Efficient red fluorescent OLEDs based on aggregation-induced emission combined with hybridized local and charge transfer state

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## Graphic Abstract:



1	Efficient red fluorescent OLEDs based on aggregation-induced emission
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14	Abstract:
15	Limited by the energy gap law and large conjugate structures, red organic
16	light-emitting diodes (OLEDs) have long been criticized for their efficiency problems.
17	The aggregation-induced emission (AIE) effect and the reverse intersystem crossing
18	process can lead to high photoluminescent quantum yields (PLQYs) and high exciton
19	utilization efficiency (EUE), two key objectives for obtaining efficient OLEDs. In this
20	work, we chose benzothiadiazole as the acceptor (A) and triphenylamine and
21	phenothiazine as the donors (Ds) to design and synthesize a D-A-D red fluorescent
22	molecule, PBTPA. Results of systematic photophysical measurements indicated
23	PBTPA to exhibit AIE trending, manifesting as aggregation-induced enhanced
24	emission and the characteristics of hybridized local and charge transfer (HLCT) states.

25	These features facilitated high solid-state luminescence efficiency and high exciton
26	utilization to be achieved. A non-doped device fabricated using PBTPA displayed a
27	red electroluminescence peak at 656 nm, corresponding to the Commission
28	International de L'Eclairage coordinates of (0.65, 0.32), and an external quantum
29	efficiency of 1.62%. By calculation, the EUE reached a value of 50%. According to
30	the results of theoretical calculations, the effective hot exciton channel between the
31	second triplet $(T_2)$ and the lowest singlet $(S_1)$ was responsible for the high EUE. This
32	EUE value is relatively good for this type of red OLEDs. Evidence indicates that
33	combining AIE and HLCT has excellent potential to aid the discovery of
34	new-generation highly efficient red OLEDs.

Keywords: D-A-D type red fluorescent molecule; aggregation-induced emission;
hybridized local and charge-transfer state; red fluorescent organic light-emitting
diodes; exciton utilization

38

### 39 **1. Introduction:**

Since Tang developed the first organic light-emitting diode (OLED) in 1987, these devices have been at the center of a great deal of research enthusiasm.<sup>1</sup> Due to the high contrast they afford, as well as their active luminescence and fast response, OLEDs are currently widely used in commercial applications.<sup>2-5</sup> Notably, photoluminescent quantum yield (PLQY) and exciton utilization efficiency (EUE) are two key parameters defining the performance of OLED devices.<sup>6, 7</sup>

46 Devices that emit light in the wavelength perceived as the color red, one of the three

47 primary colors, are still beset by many problems. In order to design red light-emitting molecules, large conjugate structures are usually necessary; these types of molecules, 48 however, tend to planarize, which causes the light they emit to shift toward longer 49 wavelengths. Furthermore, planarization tends to promote strong intermolecular 50 51 interactions, including  $\pi - \pi$  stacking interactions, which eventually favor aggregation-caused quenching (ACQ) and lead to a decrease in PLQY value.<sup>8-10</sup> Red 52 light-emitting OLEDs are thus generally less efficient than their blue and green 53 light-emitting counterparts. In order to address this issue, and on the basis of the 54 aggregation-induced emission (AIE) mechanism proposed by Tang et al. in 2001,<sup>11</sup> 55 the propeller-shaped molecular design was introduced to restrain intermolecular 56 motions in the aggregated state and further limit the non-radiative transitions among 57 molecules.<sup>12-14</sup> Over time, therefore, AIEgens like tetraphenylethenes (TPEs) have 58 expanded the AIE molecular library; importantly, such molecular species have been 59 utilized in many research fields, including those focusing on highly sensitive sensors, 60 intelligent response systems, and precision medicine.<sup>15-20</sup> A molecule named 61 2TPA-BT-N-2P with a distinct AIE effect synthesized by Liao et al. in 2020 was 62 observed to display a PLQY value of 91%.<sup>12</sup> Using the AIE concept in the design of 63 red light-emitting molecules can effectively suppress quenching during the 64 luminescence process, which helps increase the molecules' PLQY. 65

According to the energy gap law, the inherent narrow bandgap of red light emitters could bring about a substantial vibrational–rotational coupling between the ground and excited states, resulting in a reduction of the radiative transition rates and low

luminescence efficiency.<sup>21-23</sup> In order to overcome this problem, more singlet excitons need to be involved in the fluorescence emission; in other words, the exciton utilization (EUE) must be improved. According to the traditional spin–statistics rule, only 25% of the singlet excitons can participate in fluorescence emission.<sup>24, 25</sup> This limitation can however be overcome transforming large numbers of triplet excitons into singlet excitons, *via*, for instance, the triplet–triplet annihilation (TTA) mechanism,<sup>26</sup> the thermally activated delayed fluorescent (TADF) mechanism,<sup>27-29</sup>

and the hot exciton mechanism. 30, 31

In detail, in the TTA mechanism, the lowest singlet  $(S_1)$  and a ground state  $(S_0)$ 77 exciton are generated by the two lowest triplet  $(T_1)$  excitons. Notably, the maximum 78 internal quantum efficiency of TTA is 62.5%.<sup>32</sup> The TADF mechanism exploits the 79 small energy difference between  $T_1$  and  $S_1$  and the highly separated highest occupied 80 molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO); in 81 TADF, reverse intersystem crossing (RISC) is enabled, thereby ultimately maximizing 82 the use of triplet excitons.<sup>33</sup> Nevertheless, the accumulation of long-life T<sub>1</sub> excitons at 83 high current density or high brightness results in severe roll-off, an issue that has 84 always plagued TADF materials. The hot exciton mechanism is based on the RISC 85 process associated with the small energy gap between the high-lying triplet state and 86 its energetically similar singlet state; notably, hot exciton materials tend to be 87 characterized by a large energy gap between  $T_1$  and  $T_2$ , which prevents the triplet 88 excitons from being lost to internal conversion (IC).<sup>34</sup> Importantly, many hot exciton 89 compounds are also characterized by the coexistence of local luminescence (LE) state 90

