**Liquid-Crystalline Thermally Activated Delayed Fluorescence: Design, Synthesis and Application in Solution-Processed Organic Light-Emitting Diodes**

Yuanyuan Zhua,Songkun Zenga, Bing Lia,Alice J. McEllinb, Junxu Liaoc, Zhou Fanga, Chen Xiaoa, Duncan W. Bruceb\*, Weiguo Zhua\*, Yafei Wanga\*

a*School of Materials Science & Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Changzhou University, Changzhou 213164, PR China. Email:* [*zhuwg18@126.com*](mailto:zhuwg18@126.com)*;* [*qiji830404@hotmail.com*](mailto:qiji830404@hotmail.com)

*bDepartment of Chemistry, University of York, Heslington, York*, *YO10 5DD*. *Email:* [duncan.bruce@york.ac.uk](mailto:duncan.bruce@york.ac.uk)

*cSchool of Chemical Engineering and Energy Technology, Dongguan University of Technology, Dongguan, 523808, PR China.*

**Abstract**

Realizing both high efficiency and liquid-crystallinity in one molecule remains a challenge in thermally activated delayed fluorescence (TADF) emission. Herein, two isomeric compounds— *m*-DPSAc-LC and *p*-DPSAc-LC with different connection position between donor and acceptor moieties—were synthesized and characterized. Diphenylsulfone (DPS) was used as the acceptor, acridine (Ac) as the donor and biphenyl derivatives (LC) were employed as the mesogenic group. Both compounds showed a smectic mesophase evidenced by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and temperature-dependent small-angle X-ray scattering (SAXS). The compound *p*-DPSAc-LC clearly exhibited thermally activated delayed fluorescence due to the much more distorted geometry, whereas *m*-DPSAc-LC showed simple fluorescence. Compared to the parent TADF molecules without appended mesogenic groups (DPS-Ac), these liquid-crystalline emitters possessed higher hole mobilities and improved device performance. The OLEDs fabricated *via* solution processing using the liquid-crystalline compound *p*-DPSAc showed a maximum external quantum efficiency of *ca* 15% and as such is the first example of a liquid-crystalline TADF material in an OLED device.

Keywords: liquid crystal; thermally activated delayed fluorescence; diphenylsulfone; acridine; synthesis and properties; solution processable OLED;

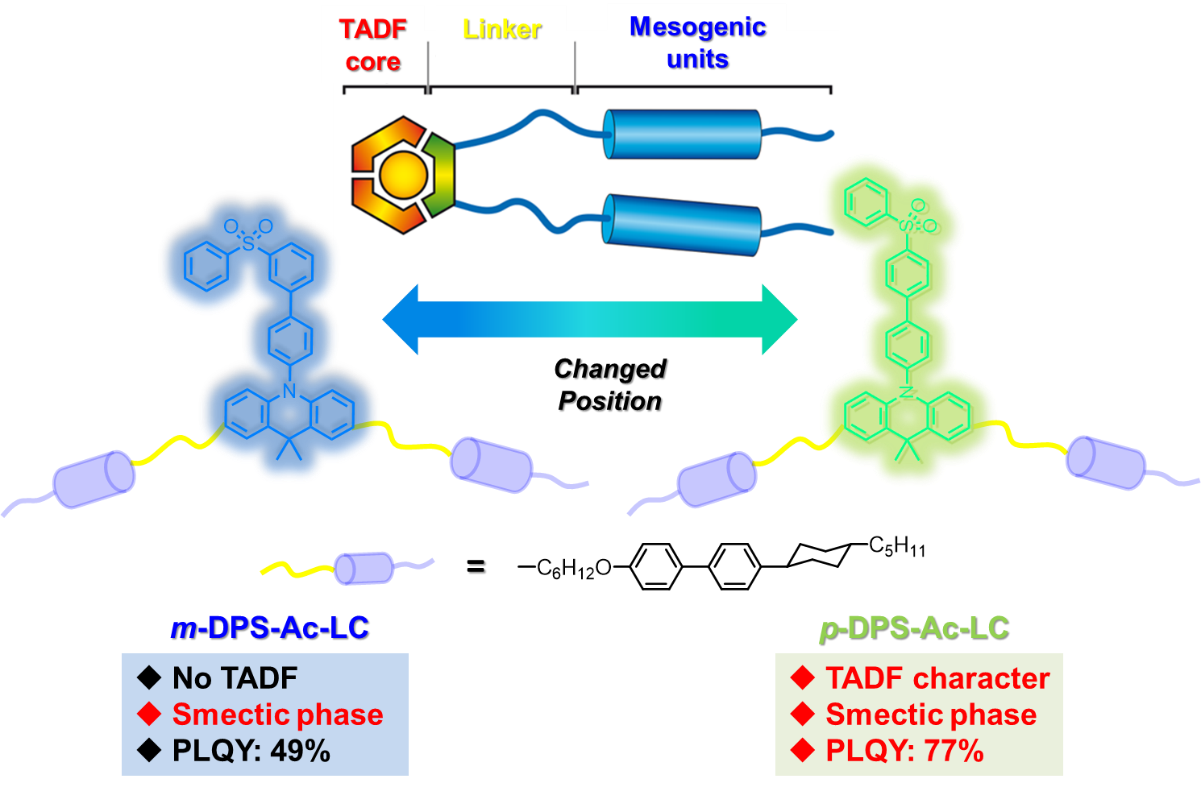
**Introduction**

Thermally activated delayed fluorescence (TADF) has become an attractive approach to emissive materials for use in organic light-emitting diodes (OLEDs) because of their 100% theoretical internal quantum efficiency (IQE) and metal-free, organic nature.1-9 In such materials, triplet excitons can up-convert to the singlet excited state through reverse intersystem crossing (*r*ISC) when there is a small energy difference (Δ*E*ST) between the lowest singlet (S1) and triplet (T1) excited states, leading to the TADF character.10-15 According to equation (1):16

(1)

there is a relationship between *k*rISC and Δ*E*ST is observed, implying that an effective method to maximize the *r*ISC process is to reduce the value of Δ*E*ST. On the other hand, the Δ*E*ST of organic molecules depends on the exchange energy between singlet and triplet states, which in turn is related to the overlap integral of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital). Based on previous results, a most effective method to construct a TADF material is to develop a twisted donor-acceptor (D-A) molecule which possesses small spatial overlap between the HOMO and LUMO, resulting in small energy separations Δ*E*ST. 17-20 Thus, many TADF emitters have been developed using this principle and the reported external quantum efficiencies (EQE) in devices can be greater than 20%.21-26 On the other hand, TADF materials with multifunctional photophysical property, such as aggregation-induced emission, triboluminescence and room-temperature phosphorescence, have been developed because of their potential application in intelligent devices. However, owing to the distorted molecular geometry required for TADF molecules, which is at odds with the molecular anisotropy required to realize liquid crystallinity, there is a single report27 of liquid-crystalline TADF materials, even though liquid crystals possess the good carrier mobilities consequent on their long-range order.28-33 Therefore, it is then of interest to integrate liquid crystallinity into TADF materials to explore the molecular structure-property relationship.

