

## Unique Electron Deficient Molecule for Thermally Activated Delayed Fluorescence Application

Mohammed Al-Mashhadani<sup>1</sup>, Muataz Ali<sup>1</sup>,  
Mustafa Abdallah<sup>1</sup>, Muna Bufaroosha<sup>2</sup> and Emad Yousif<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq

<sup>2</sup>Department of Chemistry, College of Science, United Arab Emirates University,  
Al-Ain 15551, United Arab Emirates

(\*Corresponding author's e-mail: emad\_yousif@hotmail.com)

Received: 30 July 2022, Revised: 9 December 2022, Accepted: 16 December 2022, Published: 31 May 2023

### Abstract

Utilizing purely organic materials with relatively highly emissive characteristics for designing organic light-emitting diodes (OLEDs) is fascinating since employing rare metals is unessential, hence, enormous research activities have been conducted in this field. Recently, additional efforts were devoted to designing special emitting materials demonstrating thermally activated delayed fluorescence (TADF). Molecular structures were ideally designed in a specific way using an electron-deficient molecule as an acceptor (A) and an electron-rich molecule as a donor (D) in order to minimize the overlapping between the highest occupied molecular orbital (HOMO) of the donor (D) and the lowest unoccupied molecular orbital (LUMO) of the acceptor (A). TADF requires a small band gap between the singlet excited and triplet excited states ( $\Delta E_{ST}$ ), usually less than (c.a 0.1 eV) of the luminescent material. This makes it possible to thermally harvest the excitons from the triplet excited state ( $T_1$ ) to the singlet excited state ( $S_1$ ) by a process known as reverse intersystem crossing (RISC) and then to harvest all the excitons for the fluorescence process. Thus, the design of the TADF molecular structure needs both an electron-rich segment as a donor and an electro-deficient segment as an acceptor. Up to the present, electron-deficient moieties (EDM) have been studied less than electron rich moieties (ERM) during the last few years. This review is highlighting the recent advances regarding the specific molecular designs of TADF emission materials for OLED applications, particularly, focusing on (dibenzothiophene-*S,S*-dioxide) as electron deficient molecule, which exhibits a strong electron-deficient unit and high ability of photo- and electroluminescence features.

**Keywords:** Thermally activated delayed fluorescence, OLED, Dibenzothiophene-*S,S*-dioxide, TADF, Organic light emitting diode

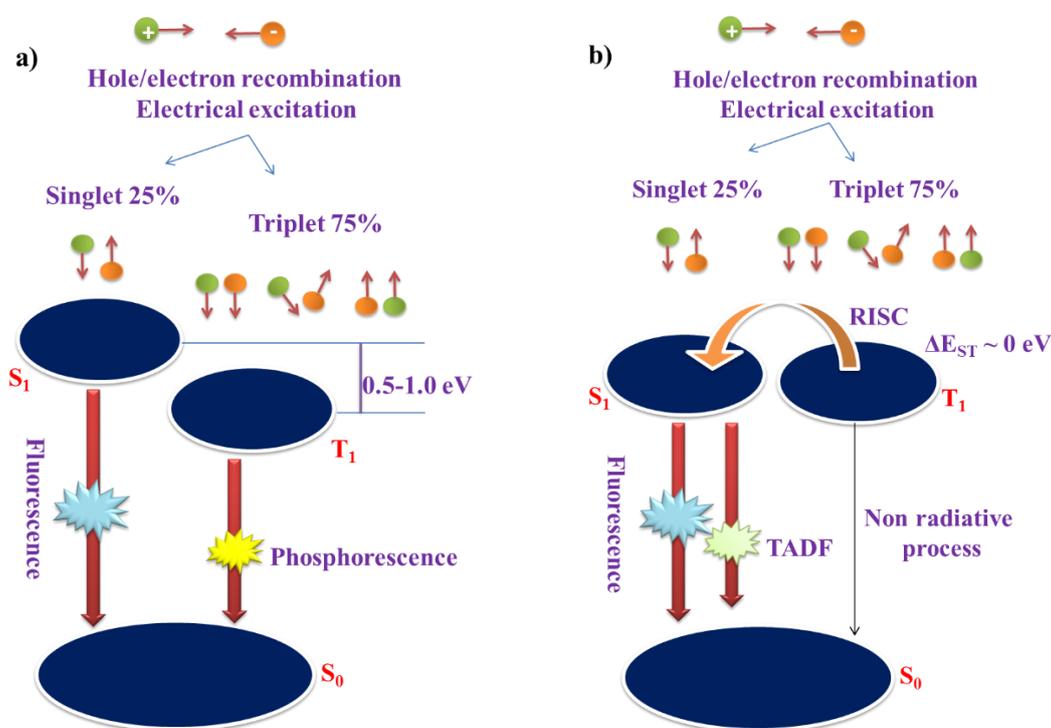
### Introduction

Over the last 3 decades, organic electronics [1,2] have been an area of active research into the synthesis of organic small molecules, oligomers, polymers, and organometallic materials. A large number of researches have been conducted to develop new molecular and polymeric structures with wonderful electronic and photo-/electro-luminescence properties [3-8]. Which were mostly applied in the design of organic light emitting diodes (OLEDs) [9-12], organic photovoltaic cells (OPVs) [13], and organic field effect transistors (OFTs) [14], fluorescence sensors [15] and organic lasers [16]. Materials designs were developed to control color, intensity, and a lifetime of emission, combining both synthetic and theoretical chemistry/physics in this field. In contrast, traditional inorganic conductors [17] and semiconductors, [18] organic electronic materials (small molecules or polymers) are mostly synthesized by applying organic synthetic strategies [19]. One of the most important advantages of organic electronics is its low cost, compared to conventional inorganic electronics [20]. Since the ground-breaking work in 1987 by Tang, organic materials for OLEDs have prospered [21], due to various adoption of such materials in light-emitting devices like mobiles, smartphones, tablets, car audio, and video systems, cameras, etc. [22]. The relatively main key point in OLEDs application is that exciton formation under electrical excitation logically gives in 25 % singlet and 75 % triplet excitons, the latter being lost as thermal energy, under room temperature conditions [23]. The pioneering research into OLED material science has been the endeavor of finding a process that can efficiently harvest the 75 % triplet excitons formed on charge recombination into emissive singlet states in small organic systems. The most efficient way known yet to

harvest the 75 % triplet excitons is *via* using thermally activated delayed fluorescence (TADF) materials, [24] as illustrated in the next sections.

### Thermally activated delayed fluorescence (TADF)

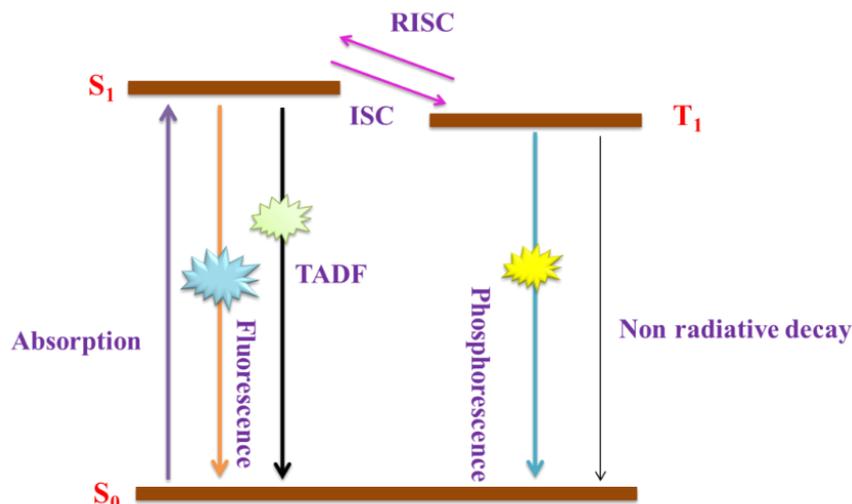
Organic electroluminescence is a process of electron-excitation, where an electron and hole are recombined in an OLED device, and form excitons in the excited state. Statistically, 25 % of excitons go to singlet state and 75 % go to triplet state as shown in **Figure 1**. These excitons decay to the ground state from excited states of different multiplicities, either singlet by a process of fluorescence (nanosecond timescale) or triplet by a process of phosphorescence (millisecond timescale) [25]. The selection rules of quantum mechanics dictate that the transition between states of the symmetric multiplicity is allowed. However, the transition of electrons is prohibited between states that are of asymmetric multiplicity (intersystem crossing with spin changes) according to the Pauli Exclusion Principle. Hence, the energy difference between singlet and triplet ( $\Delta E_{ST}$ ) is usually large (c.a 0.5 - 1.0 eV) in most organic light emitting molecules as shown in **Figure 1**. TADF process [26] attempts to overcome this issue, based on designing special organic molecules, where the  $\Delta E_{ST}$  is small as much as possible [27]. EQE (external quantum efficiency), represents the percentage of the emitted photons outside the device to the number of charges injected into it, these can be as low as 5 % for organic fluorophores from 25 % singlet excitons, after a light-out coupling efficiency  $\sim 20$  %.