with high luminescence efficiency and charge transfer (CT) state with weak exciton binding energy; these species are called hybridized local and charge transfer (HLCT) materials.<sup>35-37</sup> These types of materials can achieve high efficiency and low roll-off under non-doping conditions, while affording relatively good color purity, so they represent a suitable choice in the design of efficient red light emitters. In this context, the hot exciton material TPANZP, reported by the Ma group, displayed an EUE value

97 of 93%, in conjunction with an emission peak at  $664 \text{ nm.}^{35}$ 

In the present study, by rationally selecting donor (D) and acceptor (A), we designed 98 99 and synthesized a D-A-D type molecule dubbed 4-(7-(10-ethyl-10H-phenothiazin-3-yl)benzo[c][1,2,5]thiadiazol-4-yl)-N,N-diphenyla 100 PBTPA (see Scheme 1). Benzothiadiazole has a good 101 niline. namely. electron-accepting capacity, and it is well-planarized; benzothiadiazole's  $\Delta E_{T1-T2}$  (the 102 energy gap between  $T_1$  and  $T_2$ ) has a value of 0.97 eV, which is advantageous from 103 the standpoint of the construction of molecular species emitting long-wavelength light. 104 Triphenylamine and phenothiazine are strong electron donors. We have attached an 105 ethyl group to the N atom of phenothiazine in the hope of increasing steric hindrance, 106 and thus suppressing ACQ to a certain extent. We then performed systematic tests and 107 108 theoretical calculations on PBTPA. This molecule exhibited typical AIE and HLCT characteristics. Furthermore, we fabricated a non-doped OLED device that relied on 109 PBTPA as the light-emitting layer. This device emitted red light at 656 nm with 110 Commission International de L'Eclairage (CIE) coordinates of (0.65, 0.32) and 111 external quantum efficiency (EQE) of 1.62%, with a EUE of 50%. These data indicate 112

113	that the device displays a relatively good performance as a red emitter. Notably, the								
114	subsequent doping of this structure improved the device's efficiency. We conclude								
115	that combining AIE with HLCT is an effective design approach to manufacturing								
116	efficient red light-emitting OLEDs.								
117	2. Experimental section								
118	2.1 Materials								
119	All raw materials were commercially purchased from Aldrich Chemical Co. or								
120	Energy Chemical Co., China								
121	dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN),								
122	4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine (TAPC),								
123	1,3-bis(N-carbazolyl)benzene (mCP), 9,10-bis(2-naphthyl)anthraces (AND),								
124	1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB), and lithium fluoride (LiF).								
125	Tetrahydrofuran (THF) was distilled over metallic sodium and dimethylformamide								
126	(DMF) over calcium hydride before use. The other organic solvents and reagents were								
127	all commercially available analytical-grade products and used as received without								
128	further purification.								

129 2.2 Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AC500 spectrometer at 500 MHz and 125 MHz, respectively, when the compounds were dissolved in deuterated chloroform-*d* (CDCl<sub>3</sub>) with tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were measured using an AXIMA-CFRTM plus instrument. Differential scanning calorimetry (DSC) curves were determined on a

135	Netzsch DSC (204F1) instrument at a heating rate of $10 \square \min^{-1}$ . Thermogravimetric
136	analysis (TGA) was performed on a Netzsch (209F1) thermogravimetric analyzer in a
137	nitrogen atmosphere (50 mL min <sup>-1</sup> ) at a heating rate of 10 $\square$ min <sup>-1</sup> . UV-vis absorption
138	and fluorescence spectra of solution and films were measured by the Hitachi U-4100
139	spectrophotometer and Hitachi F-4600 spectrophotometer, respectively. In preparation
140	for the AIE test, the final product was first dissolved in THF $(10^{-4} \text{ M})$ and then mixed
141	with water to form solutions $(10^{-5} \text{ M})$ of different volume ratios. Photoluminescence
142	quantum yield was carried out with FLS-980 spectrometer. The lifetimes of nondoped
143	films were measured on an Edinburgh FLS-980 with an EPL-375 optical laser. Cyclic
144	voltammetry (CV) was performed with a BAS 100W Bioanalytical System, using a
145	glass carbon disk (diameter = 3 mm) as the working electrode, a platinum wire with a
146	porous ceramic wick as the auxiliary electrode, and Ag/Ag <sup>+</sup> as the reference electrode
147	standardized by the redox couple ferrocenium/ferrocene. All solutions were purged
148	with a nitrogen stream for 10 min before measurement. The procedure was performed
149	at room temperature, and a nitrogen atmosphere was maintained over the solution
150	during measurements.

151 *2.3 Theoretical calculation.* 

The ground-state geometry was optimized at the level of B3LYP/6-31G(d, p), spatial distributions of the HOMOs and LUMOs of the compound was obtained from the optimized ground state structure. On the basis of the optimized configuration of the ground state ( $S_0$ ), the high excitation energy levels of singlet and triplet states were evaluated using TD-M06-2X/6-31G(d, p). In order to gain further insight into the

- 157 character of excited states, natural transition orbitals (NTOs) were evaluated for  $S_1$ - $S_5$ 158 and  $T_1$ - $T_5$  states.
- 159 2.4 Device fabrication.

