3) δ (ppm)**: 167, 148, 146, 132, 130, 128, 128, 124, 121, 120, 51. **HR-MS [M+H]**<sup>+</sup> Calculated: (C<sub>22</sub>H<sub>19</sub>NO<sub>4</sub>) 361.1341; Found: 362.1387. The characterization matches that previously reported[137].

3.3.1.2 Synthesis of dimethyl 2,2'-((4-bromophenyl)azanediyl)dibenzoate (2)



Dimethyl 2,2'-(phenylazanediyl)dibenzoate (4.00 g, 11.1 mmol, 1 equiv.) was dissolved in 20 mL DCM in flask. NBS (2.10 g, 11.8 mmol, 1.1 equiv.) was added in dropping funnel in 15 mL DCM. NBS solution was added drop by drop at 0 °C. The reaction was stirred at room temperature for a night. 10 mL NaOH (0.1 M) was added and extracted with DCM (2 x 15 mL). The crude product was purified with column chromatography (1:9, EtOAc:n-hexane). White solid product was obtained. **Yield**: 85% (4.12 g). **M**<sub>p</sub>: 156-159 °C. <sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>) \delta (ppm)**: 7.71 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.45 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 2H), 7.26-7.18 (m, 6H), 6.64-6.61 (m, 2H), 3.47 (s, 6H). <sup>13</sup>**C NMR (126 MHz, CDCl<sub>3</sub>) \delta (ppm)**: 165, 146, 144, 135, 133, 132, 130, 121, 117, 114, 52.

3.3.1.3 Synthesis of 3-bromoquinolino[3,2,1-de]acridine-5,9-dione (3)



Dimethyl 2,2'-((4-bromophenyl)azanediyl)dibenzoate (4.00 g, 9.08 mmol, 1 equiv.) was combined with sodium hydroxide (1.82 g, 45.4 mmol, 5 equiv.) in 40 mL of an ethanol/water (1:1) mixture. The reaction was heated to reflux for 12 h. After cooling to room temperature, the pH was adjusted to 2-3 by addition of dilute hydrochloric acid. The diacid precipitated was collected by vacuum filtration, washed thoroughly with water, dried under vacuum. Dibenzoic acid (3.20 g, 7.76 mmol, 1 equiv.) dissolved in 30 mL DCM. Thionyl chloride (1.13 mL, 15.5 mmol, 2 equiv.) was added dropwise. The color changed from light yellow to dark yellow. 3-4 drops DMF were added, and the reaction was refluxed for 3 h. The mixture was cooled to room temperature and aluminium chloride (10.3 g, 77.6 mmol, 10 equiv.) was added slowly. The mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature and water (15 mL) was added slowly (exothermic) yellow precipitate was observed. Then the mixture was filtered by vacuum filtration and washed with hexane 3 times. The yellow product was dried under vacuum. Yield: 92% (2.69 g). Mp: 296-299 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 8.77 (ddd, J = 9.7, 7.7, 1.7 Hz, 2H), 8.64 (d, *J* = 2.4 Hz, 1H), 8.52 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.08 (dd, *J* = 11.5, 8.8 Hz, 2H), 7.80 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.74 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H) <sup>13</sup>**C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm)**: 142.9, 142.2, 141.9, 140.1, 138.4, 138.1, 137.6, 133.7, 131.5, 130.3, 129.8, 129.1, 128.1, 125.8, 125.7, 123.8, 122.9, 121.0, 118.7, 116.5, 114.2. **GC-MS** *m*/*z* Calculated: 376.20 Found: 377.00

3.3.1.4 Sythesis of 3-((4-methoxyphenyl)(phenyl)amino)quinolino-[3,2,1-de]acridine-5,9-dione (4)



Compound 3 (1.00 g, 2.66 mmol, 1 equiv.), 4-methoxy-N-phenylaniline (0.56 g, 2.79 mmol, 1.05 equiv.), NaO'Bu (0.51 g, 5.32 mmol, 2 equiv.), TTBP. HBF<sub>4</sub> (0.05 g, 0.19 mmol, 0.07 equiv.) and  $Pd_2(dba)_3$  (0.048 g, 0.053 mmol, 0.02 equiv.) were added in a schlenk tube under nitrogen. Dry toluene (12 mL) was injected to the schlenk tube and the mixture was heated to 110 °C. After 24 h, the reaction mixture was extracted with DCM (200 mL) and washed with water ( $3 \times 50$  mL). The desired product was obtained as a red solid after column chromatography (1:9 EtOAc : Hexanes). Yield: 78% (1.02 g). **R***f*: 0.5 (2:3, EtOAc:n-Hexane on silica gel). **Mp**: 217 - 219 °C. <sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>**)  $\delta$  (ppm): 8.76 (dd, J = 7.7, 1.7 Hz, 1H), 8.72 (dd, J = 7.6, 1.7 Hz, 1H), 8.51 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 2.8 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.73-7.67 (m, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 (dd, J = 9.2, 2.9 Hz, 1H), 7.34-7.30 (m, 2H), 7.19-7.13 (m, 4H), 7.08 (tt, J = 7.4, 1.2 Hz, 1H), 6.95-6.91 (m, 2H), 3.86 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm): 178.5, 178.3, 139.8, 138.8, 133.0, 132.8, 132.6, 129.5, 127.8, 126.3, 124.8, 123.3, 121.3, 120.3, 117.5, 115.1, 55.5. HR-MS [M<sup>+</sup>] Calculated: (C<sub>33</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>) 494.1630; Found: 494.1634.

3.3.1.5 Synthesis of 3-((4-hydroxyphenyl)(phenyl)amino)quinolino-[3,2,1-de]acridine-5,9-dione (5)



Compound **4** (0.80 g, 1.62 mmol, 1 equiv.) was dissolved in dry DCM (10 mL) in a schlenk flask under nitrogen cover. BBr<sub>3</sub> in DCM solution (8.1 mL, 8.09 mmol, 5 equiv.) was dropwise added to the solution at -78 °C. After 2 h water was added slowly, and the crude reaction was extracted with DCM (100 mL). The compound was further purified by silica gel column chromatography (1:1, EtOAc:n-hexane). The product was obtained as a purple solid. **Yield**: 65% (0.50 g). **R**<sub>*f*</sub>: 0.23 (2:3 EtOAc : Hexanes on silica gel). **M**<sub>P</sub>: 269-272 °C. <sup>1</sup>**H NMR (500 MHz, DMSO-d6) δ (ppm)**: 9.59 (s, 1H), 8.59 (dd, J = 7.5, 1.8 Hz, 1H), 8.54 (dd, J = 7.6, 1.8 Hz, 1H), 8.30 (d, J = 7.9 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.02 (dd, J = 9.7, 4.5 Hz, 1H), 7.81 (t, J = 7.8 Hz, 1H), 7.73-7.66 (m, 1H), 7.63 (t, J = 3.0 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.39-7.30 (m, 3H), 7.15-7.04 (m, 5H), 6.84 (d, J = 8.7 Hz, 2H). <sup>13</sup>C **NMR (126 MHz, DMSO-d6) δ (ppm)**: 177.9, 177.7, 155.7, 147.3, 145.7, 139.8, 139.7, 137.8, 133.7, 133.3, 132.8, 132.6, 130.1, 129.8, 127.1, 126.9, 125.7, 125.5, 123.9, 123.6, 123.2, 122.8, 122.7, 121.3, 117.1, 115.1 **HR-MS [M+Na]**<sup>+</sup> Calculated: (C<sub>32</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>) 480.1473; Found: 480.1444.

3.3.1.6 Synthesis of 3-((4-(4-bromobutoxy)phenyl)(phenyl)amino)quinolino[3,2,1-de]acridine-5,9-dione (6)



Compound **5** (0.650 g, 1.31 mmol, 1 equiv.) and NO<sup>t</sup>Bu (0.379 g, 3.94 mmol, 3 equiv.) were added to a dry schlenk tube under a positive N2 flow. Then dry THF (20 mL) and 1,4-dibromobutane (1.6 mL, 13.1 mmol, 10 equiv.) were sequentially added to the mixture with stirring. The reaction was stirred overnight at 65 °C. The mixture was extracted with DCM (100 mL) and washed with water ( $3 \times 100$  mL). The organic layer was concentrated under reduced pressure. Further purification was done by silica gel column chromatography (1:9 EtOAc : Hexanes on silica gel) product was obtained as a red solid. Yield: 58.1% (0.47 g). Rf: 0.6 (2:3, EtOAc:n-hexane on silica gel). Mp: 121-125 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm): 8.76 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.51 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.03 (d, J = 2.8 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.70 (t, J = 8.7 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.39 (dd, J = 9.2, 2.9 Hz, 1H), 7.33-7.30 (m, 2H), 7.18-7.13 (m, 4H), 7.08 (tt, J = 7.3, 1.2 Hz, 1H), 6.94-6.88 (m, 2H), 4.04 (t, J = 6.0Hz, 2H), 3.54 (t, J = 6.6 Hz, 2H), 2.17-2.09 (m, 2H), 2.03-1.96 (m, 2H). <sup>13</sup>C NMR (**126 MHz, CDCl<sub>3</sub>**) δ (ppm): 178.5, 178.3, 156.2, 147.1, 145.7, 133.6, 133.1, 132.6, 129.6, 127.7, 124.9, 123.8, 123.3, 121.4, 120.3, 117.6, 115.7, 67.1, 33.5, 31.6, 29.4, 27.9, 27.6, 14.1. **HR-MS** [M<sup>+</sup>] (C<sub>36</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>3</sub>) Calculated: 615.53; Found:617.1263

3.3.1.7 Synthesis of 1-(4-(4-((5,9-dioxo-5,9-dihydroquinolino[3,2,1-de]acridin-3-yl)(phenyl)amino)phenoxy)butyl)-3-methyl-1H-imidazol-3-ium hexafluorophosphate(V) (7) (DiKTa-DPA-OBuIm)