**Figure 1** Energy diagram of electrical excitation of conventional organic molecules.

When TADF compounds are exposed to energy and get excited (**Figure 2**), triplet excitons appear after an efficient transition of electrons by a process known as the inter-system crossing (ISC) process. There are 2 distinct unimolecular mechanisms for the TADF materials process known: The 1<sup>st</sup> mechanism is known as prompt fluorescence (PF). In this mechanism, decay occurs over a nanosecond timescale, from the  $S_1$  to the  $S_0$  state. While the 2<sup>nd</sup> mechanism is delayed fluorescence (DF). In this mechanism, triplet excitons are ‘harvested’ into singlet excitons by a reverse intersystem crossing (RISC) process [28]; an endothermic up-conversion of the  $T_1$  to the  $S_1$  (higher energy), hence the process being ‘thermally activated’ and thus slower over a microsecond timescale. This is shown diagrammatically in **Figure 2** [26]. For an efficient TADF process, facilitated by the DF mechanism, specifically the RISC conversion of  $T_1$  to  $S_1$ , the energy difference between these states needs to be small as much as possible close to zero. In most organic molecules, these energy levels can be separated by  $\sim 0.5 - 1.0$  eV. Special

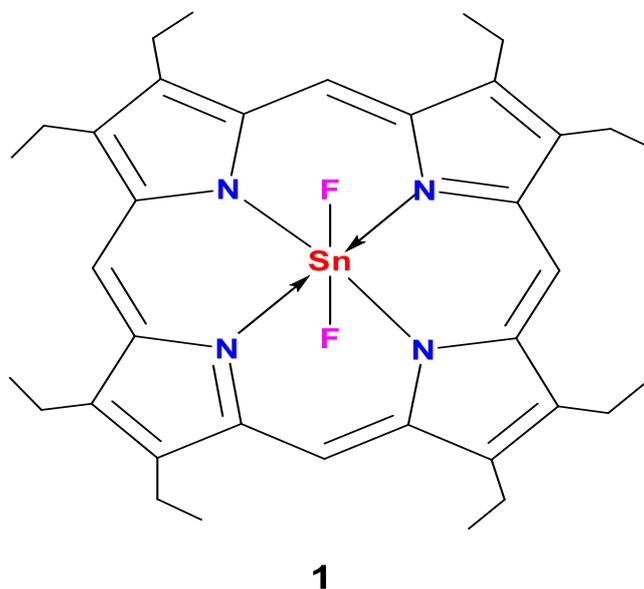
molecular design considerations can be made to lower this  $\Delta E_{ST}$  to minimize energy loss as this will be explained below.



**Figure 2** The process of photoluminescence, fluorescence, phosphorescence and the process of thermally activated delayed fluorescence.

#### TADF materials

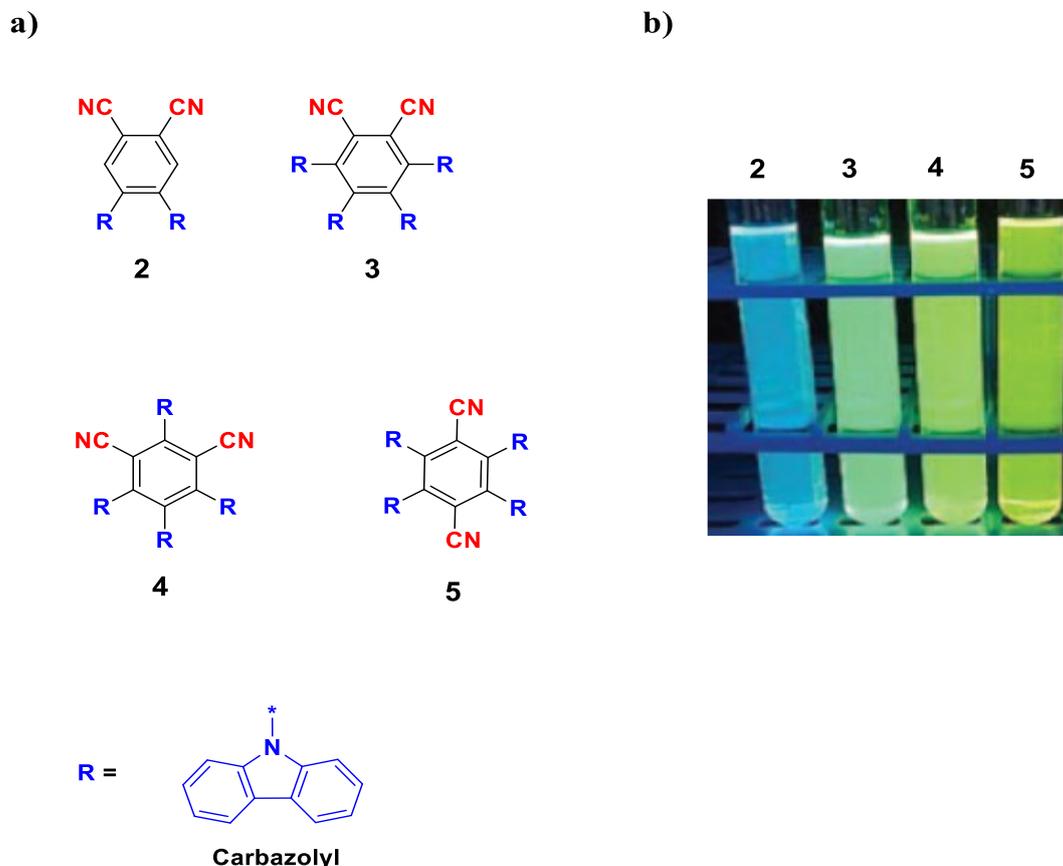
TADF phenomena were applied for the first time in OLED technology in 2009 when Endo *et al.* [29] discover a promising EQE's of c.a 13 % *via* the application of short electrical pulses to Sn (IV)-porphyrin complex (1) (**Figure 3**).



**Figure 3** First Sn (IV)-porphyrin complex as TADF materials for OLED applications.

In 2012 based on purely organic materials (rare metal-free), Uoyama *et al.* [30] synthesized a series of highly efficient TADF materials utilizing carbazolyl (works as an electron donor) and dicyanobenzene (works as an electron acceptor) moieties, based on donor-acceptor (D-A) design, (compounds 2 - 4, **Figure 4(a)**). Photoluminescence photograph of molecules 2 - 4 in toluene under long wave UV irradiation 365 nm is presented in **Figure 4(b)**. It has demonstrated a wide range of photon emissions from light blue (compound 2) to dark green (compound 5). The photoemission wavelength depends on the nature of the central accepting unit (dicyanobenzene) and the attached donating units (carbazolyl). It

has been proved that increases in attached carbazolyl units lead to enhancing the donating characteristic of the molecule which redshifts the maximum wavelength of emission.



**Figure 4** a) Molecular structures of carbazolyl dicyanobenzene compounds 2 - 4 as TADF materials. b) Photoluminescence photo of compounds 2 - 4 in toluene under exposure to UV of 365 nm [30].

The most important point of the TADF molecular design is the arrangement of a small  $\Delta E_{ST}$  (below 0.1 eV) with a relatively efficient radiative decay rate (above  $10^6 \text{ s}^{-1}$ ) to overcome the problem of losing the energy in non-radiative decay pathways, resulting in very efficient TADF emitters. Because of the conflict between these 2 categories, there is a need to accurately balance the HOMO and LUMO orbitals of the donor and acceptor units. Due to the steric hindrance, the carbazolyl moiety is obviously slanted from the plane structure of dicyanobenzene, HOMO orbitals localized on the donor unit, and the LUMO on the acceptor unit of these emitters, giving a small  $\Delta E_{ST}$ . Prior to these ground breakingly results, researchers believed that a highly efficient photoluminescence system with narrow  $\Delta E_{ST}$  from organic molecules only is impossible [30]. Adachi's group work provides that it is possible to design materials with a high photoluminescence efficiency and a small  $\Delta E_{ST}$  simultaneously. Moreover, they demonstrate an EQE of 30 %, which is clearly overcome the limitation EQE 5 % of organic fluorescence materials and close to rare metal-complexes phosphorescence-based OLED efficiency [31]. Thus, highlighting the feasibility of such materials for OLED applications. Since Adachi and co-workers demonstrated these efficiencies, they achieved more publications considering the design and synthesis of new TADF emitters [32-35].