A nondoped device was fabricated with the structure of indium-tin oxide (ITO)/ 160 dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) (5 nm)/ 161 162 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine (TAPC) (50 nm)/ PBTPA (20 nm)/ 1,3,5-Tris(3-pyridyl-3-phenyl)benzene (TmPyPB) (50 nm) / LiF (1 163 nm)/ Al (100 nm). In this structure, ITO and LiF/Al were used as the anode and 164 cathode, respectively. HATCN and TAPC served as the hole injection layer and the 165 hole transport layer, respectively. TmPyPB served as both an electron transport layer 166 and a hole blocking layer. The doped structure was indium-tin oxide (ITO)/ 167 dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) (5 nm)/ 168 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine (TAPC) (50 nm)/ 169 1,3-bis(N-carbazolyl)benzene (10nm)/ 9,10-bis(2-naphthyl)anthraces 170 mCP (AND):PBTPA 2% (20 nm)/ 1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB) (45 171 nm)/ LiF (1 nm)/Al (100 nm). In this structure, mCP served as the electron-blocking 172 layer and ADN as the host material for doping. 173

174 ITO-coated glass with a sheet resistance of  $15-20 \ \Omega \ cm^{-2}$  was used as the substrate. 175 Before device fabrication, the ITO glass substrates were cleaned with isopropyl 176 alcohol and deionized water, dried in an oven at 120 °C. After oxygen plasma 177 cleaning for 3 min and finally transferred to a vacuum deposition system with a base 178 pressure greater than  $5 \times 10^{-6}$  mbar for organic and metal deposition. The thickness of

each deposition layer was monitored using a quartz crystal thickness/ratio monitor (STM-100/MF, Sycon). The current-voltage-luminance characteristics were measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured by a Spectrascan

183 PR650 spectrophotometer. EQEs were calculated from the luminance, current density,

184 and EL spectrum according to the literature.

185 2.5 Synthesis

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The synthesis routes and molecular structures of PBTPA is depicted in **Scheme 1**. Intermediates  $M_1$ ,  $M_2$  and final product PBTPA were synthesized by Suzuki-Miyaura Cross-Coupling.<sup>38</sup> The nuclear magnetic resonance data of the intermediate products  $M_1$  and  $M_2$  (**Figure S1**) are included in the supporting information. The nuclear magnetic resonance spectrometry (**Figure S2**), mass spectrometry (**Figure S3**) and elemental analysis confirmed that we finally got the target product.

192 Synthesis of 10-ethyl-10H-phenothiazine (1)

A mixture of 10 H-phenothiazine (4.00 g, 17.6 mmol), sodium hydroxide (6.00 g, 150 193 mmol), bromoethane (2.50 g, 22.7 mmol), dimethyl sulfoxide (70 mL) was stirred at 194 room temperature for 24 hours under nitrogen atmosphere. The reaction mixture was 195 poured into water and extracted with dichloromethane for several times. The organic 196 phase was collected and dried over anhydrous MgSO<sub>4</sub>. After filtration and solvent 197 evaporation, the residue was purified via silica gel column chromatography using 198 petroleum ether/dichloromethane (10/1; v/v) as an eluent to give the product as a 199 white solid (4.80 g, 84.4%).<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.16 – 7.08 (m, 4H), 200

- 201 6.89 (td, *J* = 7.5, 1.2 Hz, 2H), 6.85 (dd, *J* = 8.1, 1.1 Hz, 2H), 3.91 (q, *J* = 7.0 Hz, 2H),
- 202 1.40 (t, J = 6.9 Hz, 3H).
- 203 Synthesis of 3-bromo-10-ethyl-10H-phenothiazine (2)

A solution of NBS (3.13 g, 17.6 mmol) in anhydrous DMF (40 mL) was added to a 204 solution of 1 (4.00 g, 17.6 mmol) in anhydrous DMF (70 mL) by dropwise at 205 0  $\Box$ . Then the mixture reacted at room temperature for 8 hours under nitrogen 206 atmosphere. The reaction mixture was poured into water and extracted with 207 dichloromethane for several times. The organic phase was collected and dried over 208 anhydrous MgSO<sub>4</sub>. After filtration and solvent evaporation, the residue was purified 209 210 via silica gel column chromatography using petroleum ether/ethyl acetate (15/1; v/v)as an eluent to give the product as a white solid. Then the white solid was 211 recrystallized from a mixture of ethyl acetate/methanol (1:3; v/v) and we got the 212 target product (3.80 g, 70.6%). <sup>1</sup>H NMR (500 MHz, Chloroform-d): 1.44 (t, J <sup>1</sup>/<sub>4</sub> 6.9 213 Hz, 3H,); 3.91 (q, 2H), 6.71 – 7.30 (m, 7H). 214

215 Synthesis

of

216 10-ethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine ( $M_1$ )

A solution of **2** (3.00 g, 9.8 mmol), bis(pinacolato)-diboron (2.98 g, 11.73 mmol), Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (0.14 g, 0.19 mmol) and KOAc (2.88 g, 29.35 mmol) in degassed dioxane (50 mL) was stirred at 90  $\Box$  for 8 h under nitrogen atmosphere. The reaction was quenched by adding deionized water, and the resulting mixture was extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulfate and concentrated in vacuum. The crude product was purified via silica gel