Compound 6 (0.43 g, 0.7 mmol, 1 equiv.) and 1-methylimidazole (1 mL, 13 mmol, 18.6 equiv.) was added to a schlenk tube under nitrogen. The mixture was stirred for 2 h at 100 °C, after cooling down to RT, ammonium hexafluorophosphate solution (2 g/2 mL) was added to the reaction mixture and stirred for 1 h. The product precipitated after addition water (3 mL) and cooled in a fridge overnight. Red precipitate was filtered by vacuum filtration and washed with water (100 mL). The product was obtained as red solid after dried under vacuum. Yield: 93% (0.54 g). Mp: 239-241 °C. <sup>1</sup>**H NMR (500 MHz, DMSO-d<sub>6</sub>) δ (ppm)**: 9.15 (s, 1H), 8.61 (d, *J* = 7.6 Hz, 1H), 8.55 (d, *J* = 7.6 Hz, 1H), 8.42 (s, 1H), 8.32 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 8.07 (d, J = 9.3 Hz, 1H), 7.86-7.80 (m, 2H), 7.75-7.68 (m, 2H), 7.64 (d, J = 2.9 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.45 (s, 1H), 7.40-7.32 (m, 4H), 7.17 (d, J = 8.8 Hz, 2H), 7.15-7.09 (m, 3H), 7.01 (d, J = 8.9, 2H), 4.27 (t, J = 7.1 Hz, 2H), 4.03 (t, J = 6.2 Hz, 2H), 1.99 (p, J = 7.3 Hz, 2H), 1.74 (p, J = 6.2 Hz, 2H). <sup>13</sup>C NMR (126 MHz, **DMSO-d<sub>6</sub>**) δ (ppm): 178.0, 156.4, 147.2, 145.5, 139.5, 137.0, 133.0, 132.7, 128.4, 124.1, 122.7, 116.3, 67.4, 48.7, 36.2, 26.8, 25.8. <sup>19</sup>F {<sup>1</sup>H} NMR (471 MHz, DMSO**d**<sub>6</sub>) δ (ppm): -70.1 (d, *J* = 710.5 Hz). <sup>31</sup>P {<sup>1</sup>H} NMR (202 MHz, DMSO-d<sub>6</sub>) δ (ppm): -144.2 (hept, J = 711.4 Hz). **HR-MS** [**M**<sup>+</sup>] (C<sub>40</sub>H<sub>33</sub>N<sub>4</sub>O<sub>3</sub>) Calculated: 617.2542; Found:617.2553.

3.3.1.8 Synthesis of 2-bromoisophthalic acid (8)



To a solution of 2-bromo-1,3-dimethylbenzene (14.0 mL, 108.1 mmol, 1 equiv.) in <sup>1</sup>BuOH (80 mL) and H<sub>2</sub>O (80 mL) was added KMnO<sub>4</sub> (42.7 g, 270.2 mmol, 2.5 equiv.) in portions while stirring at room temperature. Temperature was increased to 90 °C gradually. The reaction was stirred at 90 °C for 2 h. It was cooled to room temperature. A second batch of KMnO<sub>4</sub> (42.7 g, 270.2 mmol, 2.5 equiv.) was added. After stirring at 90 °C for 10 h, the hot reaction mixture was filtered, and the residue was washed with water (3 x 30 mL). After reducing the volume to 30 mL, the filtrate was acidified in ice-bath to pH 2 with concentrated HCl to get white precipitate. It was filtered and dried under vacuum. The product was obtained as white solid. **Yield**: 77% (20.5 g). **Mp**: 217-219 °C. <sup>1</sup>H **NMR (500 MHz, DMSO-d<sub>6</sub>) δ (ppm)**: 7.70 (d, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H). <sup>13</sup>C **NMR (126 MHz, DMSO-d<sub>6</sub>) δ (ppm)**: 173.1, 141.9, 135.9, 133.1, 121.4. The characterization matches that previously reported[180]

#### 3.3.1.9 Synthesis of dimethyl 2-bromoisophthalate (9)



In a round-bottom flask with a magnetic stirrer and a reflux condenser was added 2bromo-isophthalic acid (6 g, 0.02 mol, 1 equiv.), in 50 mL of methanol and 6 mL of H<sub>2</sub>SO<sub>4</sub>. The reaction mixture was heated to 65 °C for 16 h and poured into water (50 mL). The reaction was neutralized with NaHCO<sub>3</sub>, and the aqueous solution was washed several times with ethyl acetate. The organic layers were combined and dried under reduced pressure to afford the product as a light-yellow oil. **Yield**: 70% (5.0 g). <sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm)**: 7.73 (d, J = 7.7 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 3.97 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm): 171.2, 166.9, 135.3, 132.3, 127.1, 119.1, 60.4, 52.8, 21.1, 14.2. GC-MS *m/z* Calculated: 271.96 Found: 272.00. The characterization matches that previously reported[180]

3.3.1.10 Synthesis of 4-methoxy-N-phenylaniline (10)



Iodobenzene (9.15 g, 44.9 mmol, 1 equiv.), methoxyaniline (6.63 g, 53.8 mmol, 1.2 equiv.), K<sub>2</sub>CO<sub>3</sub> (18.6 g,135 mmol, 3 equiv.), CuI (0.598 g, 3.14 mmol, 0.07 equiv.) and CuSn (2.45 g, 13.5 mmol, 0.3 equiv.) were added in a schlenk tube under nitrogen. Then di-*n*-butyl ether (20 mL) was injected and heated to 150 °C. After 24 h, reaction was cooled down and filtered with celite followed by DCM wash several times. Water (150 mL) was added to DCM solution and the organic phase was collected. Final purification was done by column chromatography (EtOAc : Hexanes on silica gel). Corresponding fractions were combined and concentrated. The off-white precipitate formed was filtered and washed with hexane. The product was dried under vacuum. **Yield**: 30% (2.69 g). **Mp**: 103-105 °C. <sup>1</sup>**H NMR** (**500 MHz**, **CDCl**<sub>3</sub>) **δ** (**ppm**): 7.27-7.22 (m, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 7.9 Hz, 2H), 6.92-6.84 (m, 3H). <sup>13</sup>**C NMR** (**126 MHz**, **CDCl**<sub>3</sub>) **δ** (**ppm**): 155.2, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.6. **GC-MS** *m*/*z* Calculated: 199.09 Found: 199.15. The characterization matches that previously reported[181]

3.3.1.11 Synthesis of dimethyl 2-((4-methoxyphenyl)(phenyl)amino)isophthalate (11)



4-Methoxy-N-phenylaniline (2.00 g, 10.0 mmol, 1 equiv.), dimethyl 2bromoisophthalate (3.00 g, 11.0 mmol, 1.1 equiv.), K<sub>2</sub>CO<sub>3</sub> (6.94 g, 50.2 mmol, 5.0

equiv.), CuI (191 mg, 1.00 mmol, 0.10 equiv.), CuSn (183 mg, 1.00 mmol, 0.10 equiv.), 2,2,6,6-tetramethylheptane-3,5-dione (0.21 mL, 1.0 mmol, 0.10 equiv.) and di-*n*-butyl ether (10 mL) were mixed in a schlenk tube under nitrogen. The reaction mixture was stirred at 150 °C for 3 h. The mixture was cooled to RT and diluted with DCM (100 mL) The organic phase was washed with water ( $3 \times 50$  mL). The Organic layer was then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (1:9-1:4, EtOAc:n-hexane). Reletad fractions were combined and solvent was removed under reduced pressure. The mixture was diluted with hexane and kept in a freezer overnight. Yellow solid was filtered by vacuum filtration and dried under vacuum. Yield: 83% (3.25 g). Rf: 0.30 (15% EtOAc:n-hexane on silica gel). Mp: 113-116 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (**ppm**): 7.72 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 7.7 Hz, 1H), 7.12-7.18 (m, 2H), 6.94-6.95 (m, 2H), 6.88 (d, J = 7.9 Hz, 3H), 6.74-6.78 (m, 2H), 3.76 (s, 3H), 3.48 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (ppm): 167.8, 155.5, 147.8, 144.7, 140.3, 133.8, 132.5, 128.9, 125.0(4), 124.9(5), 121.5, 121.0, 114.3, 55.6, 52.3. HR-MS [M+Na]<sup>+</sup> Calculated: (C<sub>23</sub>H<sub>21</sub>NO<sub>5</sub>Na) 414.1317; Found: 414.1295.

3.3.1.12 Synthesis of 3-hydroxyquinolino[3,2,1-de]acridine-5,9-dione(12)



Compound **11** (3.00 g, 1 equiv.) was dispersed in EtOH:H<sub>2</sub>O (15 mL:15 mL) and mixed with NaOH (1.53 g, 5 equiv.). The reaction mixture was heated to reflux for 3 h. After cooling to RT, pH was adjusted to 2 - 3 by dropwise addition of dilute HCl. The resultant oily solid was kept in a fridge and sonicated for 60 min. The formed solid was then filtered by vacuum filtration and washed with water. The product was dried under vacuum. The diacid obtained was added to dry DCM (40 mL), oxalyl chloride (1.16 mL, 13.2 mmol, 2 equiv.) in a two-neck flask fitted with condenser under nitrogen. To this mixture, 3 drops of dry DMF were added. After refluxing for 3 h, the reaction flask was cooled to RT, and AlCl<sub>3</sub> (7.04 g, 52.8 mmol, 8 equiv.) was added in

portions under a positive N<sub>2</sub> flow. It was heated to reflux for 20 h. After cooled to RT, the reaction was quenched by slow addition of water (50 mL) and THF (50 mL) was added to dissolve the product. The mixture was then transferred to a separating funnel, layers are separated, the aqueous layer was washed with more DCM (100 mL x 5). Organic fractions were combined and concentrated under reduced pressure. The orange precipitate formed was washed with acetone and DCM and dried under vacuum. **Yield**: 67% (1.40 g). **R***f*: 0.23 (2:3, EtOAc:n-hexane on silica gel). **Mp**: 360-364 °C. <sup>1</sup>**H NMR** (**500 MHz**, **DMSO-d**<sub>6</sub>) **δ** (**ppm**): 10.12 (s, 1H), 8.63 (d, *J* = 7.8, 0.8 Hz, 2H), 8.33 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.83 (td, *J* = 7.3, 1.5 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 3.0 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.28 (dd, *J* = 9.2, 3.0 Hz, 1H). <sup>13</sup>**C NMR** (**126 MHz**, **DMSO-d**<sub>6</sub>) **δ** (**ppm**): 177.6, 177.5, 154.9, 139.6, 138.3, 133.3, 132.4, 132.2, 127.0, 126.7, 125.4, 124.9, 123.4, 122.8, 122.7, 122.5, 121.9, 120.7, 109.9. **HR-MS** [**M-H**]<sup>-</sup> Calculated: (C<sub>20</sub>H<sub>10</sub>NO<sub>3</sub>) 312.0661; Found: 312.0669.