Hence, it has been proven that, purely organic emitters can be used to support the TADF process. D-A (donor connected to an acceptor) systems with a distinct intra/intermolecular charge transfer (CT) character to facilitate a small  $\Delta E_{ST}$ , which is a molecular architecture that is currently being employed in TADF chemistry without the requirement of heavy metals. As per deductions,  $\Delta E_{ST}$  represents the difference between the singlet excited state ( $S_1$ ) and triplet excited state ( $T_1$ ). Thus, the HOMO orbitals of the donor and the LUMO orbitals of the acceptor subsidize the energy exchange of the D-A based molecule. Therefore, appropriate design considerations should be made to achieve a TADF emitter with optimal properties. Different approaches were utilized to achieve narrow  $\Delta E_{ST}$ . One way is to connect a

donor and an acceptor together by steric hindrances [36], such as a twist or spiro-junction, hence separating the spatial overlap of HOMO and LUMO orbitals [37]. Another design consideration is by creating a hard system throughout a strong connection between the donor and acceptor units resulting in a very rigid molecular structure, leading to an improvement in the radiative luminescence efficiency [30]. A key goal in the design principles of TADF materials is a large  $k_r$  (radiative decay rate) of  $S_1$  excitons to the  $S_0$  state, to improve electroluminescence efficiency. However as mentioned previously, a small  $\Delta E_{ST}$  and large  $K_r$  are conflicting in their feasibility. There are 2 known ways to achieve a large  $k_r$ : One way is by increasing overlap density distribution between the electronic wave functions of the ground state, in which the  $S_1$  state can start  $S_1 \rightarrow S_0$  decay to promote photoluminescence quantum yield (PLQY) of the TADF emitter. Another way is by delocalization of molecular orbitals with well-separated HOMO and LUMO levels can suppress a decrease in radiative decay rate for fluorescence ( $K_f$ ) whilst lowering  $\Delta E_{ST}$ .

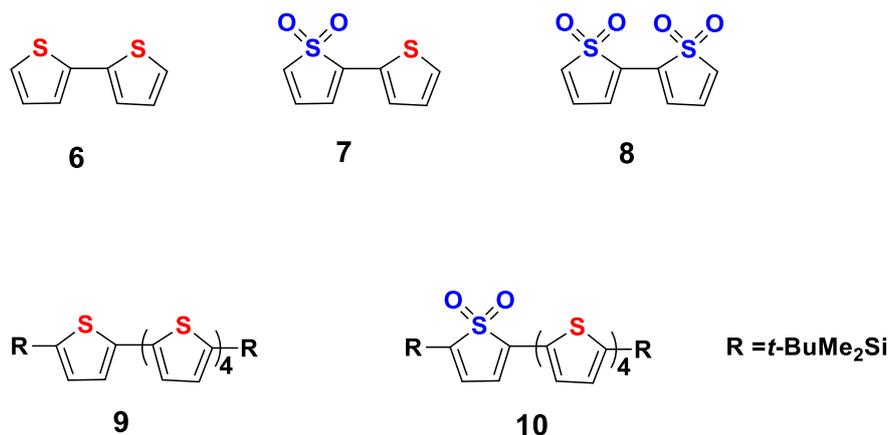
One technique to increase the overlap density distribution between the electronic wave functions of the ground state, where the  $S_1$  state can start the  $S_1 \rightarrow S_0$ . So, decay to encourage the photoluminescence quantum yield (PLQY) of the TADF emitter, is one of the 2 strategies to obtain a big  $k_r$ . Another method is to delocalize molecular orbitals with well-separated HOMO and LUMO levels in order to lower  $\Delta E_{ST}$  and inhibit a decline in the radiative decay rate for fluorescence ( $K_f$ ).

### Electron-deficient moieties for organic electronic applications

The greatest number of semiconducting conjugated organic molecules are electron-rich structure compounds (p-type), which have high HOMO energy levels for instance thiophene [38], *p*-phenylenevinylene [39], and fluorine [40] moieties. p-doped can be more straightforward to produce positive polarons in comparison to n-doped to get negative polarons, this is because they possess higher hole mobility in the materials than electron mobility and their p-doped state is usually more stable. In the last decades, electron-deficient semiconductors have been investigated less than p-type, even though the number of organic electronic applications which need electron-deficient n-type materials such as n-type transistors for full logic circuits, photovoltaics, cathode materials, and charge-transfer materials etc. [41,42]. Moreover, TADF materials for OLED applications require both the electron-rich unit as a donor and the electron-deficient unit as an acceptor [43].

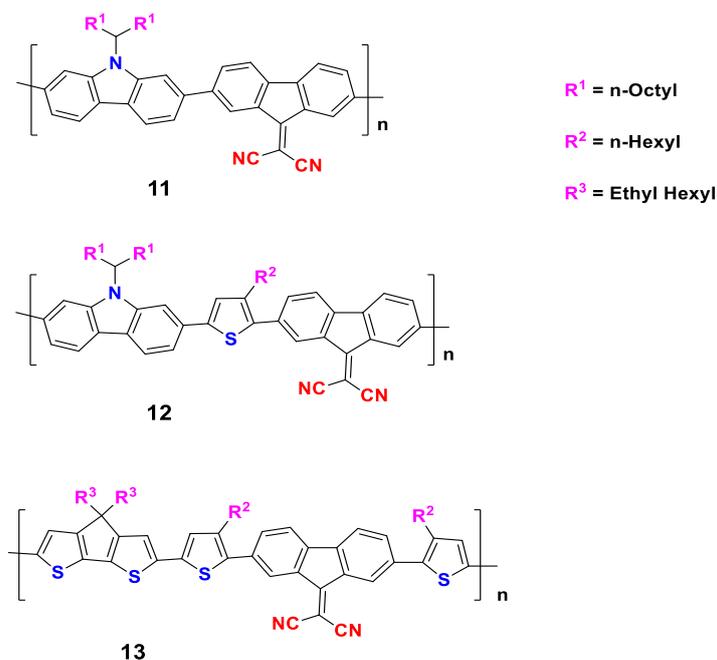
One of the challenges to research in the field of electron-deficient semiconductors is finding a special kind of structural design that has the ability to decrease the energy of LUMO orbitals. Many approaches have been implemented to reduce the LUMO energy level, particularly, in conjugated polymers [44]. The 1<sup>st</sup> approach utilizes electron-deficient heterocyclic units in the polymer chain such as oxadiazoles, benzothiadiazoles, pyridines [45], quinoxalines, thiophene-*S,S*-dioxides [46], etc. The 2<sup>nd</sup> approach is the construction of conjugated polymers based on electron-deficient heterocyclic building blocks; another approach is to use electron-withdrawing substituents on the side chains. Moreover, it is possible to use a combination of electron-withdrawing/electron-donating building blocks in the building of the polymer backbone to achieve a narrow band gap and a low LUMO level in polymers [47,48].

Barbarella *et al.* [49] first introduced thiophene-*S,S*-dioxide as an electron-deficient unit into conjugated oligomers and polymer backbones [50,51]. According to HF/3-21G ab initio calculations, the introduction of 2,2'-bithiophene (6) and its derivatives mono (7) and *bis* *S,S*-dioxides (8) (**Figure 5**) into the chemical structure has a significant impact on the orbital pattern. *S,S*-dioxides revealed the ability to reduce the energy of both HOMO and LUMO orbitals in which LUMO orbitals are remarkably affected in comparison to HOMO orbitals. This consequently leads to narrowing down the energy gap. Also, the mathematical calculation showed that SO group orbitals have slight participation with the frontier orbitals, essentially of  $\pi$ ,  $\pi^*$  type [48].