Encouraged by our previous investigations of luminescent liquid crystals,34-35 very recently, some of us designed a series of TADF-based LCs in which the emissive TADF core (terephthalonitrile) was functionalized with alkoxy-substituted carbazoles to give materials with eight or even sixteen peripheral chains.27 Although some molecules showed a columnar hexagonal mesophase, the emission efficiency remained low (*Φ*em: 1.5～18%) so that combining good TADF efficiency with liquid crystallinity remains a challenge of significance.

****

**Figure 1**. The design schematic diagram for TADF-LC materials and the molecular structures.

Inspired by our previous result, in this contribution, we continue to seek the multifunctional TADF emitters with LC property. As we know, 9,9-dimethyl-9,10-dihydroacridine (Ac) is a promising donor unit in TADF emitter due to its good hole-transporting ability, which can give a shallow HOMO energy level and thus improved hole injection. On the other hand, diphenyl sulfone (DPS) has wide application as an emitter because of its strong electron-withdrawing nature and easy chemical functionalization. Therefore, D-A-type molecules containing DPS and Ac as the acceptor and donor groups, respectively, were designed in this contribution.36-37 Following on from work developing phosphorescent liquid crystals,34 the decision was made to use a difluorobiphenyl-based mesogenic unit to functionalize the periphery of the TADF emissive core, conferring liquid crystallinity and contributing to molecular rigidity, thus enhancing the emission efficiency. To this end, two isomers of the target compound were designed and prepared – *m*-DPSAc-LC and *p*-DPSAc-LC (**Figure 1**) – with a different linking position between the donor and acceptor. In this approach, the molecule could be expected to achieve much higher emission efficiency because the nonradiative process promoted by large numbers of flexible peripheral chains can be suppressed. The preparation, structure and properties of these new materials are now discussed. As expected, compound *p*-DPSAc-LC possesses clear TADF character with very high emission efficiency of 77%. Due to the rather high molecular weight, both emitters were fabricated into OLEDs by solution-processing, which possesses many merits, such as low-cost, relatively simple preparation process and fine control of the doping concentration.38 Impressively, the solution-processable OLED based on the TADF-LC molecule presented a maximum EQE of 15%. To the best of our knowledge, this is the first example on the application of LC-TADF molecules in OLED.

**Experimental Section**

All reagents used in the experiments were purchased from commercial sources without further purification. For column chromatography, silica gel with 200 ~ 300 mesh was used. Compound 1, 1-bromo-3-(phenylsulfonyl)benzene, 1-bromo-4-(phenylsulfonyl)benzene and compound 4 were reported in our previous work.39-41



**Scheme 1**. Synthetic route of the emitters.

Reaction conditions: a) K2CO3, acetone, 80 oC,24 h; b) [Pd(PPh3)4], K2CO3, THF, 80 oC, 24 h; c) *N*-bromosuccinimide, CHCl3, RT, 12 h.

**2-(4-((6-((2,3-Difluoro-4'-(4-pentylcyclohexyl)-[1,1'-biphenyl]-4-yl)oxy)hexyl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).** A mixture of compound 1 (5.0 g, 9.1 mmol), compound 2 (2.4 g, 10.9 mmol) and K2CO3 (6.2 g, 45.5 mmol) in acetone was heated under reflux for 24 h under Ar. After cooling to RT, the reaction mixture was poured into water and extracted with CH2Cl2. The organic layer was washed with water, dried over MgSO4 and removed by rotary evaporator. The residue was purified by column chromatography on silica (Hexane/CH2Cl2, 1:1, v/v) to give a white solid. Yield: 3.4 g (5.1mmol, 57 %). m.pt: 106.1 oC. 1H NMR (400 MHz, CDCl3) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.29 (s, 2H), 7.08 (t, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.78 (t, *J* = 8.2 Hz, 1H), 4.08 (t, *J* = 6.4 Hz, 2H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.50 (t, *J* = 12.0 Hz, 1H), 1.95 – 1.81 (m, 8H), 1.57 – 1.45 (m, 7H), 1.33 (s, 20H), 1.11 – 1.02 (m, 2H), 0.90 (t, *J* = 6.9 Hz, 3H). 13C{1H} NMR(126 MHz, CDCl3) δ 161.67, 147.40, 136.50, 132.36, 128.61, 127.04, 123.50, 123.08, 113.84, 109.55, 83.51, 69.70, 67.55, 44.35, 37.31, 34.30, 33.59, 32.22, 29.13, 26.66, 25.71, 24.85, 22.73, 14.13. MALDI-MS (m/z) of C41H55BF2O4 for [M]+: calcd. 660.69; found, 660.39.

**9,9-Dimethyl-10-(3'-(phenylsulfonyl)-[1,1'-biphenyl]-4-yl)-9,10-dihydroacridine (5).** A mixture of 1-bromo-3-(phenylsulfonyl)benzene (1.0 g, 3.4 mmol),compound 4 (1.7 g, 4.1 mmol), [Pd(PPh3)4] (196 mg, 0.17 mmol), K2CO3 (2 M, 15 mL) and tetrahydrofuran (45 mL) was heated under reflux for 24 h. After completion of the reaction, extraction with CH2Cl2, drying over anhydrous MgSO4 and evaporation of the solvent were carried out. The crude mixture was purified on column chromatography using hexane/CH2Cl2 (2:1, v/v) as an eluent to get a white solid. Yield: 1.2 g (2.4 mmol, 70 %). m.pt: 182.5 oC. 1H NMR (300 MHz, CDCl3) δ 8.27 (t, *J* = 1.7 Hz, 1H), 8.05 – 7.95 (m, 3H), 7.88 – 7.85 (m, 3H), 7.67 – 7.41 (m, 8H), 7.01 –6.95 (m, 4H), 6.31 (dd, *J* = 7.9, 1.5 Hz, 2H), 1.71 (s, 6H). 13C{1H} NMR (75 MHz, CDCl3) δ 142.47, 141.75, 141.53, 141.47, 140.77, 139.02, 133.38, 132.06, 131.87, 130.12, 130.00, 129.71, 129.43, 127.79, 126.78, 126.43, 126.23, 125.36, 120.75, 114.01, 36.02, 31.31. MALDI-MS (m/z) of C33H27NO2S for [M]+: calcd. 501.18; found, 502.30.

**2,7-dDbromo-9,9-dimethyl-10-(3'-(phenylsulfonyl)-[1,1'-biphenyl]-4-yl)-9,10-dihydroacridine (6).** A chloroform solution of *N*-bromosuccinimide (20 mL, 727.3 mg, 4.09 mmol) was dropped slowly into a chloroform solution of compound 5 (30 mL, 1.0 g, 1.99 mmol) in an ice bath. Then the reaction mixture was stirred at room temperature for 24 h. Afterwards, the solvent was removed under reduced pressure and the product was purified by silica-gel chromatography using hexane/CH2Cl2 (3/1, v/v) as eluent to get a white solid. Yield: 0.8 g (1.2 mmol, 61 %). m.pt: 143.6 oC. 1H NMR (400 MHz, CDCl3) δ 8.27 (s, 1H), 7.97 – 8.03 (m, 3H), 7.93 – 7.80 (m, 3H), 7.70 – 7.49 (m, 6H), 7.38 (t, *J* = 6.5 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.19 (d, *J* = 8.8 Hz, 2H), 1.64 (d, *J* = 8.7 Hz, 6H). 13C{1H} NMR (126 MHz, CDCl3) δ 142.53, 141.39, 140.52, 139.57, 133.37, 131.71, 131.54, 129.94, 129.40, 128.15, 127.75, 126.95, 126.18, 115.79, 113.52, 30.94, 22.69. MALDI-MS (m/z) of C33H25Br2NO2S for [M]+: calcd. 659.44; found, 659.06.