223	chromatography using petroleum ether/dichloromethane (3:2; v/v) as the eluent to								
224	give the desired compound as white solid powder (1.90 g, 55%). $^{1}$ H NMR (500 MHz,								
225	Chloroform- <i>d</i> ) $\delta$ 7.64 – 7.55 (m, 2H), 7.17 – 7.06 (m, 2H), 6.89 (t, <i>J</i> = 7.5 Hz, 1H),								
226	6.84 (d, <i>J</i> = 8.1 Hz, 2H), 3.91 (q, <i>J</i> = 7.0 Hz, 2H), 1.40 (t, <i>J</i> = 6.9 Hz, 3H).								
227	Synthesis of 4-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)-N,N-diphenylaniline ( $M_2$ )								
228	A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (3.05 g, 10.38 mmol),								
229	(4-(diphenylamino)phenyl)boronic acid (3.00 g, 10.38 mmol), potassium carbonate								
230	(0.72 g, 5.21 mmol), THF (80 mL) and deionized water (20 mL), with $Pd(PPh_3)_4$								
231	(0.12 g, 0.10 mmol) acting as catalyst was refluxed at 70 °C for 24 h under nitrogen								
232	atmosphere. After the mixture was cooled down, water (35 mL) was added to the								
233	resulting solution and the mixture was extracted with dichloromethane for three times.								
234	The organic phase was dried over anhydrous magnesium sulfate and concentrated in								
235	vacuum. After filtration and solvent evaporation, the liquid was purified by silica gel								
236	chromatography using petroleum ether/dichloromethane (3:1; v/v) to afford orange								
237	solid ( $M_2$ ) (2.00 g, 42%), Compound $M_2$ was recrystallized from a mixture of								
238	trichloromethane and methanol (3:1; v/v). <sup>1</sup> H NMR (500 MHz, Chloroform-d) $\delta$ 7.90								
239	(d, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.55 (d, $J = 7.7$ Hz, 1H), 7.28 (d, $J =$								
240	18.2 Hz, 6H), 7.18 (dd, <i>J</i> = 8.3, 3.3 Hz, 6H), 7.08 (t, <i>J</i> = 7.4 Hz, 2H).								
241	<i>Synthesis</i> of								
242	4-(7-(10-ethyl-10H-phenothiazin-3-yl)benzo[c][1,2,5]thiadiazol-4-yl)-N,N-diphenyla								
243	niline ( <b>PBTPA</b> )								

244 A mixture of  $M_1$  (1.44 g, 3.91 mmol),  $M_2$  (1.80 g, 3.91 mmol), potassium carbonate

245	(0.27 g, 1.95 mmol), THF (80 mL) and deionized water (20 mL), with $Pd(PPh_3)_4$
246	(0.05 g, 0.04 mmol) acting as catalyst was refluxed at 70 $^{\circ}$ C for 24 h under nitrogen
247	atmosphere. After the mixture was cooled down, water (35 mL) was added to the
248	resulting solution and the mixture was extracted with dichloromethane for several
249	times. The organic phase was dried over anhydrous magnesium sulfate and
250	concentrated in vacuum. After filtration and solvent evaporation, the liquid was
251	purified via silica gel chromatography using petroleum ether/dichloromethane (2:1;
252	v/v) to afford jacinth solid (PBTPA) (1.20 g, 51%), pure compound PBTPA was
253	recrystallized from a mixture of trichloromethane and methanol (2:1; v/v). <sup>1</sup> H NMR
254	(500 MHz, Chloroform- <i>d</i> ) $\delta$ 7.89 – 7.85 (m, 2H), 7.83 (dd, <i>J</i> = 8.5, 2.1 Hz, 1H), 7.75
255	(d, $J = 2.1$ Hz, 1H), 7.74 – 7.69 (m, 2H), 7.30 (dd, $J = 8.6$ , 7.3 Hz, 4H), 7.23 – 7.11
256	(m, 8H), 7.07 (dd, J = 7.9, 6.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 1H), 6.95 – 6.87 (m, 2H),
257	4.01 (q, $J = 7.0$ Hz, 2H), 1.48 (t, $J = 6.9$ Hz, 3H). <sup>13</sup> C NMR (126 MHz, Chloroform- $d$ )
258	$\delta$ 154.03 , 147.43 , 144.88 , 131.54 , 130.91 , 129.84 , 129.29 , 128.18 , 127.62 ,
259	127.37 , 127.27 , 127.10 , 124.84 , 123.89 , 123.24 , 122.85 , 122.45 , 115.01 , 114.83 ,
260	53.34 , 41.91 , 12.99. MALDI-TOF MS (mass m/z): 604.1 [M <sup>+</sup> ]. Anal. calcd. for
261	C <sub>38</sub> H <sub>28</sub> N <sub>4</sub> S <sub>2</sub> : C, 75.47; H, 4.67; N, 9.26; S, 10.60. Found: C, 75.39; H, 4.682; N, 9.27;
262	S, 10.564.