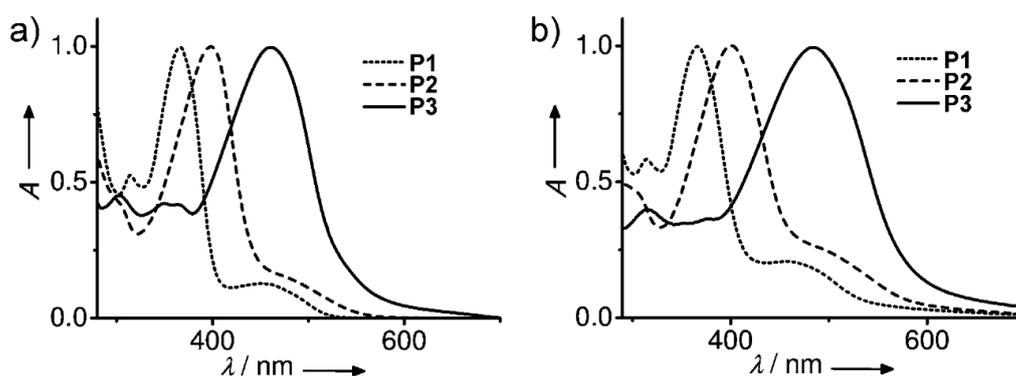


**Figure 5** Structures of the thiophene-*S,S*-dioxide oligomers 6 - 10 [48].

Cyclic voltammetry of pentamer containing *S,S*-dioxide group at one end (10) showed anodic and cathodic potentials of 1.04 and  $-1.34$ , respectively. These results were compared to data reported for oligothiophene (9). It was found that *S,S*-dioxide oxidation potential has an increment of 0.12 V whereas reduction potential became less negative by 0.79 V. In addition, LUMO orbitals of oligothiophene-containing terminal *S,S*-dioxides group appears at a lower energy level than those of the unmodified oligothiophenes. These results agree with the trends obtained through ab initio mathematical calculations [48]. Electron-deficient conjugated polymers can improve the performance of OLED devices by 2 methods, first, by increasing the electron density supplied by the metal cathode, and second, by blocking the holes on emitting layer of the cathode. Thus, balancing the electrons and holes, and increasing the chance of exciton formation. Vijayakumar *et al.* [52] designed and synthesized a new series of n-type copolymers based on the dicyanofluorene moiety. Attaching 2 cyano groups developed the dicyanofluorene segment to be a strong electron acceptor. Three co-polymers (11 - 13) were investigated by incorporating various donor moieties with dicyanofluorene (**Figure 6**). All co-polymers demonstrated a notable absorption in the UV-visible region. The maximum absorption showed a bathochromic shift toward a higher wavelength with an increasing number of thiophene moieties in the copolymer backbone (**Figure 7**). A space-charge-limited current (SCLC) study demonstrated that the electron mobility of the materials in the bulk state was 1 to 2 orders greater than that of the corresponding hole mobility, which proved the n-type nature of the polymers.



**Figure 6** Structures of co-polymers 11 - 13 [52].

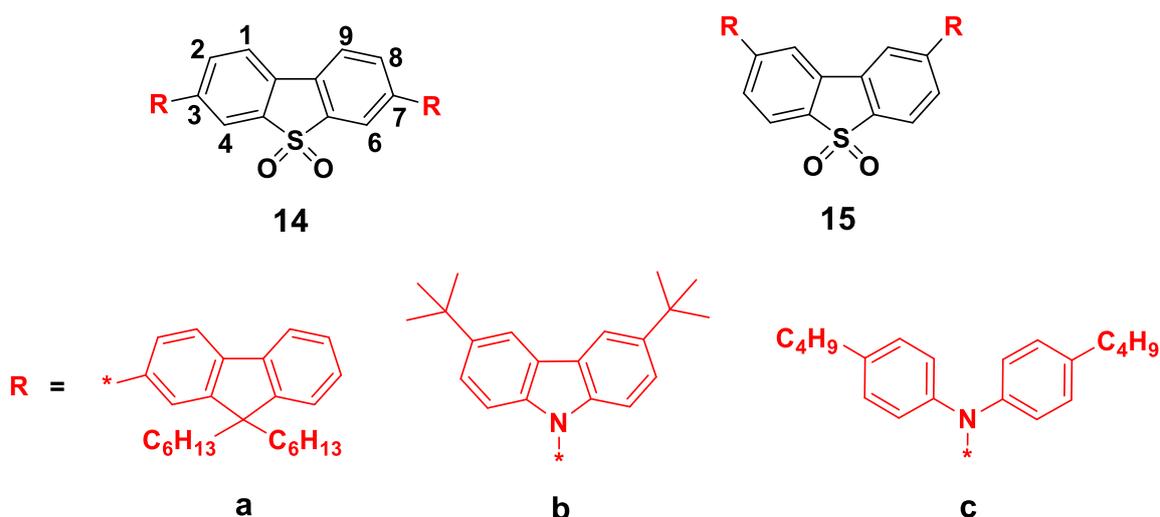


**Figure 7** Absorption spectrum of 11 - 13 (P1-P3) in a) tetrahydrofuran and b) the thin-film state [52].

Dibenzothiophene-*S,S*-dioxide is an electron-deficient moiety because of the electron-withdrawing character of the sulfonyl group making it an interesting building block to assemble conjugated materials (**Figure 8**). In 2005, Peregichka *et al.* [53] introduced dibenzothiophene-*S,S*-dioxide as an electron-deficient unit for organic electronic applications. The idea was that the dibenzothiophene-*S,S*-dioxide was topologically similar to the fluorene unit, where C(R<sub>2</sub>) bridge between the phenylene moieties is replaced by an electron-withdrawing SO<sub>2</sub> bridge, thus reducing the LUMO energy and giving the materials a higher electron affinity. Since this first important research until this article was written, over 400 papers have been published in the literature which uses dibenzothiophene-*S,S*-dioxide in organic electronic materials as an electron-deficient building block, particularly, for the design of new light-emitting copolymers [54-59]. Yet, to date of writing this review, no dibenzothiophene-*S,S*-dioxide homopolymers have been reported. Except the homopolymers were studied by Al-Mashhadani [60].

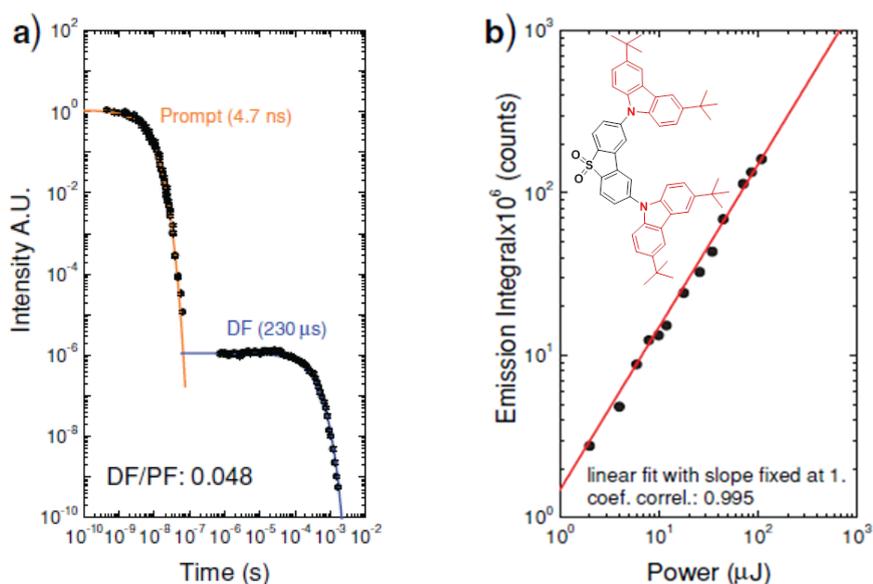
#### Dibenzothiophene-*S,S*-dioxide (DTO) for TADF materials

Dibenzothiophene-*S,S*-dioxide (DTO) is used as an electron-deficient accepting unit in TADF materials building block, due to the SO<sub>2</sub> electron withdrawing (EWG) characteristics making the structure strongly accepting electrons. Reports by Dias *et al.* [61], show the effects of substitution positions, for example, 'angular' di-substitution (15) of the acceptor unit (at C-2,8) shows a strong fluorescence when the donor contains heteroatoms (N or O), this effect extends to low temperatures (**Figure 8**). When the acceptor unit is 'linearly' disubstituted (C-3,7) 14, fluorescence is very weak regardless of the donor chemistry.



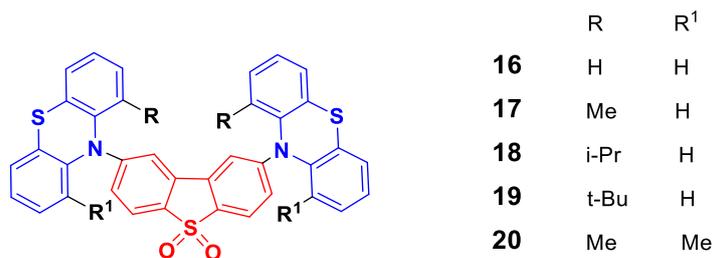
**Figure 8** Chemical structure of 14 - 15 compounds.