***m*-DPSAc-LC.** A mixture of compound 3 (1.65 g, 2.4 mmol), compound 6 (525 mg, 0.8 mmol), [Pd(PPh3)4] (138 mg, 0.04 mmol), K2CO3 (2 M, 10 mL) and tetrahydrofuran (30 mL) was heated under reflux for 24 h. After completion of the reaction, extraction with CH2Cl2, drying over anhydrous MgSO4 and evaporation of the solvent were carried out. The crude mixture was purified on column chromatography using hexane/CH2Cl2 (2/3, v/v) as an eluent to get a light yellow solid. Yield: 152 mg (0.1 mmol, 12 %). m.pt: 97.1 oC. 1H NMR (400 MHz, CDCl3) δ 8.29 (s, 1H), 8.04 – 7.97 (m, 3H), 7.91 – 7.86 (m, 3H), 7.71 – 7.37 (m, 16H), 7.28 (s, 4H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.10 – 7.05 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 4H), 6.78 (t, *J* = 8.1 Hz, 2H), 6.36 (s, 2H), 4.10 – 4.00 (m, 8H), 2.50 (t, *J* = 12.1 Hz, 2H), 1.93 – 1.81 (m, 21H), 1.52 – 1.43 (m, 5H), 1.33 – 1.25 (m, 25H), 1.10 – 1.01 (m, 5H), 0.90 (t, *J* = 7.0 Hz, 6H). 13C{1H} NMR (126 MHz, CDCl3) δ 158.15, 149.87, 147.89, 147.52, 142.89, 142.50, 141.63, 140.92, 139.14, 133.38, 132.37, 131.87, 130.02, 129.79, 129.43, 128.62, 127.79, 127.10, 126.95, 126.24, 123.54, 123.06, 114.79, 109.55, 77.31, 77.05, 76.80, 69.73, 67.91, 44.37, 37.38, 34.32, 33.61, 32.25, 29.20, 26.69, 25.81, 22.76, 14.17. MALDI-MS (m/z) of C103H111F4NO6S for [M]+: calcd. 1566.81; found, 1566.77.

**9,9-Dimethyl-10-(4'-(phenylsulfonyl)-[1,1'-biphenyl]-4-yl)-9,10-dihydroacridine (7).** Compound 1-bromo-4-(phenylsulfonyl)benzene was synthesized according to our previous work.2 The synthetic process was similar to that for compound 5 as a white solid. Yield: 1.24 g (2.5 mmol, 73 %). m.pt: 224.8 oC. 1H NMR (400 MHz, CDCl3) δ 8.10 – 7.99 (m, 4H), 7.81 (dd, *J* = 8.5, 1.9 Hz, 4H), 7.63 – 7.52 (m, 3H), 7.49 – 7.41 (m, 4H), 7.01 – 6.91 (m, 4H), 6.29 (s, 2H), 1.70 (s, 6H). 13C{1H} NMR (75 MHz, CDCl3) δ 145.22, 141.75, 141.67, 140.74, 140.58, 139.01, 133.31, 132.05, 130.15, 129.83, 129.40, 128.39, 128.07, 127.72, 126.41, 125.35, 120.78, 114.00, 36.02, 31.27. MALDI-MS (m/z) of C33H27NO2S for [M]+: calcd. 501.18; found, 502.34.

**2,7-dibromo-9,9-dimethyl-10-(4'-(phenylsulfonyl)-[1,1'-biphenyl]-4-yl)-9,10-dihydroacridine (8).**

The synthetic process was similar to that for compound 6 as a white solid. Yield: 0.76 g (1.2 mmol, 58 %). m.pt: 126.4 oC. 1H NMR (400 MHz, CDCl3) δ 8.08 – 8.00 (m, 4H), 7.81 (t, *J* = 8.3 Hz, 4H), 7.64 – 7.50 (m, 5H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.17 (d, *J* = 8.8 Hz, 2H), 1.66 (d, *J* = 8.7 Hz, 6H). 13C{1H} NMR (126 MHz, CDCl3) δ 144.84, 141.53, 140.77, 139.54, 133.32, 131.73, 131.54, 130.05, 129.35, 128.38, 128.10, 127.68, 115.77, 113.53, 36.28, 29.57. MALDI-MS (m/z) of C33H25Br2NO2S for [M]+: calcd. 659.44; found, 658.91.

***p*-DPSAc-LC.** The synthetic process was similar to that for compound *m*-DPSAc-LC as a yellow solid. Yield: 168 mg (0.11 mmol, 13 %). m.pt: 87.5 oC. 1H NMR (400 MHz, CDCl3) δ 8.08 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.84 (t, *J* = 7.4 Hz, 4H), 7.68 – 7.52 (m, 5H), 7.51 – 7.39 (m, 10H), 7.28 (s, 4H), 7.17 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.08 (td, *J* = 8.6, 2.0 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 4H), 6.78 (t, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 8.5 Hz, 2H), 4.09 (t, *J* = 6.5 Hz, 4H), 4.01 (t, *J* = 6.4 Hz, 4H), 2.50 (t, *J* = 12.1 Hz, 2H), 1.96 – 1.71 (m, 22H), 1.59 – 1.57 (m, 7H), 1.52 – 1.46 (m, 5H), 1.37 – 1.19 (m, 18H), 1.10 – 1.01 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 6H). 13C{1H} NMR (126 MHz, CDCl3) δ 158.12, 149.88, 147.86, 147.42, 145.14, 141.65, 140.89, 140.59, 139.08, 133.27, 132.33, 129.87, 129.36, 128.59, 128.37, 128.04, 127.87 – 127.00, 123.50, 123.07, 114.76, 109.54, 77.27, 77.02, 76.77, 69.70, 67.87, 44.34, 37.34, 34.29, 33.58, 32.22, 29.16, 26.66, 25.77, 22.72, 14.13. MALDI-MS (m/z) of C103H111F4NO6S for [M]+: calcd. 1566.81; found, 1566.22.

**Results and Discussion**

**Synthesis**

The synthetic route to the luminescent liquid crystal materials is depicted in **Scheme 1** and used a series of palladium-catalyzed Suzuki-Miyaura couplings with boronic acids to access the target materials; they were characterized by 1H and 13C NMR spectroscopy, mass spectrometry and HPLC (**Figure S1~S10**). As shown in **Figure S11**, thermogravimetric analysis shows that both *m*-DPSAc-LC and *p*-DPSAc-LC exhibit good thermal stability with decomposition temperatures (at 5% weight loss) of 422 and 424 oC, respectively, under scanning conditions.