3.3.1.13 Synthesis of 3-(4-bromobutoxy)quinolino[3,2,1-de]acridine-5,9-dione (13)



Compound **12** (1.25 g, 3.99 mmol, 1 equiv.) and NO'Bu (1.15 g, 12.0 mmol, 3 equiv.) was added to a schlenk tube under N<sub>2</sub> flow. Dry THF (20 mL) was injected and stirred for 30 minutes. To this solution, 1,4-dibromobutane (4.73 mL, 39.9 mmol, 10 equiv.) was added. The reaction was stirred at 65 °C for 16 h. The mixture was cooled to RT, diluted with DCM (100 mL). The DCM layer was then washed with water (3 × 50 mL). The organic layer was combined and concentrated under reduced pressure. The compound was further purified by silica gel column chromatography (3:7, EtOAc:nhexane). The fractions were combined and concentrated under reduced pressure. The yellow solid was then filtered and dried under vacuum. Product was obtained as a yellow solid. **Yield**: 40 % (0.71 g). **R***f*: 0.47 (2:3 EtOAc : Hexanes on silica gel). **Mp**: 158 - 161 °C. <sup>1</sup>H NMR (**500 MHz, CDCl<sub>3</sub>**)  $\delta$  (**ppm**): 8.80-8.73 (m, 2H), 8.51 (dd, *J*)

= 7.9, 1.7 Hz, 1H), 8.09 (dd, J = 13.4, 8.9 Hz, 2H), 7.87 (d, J = 3.1 Hz, 1H), 7.71 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.31-7.28 (m, 2H), 4.21 (t, J = 6.0 Hz, 1H), 3.55 (t, J = 6.5 Hz, 2H), 2.19-2.11 (m, 2H), 2.10-2.02 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 178.5, 178.3, 156.1, 139.8, 138.8, 133.8, 133.1, 132.7, 127.8, 127.4, 126.2, 125.0, 123.3, 122.9, 122.4, 122.0, 120.1, 108.3, 67.7, 33.4, 29.5, 27.9. HR-MS [M<sup>+</sup>] Calculated: (C<sub>24</sub>H<sub>18</sub>BrNO<sub>3</sub>) 448.0470; Found: 448.0540.

3.3.1.14 Synthesis of 3-(4-((5,9-dioxo-5,9-dihydroquinolino[3,2,1-de]acridin-3-yl)oxy)butyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate(V) (**DiKTa-OBuIm**) (14)



Compound 13 (0.7 g, 2 mmol, 1 equiv.) and 1-methylimidazole (4 mL, 80 mmol, 40 equiv.) was added to a schlenk tube under nitrogen. The reaction was stirred at 100 °C for 2 h. After cooling down to RT, ammonium hexafluorophosphate solution (3.0 g/ 3 mL) was added drop by drop to mixture and stirred for 1 h. The mixture was diluted with cold water (50 mL). Yellowish-orange precipitate was filtered by vacuum filtration and washed with water (100 mL). The product was obtained as yellow solid after dried under vacuum. Yield: 85% (0.76 g). Mp: 105-108 °C. <sup>1</sup>H NMR (500 MHz, **DMSO-d**<sub>6</sub>) δ (ppm): 9.16 (d, J = 1.7 Hz, 2H), 8.61 (dq, J = 7.7, 1.7 Hz, 2H), 8.32 (dd, J = 7.9, 1.7 Hz, 2H), 8.14-8.08 (m, 1H), 7.87-7.79 (m, 1H), 7.74-7.69 (m, 3H), 7.56 (t, J = 7.5 Hz, 1H), 7.40 (dd, J = 9.3, 3.1 Hz, 1H), 4.30 (t, J = 7.1 Hz, 2H), 4.20 (t, J = 6.3Hz, 2H), 3.87 (s, 3H), 2.09-1.98 (m, 2H), 1.88-1.75 (m, 2H). <sup>13</sup>C NMR (126 MHz, **DMSO-d**<sub>6</sub>) δ (ppm): 178.0, 177.7, 156.0, 139.8, 138.7, 133.8, 132.7, 127.1, 125.8, 125.5, 124.1, 124.0, 123.2, 122.7, 122.4, 121.0, 108.2, 67.8, 48.9, 36.2, 26.7, 25.6. <sup>19</sup>F {<sup>1</sup>H} NMR (471 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): -70.8 (d, J = 710.5 Hz). <sup>31</sup>P {<sup>1</sup>H} NMR (202 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): -144.2 (hept, J = 711.4 Hz). HR-MS [M<sup>+</sup>] Calculated: (C<sub>23</sub>H<sub>21</sub>NO<sub>5</sub>Na) 450.1812; Found: 450.1825.

#### 3.3.2 Synthesis of iTMC Emitters

 3.3.2.1 Synthesis of bis(3,5-difluoro-2-[5-(trifluoromethyl)-2pyridinyl- κN]phenyl-κC)-4,4',6,6'-tetramethyl-2,2'-bipyridine Iridium(III) trifluoromethanesulfonimide (1a)

4,4',6,6'-Tetramethyl-2,2'-bipyridine (46.7 mg, 0.22 mmol, 2.0 equiv.) and di- $\mu$ chlorotetrakis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl- $\kappa$ N]phenyl- $\kappa$ C]di iridium (103.1 mg, 0.11 mmol, 1.0 equiv.) were added to two necked round bottom flask. The reaction mixture was stirred at 150 °C for 3 h. The mixture was cooled to RT and excess LiTFSI was added. Distilled water (100 mL) was added, and the organic phase was extracted with DCM (3 x 100 mL). The organic layer was then concentrated under reduced pressure. The crude product was recrystallized with the mixture of DCM: Hexanes. Yellow crystals were obtained. **Yield**: 71% (72.6 mg). <sup>1</sup>**H NMR (500 MHz, CDCl3) δ (ppm)**: 8.46 (dd, *J* = 8.7, 3.3 Hz, 2H), 8.32 (s, 2H), 8.09 (d, *J* = 2.0 Hz, 2H), 7.70 (d, *J* = 1.8 Hz, 2H), 7.20 (s, 2H), 6.55 (td, *J* = 9.1, 4.4 Hz, 2H), 5.46 (dd, *J* = 8.3 Hz, 2H), 2.56 (s, 6H), 1.84 (s, 6H).

 3.3.2.2 Synthesis of bis(3,5-difluoro-2-[5-(trifluoromethyl)-2pyridinyl- κN]phenyl-κC)-4,4',6,6'-tetramethyl-2,2'-bipyridine Iridium(III) hexafluorophosphate (1b)

4,4',6,6'-Tetramethyl-2,2'-bipyridine (46.7 mg, 0.22 mmol, 2.0 equiv.) and di- $\mu$ chlorotetrakis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl- $\kappa$ N]phenyl- $\kappa$ C]di iridium (106.3 mg, 0.11 mmol, 1.0 equiv.) were added to two necked round bottom flask. The reaction mixture was stirred at 150 °C for 3 h. The mixture was cooled to RT and excess NH<sub>4</sub>PF<sub>6</sub> was added. Distilled water (100 mL) was added, and the organic phase was extracted with DCM (3 x 100 mL). The organic layer was then concentrated under reduced pressure. The crude product was recrystallized with the mixture of DCM: Hexanes. Yellow crystals were obtained. **Yield**: 85% (78.8 mg). 8.48 (dd, *J* = 8.8, 3.2 Hz, 2H), 8.36 (s, 2H), 8.10 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.68 (s, 2H), 7.22 (d, *J* = 3.6 Hz, 4H), 6.54 (ddd, *J* = 11.1, 8.7, 2.3 Hz, 2H), 5.46 (dd, *J* = 8.2, 2.3 Hz, 2H), 2.69 (s, 6H), 1.85 (s, 6H).

# 3.3.2.3 Synthesis of bis(3,5-difluoro-2-[5-(trifluoromethyl)-2 pyridinyl- κN]phenyl-κC)-4,4'-dimethyl-2,2'-bipyridine Iridium(III) trifluoromethanesulfonimide (2a)

4,4'-Dimethyl-2,2'-bipyridine (40.1 mg, 0.22 mmol, 2.0 equiv.) and di- $\mu$ chlorotetrakis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl- $\kappa$ N]phenyl- $\kappa$ C]di iridium (103 mg, 0.11 mmol, 1.0 equiv.) were added to two necked round bottom flask. The reaction mixture was stirred at 150 °C for 3 h. The mixture was cooled to RT and excess LiTFSI was added. Distilled water (100 mL) was added, and the organic phase was extracted with DCM (3 x 100 mL). The organic layer was then concentrated under reduced pressure. The crude product was recrystallized with the mixture of DCM: Hexanes. Yellow crystals were obtained. **Yield**: 83% (83.3 mg). <sup>1</sup>**H** NMR (500 MHz, **CDCl3**)  $\delta$  (**ppm**): 8.70 (s, 2H), 8.42 (dd, *J* = 8.8, 3.2 Hz, 2H), 8.04 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 5.6 Hz, 2H), 7.58 (s, 2H), 7.36 (d, *J* = 5.6 Hz, 2H), 6.65 (ddd, *J* = 11.9, 8.9, 2.3 Hz, 2H), 5.63 (dd, *J* = 8.1, 2.3 Hz, 2H), 2.69 (s, 6H).