**Figure 9(a)** shows the Prompt fluorescence (PF) in addition to delayed fluorescence (DF) [61]. The DF/PF ratio and lifetimes data were collected and analyzed for time intervals spanning 9 orders of magnitude using exponential decay laws in a single experiment. PF Intensity was experimentally calculated at room temperature from a plot of the emission intensity (**Figure 9(a)**). This makes it possible to measure PF and DF intensities in a single experiment. On the other hand, **Figure 9(b)** indicates that the DF intensity has a strong linear dependency throughout the excitation range. The pure thermally aided nature of the TADF mechanism in 15b is shown by this behaviour. It has been shown that angular versus linear material topologies, the presence of a 3-n triplet state, and charge transfer states with extremely low exchange energy are all necessary to adequately explain the discovery of TADF in ICT materials with relatively high singlet 1 CT-triplet 3 energy splitting. This TADF mechanism has been proven to convert triplet states to singlet ones with about 100 % efficiency.



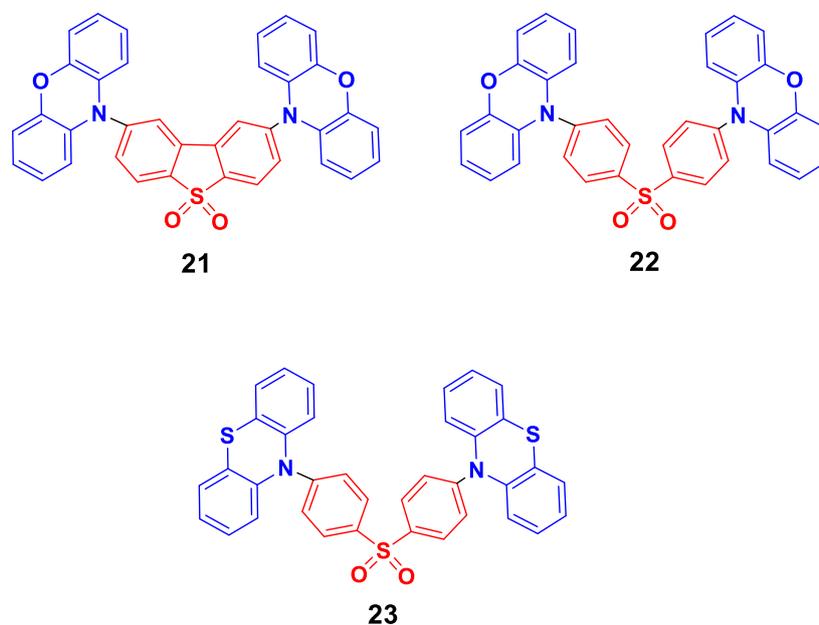
**Figure 9** a) Prompt fluorescence (PF) and delayed fluorescence (DF) for compound 15b. b) Variation of DF intensity for compound 15b [61].

The same group in 2016 has introduced a series of new thiophene-*S,S*-dioxide derivatives modified with phenothiazine derivatives as charge transfer molecules (16 - 20) as shown in **Figure 10** [62]. They proved that increasing steric restriction around the donor-acceptor bond considerably leads to change in the contributions from TADF and phosphorescence. Their work has proven that when 1-(and 9) position(s) of the phenothiazine undergo a substitution reaction with a bulky group, a strong phosphorescence will take place and no TADF will appear at room temperature. The work of Dias *et al.* [27], showed that the rigid near perpendicular D-A-D molecular geometry is critical to minimize  $\Delta E_{ST}$ . In this work, they demonstrated that the efficiency of TADF materials is significantly controlled by 2 factors. First, the electronic coupling between the local triplet, ( $^3LE$ ), and the charge transfer singlet states, ( $^1CT$ ,  $^3CT$ ) forms an interconversion of singlet and triplet states by the spin orbit charge transfer mechanism, a 2<sup>nd</sup> order process mediated by vibronic coupling. The other factor is the need for the D-A geometry to be dynamically swinging about D-A orthogonality.



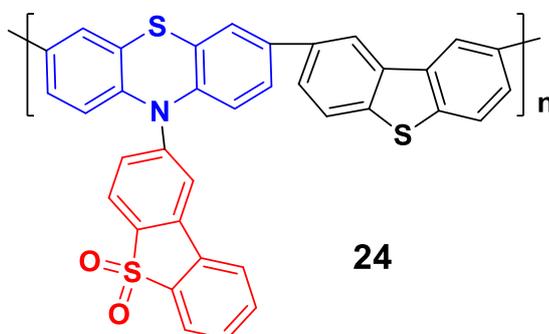
**Figure 10** Chemical structure of D-A-D molecules 16 - 20.

Tang and co-workers synthesised a series of D-A-D materials 16, 21 - 23 for TADF applications see **Figures 10 and 11** [63]. These compounds are designed in a way to suppress the intermolecular rotation and vibration and to create aggregate which has strong emission features. The flexible conformations of the molecular structure can affect the interactions, especially  $\pi$ - $\pi$  interactions, and consequently reduces the non-radiative decay of the aggregates. The twist angle between the donor and acceptor can critically influence the  $\Delta E_{ST}$ , since it can increase the separation of HOMO and LUMO orbitals and reduces  $\Delta E_{ST}$  values and so delayed fluorescence.



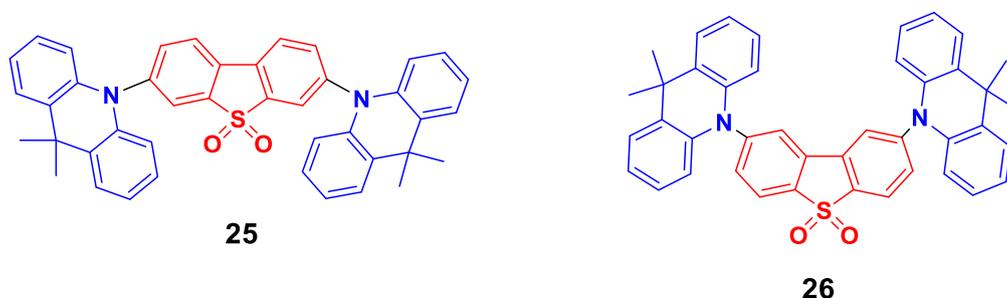
**Figure 11** Chemical structure of D-A-D molecules 21 - 23.

The photo-physics properties of phenothiazine–dibenzothiophene-*S,S*-dioxide 16 have been investigated in detail [64]. The compound 16 showed an obvious thermally activated delayed fluorescence due to a closely perpendicular angular arrangement between dibenzothiophene-*S,S*-dioxide and phenothiazine moieties. TADF of compound 16 improved when the CT energy of the triplets in the excited state was split into singlet-triplet states combined with improving spin orbit coupling. Due to such behaviour, the EQE efficiency was very high (about 19 %) making it a good candidate to be used industrially to fabricate different devices. The brilliant performance of this unit inspired this research group to investigate its performance when introduced to organic conjugated polymer 24 (**Figure 12**) based on 16 as a monomer. The new polymer has shown efficient TADF properties with triplet harvesting, in which the new material was fabricated into a device via solution processing. However, EQE performance of the new polymer was lower than that of a small molecule in terms of TADF OLEDs devices. However, this work starts a new area of research to explore TADF on a macromolecular level in LEDs, using more convenient methods to deposit on a larger area such as spin-coating and inkjet printing.



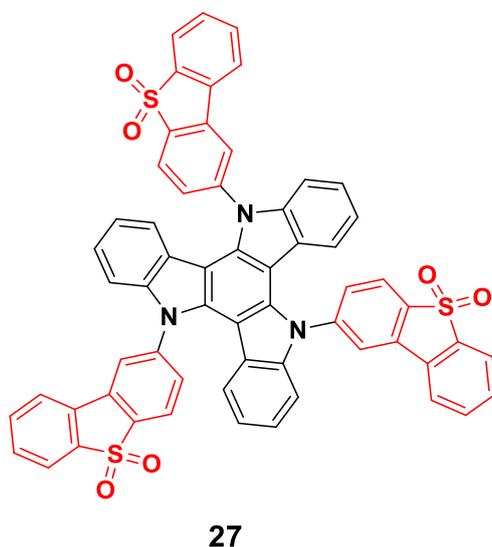
**Figure 12** Chemical structure of conjugated polymer 24.