263 **3. Results and discussion** 

264 *3.1 Synthesis and Characterization* 

The synthetic route and molecular structure of PBTPA are depicted in Scheme 1.
Detailed synthetic steps and NMR data of the intermediate products are included in

the supporting information. Intermediates M1 and M2 and the final product PBTPA 267 were synthesized by Suzuki-Miyaura cross-coupling.<sup>38</sup> NMR (Figure S2) and mass 268 269 spectrometry (Figure S3) data confirmed that we had obtained the target product. 3.2 Thermal properties and electrochemical properties 270 271 As part of the development of the fabrication process of OLEDs, ensuring that the light emitter is thermally stable, from a structural and activity standpoint, is essential. 272 We measured PBTPA's thermal stability by thermogravimetric analysis and 273 differential scanning calorimetry (DSC) conducted in a nitrogen atmosphere. As can 274 be evinced from the data reported in Figure 1a and listed in Table 1, the 275 decomposition temperature (T<sub>d</sub>, corresponding to 5% weight loss) for PBTPA was 276 410 °C. A high T<sub>d</sub> value implies that a molecule has excellent thermal stability, and it 277 is suitable to be employed in the vacuum deposition technique. According to the DSC 278 curves, the glass-transition temperature (Tg) of PBTPA was 119 °C. A Tg value this 279 high guarantees the emitter's morphological stability under heating, which allows the 280 molecule to display a consistent activity. 281

In order to test the electrochemical properties of PBTPA, cyclic voltammetry measurements were conducted. As can be evinced from the data reported in **Figure 1b** and **Table 1**, PBTPA's reduction potential was found to be -1.61 V and its oxidation potential -0.38 V. The fact that the oxidation and reduction curves were reversible indicated that the molecule could gain and lose electrons stably, which can use relieved in OLED devices as a luminous layer. The values for the energy levels of the HOMO and LUMO of PBTPA were calculated to be -4.98 eV and -3.10 eV, respectively, which means that the value of the HOMO-LUMO gap was 1.88 eV,

- 290 consistent with red light emission.
- 291 3.3 Photophysical Properties

In Figure 2a are reported the UV-vis absorption and photoluminescence (PL) spectra 292 of PBTPA in toluene ([PBTPA] =  $1 \times 10^{-5}$  M). Two absorption peaks were observed at 293 310 nm and 461 nm. The sharp, strong absorption peak at 310 nm is mainly due to the 294  $\pi$ - $\pi$ \* transition of the phenothiazine and triphenylamine fragments in the molecular 295 skeleton. The absorption band of PBTPA in the 370-550 nm wavelength range is the 296 result of an intramolecular charge transfer (ICT). Notably, measuring the UV-vis 297 absorption spectra in solvents with different polarities (Figure S4) was not associated 298 with any significant changes in the spectrum's shape and position, indicating that the 299 value of the ground-state dipole moment is very constant. The emission peak of 300 PBTPA was observed at 629 nm, and it was characterized by a PLQY value of 50.9% 301 in pure toluene solution. 302

The data in Figure 2b illustrate the solvation effect, whereby the peaks in the PL 303 spectrum of PBTPA shift in wavelength as a function of the solvent's polarity. In 304 particular, the said spectrum red-shifted by 74 nm on going from hexane to 305 acetonitrile as solvent. The formation of a new energy balance between the solvent 306 and the excited molecule is essential for the mentioned red shift in the PL spectrum to 307 be observed. This solvatochromic effect indicated the presence of a CT component in 308 309 the excited state. Notably, the PLQY value for PBTPA decreased steeply from 88% in hexane to 3.6% in acetonitrile. In detail, in the low-polarity hexane solution, the 310

PLQY of PBTPA was relatively large. As the solvent polarity increased, however, the PLQY value decreased to 50.9% in the medium-polarity toluene, and to 57.9% in butyl ether. In the highly polar acetone and acetonitrile, PLQY decreased drastically to 4.3% and 3.6%, respectively. This downward trend of PLQY in higher polarity solutions was caused by an increasing CT component that competes with LE.

316 In order to further delve into the solvation effect, a Lipper-Mataga solvation model, whereby the Stokes shift values are plotted against the polarity of the solvent, was 317 constructed. The calculated dipole moment of excited PBTPA is 11.2 D, and the 318 ground dipole moment has a value of 3.2 D. The dipole moment of the excited 319 molecule is thus larger than that of the ground state, and it is smaller than that of the 320 typical CT molecule DMABN (23 D)<sup>39</sup>; once again, the constant slope of the line 321 322 (Figure 2c) implied that the excited state of the molecule is a typical hybrid state composed of both CT and LE. 323

The lifetime curve in Figure 2d indicated that PBTPA in film form is characterized by 324 a short fluorescence lifetime (4.7 ns). In fact, the lifetime curve presented a single 325 exponential decay. The lack of a fluorescence delay illustrated well the fact that the 326 molecule's behavior does not conform to the TADF or the TTA mechanisms. 327 Employing equations  $K_r = \Phi_f / \tau$  and  $K_{nr} = 1/\tau - K_r$ , where  $\Phi_f$  represents the molecule's 328 fluorescence efficiency (16.2% for PBTPA in film) and  $\tau$  represents the molecule's 329 transient fluorescence lifetime (4.71 ns for PBTPA in film), we were able to calculate 330 PBTPA's radiation rate (K  $_r$  = 3.4  $\times$  10  $^7$   $s^{-1}$ ) and the same molecule's non-radiation rate 331  $(K_{nr} = 17.8 \times 10^7 \text{ s}^{-1})$ . Notably, the lifetime of PBTPA in the film phase (4.71 ns) was 332

similar to its counterpart measured in acetonitrile solution (4.70 ns). However, the film's PLQY value (16.2%) was more than four-fold higher than that of acetonitrile (3.6%). This difference might be attributed to the luminescence of PBTPA in acetonitrile solution is a single molecule process, in contrast to the thin film case, where molecules are aggregated and exhibit an AIE effect, which increases PL efficiency.