#### 3.4 Device Fabrication

The device production steps were started with the preparation of the anode substrate and after the thin films of organic material used as the active layer were formed, the device production was completed by coating the cathode material.

ITO coated glass substrates were prepared with the help of diamonds with dimensions of 3.0 x 3.0 cm. The ITOs, which were cleaned by chemical method (in ultrasonic baths for 30 minutes in toluene, acetone, and isopropyl alcohol each), were removed from the surface with nitrogen gas and the isopropyl alcohol on them. The cleaned ITOs were kept in  $O_2$  plasma at  $10^{-2}$  mbar 60 W for 3 minutes to remove foreign impurities that may remain on the surface. PEDOT:PSS used as HTM was coated on ITO glass at 4000 rpm. Thin films were annealed at 120°C for 30 minutes.

According to the previous studies, thickness optimization studies, the densities of iridium complexes were prepared in acetonitrile at a concentration of 20 mg/ml. Within the scope of the optimization studies, the thicknesses of the thin films obtained by using different spin speeds of 1000 and 1500 rpm for iTMC emitters. The active

layer coating was carried out by taking 250  $\mu$ l of these prepared solutions and coating on ITO/PEDOT:PSS at 1500 rpm (optimal coating speed) by a spin coating method. The thin films were annealed under T<sub>g</sub> temperature for 30 minutes in a vacuum oven at 100 °C and the solvent was evaporated for iTMC emitters. The electron transport layer was formed by the cathode vacuum thermal evaporation method. The ambient pressure is 3x10<sup>-6</sup> mbar. The Al cathode material was coated on ITO/PEDOT:PSS/iTMC. The thin films were spin coated at 2000 rpm, 60 seconds and annealed at 75 degrees for 5 minutes. Device configuration is ITO/PEDOT:PSS/Active Film/Al for ionic small molecules.

# Chapter 4

### Results

#### 4.1 Compound Characterization

#### 4.1.1 Molecular Characterization

Intermediates (8)[180], (9)[180] and (10)[181] were synthesized according to previous literature. Br-DiKTa was synthesized in 4 steps. The first step was Buchwald-Hartwig cross coupling reaction between aniline and methyl 2-iodobenzoate which gave the dimethyl 2,2'-(phenylazanediyl)dibenzoate (1) in a moderate yield (56%). 2,2'-((4-Bromophenyl)azanediyl)dibenzoate (2) was obtained from the bromination reaction of compound (1) using NBS. After the saponification reaction, Br-DiKTa was obtained by Friedel-Crafts acylation with SOCl<sub>2</sub> AlCl<sub>3</sub>. 3-((4and Methoxyphenyl)(phenyl)amino)quinolino[3,2,1-de]acridine-5,9-dione (4) was obtained by Buchwald-Hartwig cross coupling reaction between 4-methoxy-Nphenylaniline and 3-bromoquinolino[3,2,1-de]acridine-5,9-dione in high yield. Compound (5) obtained the demethylation of the 3-((4was by methoxyphenyl)(phenyl)amino)quinolino[3,2,1-de]acridine-5,9-dione (4) with boron tribromide. For alkylation step for both intermediate (compound 5 and 12) used same condition, in the presence of NaO'Bu and THF gave compound 6 and 13, respectively. Final compounds (DiKTa-OBuIm and DiKTa-DPA-OBuIm) were obtained by the reaction of 1-methylimidazole at 100 °C followed by exchange of  $PF_6^-$  anion. All compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy, and mass spectrometry.



Scheme 4.1: (i) K<sub>2</sub>CO<sub>3</sub>, CuSn, CuI, di-n-butyl ether, 150 °C. (ii) NaOH, ethanol:water (1:1) reflux (iii) AlCl<sub>3</sub>, SOCl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, reflux (iv) Pd<sub>2</sub>(dba)<sub>3</sub>, NaO<sup>t</sup>Bu, TTBP.HBF<sub>4</sub>, toluene, reflux (v) BBr<sub>3</sub>, 0 °C, CH<sub>2</sub>Cl<sub>2</sub> (vi) NaO<sup>t</sup>Bu, 1,4dibromobutane, THF, reflux (vii) 1-methylimidazole, 100 °C, 2 h, NH<sub>4</sub>PF<sub>6</sub>



Scheme 4.2: (i) KMnO<sub>4</sub>, t-BuOH:water (1:1), 90 °C, 12 h (ii) MeOH, H<sub>2</sub>SO<sub>4</sub>, 65 °C, 16 h (iii) K<sub>2</sub>CO<sub>3</sub>, CuI, CuSn, di-n-butyl ether, 150 °C (iv) K<sub>2</sub>CO<sub>3</sub>, di-n-butyl ether, CuI, CuSn, 150 °C, 3 d (v)1. EtOH:water (1:1), NaOH 2. (COCl)<sub>2</sub>, AlCl<sub>3</sub>, reflux, 18 h (vi) 1,4-dibromobutane, Na<sup>t</sup>OBu, THF (vii)1-methylimidazole, 100 °C, 2 h, NH<sub>4</sub>PF<sub>6</sub>

Iridium complexes were synthesized with the di- $\mu$ -chlorotetrakis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl- $\kappa$ N]phenyl- $\kappa$ C]di iridium and two equivalent of N^N ligand followed by exchange of the counterion (NH<sub>4</sub>PF<sub>6</sub>/LiTFSI) according to the current literature procedure. 4,4',6,6'-Tetramethyl-2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine ligands were used as ancillary ligand. 3,5-Difluoro-2-[5-

(trifluoromethyl)-2-pyridinyl was cyclometalated ligand for iridium complexes. The complexes were purified by crystallization in the dichloromethane hexane solvent system. Synthetic pathway of complexes is given in Scheme 4.3. Auxiliary ligand 1 [182] and ligand 2[183] are already in the literature. Crystal structure of ligand 1 were studied within the scope of this thesis.



Scheme 4.3: Synthetic pathway of iridium complexes 1a, 1b and 2a

In the <sup>1</sup>H NMR spectrum of ligand 1, aromatic ring protons were observed at 6.97 and 7.99 ppm as a singlet. Methyl protons were located 2.58 and 2.37 ppm. For ligand 2, aromatic ring protons were at 8.49 ppm (doublet), 8.19 ppm (singlet) and 7.08 ppm (doublet). Methyl protons were observed at 2.38 ppm as a singlet. These results are compatible with the previous literature[184].

In <sup>1</sup>H NMR spectra of **1a** and **1b** complexes, aromatic ring protons were observed between 8.46-5.46 ppm and 8.48-5.46 ppm, respectively. Methyl protons located at *ortho* position were observed at 2.56 ppm and those located *para* position were observed at 1.84 ppm as singlet.

In <sup>1</sup>H NMR spectrum of **2a** complex, aromatic protons and methyl protons were observed between 8.70-5.63 and 2.69 ppm, respectively.

#### 4.1.2 Electrochemical Characterization

The electrochemical properties of the emitters were studied by cyclic voltammetry (CV) in degassed acetonitrile with  $[^{n}Bu_{4}N]PF_{6}$  as the supporting electrolyte, and the values reported versus SCE. The CV and DPV spectra are shown in Fig. 4.1 and the data for oxidation/ reduction potentials ( $E_{ox}/E_{red}$ ) are summarized in Table 4.1.



Figure 4.1: Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) of DiKTa-OBuIm (green) and DiKTa-DPA-OBuIm (red) in degassed acetonitrile with 0.1 M [ $nBu_4N$ ]PF<sub>6</sub> as the supporting electrolyte and Fc<sup>+</sup>/Fc as the internal reference (0.38 V vs SCE)[178] Scan rate = 100 mV s<sup>-1</sup>

Table 4.1: Oxidation/ reduction potentials and HOMO/LUMO values of DiKTa derivatives

	E <sub>ox</sub> <sup>a</sup> /V	Ered <sup>a</sup> /V	HOMO <sup>b</sup> /eV	LUMO <sup>b</sup> /eV	$\Delta E_{H-L}^{c}/eV$
DiKTa-OBuIm <sup>a</sup>	1.05	-1.67	-5.85	-3.13	2.72
DiKTa-DPA-OBuIm <sup>a</sup>	0.44	-1.61	-5.24	-3.18	2.06
DiKTa <sup>a</sup>	1.66	-1.33	-5.93	-3.11	2.82
<b>DDiKTa</b> <sup>b</sup>	1.63	-1.27	-	-	-
Mes3DiKTa	1.54	-1.28	-5.86	-3.26	2.59
3-PhQAD	_	-	-6.20	-3.38	2.82
7-PhQAD	-	-	-6.19	-3.40	2.79

<sup>a</sup> In degassed MeCN with 0.1 M ["Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte and Fc/Fc<sup>+</sup> as the internal reference (0.38 V vs. SCE). <sup>b</sup>In degassed DCM with 0.1 M ["Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte and Fc/Fc<sup>+</sup> as the internal reference (0.46 V vs. SCE). <sup>b</sup>The HOMO and LUMO energies were determined using the relation  $E_{\text{HOMO/LUMO}} = -(E_{\text{ox}} / E_{\text{red}} + 4.8)$  eV, where  $E_{\text{ox}}$  and  $E_{\text{red}}$  are the anodic and cathodic peak potentials, respectively calculated from DPV related to Fc/Fc<sup>+</sup>. <sup>c</sup> $E_{\text{H-L}} = |E_{\text{HOMO}} - E_{\text{LUMO}}|$ .

**DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** show reversible reduction and reversible oxidation waves. The  $E_{ox}$  and  $E_{red}$  determined from the DPV peaks and values were found as 1.05/0.44 and -1.67/-1.61 V, respectively. The HOMO is more highly affected by the addition of donor units. Decreased  $\Delta E$  **DiKTa-DPA-OBuIm** can be due to the increased conjugation compared to **DiKTa-OBuIm**. **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** have LUMO values that match DiKTa (-3.11 eV), indicating that reduction happens on the DiKTa core in both compounds.

The electrochemical properties of the ligands and iridium complexes were studied by CV measurements in a 0.1 M solution of ["Bu<sub>4</sub>N]PF<sub>6</sub> in acetonitrile. CVs of ligand **1** and ligand **2** is given in Figure 4.2. Ligand **1** has a reduction potential of -0.69V V and its oxidation peak of approximately is at -0.54V. The reduction potential of ligand **2** is observed at -0.73 V with an oxidation peak of -0.37V. The HOMO energy levels of ligands were calculated by the optical band gap  $(E_g^{opt})$ . One of the ways followed in the literature is calculated by drawing a tangent line from the top of the absorption curve to the wavelength where it ends, and substituting the corresponding wavelength in the equation,  $\Delta E_g^{opt} = \frac{1241}{\lambda nm}$ [185,186]. Optical band gaps are found to be 4.01 and 4.09 eV, respectively.



Figure 4.2: Cyclic voltammograms (CVs) of ligand 1 and ligand 2

Table 4.2: Oxidation/reduction potentials and HOMO/LUMO values of iridium (III	I)
complexes and ligands	

	Eox <sup>a</sup> /V	Ered <sup>a</sup> /V	HOMO <sup>b</sup> /eV	LUMO <sup>b</sup> /eV	ΔEн-l/eV
Ligand 1	-	-0.69	-7.72	-3.71	-4.01
Ligand 2	-	-0.73	-7.76	-3.67	-4.09
1a	+1.70	-0.75	-6.10	-3.65	-2.45
1b	+1.68	-0.72	-6.08	-3.68	-2.40
2a	+1.63	-0.66	-6.03	-3.74	-2.29

<sup>a</sup> In degassed MeCN with 0.1 M [<sup>*n*</sup>Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte, <sup>b</sup>The HOMO and LUMO energies were determined using the relation  $E_{\text{HOMO/LUMO}} = -(E_{\text{ox}} / E_{\text{red}} + 4.4)$  eV, where  $E_{\text{ox}}$  and  $E_{\text{red}}$  are the anodic and cathodic peak potentials.

CVs of complexes **1a**, **1b** and **2a** are given in Figure 4.3. For the Ir(III) complexes, the desired optical properties can be obtained by the changing of the ligand structure. The electron density of the HOMO to be located on the metal centre and on the C^N ligands

while the LUMO is largely located on the N^N ancillary, distributions characteristic of cationic Ir(III) complexes. While the HOMO energy level of Ir(C^N)(III) complexes is usually determined by the iridium metal-centered d orbitals, the LUMO energy level is determined by the p-orbitals in the ligands[187]. In Ir(III) complexes, an electron leaves the center of the metal, causing oxidation with the conversion of Ir(III)/Ir(IV). The electron withdrawing groups will reduce the electron density around the metal center, resulting in a lower HOMO energy level[188]. The reduction potentials of the Ir(III) complexes are associated with the N^N ligand and the oxidation potentials with the C^N ligand. The oxidation peak of complexes change between +1.70 and +1.63 V, which is attributed to the Ir(III)/(IV) redox with contributions from the C^N ligands. The reduction peak of complexes changes between -0.66 and -0.75 V. Complexes **1a** and **1b** have a similar oxidation/reduction potential because of having the same cationic structures. As it can be understood, changing the anion has no effect on the oxidation/reduction potentials.



Figure 4.3: CVs of complexes **1a**, **1b** and **2a** in degassed acetonitrile solution with 0.1 M [*n*Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte

#### 4.1.3 Photophysical Characterization

Solution-state photophysical measurements; absorption and steady-state emission spectra of **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** in dilute acetonitrile solution are given in Figure 4.4. The absorption spectra show two main bands. The lowest energy absorption band for **DiKTa-OBuIm** at 453 nm ( $\varepsilon = 17 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) is red-shifted and slightly more intense compared to parent **DiKTa** at 436 nm, ( $\varepsilon = 14 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) due to the increased conjugation in **DiKTa-OBuIm**. This band is assigned to a short-range charge transfer transition (SRCT) that is characteristic for MR-TADF compounds. The Stokes shift is 54 nm (2361 cm<sup>-1</sup>) for **DiKTa-OBuIm**. The lowest energy absorption band in **DiKTa-OPA-OBuIm** is red-shifted and less intense ( $\varepsilon = 6$ 

×  $10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) than **DiKTa-OBuIm**, which attributed to a transition with significant long-range charge transfer (LRCT) character. As expected from D-A compounds, the Stokes shift is larger at 75 nm (2761 cm<sup>-1</sup>). **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** exhibited broad green ( $\lambda_{PL} = 507 \text{ nm}$ , FWHM = 75 nm) and red ( $\lambda_{PL} = 563 \text{ nm}$ , FWHM = 92 nm) emissions in MeCN. The photoluminescence quantum yield,  $\Phi_{PL}$ , in MeCN for **DiKTa-OBuIm** is 48% which decreases in air to 34%. The emission is much weaker in **DiKTa-DPA-OBuIm**, reflecting both the smaller oscillator strength of the transition to S<sub>1</sub> and the greater non-radiative decay due to the energy gap law ( $\Phi_{PL} =$ 11% and 7%, respectively under vacuum and in air) in MeCN. The S<sub>1</sub> and T<sub>1</sub> levels were measured from the onsets of fluorescence (2.66 eV) and phosphorescence spectra (2.41 eV) in 2-MeTHF glass at 77 K. **DiKTa-OBuIm** possesses a  $\Delta E_{ST}$  of 0.25 eV. Unfortunately, **DiKTa-DPA-OBuIm** was insoluble in 2-MeTHF and so the measurement could not be made. No delayed component was observed in MeCN solution under vacuum for either of the compounds.



Figure 4.4: Solution-state photophysical measurements: absorption and steady-state emission spectra at 300 K measured in THF.  $\lambda_{exc} = 453$  nm for **DiKTa-OBuIm** and  $\lambda_{exc} = 488$  nm for **DiKTa-DPA-OBuIm** 

The photoluminescence properties of **DiKTa-DPA-OBuIm** and **DiKTa-OBuIm** were investigated as neat films and as 1wt% in mCP (1,3-bis(*N*-carbazolyl)benzene), 1wt % in PMMA and 1wt% in blue ionic host doped films (Figure 4.5).


Figure 4.5: Thin film PL spectra for a) DiKTa-OBuIm and b) DiKTa-DPA-OBuIm

The  $\lambda_{PL}$  are 499 nm and 577 nm for **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** in mCP, respectively. The neat film photoluminescence quantum yields were measured. The highest PLQY were found as 70.6% and 61.0% in mCP for **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm**, respectively. The photophysical properties are summarized in Table 4.3. The enhance in PLQY in N<sub>2</sub> can be attributed to TADF. In air, the triplet states of molecules are quenched by oxygen dissolved in the solution, leading suppressed TADF and the lower PLQY. The removal of oxygen from the solution by bubbling N<sub>2</sub> gas through it allows triplet states to exist[189].

Table 4.3: PLQY measurements of DiKTa-OBuIm and DiKTa-DPA-OBuIm in drop casted thin films

	Film type	Host	Concentration	PLQY	PLQY	λexc	$\lambda_{PL}$
	rim type	11050	Concentration	(%) air	(%) N2	(nm)	(nm)
	Neat	-	Neat	9.0	9.0	420	554
OBuIm	1wt% in mCP	mCP	1wt%	57.2	70.6	340	499
	1wt% in PMMA	PMMA	1wt%	27.5	33.0	440	514
DiKTa-	Neat	-	Neat	-	-	550	679
DPA-	1wt% in mCP	mCP	1wt%	53.3	61.0	340	577
OBuIm	1wt% in PMMA	PMMA	1wt%	20.5	26.2	465	577

Time-resolved PL measurements of the thin films were carried out using an iCCD camera. The singlet-triplet energy gap ( $\Delta E_{ST}$ ) was determined from the difference in energy of the onset of the prompt fluorescence and phosphorescence spectra in 2-MeTHF solution measured at 77 K (Figure 4.6). The calculated  $\Delta E_{ST}$  value (0.31 eV) for **DiKTa-OBuIm** was found to be 0.16 eV experimentally from the onset of these spectra.



Figure 4.6: Prompt fluorescence (at 77K) and phosphorescence spectra (at 77K) of DiKTa-OBuIm in 2-MeTHF

The temperature-dependent time-resolved emission decay characteristics of **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** in mCP is shown in Figure 4.7. Two emitters exhibit very small change in the decay with temperature.



Figure 4.7: (a) Steady-state emission spectra of DiKTa-OBuIm and DiKTa-DPA-OBuIm in 1wt% doped mCP films. (b) Temperature-dependent time resolved PL decays of DiKTa-OBuIm in 1wt% doped mCP films. λ<sub>exc.</sub> = 379 nm. (c)
Temperature-dependent time resolved PL decays of DiKTa-DPA-OBuIm in 1wt% doped mCP films. λ<sub>exc.</sub> = 379 nm

The absorption and PL spectra of ligands **1** and **2** are given in Figure 4.8. The maximum absorption peaks were observed at 244 and 290 nm for ligand 1 and 242 and 281 nm for ligand 2. These absorption bands are attributed to  $\pi \rightarrow \pi^*$  transitions. In the ligand 2 spectrum, maximum absorption peak blue shifted because of the increasing of weak electron donating methyl groups. Pyridine is a naturally electron-deficient aromatic ring that has been utilized to create complexes that Ir(III) complexes by attaching to the phenyl ring in ppy. The PL yield increases due to the methyl group in the *meta* position of the phenyl rings relative to the iridium atom. It is known that the methyl groups attached at the *meta* position with respect to the Ir metal atom have

a great influence on absorption, emission, redox potentials and electroluminescence[190]. Additionally, the LEC performances of complexes containing TFSI<sup>-</sup> anion were higher than complexes containing  $PF_6^-$  anion due to the electron delocalization of the anion and its high conductivity [191,192].



Figure 4.8: Absorption and PL spectra of ligands 1 and 2 in MeCN

The absorption and PL spectra of iridium complexes are given in Figure 4.9. The maximum absorption wavelength of the **1a** and **2a** complexes in MeCN showed a maximum at 257 and 248nm with a shoulder at 313 and 291nm, respectively. For complex **1b**, absorption peaks were observed at 302 and 259 nm, respectively. The strong absorption bands of complexes at 250 nm are due to ligand-centered (<sup>1</sup>LC)  $\pi$ - $\pi$ <sup>\*</sup> transitions on ligands, while weak absorption intensity ranging from 270-300 nm is spin-permitted metal-to-ligand charge transfer (<sup>1</sup>MLCT)[193]. Metal-centered charge transitions can be explained by the strong heavy atom effect of Ir(III) complexes on the spin-orbit coupling[194-196].



Figure 4.9: Normalized absorption and PL spectra of 1a, 1b and 2a complexes in MeCN

#### 4.1.4 Crystallographyic Studies

Within the scope of the thesis, the structure of **1**, **1a** and **1b** molecules was clarified with single crystal. The diffraction data of these compounds were collected on a Rigaku-Oxford XCalibur EOS-CCD detector diffractometer (MoK<sub> $\alpha$ </sub> radiation graphite monochromator,  $\lambda = 0.71073$  Å). The processing of data was carried out in CrysAlis Pro software. Data reduction and analytical absorption corrections were performed by CrysAlis Pro program[197]. Using Olex2[198], the structures were solved using ShelXT structure solution program, employing Intrinsic Phasing method[199]. The model was refined by full-matrix least-squares on F<sup>2</sup> in SHELXL[200]. All nonhydrogen atoms were refined anisotropically and hydrogen atoms were added to the structure in idealized positions and further refined according to the riding model.

Ligand 1 crystals were obtained from slow evaporation of ethyl acetate. Bond lengths, bond angles and torsion Angles (°) of **1** are also given in Table 4.4 and Table 4.5. Image of ligand **1** and packing image of the ligand 1 in the b-axis obtained with the Ortep program are given in Figure 4.10 and Figure 4.11, respectively.

Table 4.4: Selected Bond Lengths (Å) of ligand 1 (Asymmetric unit is constructed by the symmetry operations with the symmetry code <sup>1</sup>: 1-X,1-Y,+Z) and Bond Angles (°) of **L** (symmetry code <sup>1</sup>: 1-X,1-Y,+Z)

Bond Lenghts (Å)						
N1-C1	1.375(8)	N1-C5	1.354(6)			
C1-C1 <sup>1</sup>	1.484(4)	C1-C2	1.347(8)			
C2-C3	1.379(6)	C3-C4	1.366(10)			
C3-C7	1.516(9)	C4-C5	1.397(10)			
C5-C6	1.482(9)	-	-			

Bond An	gles (°)	Torsion Ar	igles (°)
C5-N1-C1	119.3(6)	N1-C1-C2-C3	-0.3(4)
N1-C1-C1 <sup>1</sup>	118.7(3)	C1-N1-C5-C4	-0.7(7)
C2-C1-N1	122.6(2)	C1-N1-C5-C6	179.5(5)
C2-C1-C11	118.7(3)	C1 <sup>1</sup> -C1-C2-C3	179.3(4)
C1-C2-C3	118.4(5)	C1-C2-C3-C4	-0.2(7)
C2-C3-C7	118.5(7)	C1-C2-C3-C7	-178.7(4)
C4-C3-C2	120.3(6)	C2-C3-C4-C5	0.2(4)
C4-C3-C7	121.2(5)	C3-C4-C5-N1	0.2(4)
C3-C4-C5	120.2(2)	C3-C4-C5-C6	-180.0(6)
N1-C5-C4	119.2(6)	C5-N1-C1-C11	-178.8(4)
N1-C5-C6	120.0(7)	C5-N1-C1-C2	0.8(4)
C4-C5-C6	120.8(5)	C7-C3-C4-C5	178.7(6)

Table 4.5: Selected Bond angles and torsion Angles (°) of ligand 1 (symmetry code <sup>1</sup>: 1-X, 1-Y, +Z)

According to the results, ligand 1 was in the orthorhombic crystal system (Table 4.5). Image of ligand 1 and its packing image in the b-axis obtained with the Ortep program are given in Figure 4.10 and Figure 4.11, respectively.



Figure 4.10: Image of ligand 1 obtained with the Ortep program



Figure 4.11: Packing image of the ligand 1 in the b-axis

Structures	1	1a	1b	
Empirical formula	$C_{14}H_{16}N_2$	$C_{38}H_{26}F_{16}IrN_4P$	$C_{40}H_{26}F_{16}IrN_5O_4S_2$	
Formula weight	212.29	1065.8	1200.98	
Temperature/K	150.00(10)	293(2)	293(2)	
Crystal system	orthorhombic	monoclinic	triclinic	
Space group	Aea2	P21/n	P-1	
a/Å	11.9585(6)	14.1052(6)	12.0989(8)	
b/Å	6.3028(3)	20.3937(6)	13.1950(8)	
c/Å	15.7676(12)	14.8992(7)	15.7971(7)	
α/°	90	90	83.513(4)	
β/°	90	104.265(4)	70.362(5)	
γ/°	90	90	69.798(5)	
Volume (Å <sup>3</sup> )	1188.44(12)	4153.7(3)	2229.1(2)	
Z	4	4	2	
$\rho_{calc}(g/cm^3)$	1.19	1.704	1.789	
$\mu/\text{mm}^{-1}$	0.07	3.358	3.202	
F(000)	456	2072	1172	
$Crystal size/mm^3$	$0.362 \times 0.3 \times$	0.27  imes 0.16  imes	0 59 × 0 28 × 0 11	
	0.118	0.13	0.20 0.11	
Radiation		Mo K $\alpha$ ( $\lambda = 0.71$	.073)	
$2\Theta$ range /°	6.814 to 52.742	6.036 to 50.052	5.82 to 52.856	
	$-14 \le h \le 14$	$-16 \le h \le 16$	$-14 \le h \le 15$	
Index ranges	$-7 \le k \le 7,$	$-24 \le k \le 24,$	$-16 \le k \le 14$	
	$-19 \le l \le 19$	$-17 \le l \le 17$	-17 ≤1 ≤ 19	
Reflections collected	8060	47938	15942	
	1221	7323	15942	
Independent reflections	$[R_{int}=0.0439,$	$[R_{int}=0.0760,$	[R <sub>int</sub> =-,	
	R <sub>sigma</sub> =0.0294]	$R_{sigma} = 0.0557$ ]	R <sub>sigma</sub> =0.0900]	
Data/restraints/parameters	1221/1/75	7323/72/571	15942/113/674	
Goodness-of-fit on F2	1.04	1.01	0.865	
Final R indexes	$R_1=0.0449,$	$R_1=0.0400,$	$R_1 = 0.0377,$	
[I>=2σ (I)]	wR <sub>2</sub> =0.1183	$wR_2 = 0.0803$	wR <sub>2</sub> =0.0738	
Final R indexes [all data]	R1 = 0.0651,	$R_1 = 0.0713,$	$R_1 = 0.0585,$	
	wR2 = 0.1343	wR <sub>2</sub> =0.0911	wR <sub>2</sub> =0.0763	
Largest diff. peak/hole/eÅ <sup>-3</sup>	0.20/-0.18	1.16/-0.44	1.26/-0.74	

Table 4.5: X-ray data collection of molecules, crystallographic characterization and structure analysis parameters

**1a** and **1b** crystals were grown from dichloromethane/hexane solution by slow evaporation of the solvents. They were crystallized in the monoclinic and triclinic crystal system (Table 4.5). In both complexes, fluorine atoms of  $CF_3$ — groups are refined as disordered positions. Image of **1a** and **1b** complexes obtained with the Ortep program were given in Figure 4.12. Packing image in the b-axis of the **1a** and **1b** complexes are given in Figure 4.13 and Figure 4.14, respectively. Selected bond

lengths and bond angles for complexes **1a** and **1b** are given in Table 4.6 and Table 4.7, respectively.

	1a	1b		
Ir7—N1	2.185(4)	Ir1—N1	2.206(5)	
Ir7—N2	2.206(4)	Ir1—N2	2.199(4)	
Ir7—N3	2.065(4)	Ir1—N3	2.029(4)	
Ir7—N4	2.037(4)	Ir1—N4	2.043(5)	
Ir7—C1	2.003(5)	Ir1–C1	2.006(6)	
Ir7–C13	2.005(6)	Ir1–C13	2.009(6)	

Table 4.6: Selected Bond Lengths (Å) for complexes 1a and 1b

Table 4.7: Selected Bond Angles (°) for complexes 1a and 1b

1a					1b			
N1-Ir7-N2	75.64(14)	C1-Ir7-N3	96.1(2)	N2—Ir1—N1	76.08(18)	C1–Ir1–N2	105.1(2)	
N3—Ir7—N1	93.29(17)	C1-Ir7-N4	81.1(2)	N3—Ir1—N1	98.11(19)	C1–Ir1–N3	80.7(2)	
N3—Ir7—N2	84.20(15)	C1–Ir7–C13	82.4(2)	N3-Ir1-N2	90.03(17)	C1–Ir1–N4	96.5(2)	
N4—Ir7—N1	93.14(16)	C13–Ir7–N1	172.25(19)	N3—Ir1—N4	175.81(19)	C1–Ir1–C13	81.5(2)	
N4—Ir7—N2	98.75(16)	C13–Ir7–N2	99.84(17)	N4—Ir1—N1	84.56(19)	C13–Ir1–N1	97.4(2)	
N4—Ir7—N3	173.42(18)	C13–Ir7–N3	79.9(2)	N4-Ir1-N2	93.75(18)	C13–Ir1–N2	171.6(2)	
C1-Ir7-N1	102.09(17)	C13–Ir7–N4	93.8(2)	C1-Ir1-N1	178.34(19)	C13–Ir1–N3	96.2(2)	
C1-Ir7-N2	177.72(19)			C13–Ir1–N4	80.2(2)			



Figure 4.12: Image of **1a** (top) and **1b** (bottom) complexes obtained with the Ortep program



Figure 4.13: Packing image of the complexes **1a** in the b-axis



Figure 4.14: Packing image of the complexes 1b in the b-axis

### 4.1.5 Computational Studies

The energies of frontier molecular orbitals (HOMO, HOMO-1, LUMO and LUMO+1) of **DiKTa-DPA-OBuIm** and **DiKTa-OBuIm** were calculated based on the optimized ground state gas-phase geometry using Density Functional Theory (DFT) with the PBE0 functional and the 6-31G(d,p) basis set (Figure 4.15 and Figure 4.16). Calculations for both molecules were made with the methyl and butyl chain. Increasing the number of carbons in the alkyl chain did not change the frontier molecular orbital energies. The energies of HOMO/HOMO-1 and LUMO/LUMO+1 of **DiKTa-DPA-OBuIm** molecule were found to be -1.2/-2.1 eV and -5.1/-6.2 eV. The energies of HOMO/HOMO+1 of **DiKTa-OBuIm** molecule were found to be -1.3/-2.1 eV and -5.9/-7.0 eV.



Figure 4.15: Isocontour plots of the HOMO/HOMO–1 and LUMO/LUMO+1 orbitals calculated in the gas phase at the PBE0/6-31G(d,p) level of **DiKTa-DPA-OBuIm** with methyl and butyl chain



Figure 4.16: Isocontour plots of the HOMO/HOMO–1 and LUMO/LUMO+1 orbitals calculated in the gas phase at the PBE0/6-31G(d,p) level of **DiKTa-OBuIm** with methyl and butyl chain

HOMO is mainly located on the diphenylamine moiety and LUMO is located on DiKTa core for the **DiKTa-DPA-OBuIm** molecule. The highest occupied molecular orbital (HOMO) in **DiKTa-OBuIm** is also localized on the **DiKTa** core and the electron density distribution of this molecule is reminiscent to that of a MR-TADF compound and is nearly identical to that of the parent emitter, **DiKTa**. There is a big difference in both the electron density distribution and the HOMO energy between the two emitters. For **DiKTa-DPA-OBuIm**, the HOMO is mainly localized on the DPA unit, but with some delocalization onto to the **DiKTa** core, resulting in a destabilization of this orbital from -5.91 eV in **DiKTa-OBuIm** to -5.19 eV in **DiKTa-DPA-OBuIm**. Compound **DiKTa-DPA-OBuIm** can thus be considered a donor-acceptor system. The calculated energies of molecules and DiKTa derivatives reported are summarized in Table 4.8.

Compound	HOMO / eV	LUMO / eV	$\Delta E_{\text{H-L}} / \text{eV}$
DiKTa	-5.94	-2.31	3.63
DDiKTa	-6.04	-2.34	3.70
DiKTa-OBuIm	-5.91	-2.17	3.77
DiKTa-DPA-OBuIm	-5.17	-2.10	3.02

 Table 4.8: The calculated energies of emitters and DiKTa derivatives

The HOMO and LUMO energy levels of **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** were found to be -5.91, -5.17 eV and -2.17, -2.10 eV, respectively. The calculated HOMO level of **DiKTa-DPA-OBuIm** is -5.17 eV, which is 0.77 eV higher than the parent molecule **DiKTa** due to the addition of electron donating DPA unit.

Difference density plots with respect to the gas phase ground state for  $S_1$  and  $T_1$  excited state for **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** calculated by highly correlated quantum chemical calculations at the spin-component scaling second-order approximate coupled-cluster (SCS-CC2) method with the cc-pVDZ level (Figure 4.17).



Figure 4.17: Difference density plots of S<sub>1</sub>, S<sub>2</sub>, T<sub>1</sub> and T<sub>2</sub> excited states of **DiKTa-OBuIm** (a) and **DiKTa-OPA-OBuIm** (b) calculated in the gas phase at the SCS-CC2/cc-pVDZ level. f indicates the oscillator strength

The oscillator strength, *f*, for the transition from  $S_0$  to  $S_1$  was found to be 0.1967 and 0.1607 for **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm**, respectively. The  $S_1$  energies are 3.30 eV for **DiKTa-OBuIm** and 3.07 eV for **DiKTa-DPA-OBuIm**, while the  $T_1$  energies decrease to 2.99 eV and 2.82 eV, respectively.  $\Delta E_{ST}$  values are found to be 0.31 eV and 0.25 eV for **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm**, respectively.  $S_1$ ,  $T_1$  and  $\Delta E_{ST}$  energies of **DiKTa**, **Mes<sub>3</sub>DiKTa**, **DDiKTa**, **3-PhQAD** and **7-PhQAD** are summarized in the Table 4.9. The calculated lowest singlet and triplet energy levels of two ionic **DiKTa** compounds slightly lower than DiKTa derivatives reported

before[137,159,201]. These small singlet-triplet energy gaps,  $\Delta E_{ST}$ , are small enough to permit the reverse intersystem crossing (RISC) from T<sub>1</sub> to S<sub>1</sub> at ambient temperatures. Thus, **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** are expected to be potential TADF emitters.

Compound	<b>S</b> <sub>1</sub> (eV)	<b>T</b> <sub>1</sub> ( <b>eV</b> )	$\Delta E_{\rm ST} ({\rm eV})$
DiKTa	3.45	3.18	0.27
DDiKTa	3.39	3.12	0.27
Mes <sub>3</sub> DiKTa	3.32	3.06	0.26
3-PhQAD	3.39	3.13	0.26
7-PhQAD	3.36	3.09	0.27
DiKTa-OBuIm	3.30	2.99	0.31
DiKTa-DPA-OBuIm	3.07	2.82	0.25

Table 4.9: S1, T1 and  $\Delta E_{ST}$  energies of DiKTa-OBuIm and DiKTa-DPA-OBuIm and DiKTa derivatives reported

### **4.2 Device Applications**

### 4.2.1 Device Applications of Ionic Small Molecules

For the fabricating LEC device with ionic small molecule emitters, the steps listed below were done:

- Neat film emitter was dissolved in acetonitrile.
- Emitter/small molecule host was dissolved in acetonitrile.
- Emitter/mCP was dissolved in dichloromethane.
- Emitter/mCP/polyelectrolyte was dissolved in dichloromethane.
- mCP/Host concentration/neat film concentration = 20 mg/mL.

Molecular structure of ionic liquid (BMIM:PF<sub>6</sub>), Polyelectrolyte: PEO (polyethylene glycol)/TMPE/Hybrane used in device fabrication are given in Figure 4.18.



Figure 4.18: The structure of ionic liquid (BMIM:PF<sub>6</sub>), Polyelectrolyte: PEO (polyethylene glycol)/TMPE/Hybrane used in device fabrication

The LEC device structure of the emitters is ITO/PEDOT:PSS/Active Film/Al configuration. The device structure of two emitters and the names of the devices are given in Table 4.10.

Emitter	Active Layer	Ionic Liquid (1:0.25 molar ratio host/IL)	Device
	1% wt in mCP (DCM)	BMIM:PF <sub>6</sub>	1A
DIVTO	1% wt in mCP + polyelectrolyte	BMIM:PF <sub>6</sub>	1B
OBulm	1% wt in host (MeCN)	BMIM:PF <sub>6</sub>	1C
OBuiii	1% wt in host (MeCN)	Without IL	1D
	Only Green Emitter	Without IL	1E
	1% wt in mCP (DCM)	BMIM:PF <sub>6</sub>	2A
DiKTa-	1% wt in host (MeCN)	BMIM:PF <sub>6</sub>	2B
DPA-	1% wt in host (MeCN)	Without IL	2C
OBuIm	1% wt in green host (MeCN)	Without IL	2D
	Only Red Emitter	Without IL	2E

Table 4.10: The device structure of two emitters and the names of the devices

For the device 1A, 1B and 2A, ionic liquid (BMIM:PF<sub>6</sub>) was added to improve the mobility in the active layer but no turn-on was observed because of the film degraded after annealing/thermal evaporation. Polyelectrolyte (PEO/TMPE/Hybrane) was added to improve mobility of the devices, but this did not avail.

For the device 1C, 1D, 2B and 2C, no degradation was observed after film preparation. Devices 1C and 2B, which include ionic liquid, exhibited very low luminance. Devices 1D and 2C which do not include ionic liquid worked as LECs but short-lived, which can be attributed to quenching mechanism between the emitters DiKTa-OBuIm or DiKTa-DPA-OBuIm and the host molecule.

It has been reported that the overgrowth of the doped regions after establishment of the "p-i-n" junction causes degradation of LECs due to narrowed intrinsic region and increased exciton-polaron quenching[202]. In LECs with LiF layers, it shows faster growth of n-doped regions, leading to reduced operational stability. Experimental results strongly suggest that overgrowth of doped regions plays an important role in the degradation of TADF LECs[166].