Through the work of Kim *et al.* [65], 25 - 26 compounds (**Figure 13**) have been synthesized, comparing the photophysical properties of C-2,8 substitution (26) vs. C-3,7 substitution (25). The  $\Delta E_{ST}$  for 2,8 di-substitution 0.09 eV, relative to 0.26 eV for 3,7 substitutions.  $K_{RISC}$  for 2,8-substitution was reported,  $6.1 \times 10^3 \text{ s}^{-1}$  compared to  $6.5 \times 10^2 \text{ s}^{-1}$  for 3,7. It was demonstrated that (C-2,8) substitution on the donor units can significantly increase both photoluminescence (PL) and electroluminescence (EL) characteristics.



**Figure 13** Chemical structure of D-A-D molecules (25 - 26).

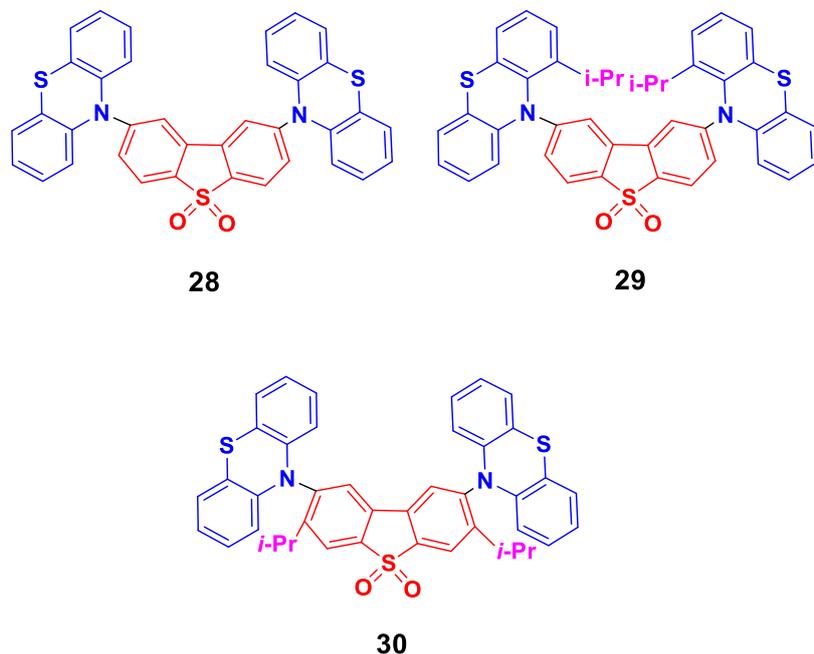
Santos *et al.* [66], in 2018, introduced a new design for TADF emitters. Their approach includes a rigid donor core linked to acceptors which is a very uncommon design of the TADF emitter where the acceptor represents the core, the system as illustrated in **Figure 14** (compound 27). They have demonstrated that reverse intersystem crossing (RISC) speeds in organic material, allow for quicker utilization of triplet excited states than Ir-based phosphorescent materials. Within 0.2 eV, a combination of the inverted structure and numerous donor-acceptor contacts generated up to 30 vibronically linked singlet and triplet states, which were used in RISC. This boosts the RISC rate significantly, resulting in fluorescence decay times as short as 103.9 nanoseconds. This emitter likewise has a low singlet-triplet gap and an emission quantum yield of around 1. Green organic light-emitting diode devices with an EQE of more than 30 % have been shown.



**Figure 14** Chemical structure of D-A<sub>3</sub> molecules 27.

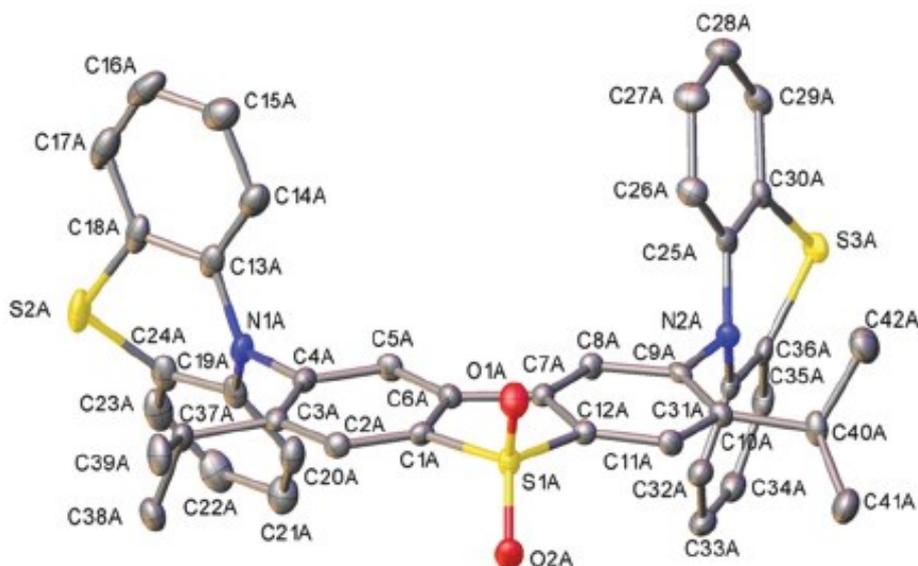
Recently, a new strategy has been developed for TADF materials depending on the conformational structure of the molecules [67]. Phenothiazine was used as an electron donor (D) and dibenzothiophene-*S,S*-dioxide as an electron acceptor (A) unit, linked as dimer D-A or trimer D-A-D materials as shown in **Figure 15**. The study investigated the influence of steric hindrance on the molecule geometry to improve the TADF emission. It showed that the substitution of bulky group at donor moiety approve an axial geometry which leads to an increase in the energy level of the singlet state, thus, the luminescence efficiency reduces. However, the substitution on the acceptor moiety was approved an equatorial

conformer where the luminescence efficiency was very strong and proved an excellent TADF emission even with a small singlet-triplet energy gap (0.2 eV).

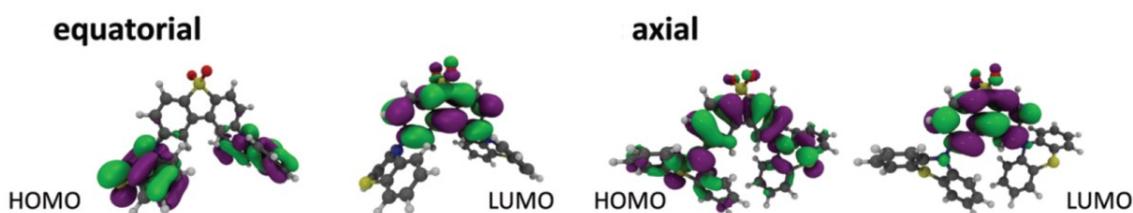


**Figure 15** Chemical structure of D-A-D molecules 28 - 30.

The crystal structure of 30 as determined by X-ray measurements is shown in **Figure 16**. Thiazine moieties have equatorial orientations in this molecule and are folded inward along the N-S vectors. Although the donor-acceptor p-conjugation is precluded in either case, and the nitrogen atom's lone pair interacts with the donor's arene rings rather than the acceptor's, the twist angles ( $t_1$ ,  $t_2$ ) around the C(A)-N bonds are somewhat asymmetrical: 86 - 881 and 66 - 741, indicating the extent of conformational flexibility. Computational analysis of molecule 28 D-A-D revealed that it can have many stable conformers, including the H-intra and H-Xtra folded conformers of the phenothiazine [68]. As seen in **Figure 17** for compound 28, this permits parallel quasi-axial (ax) and perpendicular quasi-equatorial (eq) conformers to arise.



**Figure 16** X-ray single crystals of molecular structure of compound 30 [68].



**Figure 17** DFT (M062X) calculation of Kohn–Sham ground and excited orbitals for molecule 28 [68].

## Conclusions

To conclude, the investigation of organic light emitting diodes as TADF materials might be the future of display and lighting engineering and it's a promising candidate to be used in endless potential applications. TADF is a phenomenon that can be supported using synthetic chemistry in applicable charge transfer molecules. The design of organic TADF emitters requires donor D and acceptor A with high and efficient stability in order to achieve a narrow  $\Delta E_{ST}$ . Dibenzothiophene-*S,S*-dioxide is a recommended candidate since it has a relatively strong acceptor characteristic to support the separation of HOMO orbitals of the donor apart from the LUMO orbitals of the acceptor enabling the intramolecular charge transfer (ICT) state with a small  $\Delta E_{ST}$ . Even though there are more options to be explored, many possibilities need to be studied further. Finally, we hope this review has provided an enjoyable and clear conclusion for current researchers in this field and will attract more researchers to devote their effort to developing this interesting line of work. The majority of moieties that have been applied yet for TADF applications are small organic molecules so it could be tried to investigate more polymeric materials in the future.

## Acknowledgments

We would like to thank College of Science, Al-Nahrain University, Iraq for their support during the writing this review.

## References

- [1] J Ferraris, DO Cowan, V Walatka and JH Perlstein. Electron transfer in a new highly conducting donor-acceptor complex. *J. Am. Chem. Soc.* 1973; **2**, 948-9.
- [2] H Shirakawa, EJ Louis, AG MacDiarmid, CK Chiang and AJ Heeger. Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)<sub>x</sub>. *Chem. Soc. Chem.* 1977; **16**, 578-80.
- [3] DF Perepichka, IF Perepichka, H Meng and F Wudl. *Light-emitting polymers*. In: ZR Li and H Meng (Eds.). *Organic light-emitting materials and devices*. CRC Press, Florida, 2006, p. 45-293.
- [4] TA Skotheim and JR Reynolds. *Handbook of conducting polymers*. 3<sup>rd</sup> eds. CRC Press, Florida, 2007.
- [5] Y Chujo. *Conjugated polymer synthesis: Methods and reactions*. 4<sup>th</sup> eds. Wiley-VCH, Weinheim, Germany, 2010, p. 331.
- [6] M Leclerc and JF Morin. *Design and synthesis of conjugated polymers*. 1<sup>st</sup> ed. Wiley-VCH, Weinheim, Germany, 2010, p. 379.
- [7] AC Grimsdale, KL Chan, RE Martin, PG Jokisz and AB Holmes. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chem. Rev.* 2009; **109**, 897-1091.
- [8] X Zhaoab and X Zhan. Electron transporting semiconducting polymers in organic electronics. *Chem. Soc. Rev.* 2011; **40**, 3728-43.
- [9] JH Burroughes, DDC Bradley, AR Brown, RN Marks, K Makcay, RH Friend, PL Burn and AB Holmes. Light-emitting diodes based on conjugated polymers. *Nature* 1990; **347**, 539-41.
- [10] RH Friend, GJ Denton, JJM Halls, NT Harrison, AB Holmes, A Köhler, A Luxb, SC Moratti, K Pichler, N Tessler and K Towns. Electronic processes of conjugated polymers in semiconductor device structures. *Synth. Met.* 1997; **84**, 463-70.
- [11] MT Bernius, M Inbasekaran, J O'Brien and W Wu. Progress with light-emitting polymers. *Adv. Mat.* 2000; **12**, 1737-50.

- [12] GM Farinola and R Ragni. Electroluminescent materials for white organic light emitting diodes. *Chem. Soc. Rev.* 2011; **40**, 3467-82.
- [13] K Zhao, L Ye, W Zhao, S Zhang, H Yao, B Xu, M Sun and J Hou. Enhanced efficiency of polymer photovoltaic cells via the incorporation of a water-soluble naphthalene diimide derivative as a cathode interlayer. *J. Mater. Chem. C* 2015; **3**, 9565-71.
- [14] C Di, F Zhang and D Zhu. Multi-functional integration of organic field-effect transistors (OFETs): Advances and perspectives. *Adv. Mater.* 2012; **25**, 1-18.
- [15] S Ghosh, AS Alghunaim, MH Al-mashhadani, MP Krompiec, M Hallett and IF Perepichka. 4,5-Diazafluorene co-oligomers as electron deficient light-emitting materials and selective fluorescence sensors for mercury(II) cations. *J. Mater. Chem. C* 2018; **6**, 3762.
- [16] Y Chujo. *Conjugated polymer synthesis: Methods and reactions*. Wiley-VCH, Weinheim, Germany, 2010, p. 328.
- [17] P Knauth, Inorganic solid Li ion conductors: An overview. *Solid State Ion.* 2009; **180**, 911-6.
- [18] Y Sun and JA Rogers. Inorganic semiconductors for flexible electronics. *Adv. Mater.* 2007; **19**, 1897-916.
- [19] Y Yang and F Wudl. Organic electronics: From materials to devices. *Adv. Mater.* 2009; **21**, 1401-3.
- [20] SR Forrest. The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature* 2004; **428**, 911-8.
- [21] CW Tang and SA Vanslyke. Organic electroluminescent diodes. *Appl. Phys. Lett.* 1987; **51**, 913-5.
- [22] MT Bernius, M Inbasekaran, J O'Brien and W Wu. Progress with light-emitting polymers. *Adv. Mater.* 2000; **12**, 1737-50.
- [23] MA Baldo, DF O'Brien, ME Thompson and SR Forrest. Excitonic singlet-triplet ratio in a semiconducting organic thin film. *Phys. Rev.* 1999; **B60**, 14422-8.
- [24] Y Tao, K Yuan, T Chen, P Xu, H Li, R Chen, C Zheng, L Zhang and W Huang. Thermally activated delayed fluorescence materials towards the breakthrough of organoelectronics. *Adv. Mater.* 2014; **26**, 7931-58.
- [25] U Mitschke and P BaÈuerle. The electroluminescence of organic materials. *J. Mater. Chem.* 2000; **10**, 1471-507.
- [26] Z Yang, Z Mao, Z Xie, Y Zhang, S Liu, J Zhao, J Xu, Z Chi and MP Aldred. Recent advances in organic thermally activated delayed fluorescence materials. *Chem. Soc. Rev.* 2017; **46**, 915-1016.
- [27] FB Dias, J Santos, DR Graves, P Data, RS Nobuyasu, MA Fox, AS Batsanov, T Palmeira, MN Berberan-Santos, MR Bryce and AP Monkman. The role of local triplet excited states and D-A relative orientation in thermally activated delayed fluorescence: Photophysics and devices. *Adv. Sci.* 2016; **3**, 1-10.
- [28] U Shakeel and J Singh. Study of processes of reverse intersystem crossing (RISC) and thermally activated delayed fluorescence (TADF) in organic light emitting diodes (OLEDs). *Org. Electron.* 2018; **59**, 121-4.
- [29] A Endo, M Ogasawara, A Takahashi, D Yokoyama, Y Kato and C Adachi. Thermally activated delayed fluorescence from  $sn4+$ -porphyrin complexes and their application to organic light-emitting diodes - a novel mechanism for electroluminescence. *Adv. Mater.* 2009; **21**, 4802-6.
- [30] H Uoyama, K Goushi, K Shizu, H Nomura and C Adachi. Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature* 2012; **492**, 234-8.
- [31] C Adachi, MA Baldo, ME Thompson and SR Forrest. Nearly 100 % internal phosphorescence efficiency in an organic light emitting device. *J. Appl. Phys.* 2001; **90**, 5048-51.
- [32] C Adachi. Third-generation organic electroluminescence materials. *Jpn. J. Appl. Phys.* 2014; **53**, 1-11.
- [33] T Bui, F Goubard, M Ibrahim-Ouali, D Gigmes and F Dumur. Thermally activated delayed fluorescence emitters for deep blue organic light emitting diodes: A review of recent advances. *Appl. Sci.* 2018, **8**, 494-517.
- [34] M Sarma and K Wong. Exciplex: An intermolecular charge-transfer approach for TADF. *ACS Appl. Mater. Interfaces* 2018; **10**, 19279-304.
- [35] CA Voll, G Markopoulos, TC Wu, M Welborn, JU Engelhart, S Rochat, GD Han, GT Sazama, TA Lin, TV Voorhis, MA Baldo and TM Swager. Lock-and-key exciplexes for thermally activated delayed fluorescence. *Org. Lett.* 2020; **2**, 1-10.
- [36] K Nasu, T Nakagawa, H Nomura, C Lin, C Cheng, M Tseng, T Yasuda and C Adachi. A highly luminescent spiro-anthracenone-based organic light-emitting diode exhibiting thermally activated delayed fluorescence. *Chem. Commun.* 2013; **49**, 10385-7.