To explore the AIE characteristics, we confirmed the PL spectra of PBTPA in the 339 mixture solutions. Based the data reported in Figure 3a, b, it can be evinced that 340 341 PBTPA had an emission at 674 nm with a broad full width at half maximum in pure THF. The PL intensity began to decrease as the water fraction  $(f_w)$  in the solvent 342 increased. However, it increased dramatically after fw reached a value of 50%. 343 Interestingly, a red shift of 15 nm occurred in PBTPA's emission spectrum from 80% 344  $f_w$  to 90%  $f_w$ . This observation might be due to a certain degree of change occurring in 345 the molecular aggregation state of PBTPA when  $f_w$  reaches the value of 90%, making 346 the molecular configuration more planar, so that the increase in PL intensity at 90%  $f_w$ 347 was not apparent as the red shift occurred. The AIE trend for the molecule can be 348 called aggregation-induced enhanced emission. The low PL strength of PBTPA at f<sub>w</sub> 349 values below 50% can be attributed to the molecule was combinations of donors and 350 acceptor units, which may trigger a twisted intramolecular charge transfer leading to 351 emission annihilation, as the solution's polarity increases.<sup>40, 41</sup> According to the theory 352 of restricted intermolecular motion, hindrance to the free rotation of the benzene ring 353 in the propeller-like configuration of triphenylamine and inhibition of the 354

355 conformation change of phenothiazine are the main causes of the AIE phenomenon.<sup>42</sup>

356 3.4 Theoretical Calculations

In order to verify that PBTPA's molecular design conforms to the energy distribution 357 of typical HLCT materials, we performed time-dependent density functional theory 358 (TDDFT) calculations on PBTPA. The geometry configuration and frontier molecular 359 orbitals (FMOs) were optimized by B3LYP/6-31G (d, p) in the Gaussian09 package. 360 The natural transition orbits (NTOs) were obtained at the level of M062X/6-31G (d, 361 p). The optimized geometry configuration depicted in Figure 4a for this D-A-D 362 molecule includes a phenothiazine unit characterized by a dihedral angle of 40°. The 363 value for the twist angle of the phenothiazine and triphenylamine units adjacent to 364 benzothiadiazole in PBTPA is 33°. Importantly, this moderately distorted structure 365 favors the formation of CT states. PBTPA's FMOs (Figure S6) are such that the 366 HOMO of the molecule is distributed horizontally throughout the molecule's 367 backbone. By contrast, the LUMO is mainly localized vertically on the 368 benzothiadiazole unit and, to a lesser extent, on the adjacent aromatic rings. The 369 partial overlap of HOMO to LUMO transition suggested that PBTPA possesses both 370 CT character and  $\pi$ - $\pi$ \* transition of local luminescence. 371

In order to explore further the characteristics of HLCT, we investigated the excited states of PBTPA. The NTOs showed the hole-particle distribution of the first five singlets and the first five triplets (**Figure S7**) and corresponding energy level diagram. As can be evinced from **Figure 4a**, the lowest-energy singlet (S<sub>1</sub>) of PBTPA exhibits the orbital characteristics of LE and CT hybridization, with a certain degree of overlap

377	between the holes and particles. The oscillator strength is 0.7135, which means that $S_1$
378	is the primary energy level for radiation transition. The lowest-energy triplet $(T_1)$
379	mainly showed the hybridization state, with the particles and holes concentrated on
380	benzothiadiazole, an arrangement that is not conducive to the establishment of a weak
381	exciton binding interaction. The results of the energy level calculations (Figure 4b)
382	indicated that the magnitude of $\Delta E_{(T1-S1)}$ (0.84 eV) is not conducive to the formation
383	of the "cold exciton" channel for the TADF-type RISC process. The $T_2$ state
384	presented a CT-dominated hybrid state, resulting in the $\Delta E_{(T2-S1)}$ value to be 0.17 eV,
385	a small enough value to afford the possibility for the hot exciton RISC process from
386	$T_2$ to $S_1$ to occur. The value of $\Delta E_{(T1-T2)}$ is 1.01 eV, which is substantial enough to
387	render $K_{\text{RISC}}$ more favorable in the process of competing with the IC rate $K_{\text{IC}}.$ In the
388	excited state, a $T_2 \rightarrow S_1$ "hot exciton" channel formed, which changes the spin
389	characteristics of some triplet excitons to singlet excitons for fluorescence emission.
390	The results of the theoretical calculations performed indicated, therefore, that the
391	molecular energy distribution of PBTPA displayed the characteristics that would
392	favor HLCT, which is expected to break the 25% quantum statistical limitation, thus
393	affording the means to construct an efficient OLED.