Figure 4.19: Voltage-Time and Luminance-Time graphs of devices 1D (left) and 2C (right) (Driven with a pulsed average current of 50 A m<sup>-2</sup>)

It has been reported that the overgrowth of the doped regions after establishment of the "p-i-n" junction causes degradation of LECs due to narrowed intrinsic region and increased exciton-polaron quenching[202]. In LECs with LiF layers, it shows faster growth of n-doped regions, leading to reduced operational stability. Experimental results strongly suggest that overgrowth of doped regions plays an important role in the degradation of TADF LECs[166].

The driving voltage fell when the pulsed current bias was applied, demonstrating that the devices work as LECs. Light emission is detected at around ~5 V, with values of 15cd m<sup>-2</sup> for the device with **DiKTa-DPA-OBuIm** and around 2 cd m<sup>-2</sup> for the devices with **DiKTa-OBuIm** and the host-guest system, each at 8 V. The brightness steadily reduced with time during constant-current operation. After 10 minutes, devices 1D and 2C showed 1.03 cd m<sup>-2</sup> and 2.07 cd m<sup>-2</sup> brightness. A recently

published study on small molecule LECs shows that a much higher bias voltage is required to exhibit device response time [166].

For the LEC devices fabricated with 2D, 1E and 2E, optimal quality films could not be obtained. The devices did not work as LECs. They were also tested as "OLEDs" (JL-V), the luminance values obtained were not very high. The electroluminescence-wavelength graph is presented in Figure 4.20.



Figure 4.20: Electroluminescence spectra of the device 1E, 2E and 2D



Figure 4.21: Current Density-Voltage and Luminance-Voltage graphs for 1E (a) 2E (b) and 2D (c) devices

The separation of the ions to the electrode interfaces reduces the injection barrier for electrons and holes. The brightness gradually increased with voltage, indicating that ionic mobility is slow or electronic carrier injection is slow due to a substantial energy barrier at one of the interfaces. With the devices 2E and 2D 2.47cd m<sup>-2</sup> and 2.85cd m<sup>-2</sup> brightness was obtained with the  $\lambda_{EL}$  max at 645 and 586 nm, respectively. Device 1E exhibited better brightness with the value of 17.14cd m<sup>-2</sup> ( $\lambda_{EL}$  max at 534 nm) compared to the LEC device based on the ionic TADF emitters Pym-CZ and Pym-<sup>*t*</sup>BuCZ [167].

#### 4.2.2 Device Applications of Iridium Complexes



The LEC device configuration of the Ir(III) complexes is ITO/PEDOT:PSS/iTMC/Al.

Figure 4.22: a) Normalized EL spectra b) Luminance-voltage curve c) current density -wavelength curve and luminous efficiency-current density curve of 1b and 2a complexes

LEC device performance of complexes **1b** and **2a** are summarized in Table 4.11. When the performance is considered, it is clear that the thin films prepared under the 1000 rpm showed better results compared to the results of the thin films prepared under 1500 rpm. Under 12 V voltage bias, LEC device based on **1b** (for 1000 rpm), the maximum current density, luminance and luminous power efficiency were found to be 1338 mA cm<sup>-2</sup>, 17.97 cd m<sup>-2</sup> and  $3.64 \times 10^{-4}$  lm W<sup>-1</sup>, respectively. LEC device with **2a** showed better results with maximum current density, luminance and luminous power efficiency of 1529 mA cm<sup>-2</sup>, 30.95 cd m<sup>-2</sup> and 7.77 x 10<sup>-4</sup> lm W<sup>-1</sup>, respectively.

The results showed that the luminance values obtained under the same voltage were very low when compared with the literature values [169]–[172].

Device	rpm	Driving Voltage (V)	Current Density (mA/cm <sup>2</sup> ) at 12 V	Luminance (cd/m <sup>2</sup> ) at 12 V	Luminous Efficiency (lm/W) at 12 V
1b	1000	9.3	1338	17.97	3.64 x 10 <sup>-4</sup>
	1500	11.5	1391	1.66	2.84 x 10 <sup>-4</sup>
20	1000	10.0	1529	30.95	7.77 x 10 <sup>-4</sup>
24	1500	10.1	1651	17.71	5.83 x 10 <sup>-4</sup>

Table 4.11: LEC Device performance results of **1b** and **2a** complexes

To get better results, same materials were coated from the solution of acetonitrile:1,2dichlorobenzene (2:3).



Figure 4.23: a) Luminance-voltage curve and b) current-voltage curve of LEC devices based on **1a**, **1b** and **2a** complexes

Luminance-voltage and current-voltage curves of the LEC devices based on **1a**, **1b** and **2a** complexes are given in Figure 4.23.

It has been clearly seen that the thin films prepared with the acetonitrile:1,2dichlorobenzene (2:3) showed worse results compared to the results of the thin films prepared only acetonitrile solutions. Unfortunately, we could not obtain better luminous efficiency with these devices. It has been understood that it is necessary to work in optimal conditions to obtain better device results.

# Chapter 5

# Conclusion

Two new ionic organic small molecules (**DiKTa-DPA-OBuIm** and **DiKTa-OBuIm**) have been synthesized and characterized. Ground state geometry optimization was done using standard DFT and excited state calculations were done using Turbomole software. The theoretical calculations predicted small  $\Delta E_{ST}$  (0.31 eV and 0.25 eV), which is a key factor in achieving TADF. Both emitters exhibited good solubility in common organic solvents, thus solution processing is possible with emitters. Photophysical properties have been investigated for the emitters for understanding the emission color, efficiency, TADF properties and their potential as active materials for LECs. The emitter, **DiKTa-OBuIm** showed a green emission ( $\lambda_{PL} = 499$  nm; PLQY = 70%) in 1wt% doped in mCP film. On the other hand, **DiKTa-DPA-OBuIm** exhibited red shifted emission, ( $\lambda_{PL} = 577$  nm; PLQY = 61%) in 1wt% doped in mCP film. Both emitters presented good electrochemical reversibility in their oxidation and reduction cycles. LEC device based on **DiKTa-OBuIm** and **DiKTa-DPA-OBuIm** showed better performance without ionic liquids compared to the ones with ionic liquids.

Three new cationic iridium (III) complexes have been synthesized and characterized. The structure of ligand 1, complexes **1a** and **1b** have been identified by single crystal. Photophysical and electrochemical properties have been investigated. They showed electrochemical reversibility in their oxidation and reduction cycles which are needed for an active material in the LEC device. LEC devices have been fabricated based on iridium complexes. LEC device with **2a** showed better results with maximum current density, luminance and luminous power efficiency of 1529 mA cm<sup>-2</sup>, 30.95 cd m<sup>-2</sup> and 7.77 x 10<sup>-4</sup> lm W<sup>-1</sup>, respectively.

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# Appendix A









Figure A4.<sup>13</sup>C NMR of **2** in CDCl<sub>3</sub>.



Figure A5.<sup>1</sup>H NMR of **3** in CDCl<sub>3</sub>.



Figure A6.<sup>13</sup>C NMR of **3** in CDCl<sub>3</sub>.



Figure A7.<sup>1</sup>H NMR of **4** in CDCl<sub>3</sub>.



Figure A8.<sup>13</sup>C NMR of **4** in CDCl<sub>3</sub>.



Figure A9.<sup>1</sup>H NMR of **5** in DMSO-d8.



Figure A10.<sup>13</sup>C NMR of **5** in DMSO-d8.



Figure A11. HRMS of **5**.







Figure A13.<sup>13</sup>C NMR of **6** in CDCl<sub>3</sub>.



Figure A14. HRMS of 6 in CDCl<sub>3</sub>.



Figure A15.<sup>1</sup>H NMR of **DiKTa-OBuIm** in DMSO.



Figure A16.<sup>13</sup>C NMR of **DiKTa-OBuIm** in DMSO.













Figure A21. <sup>13</sup>C NMR of 8 in CDCl<sub>3</sub>



Figure A22. <sup>1</sup>H NMR of 9 in CDCl<sub>3</sub>



Figure A24. <sup>1</sup>H NMR of 10 in CDCl<sub>3</sub>



Figure A26. <sup>1</sup>H NMR of 11 in CDCl<sub>3</sub>



Figure A27. <sup>13</sup>C NMR of 11 in CDCl<sub>3</sub>



Figure A28. GC-MS of 11



Figure A30. <sup>13</sup>C NMR of 12 in DMSO



Figure A32. <sup>1</sup>H NMR of 13 in CDCl<sub>3</sub>.



Figure A33. <sup>13</sup>C NMR of 13 in CDCl<sub>3</sub>.



Figure A34. HRMS of 13.



Figure A35. <sup>1</sup>H NMR of **DiKTa-DPA-OBuIm** in DMSO



Figure A36. <sup>13</sup>C NMR of **DiKTa-DPA-OBuIm** in DMSO



Figure A38. <sup>19</sup>F NMR of **DiKTa-DPA-OBuIm** in DMSO



Figure A39. HRMS of **DiKTa-DPA-OBuIm**.



Figure A40. <sup>1</sup>H NMR of ligand 1 in CDCl<sub>3</sub>.



Figure A41. <sup>1</sup>H NMR of ligand 2 in CDCl<sub>3</sub>.



Figure A42. <sup>1</sup>H NMR of complex 1a in CDCl<sub>3</sub>.



Figure A43. <sup>1</sup>H NMR of complex 1b in CDCl<sub>3</sub>.



Figure A44. <sup>1</sup>H NMR of 2a in CDCl<sub>3</sub>.

# Appendix B

Projects

### 1. 2214A International Doctoral Research Fellowship Programme (TUBITAK)

Project name: Fabrication of White Light Emitting LEC Device Using Organic Small Molecule

### 2. BAP project

Project name: Synthesis of New Materials and Optoelectronic Application For Lighting Chemical Cells

Project no: 2019-TDR-FEBE-0007

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