- [37] M Numata, T Yasuda and C Adachi. High efficiency pure blue thermally activated delayed fluorescence molecules having 10H-phenoxaborin and acridan units. *Chem. Commun.* 2015; **51**, 9443-6.
- [38] A Mishra, C Ma and P Bauerle. Functional oligothiophenes: Molecular design for multidimensional nanoarchitectures and their applications. *Chem. Rev.* 2009; **109**, 1141-276.
- [39] AJ Blayney, IF Perepichka, F Wudl and DF Perepichka. Advances and challenges in the synthesis of poly(p-phenylene vinylene)-based polymers. *Isr. J. Chem.* 2014; **54**, 674-88.
- [40] AC Grimsdale, KL Chan, RE Martin, PG Jokisz and AB Holmes. Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices. *Chem. Rev.* 2009; **109**, 897-1091.
- [41] Y Olivier, D Niedzialek, V Lemaur, W Pisula, K Müllen, U Koldemir, JR Reynolds, R Lazzaroni, J Cornil and D Beljonne. High-mobility hole and electron transport conjugated polymers: How structure defines function. *Adv. Mater.* 2014; **26**, 2119-36.
- [42] J Choi, KH Kim, H Yu, C Lee, H Kang, I Song, Y Kim, JH Oh and BJ Kim. Importance of electron transport ability in naphthalene diimide based polymer acceptors for high-performance, additive-free, all polymer solar cells. *Chem. Mater.* 2015; **27**, 5230-7.
- [43] Y Lee, SJ Woo, JJ Kim and JI Hong. Linear-shaped thermally activated delayed fluorescence emitter using 1,5-naphthyridine as an electron acceptor for efficient light extraction. *Org. Electron.* 2020; **78**, 105600.
- [44] J Choi, H Song, N Kim and FS Kim. Development of n-type polymer semiconductors for organic field-effect transistors. *Semicond. Sci. Tech.* 2015; **30**, 1-16.
- [45] H Chen, M Nikolka, A Wadsworth, W Yue, A Onwubiko, M Xiao, AJP White, D Baran, H Siringhaus and I McCulloch. A thieno[2,3-b]pyridine-flanked diketopyrrolopyrrole polymer as an n-type polymer semiconductor for all-polymer solar cells and organic field-effect transistors. *Macromolecules* 2018; **51**, 71-9.
- [46] F Mariano, M Mazzeo, Y Duan, G Barbarella, L Favaretto, S Carallo, R Cingolani and G Gigli. Very low voltage and stable p-i-n organic light-emitting diodes using a linear S,S-dioxide oligothiophene as emitting layer. *Appl. Phys. Lett.* 2009; **94**, 1-3.
- [47] W Li, L Yan, H Zhou and W You. A general approach toward electron deficient triazole units to construct conjugated polymers for solar cells. *Chem. Mater.* 2015; **27**, 6470-6.
- [48] C Arbizzani, G Barbarella, A Bongini, L Favaretto, M Mastragostino, P Ostojica, O Pudova and M Zambianchi. Oligothiophene-S,S-dioxides: Towards n-type semiconductor oligothiophenes? *Opt. Mater.* 1998; **9**, 43-5.
- [49] G Barbarella, L Favaretto, G Sotgiu, M Zambianchi, A Bongini, C Arbizzani, M Mastragostino, M Anni, G Gigli and R Cingolani. Tuning solid-state photoluminescence frequencies and efficiencies of oligomers containing one central thiophene-S,S-dioxide unit. *J. Am. Chem. Soc.* 2000; **122**, 11971-8.
- [50] E Tedesco, BM Kariuki, KDM Harris, RL Johnston, O Pudova, G Barbarella, EA Marseglia, G Gigli and R Cingolani. Structural aspects of high-efficiency blue-emitting 2,5-Bis(trimethylsilyl)thiophene-S,S-dioxide and related materials. *J. Solid State Chem.* 2001; **161**, 121-8.
- [51] N Camaioni, G Ridolfi, V Fattori, L Favaretto and G Barbarella. Oligothiophene-S,S-dioxides as a class of electron-acceptor materials for organic photovoltaics. *Appl. Phys. Lett.* 2004; **84**, 1901-3.
- [52] C Vijayakumar, A Saeki and S Seki. Optoelectronic Properties of dicyanofluorene-based n-type polymers. *Chem. Asian J.* 2012; **8**, 1845-52.
- [53] II Perepichka, IF Perepichka, MR Bryce and LO Pålsson. Dibenzothiophene-S,S-dioxide-fluorene co-oligomers. Stable, highly-efficient blue emitters with improved electron affinity. *Chem. Commun.* 2005; **27**, 3397-9.
- [54] C Li, Y Wang, D Sun, H Li, X Sun, D Ma, Z Ren and S Yan. Thermally activated delayed fluorescence pendant copolymers with electron- and hole-transporting spacers. *ACS Appl. Mater. Interfaces* 2018; **10**, 5731-9.
- [55] F Yang, K Sun, ZJ Cao, Z Hui Li and MS Wong. Synthesis and functional properties of oligofluorenyl-dibenzothiophene-S,S-dioxides end-capped by diphenylamine moieties. *Synth. Met.* 2008; **158**, 391-5.
- [56] S Fujii, Z Duan, T Okukawa, Y Yanagi, A Yoshida, T Tanaka, G Zhao, Y Nishioka and H Kataura. Synthesis of novel thiophenophenylene oligomer derivatives with a dibenzothiophene-5,5-dioxide core for use in organic solar cells. *Phys. Status Solidi.* 2012; **B249**, 2648-51.

- [57] FB Dias, KN Bourdakos, V Jankus, KC Moss, KT Kamtekar, V Bhalla, J Santos, MR Bryce and AP Monkman. Triplet harvesting with 100 % efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters. *Adv. Mater.* 2013; **25**, 3707-14.
- [58] X Zhan, Z Wu, Y Lin, S Tang, J Yang, J Hu, Q Peng, D Ma, Q Lia and Z Li. New AIEgens containing dibenzothiophene-*S,S*-dioxide and tetraphenylethene moieties: similar structures but very different hole/electron transport properties. *J. Mater. Chem. C* 2015; **3**, 5903-9.
- [59] C Fan, C Duan, Y Wei, D Ding, H Xu and W Huang. Dibenzothiophene-based phosphine oxide host and electron-transporting materials for efficient blue thermally activated delayed fluorescence diodes through compatibility optimization. *Chem. Mater.* 2015; **27**, 5131-40.
- [60] MH Al-mashhadani. 2019, Dibenzothiophene-*S,S*-dioxide based conjugated molecular and polymeric materials for organic electronics. Ph.D thesis. Bangor University, Bangor, England.
- [61] FB Dias, KN Bourdakos, V Jankus, KC Moss, KT Kamtekar, V Bhalla, J Santos, MR Bryce and AP Monkman. Triplet harvesting with 100 % efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters. *Adv. Mater.* 2013; **25**, 3707-14.
- [62] JS Ward, RS Nobuyasu, AS Batsanov, P Data, AP Monkman, FB Dias and MR Bryce. The interplay of thermally activated delayed fluorescence (TADF) and room temperature organic phosphorescence in sterically-constrained donor-acceptor charge-transfer molecules. *Chem. Commun.* 2016; **52**, 2612-5.
- [63] S Gan, W Luo, B He, L Chen, H Nie, R Hu, A Qin, Z Zhao and BZ Tang. Integration of aggregation-induced emission and delayed fluorescence into electronic donor-acceptor conjugates. *J. Mater. Chem. C* 2016; **4**, 3705-8.
- [64] RS Nobuyasu, Z Ren, G Griffiths, AS Batsanov, P Data, S Yan, AP Monkman, MR Bryce and FB Dias. Rational design of TADF polymers using a donor-acceptor monomer with enhanced TADF efficiency induced by the energy alignment of charge transfer and local triplet excited states. *Adv. Opt. Mater.* 2016; **4**, 597-607.
- [65] JU Kim, SS Reddy, LS Cui, H Nomura, S Hwang, DH Kim, H Nakanotani, SH Jin and C Adachi. Thermally activated delayed fluorescence of bis(9,9-dimethyl-9,10-dihydroacridine) dibenzo[*b,d*]thiophene 5,5-dioxide derivatives for organic light-emitting diodes. *J. Lumin.* 2017; **190**, 485-91.
- [66] PL dos Santos, JS Ward, DG Congrave, AS Batsanov, J Eng, JE Stacey, TJ Penfold, AP Monkman and MR Bryce. Triazatruxene: A rigid central donor unit for a D-A3 thermally activated delayed fluorescence material exhibiting sub-microsecond reverse intersystem crossing and unity quantum yield via multiple singlet-triplet state pairs. *Adv. Sci.* 2018; **5**, 1700989.
- [67] RS Nobuyasu, JS Ward, J Gibson, BA Laidlaw, Z Ren, P Data, AS Batsanov, TJ Penfold, MR Bryce and FB Dias. The influence of molecular geometry on the efficiency of thermally activated delayed fluorescence. *J. Mater. Chem. C* 2019; **7**, 6672-84.
- [68] MK Etherington, F Franchello, J Gibson, T Northey, J Santos, JS Ward, HF Higginbotham, P Data, A Kurowska, PL Dos Santos, DR Graves, AS Batsanov, FB Dias, MR Bryce, TJ Penfold and AP Monkman. Regio- and conformational isomerization critical to design of efficient thermally-activated delayed fluorescence emitters. *Nat. Commun.* 2017; **8**, 14987.