394 *3.5 Electroluminescence Properties* 

Based on the previously discussed electrochemical and thermal stability of PBTPA, we employed the vacuum deposition technique to fabricate a non-doped OLED comprising this red light emitter. The structure of this OLED, which we dubbed device I, is indium-tin oxide (ITO)/

399	dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) (5 nm)/
400	4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine (TAPC) (50 nm)/
401	PBTPA (20 nm)/ 1,3,5-Tris(3-pyridyl-3-phenyl)benzene (TmPyPB) (50 nm)/ LiF (1
402	nm)/ Al (100 nm). In this structure, ITO and LiF/Al were used as the anode and
403	cathode, respectively. HATCN and TAPC served as the hole injection layer and the
404	hole transport layer, respectively. PBTPA was used as the emitting material layer.
405	TmPyPB functioned as both an electron transport layer and a hole blocking layer.
406	Details of the electroluminescence performance of device I are listed in Table 2.
407	Device I achieved a maximum EQE value of 1.62%, and it was characterized by an
408	emission peak at 656 nm (Figure 5a) with CIE coordinates of (0.65, 0.32) in the
409	red-light region, which close to the red primary color standard set by REC709 (0.64,
410	0.33). Device I exhibited a low efficiency roll-off, at 100 cd m <sup>-2</sup> , the EQE was 1.33%,
411	which was 82% of the maximum EQE.
412	We went on to explore the utilization of excitons in the electroluminescence process.

413 The current density-luminance relationships of device I, reported in Figure S8 c, 414 presents a linear correction rather than quadratic relationship, so we can conclude that a TTA mechanism of P-type delayed fluorescence is not compatible with device I.<sup>43, 44</sup> 415 In order to calculate the specific exciton utilization, we introduced the equation  $\eta_{EOE} =$ 416  $\eta_{out} \cdot \eta_{rec} \cdot \eta_{pl} \cdot \eta_s$ , where  $\eta_s$  is the radiative exciton ratio,  $\eta_{out}$  is the light outcoupling 417 efficiency (its value is generally assumed to be 20%),  $\eta_{\rm pl}$  is the film 418 photoluminescence efficiency, and  $\eta_{\rm rec}$  is the fraction of exciton formation of the 419 injected charge carriers, which reaches its ideal value of 100% only if holes and 420

421	electrons are fully balanced and completely recombined to form excitons.								
422	Calculations indicate the exciton utilization efficiency of device I to be 50%.								
423	Therefore, device I exceeded the spin statistic limitation by 25%, allowing the goal of								
424	efficient luminescence to be achieved.								
425	As a way to improve the performance of turn-on voltage and maximum brightness of								
426	the device, the doped device II, with an optimized structure, was assembled. Detailed								
427	data for this species are reported in Table 2, Figure 5b and Figures S9. Device II								
428	consisted of indium-tin oxide (ITO)/								
429	dipyrazino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile (HATCN) (5 nm)/								
430	4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine (TAPC) (50 nm)/								
431	1,3-bis(N-carbazolyl)benzene mCP (10 nm)/ 9,10-bis(2-naphthyl)anthraces (AND):								
432	PBTPA2% (20 nm)/ 1,3,5-tris(3-pyridyl-3-phenyl)benzene (TmPyPB) (45 nm)/ LiF (1								
433	nm)/ Al (100 nm). In this structure, mCP served as the electron-blocking layer and								
434	ADN as the host material for doping. The efficiency of this device improved								
435	significantly in comparison with device I. In particular, device II was found to be								
436	characterized by an EQE of 4.86%, with an emission peak at 604 nm and CIE								
437	coordinates of (0.55, 0.43); moreover, the voltage at 1cd $A^{-1}$ was reduced to 3.4 V.								
438	Notably, although doping device II overcame the problem associated with carrier								
439	transport imbalance and achieved a huge improvement in efficiency over device I, it								
440	did so at the expense of color purity.								

**4. Conclusions** 

442	We designed the D–A–D-structured, red light emitter PBTPA. The stable thermal and
443	electrochemical properties of PBTPA indicated the potential of this species to be used
444	to fabricate OLED devices. Solvatochromic measurements indicated the molecule to
445	display a significant ICT, leading to an increase in polarity; the Lippert-Mataga
446	model combined with data on the film single-component lifetime at the nanosecond
447	level demonstrated that the excited state $S_1$ of the molecule is characteristic of HLCT.
448	PBTPA was also characterized by AIE. The non-doped device fabricated using
449	PBTPA achieved red light emission at 656 nm with CIE coordinates of (0.65, 0.32)
450	and EQE of 1.62%, and the exciton utilization reached a value of 50%. This device
451	thus displays a relatively good performance as red light emitting material. TDDFT
452	calculations indicated PBTPA to be characterized by a large $\Delta E_{T1-T2}$ value (1.01 eV)
453	and a small $\Delta E_{T2-S1}$ (0.17 eV) value, so that an active hot exciton channel between $T_2$
454	and $S_1$ can be formed. This design idea of AIE combined with HLCT demonstrates the
455	great potential for the manufacture of PBTPA-based efficient red-light fluorescent
456	emitters.

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601									
602	Captions								
603	Scheme 1. Synthetic steps to product PBTPA: a) Dimethyl sulfoxide, NaOH,								
604	1-bromoethane, 24 h; b) dimethylformamide, N-bromosuccinimide, overnight; c)								
605	potassium acetate, Pd(dppf) <sub>2</sub> Cl <sub>2</sub> , 90 °C, 8 h, N <sub>2</sub> protection; d) K <sub>2</sub> CO <sub>3</sub> , Pd(pph <sub>3</sub> ) <sub>4</sub> ,								
606	THF/H <sub>2</sub> O, 70 °C, 24 h, N <sub>2</sub> protection.								
607									
608	Figure 1. Thermal and electrochemical properties of PBTPA. a) Thermogravimetric								

analysis and differential scanning calorimetry curves of PBTPA; b) Cyclic voltammograms of PBTPA. Eg: energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).  $T_d$ : decomposition temperature (corresponding to 5% weight loss);  $T_g$ : glass-transition temperature.