**Single crystal analysis**

****

**Figure 2**. Single crystal structure and molecular packing in: (a, b) *m*-DPSAc-LC and (c, d) *p*-DPSAc-LC.

Single crystals of both emitters were obtained by slow and careful evaporation of CHCl3/hexane (*v/v*=1:1) solutions at room temperature. The crystal structures and molecular packing in these crystals are depicted in **Figure 2** and **Figure S12~S14**, and all relevant data are listed in **Table S5**. Compound *m*-DPSAc-LC crystallizes in the monoclinic crystal system with a space group of *P*21, whereas *p*-DPSAc-LC crystallizes in the triclinic crystal system within space group *P*-1. The former crystallizes with two molecules in the unit cell and two molecules of chloroform, and shows some disorder of one of the cyclohexyl rings. As shown in **Figure 2**, the emitters present quite different conformations with *p*-DPSAc-LC adopting a bent, rather angular structure, whereas in *m*-DPSAc-LC the structure is much more open. The angular nature of *p*-DPSAc-LC arises primarily from some *gauche* C–C–C angles in the hexamethylene chain linking the mesogenic unit to the central dihyroacridine on one side of the molecule. The other significant different between the two is that in *p*-DPSAc-LC, the dihydroacridine ring is bevelled about the 1,4-C–N axis of the central ring so that the planes of the two peripheral phenyl rings make an angle of 31.41°. In *m*-DPSAc-LC, however, the dihydroacridine ring is close to planar and the planes of the two peripheral phenyl rings make an angle of only 4.94° (**Figure S12**). The dihedral angles between the Ac and DPS moieties for *m*-DPSAc-LC and *p*-DPSAc-LC are of 46.96o and 72.19o, respectively (**Figure S12**) and this particularly twisted molecular geometry of *p*-DPSAc-LC is beneficial in minimizing Δ*E*ST value, leading to better TADF characteristics.The bent nature of *p*-DPSAc-LC creates a sort of pocket into which chain fragments on neighbouring molecules fit as part of the packing motif. This is illustrated in **Figure S14**, in which it is also possible to see an antiparallel arangement of *ortho*-difluorophenyl fragments. Other intramolecular short contacts can be found as a function of the packing.

**Theoretical Calculations**

****

**Figure 3**. The frontier molecular orbitals HOMO and LUMO, as well as the energy gap (Δ*E*ST) between singlet and triplet excited states.

The geometric and electronic structure natures of both emitters were calculated based on the crystal structures using density functional theory (DFT) and time-dependent DFT (TD-DFT) using Gaussian 09 at the level of M06-2X/6-31G(d,p). As seen from **Figures 3** and **S15**, both emitters show a similar twisted molecular geometry, in which the acridine moiety and the benzene linker are almost perpendicular. Such large torsional angles can facilitate the spatial separation between the HOMO and LUMO of the compounds. Thus, the LUMOs are mainly distributed on both diphenyl sulphone and the benzene linker, while the HOMOs arise from the donor (acridine) fragment. The energy gaps (Δ*E*ST) are calculated to be 0.484 and 0.408 eV for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively. Notably, the linker position between donor and acceptor plays a key role in the energy gap. To further understand the characters of the S0→S1 and S0→T1 transitions, natural transition orbitals (NTOs) analysis was performed for the excited state (Sn and Tn) using TD-DFT (**Figure S15**). Completely spatial separation is observed between the holes and particles in the S1 state, while substantial overlap occurs between the holes and particles in the T1 state. These results imply that the charge transfer (CT) nature and local excitation (LE) character are assigned to the singlet and triplet excited state, respectively. In this case, efficient spin-orbit coupling (SOC, El-Sayed rule) can be achieved between the 1CT and 3LE (**Table S1**). Based on the calculation results, it could be concluded that *p*-DPSAc-LC would exhibit an excellent TADF character due to the relatively small Δ*E*ST level.

**Liquid crystalline behavior**

The liquid-crystalline properties of the emitters were investigated using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and variable-temperature small-angle X-ray scattering (SAXS).

The behavior of these materials is not totally straightforward and reference to the DSC traces, recorded under N2, provides a useful starting point, noting that the traces do not show the melting points [87.5 °C and 97.1 °C for *p*-DPSAc-LC and *m-*DPSAc-LC, respectively (observed in conventional melting point apparatus, **Table S2**)] as the samples are not always obtained in their crystalline state from solution. Thus, for *m*-DPSAc-LC, the second heating cycles essentially show a small endothermic event at 113 °C (**Figures 4a and S16a**), which simply reverses on cooling. Optical microscopy shows the observed phase to be birefringent and, while it did not prove possible to obtain a well-developed texture, the features that can be observed are consistent with a SmA phase (**Figure 4b**). This is consistent with the SAXS data, obtained well below the clearing point, which show a single strong reflection at 2** = 1.9° attributed as the *d*001 reflection and corresponding to a layer spacing of 45.3 Å (**Figure 4c**). The length of the fully extended molecule (from the X-ray structure of *m*-DPSAc-LC) is 68.1 Å and so to be accommodated into a smaller layer dimension, clearly there is significant interdigitation and/or chain folding. There is also a generally broader reflection at 2** ≈ 4.6° which corresponds to a periodicity of about 19 Å, which will be discussed below (**Figure 4d**).

By DSC, the behavior of *p*-DPSAc-LC is broadly similar in terms of simple clearing (**Figure S16b**), with an endothermic clearing event at 100 °C, which reverses on cooling. To further explore the phase transition, as an example, compound *p*-DPSAc-LC was measured at different heating and cooling rate (5, 10 and 20 oC min-1, **Figure S17**). It is noted that almost identical phase transition temperatures were observed. This compound did not give usable optical textures by microscopy, but SAXS data showed a strong reflection at 2** = 1.7°, which by analogy with *m*-DPSAc-LC is assigned as arising from *d*001 and therefore corresponds to a layer spacing of 51.3 Å, again with a broader reflection at slightly higher angle.



**Figure 4**. (a) DSC curves of *m*-DPSAc-LC; (b) POM image of *m*-DPSAc-LC at 85 oC upon cooling process (Note: the magnification is x100. Scale bar is 250 m.); SAXS patterns on cooling of (c) *m*-DPSAc-LC (94 °C) and (d) *p*-DPSAc-LC (82 °C).

Thus, the mesophase is fluid in nature and, despite the presence of what is in effect a destabilizing lateral diphenylsulfoxide group, the materials are essentially calamitic. Indeed, the fact that the clearing points are so close in temperature suggests that the different spatial disposition of the diphenylsulfoxide group in the two isomers has relatively little effect on the identity or stability of the liquid crystal phase. Thus, with a single reflection, noting the essentially calamitic nature of the molecules and with such evidence that could be gleaned from the optical microscopy, the assignment as SmA is secure. However, with a fully extended length of nearly 70 Å and observed layer spacings of between 45-50 Å, how might the packing be understood? In fact, a clue comes from the observation that the distance from the end of the mesogenic unit to the sulfoxide group, measured in the structure of *p*-DPSAc-LC, is ≈46 Å (**Figure S13**). Thus, it is possible that the materials adopt a more hairpin-like structure, which would allow interdigitation in order to fill space (**Figure S14**). The observed layer spacings would then be quite consistent with the length of one mesogenic group plus the diphenylsulfoxide. Furthermore, considering how this would organize reveals the possibility of a longer-distance correlation between dimethyldihydroacridine units, that would be on the order of the observed wider-angle spacing of *ca* 19 Å. Of necessity, this correlation would be orthogonal to the layer direction and so formally the organization would lead to biaxiality, but X-ray is only able to reveal local correlations and so it is not possible to say that the phase itself is biaxial. However, on the basis of the optical texture obtained, assignment as a biaxial SmA phase is not supported.

**Photophysical Properties**



**Figure 5**. (a) UV absorption spectra measured in toluene (inset: the zoomed absorption region between 350 and 450 nm); (b) PL spectra in toluene with the excitation wavelength of 335 nm (inset: the emission pictures of the emitters under UV light irradiation (365 nm). The blue color is *m*-DPSAc-LC, while the green color is *p*-DPSAc-LC); (c) PL spectra in doped PMMA (10 wt%) with the excitation wavelength of 335 nm.

**Table 1.** Photophysical data of the emitters

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Compounds** | ***aλ*abs**  **/nm** | ***aλ*em**  **/nm** | ***bλ*em**  **/nm** | *b****τ*p**  **/ns** | *b****Φ*p**  **/%** | *b****τ*d**  **/µs** | *b****Φ*d**  **/%** | *b****Φ*total /%** | *c****T*d**  **/oC** | **Δ*E*ST**  **/eV** | ***Egopt***  **/eV** |
| *m*-DPSAc-LC | 287, 332 | 465 | 462 | 10.48 | 48.5 | / | / | 48.5 | 422 | 0.38 | 3.08 |
| *p*-DPSAc-LC | 291, 330 | 498 | 523 | 13.93 | 58.79 | 3.9 | 18.61 | 77.4 | 424 | 0.05 | 2.94 |

a: in toluene; b: 10 wt% in PMMA; c: in N2 with the heating rate of 20 oC min-1.

**Figure 5** depicts the absorption and photoluminescent (PL) properties of both emitters in solution and doped at 10 wt% loading in a PMMA film at room temperature. As shown in **Figure 5a**, almost identical absorption spectra with two main absorption bands are found for both emitters. The strong absorption band between 280 and 350 nm originates from the ππ\* transition of the aromatic system, while the very weak absorption band in the region of 350-450 nm (**Figure 5a inset**) is assigned to the intramolecular charge transfer (ICT) transition from Ac to acceptor DPS moiety. Compared to *m*-DPSAc-LC, *p*-DPSAc-LC exhibits a more distinct ICT transition owing to the extended conjugation arising from *para* substitution (**Figure 5a inset**).

Intense blue and green emission with maximum emission peaks at 465 and 498 nm were observed for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively (**Figure 5b** and **inset**). A red shift of 34 nm is observed for *p*-DPSAc-LC relative to *m*-DPSAc-LC due to its stronger ICT effect. Compared to the prototype TADF emitters (**Figure S18**), red-shifted emission spectra were observed for both liquid crystal emitters, implying a strong ICT effect modified by the donor nature of alkoxy chains. The broad and structureless emission shape clearly indicates that the emissions arise from the charge transfer (CT) excited state and solution-dependent PL spectra obtained at room temperature (**Figure S19**) showed distinct solvatochromism for both emitters supporting the assignment as CT transitions. Compound *p*-DPSAc-LC displays a PL spectrum when doped into a PMMA film (523 nm, **Figure 5c** and **Table 1**) that is red-shifted (25 nm) compared to the emission in solution, while almost identical emission spectra are observed for *m*-DPSAc-LC in both solution and film (462 nm, **Figure 5c** and **Table 1**). The different emission behavior in the PMMA film reveals the different intermolecular interaction due to the different molecular geometry (*vide supra*).

In order to investigate the TADF character of the emitters, the low temperature (77 K) fluorescence and phosphorescence were measured in 10 wt%-doped PMMA film (**Figure 6a** and **6b**). According to the onset of low-temperature emission, values for Δ*E*ST between S1 and T1 are evaluated to be 0.38 eV and 0.05 eV for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively. Such a small Δ*E*ST value in *p*-DPSAc-LC can evidently facilitate the *r*ISC process, whereas the energy gap is too large in *m*-DPSAc-LC. Then, the transient PL decay measurements were performed on the same films at room temperature (**Figure 6c**-**6e**), where it was found that *m*-DPSAc-LC shows only the prompt emission component with the lifetime of 10.48 ns (**Figure 6c**), typical of conventional fluorescence. Conversely, the film of *p*-DPSAc-LC displayed both prompt (**Figure 6d**) and delayed fluorescence components (**Figure 6e**), with the prompt component in the nanosecond region (13.93 ns), while the delayed component is in the microsecond region (3.9 μs). Therefore, compound *p*-DPSAc-LC is unambiguously assigned as possessing TADF character consistent with the tiny value of Δ*E*ST and the observed transient PL decay. Further, temperature-dependent transient PL curves of *p*-DPSAc-LC demonstrate that the delayed components gradually increase with the temperature, a character typical of TADF behavior. The absolute PLQY (photoluminescent quantum yield) values of the doped film are then found to be 48.5% and 77.4% for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively, higher values than those of their corresponding prototype compounds (*m*-DPSAc: 13.1%; *p*-DPSAc: 37.8%). Based on the PLQY and lifetime, the photophysical constants of *p*-DPSAc-LC, such as the rate constants of fluorescence (*k*r), nonradiative transition (*k*nr), intersystem crossing (*k*ISC) and reverse intersystem crossing (*k*rISC), were calculated. As shown in **Table S3**, *p*-DPSAc-LC shows a moderate value of *k*rISC of 1.97 × 105 s-1 and *k*d of 2.56 × 105 s-1 after introduction of the mesogenic groups. On the other hand,a much larger *k*nr of 1.41 × 105 s-1 was observed for *p*-DPSAc-LC due to the peripheral flexible chains.

In order to further explore the emission efficiency, the PLQYs in neat film/doped mCP were measured to be 34.3/38.9% and 54.7/66.5% for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively (**Figure S20**). After annealing, enhanced PLQYs of 39.1/45.2% and 55.5/69.2% are observed for *m*-DPSAc-LC and *m*-DPSAc-LC, respectively. These results demonstrate that the annealing procedure has some effect on the emission efficiency.

Histogram

Description automatically generated

**Figure 6**. Low-temperature fluorescence and phosphorescence (delayed 1 ms) of *m*-DPSAc-LC (a) and *p*-DPSAc-LC (b) doped in PMMA film; transient PL decay of *m*-DPSAc-LC (c); transient PL decay of *p*-DPSAc-LC (d and e); temperature-dependent transient PL decay of *p*-DPSAc-LC (f).

Then the temperature-dependent PL profiles were obtained in neat film between 100 and 470 K under a N2 atmosphere. As shown in **Figure S22**, the behavior of both compounds was similar and the emission intensity gradually increased from 100 to 280 K with a concomitant red shift and increase in the FWHM (full width at half maximum). These phenomena can be ascribed to the ordered molecular packing in the crystal state. Conversely, the emission intensity sharply decreases when the temperature is above 340 K, owing to the increased non-irradiative process at high temperature. Obviously, the different phase state has a significant effect on the emission property.

**Electrochemical Response**

The redox behavior of the materials was investigated by cyclic voltammetry in CH3CN (see experimental part), and the resulting voltammograms are shown in **Figure S23**. Both materials showed an oxidation process which, owing to the fact that the donor fragment is the same in both, exhibited a common onset potential *E*ox = 0.88 V (*E*Fc/Fc+ = 0.46 V is used as a reference). Interestingly, the two compounds show different electron-transfer kinetics at the electrode (slower for *m*-DPSAc-LC). From these data, the estimated HOMO values are –5.22 eV according to the equation *E*HOMO = –(*E*ox - *E*Fc/Fc+ + 4.8) eV42,43 and from the edge absorption, the optical band gaps (*E*opt) were evaluated to be 3.08 and 2.94 eV for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively. Based on *E*HOMO= (*E*HOMO + *E*opt) eV, the LUMO values are determined to be –2.14 for *m*-DPSAc-LC and –2.28 eVfor *p*-DPSAc-LC.

**Hole transporting properties**



**Figure 7**. Current density-voltage curves of the hole- (a) and electron-only (b) devices.

To gain insight into the influence of liquid crystallinity on charge transport character, both hole- and electron-only devices (non-doped) based on the liquid-crystalline emitters and the prototype TADF materials (*m*-DPSAc and *p*-DPSAc – **Figure S18**) were fabricated with a device structure of ITO/PEDOT:PSS (40 nm)/EML (30 nm)/MoO3 (10 nm)/Al (120 nm). The relevant data are listed in **Table S3**. As depicted in **Figure 7a**, the current density-voltage (*J*-*V*) curves showed that the LC emitters exhibited clearly larger hole mobilities than the corresponding conventional TADF molecules when an annealing temperature of 60 oC was employed. According to the formula *J* = (9/8)*ε*0*ε*r*μ*(*V*/*d*3)44 (**Table S4**), the hole mobilities of *m*-DPSAc-LC /or *p*-DPSAc-LC based devices were 9.19 × 10-4 and 9.56 × 10-4 cm2 V–1 s–1, respectively. However, the mobilities for *m*-DPSAc and *p*-DPSAc were lower at 8.38 × 10-4 and 5.67 × 10-4 cm2 V–1 s–1, respectively. When the annealing temperature was 90 oC, the LC molecules displayed improved hole mobilities of 1.11 × 10-3 and 9.74 × 10-4 cm2 V–1 s–1 for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively, probably due to the increased fluidity in the mesogenic phase. Then the hole mobilities of the emitters in the mCP host matrix were explored further. Similarly, the hole mobilities of *m*-DPSAc-LC and *p*-DPSAc-LC in host matrix were recorded at 9.43 × 10-4 and 8.23 × 10-4 cm2 V–1 s–1, respectively, which is higher than their corresponding non-LC emitter (**Table S4**), especially for *p*-DPSAc-LC. On the other hand, the LC emitters possess large or considerable electron mobility in the host matrix with the prototype emitter. Therefore, these LC molecules have a positive effect on enhancement the hole mobility, probably achieving a better device performance than the traditional TADF molecules.

**Electroluminescent Properties**

To evaluate the electroluminescence (EL) properties, solution-processed OLEDs using each emitters as the dopant were fabricated with the configuration of ITO/PEDOT:PSS (40nm)/mCP:**dopant** (20 wt%, 35 nm)/DPEPO (9 nm)/Tmpypb(45 nm)/LiF (0.5 nm)/Al (120 nm). The device structure and relevant molecular structures are listed in **Figure 8a** and **S24a**, respectively.

As shown in **Figure 8b** inset, both devices show EL spectra analogous with their PL profiles, implying the emissions in device generates from the intrinsic emitters. The maximum emission peaks at 474 and 500 nm are observed for *m*-DPSAc-LC and *p*-DPSAc-LC, respectively. Accordingly, their CIE (Commission Internationale de L'Eclairage) coordinates are (0.18, 0.23) and (0.21, 0.44), respectively (**Figure S24b**) and, in addition, the absence of emission from the host matrix suggests that there is a complete energy transfer between the host and dopant. Impressively, the EL spectrum of *p*-DPSAc-LC displays a narrower FWHM (*ca* 80 nm) than that of *m*-DPSAc-LC (*ca* 100 nm). **Figure 8c** shows the current density-voltage-luminance (*J*-*V*-*L*) curves of the devices and it is noted that the turn-on voltages (*V*turn-on: at 1 cd m-2) of *m*-DPSAc-LC and *p*-DPSAc-LC based



**Figure 8**. (a) Structure and energy diagram; (b) EL spectra (inset) and EQE-current density curves; (c) current density-voltage-luminance curves; (d) EQE values of both prototype and liquid crystal molecules.

devices are both 4.4 V. Due to the harvesting of both *S*1 and *T*1 excitons in TADF molecules, compound *p*-DPSAc-LC displays the better device performance with a maximum EQE (**Figure 8b**) of 14.9%, a current efficiency (CE) of 38.1 cd A-1 and a luminance (L) of 1413 cd m-2. These data are much better than those of the prototype TADF molecule of *p*-DPSAc (EQE: ~6.5%, **Figure 8d** and **S25**) and very much better than those for *m*-DPSAc-LC, which shows simple fluorescence (maximum EQE = 2.9%, CE = 5.8 cd A-1 and L = 180 cd m-2) and are subject to a theoretical maximum EQE value of 5%.

**Conclusions**

In summary, two novel luminescent liquid crystal molecules showing a SmA phase and based on an emissive TADF core and peripheral mesogenic moieties were synthesized and characterized. While bothmaterials showed clear liquid-crystalline properties, only *p*-DPSAc-LC showed TADF behavior owing to the large distortion between donor and acceptor units. Compared to the prototype TADF emitters, both luminescent liquid crystal emitters displayed much better emission efficiency and it was demonstrated that hole mobilities were superior in neat films of the liquid-crystalline materials compared to their non-liquid-crystalline 'parents'. Excellent performance was observed in devices prepared using *p*-DPSAc-LC or *m*-DPSAc-LC in the emissive layer, with the former (TADF) material showing more efficient emission. Thus, the solution-processed OLED achieved a maximum EQE of ca. 15% when *p*-DPSAc-LC was used in the emitter, which is the first example of a liquid-crystalline TADF material in an OLED device.

**Acknowledgements**

Financial support was provided by the National Natural Science Foundation of China (Nos. 51773021, 51911530197), the Six Talent Peaks project in Jiangsu Province (XCL-102). DWB and YW thank the Royal Society and the NSFC for an International Joint Project Grant and AJM thanks the University of York for financial support. The NMR testing was provided by Analysis and Testing Center, NERC Biomass of Changzhou University.

**Supporting Information**

The detailed experimental method, synthesis, NMR data, additional photophysical data and single crystal data supplied as Supporting Information.

**References**

1. Cai, X.; Su, S.-J., Marching Toward Highly Efficient, Pure-Blue, and Stable Thermally Activated Delayed Fluorescent Organic Light-Emitting Diodes. *Adv. Funct. Mater.* **2018,** *28*, 1802558.
2. Hong, G.; Gan, X.; Leonhardt, C.; Zhang, Z.; Seibert, J.; Busch, J. M.; Brase, S., A Brief History of OLEDs-Emitter Development and Industry Milestones. *Adv. Mater.* **2021,** *33*, e2005630.
3. Khan, A.; Tang, X.; Zhong, C.; Wang, Q.; Yang, S. Y.; Kong, F. C.; Yuan, S.; Sandanayaka, A. S. D.; Adachi, C.; Jiang, Z. Q.; Liao, L. S., Intramolecular-Locked High Efficiency Ultrapure Violet-Blue (CIE‐y <0.046) Thermally Activated Delayed Fluorescence Emitters Exhibiting Amplified Spontaneous Emission. *Adv. Funct. Mater.* **2021,** *31*, 2009488.
4. Godumala, M.; Choi, S.; Cho, M. J.; Choi, D. H., Recent Breakthroughs in Thermally Activated Delayed Fluorescence Organic Light Emitting Diodes Containing Non-Doped Emitting Layers. *J. Mater. Chem. C* **2019,** *7*, 2172-2198.
5. Jiang, T.; Liu, Y.; Ren, Z.; Yan, S., The Design, Synthesis and Performance of Thermally Activated Delayed Fluorescence Macromolecules. *Polym. Chem.* **2020,** *11*, 1555-1571.
6. Wong, M. Y.; Zysman-Colman, E., Purely Organic Thermally Activated Delayed Fluorescence Materials for Organic Light-Emitting Diodes. *Adv. Mater.* **2017,** *29*, 1605444.
7. Yu, H.; Song, X.; Xie, N.; Wang, J.; Li, C.; Wang, Y., Reversible Crystal‐to‐Crystal Phase Transitions with High‐Contrast Luminescent Alterations for a Thermally Activated Delayed Fluorescence Emitter. *Adv. Funct. Mater.* **2020,** *31*, 2007511.
8. Li, B.; Yang, Z.; Gong, W.; Chen, X.; Bruce, D. W.; Wang, S.; Ma, H.; Liu, Y.; Zhu, W.; Chi, Z.; Wang, Y., Intramolecular Through‐Space Charge Transfer Based TADF‐Active Multifunctional Emitters for High Efficiency Solution‐Processed OLED. *Adv. Opt. Mater.* **2021,** *9*, 2100180.
9. Kim, J. U.; Park, I. S.; Chan, C. Y.; Tanaka, M.; Tsuchiya, Y.; Nakanotani, H.; Adachi, C., Nanosecond-Time-Scale Delayed Fluorescence Molecule for Deep-blue OLEDs with Small Efficiency Rolloff. *Nat. Commun.* **2020,** *11*, 1765.
10. Chan, C. Y.; Cui, L. S.; Kim, J. U.; Nakanotani, H.; Adachi, C., Rational Molecular Design for Deep‐Blue Thermally Activated Delayed Fluorescence Emitters. *Adv. Funct. Mater.* **2018,** *28*, 1706023.
11. Konidena, R. K.; Lim, J.; Lee, J. Y., A Novel Molecular Design Featuring the Conversion of Inefficient TADF Emitters into Efficient TADF Emitters for Deep-blue Organic Light Emitting Diodes. *Chem. Eng. J.* **2021,** *416*, 129097.
12. Li, Y.; Wang, K.; Liao, Q.; Fu, L.; Gu, C.; Yu, Z.; Fu, H., Tunable Triplet-Mediated Multicolor Lasing from Nondoped Organic TADF Microcrystals. *Nano Lett.* **2021,** *21*, 3287-3294.
13. Sun, S.; Wang, J.; Chen, L.; Chen, R.; Jin, J.; Chen, C.; Chen, S.; Xie, G.; Zheng, C.; Huang, W., Thermally Activated Delayed Fluorescence Enantiomers for Solution-processed Circularly Polarized Electroluminescence. *J. Mater. Chem. C* **2019,** *7*, 14511-14516.
14. Xie, F.-M.; Zhou, J.-X.; Li, Y.-Q.; Tang, J.-X., Effects of the Relative Position and Number of Donors and Acceptors on the Properties of TADF Materials. *J. Mater. Chem. C* **2020,** *8*, 9476-9494.
15. Liu, H.; Liu, Z.; Li, G.; Huang, H.; Zhou, C.; Wang, Z.; Yang, C., Versatile Direct Cyclization Constructs Spiro-acridan Derivatives for Highly Efficient TADF emitters. *Angew. Chem., Int. Ed.* **2021,** *60*, 12376-12380.
16. Im, Y.; Kim, M.; Cho, Y. J.; Seo, J.-A.; Yook, K. S.; Lee, J. Y., Molecular Design Strategy of Organic Thermally Activated Delayed Fluorescence Emitters. *Chem. Mater.* **2017,** *29*, 1946-1963.
17. Gužauskas, M.; Narbutaitis, E.; Volyniuk, D.; Baryshnikov, G. V.; Minaev, B. F.; Ågren, H.; Chao, Y.-C.; Chang, C.-C.; Rutkis, M.; Grazulevicius, J. V., Polymorph Acceptor-Based Triads with Photoinduced TADF for UV Sensing. *Chem. Eng. J.* **2021,** *425*, 131549.
18. Kim, J. H.; Yun, J. H.; Lee, J. Y., Recent Progress of Highly Efficient Red and Near-Infrared Thermally Activated Delayed Fluorescent Emitters. *Adv. Opt. Mater.* **2018,** *6*, 1800255.
19. Rajamalli, P.; Senthilkumar, N.; Huang, P. Y.; Ren-Wu, C. C.; Lin, H. W.; Cheng, C. H., New Molecular Design Concurrently Providing Superior Pure Blue, Thermally Activated Delayed Fluorescence and Optical Out-Coupling Efficiencies. *J. Am. Chem. Soc.* **2017,** *139*, 10948-10951.
20. Xia, G.; Qu, C.; Zhu, Y.; Ye, J.; Ye, K.; Zhang, Z.; Wang, Y., A TADF Emitter Featuring Linearly Arranged Spiro-Donor and Spiro-Acceptor Groups: Efficient Nondoped and Doped Deep-Blue OLEDs with CIEy <0.1. *Angew. Chem., Int. Ed.* **2021,** *60*, 9598-9603.
21. Jiang, P.; Miao, J.; Cao, X.; Xia, H.; Pan, K.; Hua, T.; Lv, X.; Huang, Z.; Zou, Y.; Yang, C., Quenching-Resistant Multiresonance TADF Emitter Realizes 40% External Quantum Efficiency in Narrowband Electroluminescence at High Doping Level. *Adv. Mater.* **2021**, e2106954.
22. Jin, J.; Jiang, H.; Yang, Q.; Tang, L.; Tao, Y.; Li, Y.; Chen, R.; Zheng, C.; Fan, Q.; Zhang, K. Y.; Zhao, Q.; Huang, W., Thermally Activated Triplet Exciton Release for Highly Efficient Tri-Mode Organic Afterglow. *Nat. Commun.* **2020,** *11*, 842.
23. Yang, T.; Cheng, Z.; Li, Z.; Liang, J.; Xu, Y.; Li, C.; Wang, Y., Improving the Efficiency of Red Thermally Activated Delayed Fluorescence Organic Light-Emitting Diode by Rational Isomer Engineering. *Adv. Funct. Mater.* **2020,** *30,* 2002681.
24. Chen, Y.; Zhang, D.; Zhang, Y.; Zeng, X.; Huang, T.; Liu, Z.; Li, G.; Duan, L., Approaching Nearly 40% External Quantum Efficiency in Organic Light Emitting Diodes Utilizing a Green Thermally Activated Delayed Fluorescence Emitter with an Extended Linear Donor-Acceptor-Donor Structure. *Adv. Mater.* **2021,** *33*, e2103293.
25. Li, W.; Li, M.; Li, W.; Xu, Z.; Gan, L.; Liu, K.; Zheng, N.; Ning, C.; Chen, D.; Wu, Y. C.; Su, S. J., Spiral Donor Design Strategy for Blue Thermally Activated Delayed Fluorescence Emitters. *ACS Appl. Mater. Interfaces* **2021,** *13*, 5302-5311.
26. Liu, H.; Liu, Z.; Li, G.; Huang, H.; Zhou, C.; Wang, Z.; Yang, C., Versatile Direct Cyclization Constructs Spiro-acridan Derivatives for Highly Efficient TADF emitters. *Angew. Chem., Int. Ed.* **2021,** *60*, 12376-12380.
27. Suleymanova, A. F.; Shafikov, M. Z.; Whitwood, A. C.; Czerwieniec, R.; Bruce, D. W., Liquid-crystalline TADF Materials Based on Substituted Carbazoles and Terephthalonitrile. *J. Mater. Chem. C* **2021,** *9*, 6528-6535.
28. Iino, H.; Usui, T.; Hanna, J., Liquid Crystals for Organic Thin-film Transistors. *Nat. Commun.* **2015,** *6*, 6828.
29. Kang, D. G.; Park, M.; Kim, D. Y.; Goh, M.; Kim, N.; Jeong, K. U., Heat Transfer Organic Materials: Robust Polymer Films with the Outstanding Thermal Conductivity Fabricated by the Photopolymerization of Uniaxially Oriented Reactive Discogens. *ACS Appl. Mater. Interfaces* **2016,** *8*, 30492-30501.
30. Yi, C. L.; Ko, C. L.; Yeh, T. C.; Chen, C. Y.; Chen, Y. S.; Chen, D. G.; Chou, P. T.; Hung, W. Y.; Wong, K. T., Harnessing a New Co-Host System and Low Concentration of New TADF Emitters Equipped with Trifluoromethyl- and Cyano-Substituted Benzene as Core for High-Efficiency Blue OLEDs. *ACS Appl. Mater. Interfaces* **2020,** *12*, 2724-2732.
31. Kato, T.; Uchida, J.; Ichikawa, T.; Sakamoto, T., Functional Liquid Crystals towards the Next Generation of Materials. *Angew. Chem., Int. Ed.* **2018,** *57*, 4355-4371.
32. Liu, Y.; You, L. H.; Lin, F. X.; Fu, K.; Yuan, W. Z.; Chen, E. Q.; Yu, Z. Q.; Tang, B. Z., Highly Efficient Luminescent Liquid Crystal with Aggregation-Induced Energy Transfer. *ACS Appl. Mater. Interfaces* **2019,** *11*, 3516-3523.
33. Nishikawa, H.; Shiroshita, K.; Higuchi, H.; Okumura, Y.; Haseba, Y.; Yamamoto, S. I.; Sago, K.; Kikuchi, H., A Fluid Liquid-Crystal Material with Highly Polar Order. *Adv. Mater.* **2017,** *29*, 1702354.
34. Wang, Y.; Cabry, C. P.; Xiao, M.; Male, L.; Cowling, S. J.; Bruce, D. W.; Shi, J.; Zhu, W.; Baranoff, E., Blue and Green Phosphorescent Liquid-Crystalline Iridium Complexes with High Hole Mobility. *Chem. - Eur. J.* **2016,** *22*, 1618-1621.
35. Tan, S.; Wu, X.; Zheng, Y.; Wang, Y., Synthesis and Properties of Novel N,C,N terdentate Skeleton Based on 1,3-Di(pyridin-2-yl)benzene Moiety—New Tricks for Old Dogs. *Chin. Chem. Lett.* **2019,** *30*, 1951-1954.
36. Zhan, L.; Chen, Z.; Gong, S.; Xiang, Y.; Ni, F.; Zeng, X.; Xie, G.; Yang, C., A Simple Organic Molecule Realizing Simultaneous TADF, RTP, AIE, and Mechanoluminescence: Understanding the Mechanism Behind the Multifunctional Emitter. *Angew. Chem., Int. Ed.* **2019,** *58*, 17651-17655.
37. Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C., Efficient Blue Organic Light-Emitting Diodes Employing Thermally Activated Delayed Fluorescence. *Nat. Photonics* **2014,** *8*, 326-332.
38. Huang, T.; Jiang, W.; Duan, L., Recent Progress in Solution Processable TADF Materials for Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2018,** *6*, 5577-5596.
39. Wang, Y.; Cabry, C. P.; Xiao, M.; Male, L.; Cowling, S. J.; Bruce, D. W.; Shi, J.; Zhu, W.; Baranoff, E., Blue and Green Phosphorescent Liquid-Crystalline Iridium Complexes with High Hole Mobility. *Chem. - Eur. J.* **2016,** *22*, 1618-1621.
40. Li, B.; Yang, Z.; Gong, W.; Chen, X.; Bruce, D. W.; Wang, S.; Ma, H.; Liu, Y.; Zhu, W.; Chi, Z.; Wang, Y., Intramolecular Through‐Space Charge Transfer Based TADF‐Active Multifunctional Emitters for High Efficiency Solution‐Processed OLED. *Adv. Opt. Mater.* **2021,** *9*, 2100180.
41. Zhou, D.; Ryoo, C.; Liu, D.; Wang, S.; Qian, G.; Zheng, Y.; Park, S. Y.; Zhu, W.; Wang, Y., Cruciform Molecules Bearing Bis(phenylsulfonyl)benzene Moieties for High-Efficiency Solution Processable OLEDs: When Thermally Activated Delayed Fluorescence Meets Mechanochromic Luminescence. *Adv. Opt. Mater.* **2020,** *8*, 1901021.
42. Gupta, A. K.; Li, W.; Ruseckas, A.; Lian, C.; Carpenter-Warren, C. L.; Cordes, D. B.; Slawin, A. M. Z.; Jacquemin, D.; Samuel, I. D. W.; Zysman-Colman, E., Thermally Activated Delayed Fluorescence Emitters with Intramolecular Proton Transfer for High Luminance Solution-Processed Organic Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2021,** *13*, 15459-15474.
43. Suresh, S. M.; Duda, E.; Hall, D.; Yao, Z.; Bagnich, S.; Slawin, A. M. Z.; Bassler, H.; Beljonne, D.; Buck, M.; Olivier, Y.; Kohler, A.; Zysman-Colman, E., A Deep Blue B,N-Doped Heptacene Emitter That Shows Both Thermally Activated Delayed Fluorescence and Delayed Fluorescence by Triplet-Triplet Annihilation. *J. Am. Chem. Soc.* **2020,** *142*, 6588-6599.
44. Dias, F. B.; Penfold, T. J.; Monkman, A. P., Photophysics of thermally activated delayed fluorescence molecules. *Methods Appl. Fluoresc.* **2017,** *5*, 012001.

**Table of Contents**

****