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596

615 **Figure 2.** Photophysical properties of PBTPA. a) UV-vis absorption and 616 photoluminescence (PL) spectra of PBTPA in toluene solution  $(10^{-5} \text{ M})$ . b) Solvation

28

- 617 effect on the PL spectra of PBTPA. c) Linear fitting of the Lippert–Mataga model for
- 618 PBTPA. d) Transient PL decay spectrum of PBTPA in neat film form.
- 619

Figure 3. Dependence of PBTPA photoluminescence (PL) on the amount of water present in a H<sub>2</sub>O/THF mixture used as PBTPA's solvent. a) PL spectra of PBTPA  $(10^{-5} \text{ M})$  in H<sub>2</sub>O/THF mixtures characterized by different water fractions. b) PL intensity of a PBTPA solution  $(10^{-5} \text{ M})$  in an H<sub>2</sub>O/THF mixture *versus* the water fraction in the mixed solvent.

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Figure 4. Results of time-dependent density functional theory (TDDFT) calculations performed on PBTPA. a) Optimized molecular geometry and natural transition orbits for the  $S_1/S_0$ ,  $T_1/S_0$ , and  $T_2/S_0$  transitions of PBTPA. b) Energy level diagram for PBTPA. HLCT: hybridized local and charge transfer; hRISC: high-lying reverse intersystem crossing

631

Figure 5. Performance as red organic light-emitting diodes of non-doped devices I
and doped II. a) and b) External quantum efficiency (EQE) *versus* luminance curves
and normalized electroluminescence spectra at 8 V of device I and II. c) Energy levels
and structures of devices I and II. d) Commission International de L'Eclairage (CIE)
coordinates of devices I and II.

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Journal Pre-proof								
Table 1								
Compound	$\lambda_{abs}\left(s ight)$	$\lambda_{PL}(s/f)$	Tg/Tm	T <sub>d</sub>	НОМО	LUMO	$E_g$	$\eta_{PL}(s/f)$
	[nm] <sup>a)</sup>	[nm] <sup>b)</sup>	$[^{o}C]^{c)}$	$[^{o}C]^{d)}$	$[eV]^{e)}$	$[eV]^{e)}$	$[eV]^{f)}$	[%] <sup>g)</sup>
PBTPA	314/461	628/677	119/177	410	-4.98	-3.10	1.88	50.9/16.2

 $^{a}\lambda_{abs}$  (s): absorption wavelength in dilute toluene solution (10<sup>-5</sup> M);

 ${}^{b}\lambda_{PL}$  (s): emission peak in dilute toluene solution;  $\lambda_{PL}$  (f): emission peak in vacuum-deposited neat film;

<sup>c</sup>T<sub>g</sub>: glass-transition temperature; T<sub>m</sub>: melting temperature;

<sup>d</sup>T<sub>d</sub>: decomposition temperature;

<sup>e</sup>Energy level of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) confirmed by cyclic voltammetry;

 ${}^{f}E_{g}$ : energy gap between HOMO and LUMO (LUMO – HOMO);

 ${}^{g}\eta_{PL}(s)$ : fluorescence quantum yield in toluene (10<sup>-5</sup> M);  $\eta_{PL}(f)$ : fluorescence quantum

yield in neat film.

device	V <sub>turn-on</sub>	CE <sub>max</sub>	PE <sub>max</sub>	EQE <sub>max</sub>	L <sub>max</sub>	$\lambda_{EL}$	$V_{\text{end}}$	CIE	EUE
	[V] <sup>a)</sup>	[cd	[lm	[%] <sup>d)</sup>	[cd	[nm] <sup>f)</sup>	[V] <sup>g)</sup>	$[X,Y]^{h)}$	[%] <sup>i)</sup>
		$A^{-1}]^{b)}$	W <sup>-1</sup> ] <sup>c)</sup>		m <sup>-2</sup> ] <sup>e)</sup>				
Ι	7.20	0.87	0.37	1.62	585	656	14.80	0.65,0.32	50.0
II	3.40	9.92	8.20	4.86	7913	604	12.80	0.55,0.43	\
<sup>a</sup> Turn-on voltage at the luminescence of 1 cd m <sup>-2</sup> ;									
<sup>b</sup> Maximal current efficiency;									
<sup>c</sup> Maximal power efficiency;									
<sup>d</sup> EQE <sub>max</sub> : Maximal external quantum efficiency;									
<sup>e</sup> Maxi	mal lumi	nescence;	;						
<sup>f</sup> Maxi	mal elect	rolumines	scence pe	ak value;					
<sup>g</sup> Voltage at maximum brightness;									

Table	2.
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<sup>h</sup>Commission International de L'Eclairage coordinates; observer: 2°; obtained at 8 V;

<sup>i</sup>Maximal exciton utilization efficiency.

















Figure 5



### Scheme 1.



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Highlights:

- A novel D-A-D-type red fluorescent emitter, PBTPA, was designed and synthesized.
- It displayed aggregation-induced emission and hybridized local and charge • transfer.
- Non-doped OLED had 50% EUE, efficient hot exciton channel, low-efficiency roll-off.

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Yuan Yu and Runze Wang conducted the synthesis and the photophysical characterizations of the materials. Miao Cang, Lei Xu fabricated the OLED for the materials and estimated the OLED performances. Wei Cui, Mizhen Sun and Huayi Zhou are responsible for the basic testing and analysis of thermal and electrochemical properties. Yuan Yu wrote the paper, and all the authors revised it. Shanfeng Xue and Wenjun Yang supervised the whole work.

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### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: