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Highly twisted bipolar emitter for efficient nondoped deep-blue electroluminescence

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Graphical Abstract



ACCEPTED	MANUS	CRIPT

1	Highly Twisted Bipolar Emitter for Efficient Nondoped	
2	Deep-Blue Electroluminescence	
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10		
11	Abstract: Three novel bipolar deep-blue emitter	ſS,
12	1-(4-(<i>tert</i> -butyl)phenyl)-2-(4-(9,9-diphenylacridin-10(9H)-yl)phenyl)-1H-phenanthro)[
13	9,10- <i>d</i>]imidazole (DPACTPI	I),
14	1-(4-(<i>tert</i> -butyl)phenyl)-2-(4'-(9,9-diphenylacridin-10(9 <i>H</i>)-yl)-[1,1'-biphenyl]-4-yl)-2	1
15	<i>H</i> -phenanthro[9,10- <i>d</i>]imidazole (DPACPhTPI) ar	nd
16	2-(4-(9,9-diphenylacridin-10(9H)-yl)phenyl)-1-(4-(trifluoromethyl)phenyl)-1H-phenyl)	a
17	nthro[9,10-d]imidazole (DPACFPPI), employing the done	or
18	9,9-diphenyl-9,10-dihydroacridine (DPAC) and the acceptor, phenanthroimidazol	le,
19	were designed and synthesized. The highly twisted conformations between DAPC ar	nd
20	phenanthroimidazole in the molecules efficiently interrupt molecular π -conjugation	on
21	and inhibit π - π intermolecular interactions, resulting in good thermal stability ar	nd
22	efficient deep-blue emission. The three phenanthroimidazole derivatives in non-dope	ed

23	OLEDs exhibited deep-blue emission. In particular, DPACPhTPI-based nondoped
24	device showed an excellent performance with maximum external quantum efficiency
25	(EQE) of 3.50%, maximum current efficiency (CE) of 1.38 cd/A, maximum power
26	efficiency (PE) of 1.40 lm/W and CIE coordinate of (0.156, 0.047), which is among
27	the best results for OLEDs with a similar color. The high radiative exciton utilization
28	could be resulted from hybridized local and charge transfer (HLCT).
29	

30 Keywords: Deep-blue, Phenanthroimidazole, Twisted, Bipolar

31

32 **1. Introduction**

Organic light emitting diodes (OLEDs) have attracted much attention owing to 33 34 their superior potential applications in full-color flat-panel displays and solid-state lighting [1-2]. Three basic colors (blue, green and red) are essential to the full color 35 displays. Red and green phosphorescent OLEDs have already satisfied the 36 commercial requirement in efficiency and stability, while the blue OLEDs are still 37 one of the bottlenecks for the further application of OLEDs. In recent decades, great 38 effort has been made to develop deep blue phosphorescent emitters. Unfortunately, 39 blue phosphorescent OLEDs are still not stable enough for practical applications [3-5]. 40 Recently, thermally activated delayed fluorescence (TADF) has drawn great attention 41 of researchers due to the possibility of solving the problems of blue OLEDs [6-8]. 42 While most TADF molecules, which consist of donor and acceptor groups with 43 separated HOMO (highest occupied molecular orbital) and LUMO (lowest 44

unoccupied molecular orbital) to decrease the singlet-triplet energy gap, exhibit broad
and structureless emission bands. It's difficult to develop a deep-blue TADF emitters
due to the large stokes shift [9-11]. Highly efficient deep-blue TADF OLEDs with
CIE_y less than 0.1 and low efficiency roll-off at high brightness are rare [12]. Thus,
efficient fluorescent materials are still considered to be promising for the realization
of efficient and stable deep-blue devices.

Constructing bipolar molecules has been proved to be an effective strategy to 51 develop highly efficient blue electroluminescence materials [13-18]. Bipolar emitting 52 53 materials can achieve better balanced charge carriers and a broad exciton formation zone, consequently simplifying the device configurations and improving the device 54 performance. Nevertheless, the intramolecular charge transfer (ICT) interaction 55 56 between the donor and acceptor usually decreases the energy gap and leads to a fluorescence maximum redshift. In order to construct a deep blue molecule in a D-A 57 system, the donor and acceptor should be very carefully selected to regulate the ICT 58 energy. Phenanthroimidazole is an ideal building block for deep blue/violet 59 light-emitting materials. It exhibits electron-donating properties when an 60 electron-withdrawing moiety is attached to the imidazole ring, but it shows electron 61 withdrawing properties when linked with an electron donor [14, 19-22]. However, 62 many phenanthroimidazole derivatives suffered from a large redshift in the solid state 63 due to π - π stacking [22-25], even shifted to blue-green region. Using bulky building 64 blocks is an effective method to inhibit molecular aggregation or π - π stacking in the 65 solid state [26-27]. Moreover, a twisted structure could not only avoid π - π stacking in 66

67 the solid state [28-32] but also break the π conjugation to achieve a deep-blue 68 emission.

69 Inspired by this, we designed and synthesized three new blue-emissive materials based on phenanthroimidazole and 9,9-diphenyl-9,10-dihydroacridine. DPAC was 70 chosen as an electron donor for its good hole-transporting mobility [33] and large 71 intramolecular torsion angle induced by the steric repulsion between the hydrogen 72 atoms of the cross-linking phenylene [34]. Additionally, the sp³ C atom endows 73 DPAC unit with more rigidity and bulkiness. Furthermore, we introduce the tert-butyl 74 75 and trifluoromethyl group to the N1-substitution of phenanthroimidazole unit, which can improve the solubility of the compounds in organic solvents, enhance the 76 morphological stability and suppress the formation of aggregation or π - π stacking in 77 78 the solid state. As expected, the three compounds exhibit excellent thermal stability, bipolar carrier transport ability and deep-blue emission in the solid state. Nondoped 79 OLEDs based on the three novel emitters show deep-blue light emissions. The 80 **DPACPhTPI**-based device exhibited excellent EL performance with CIE coordinates 81 of (0.156, 0.047), low turn-on voltage of 3.0 V, high external quantum efficiency 82 (EQE) of 3.5%, current efficiency (CE) of 1.38 cd/A, and power efficiency (PE) of 83 1.40 lm/W, which is comparable to the reported high-efficiency OLEDs with similar 84 85 color.

86 2. Experimental section

87 2.1. Material and method

All the reagents and solvents used for the syntheses and measurements were 88 purchased from commercial suppliers and were used without further purification 89 unless otherwise noted. ¹H NMR and ¹³C NMR spectra were conducted on a 90 Bruker-AF301 AT 400 MHz spectrometer. Mass spectra were recorded using an 91 Agilent (1100 LC/MSD Trap) using APCI ionization. High-resolution mass 92 spectrometry (HRMS) were carried out on a Bruker Daltonics SolariX 7.0T 93 spectrometer using APCI ionization. Elemental analyses of carbon, hydrogen, and 94 nitrogen were performed on an Elementar (Vario Micro cube) analyzer. 95 Thermogravimetric analyses (TGA) were undertaken using a PerkinElmer 96 Instruments (Pyris1 TGA) under nitrogen atmosphere at a heating rate of 10 \Box /min 97 from 30 to $600\Box$. The differential scanning calorimetry (DSC) was performed on a 98 TA Q2000 DSC instrument under nitrogen at a heating rate of 10^{-/}min from 30 to 99 250 \square . The glass transition temperature (T_g) was determined from the second heating 100 UV-Vis spectra were measured using a Shimadzu UV-VIS-NIR 101 scan. Spectrophotometer (UV-3600). Photoluminescence (PL) spectra were recorded on a 102 Hitachi F-7000 fluorescence spectrophotometer. The photoluminescence quantum 103 yields (PLQYs) were measured in DCM using 9,10-diphenylanthracene as a standard 104 $(\Phi=0.90$ in cyclohexane). Cyclic voltammetry (CV) was performed on a 105 computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature 106 with a conventional three electrode cell, which consisted of a platinum wire counter 107 electrode, an Ag/AgNO₃ (0.1 M) reference electrode and a Pt carbon working 108 electrode of 2 mm diameter. Oxidations of all compounds were performed in dried 109

110	dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate
111	(Bu_4NPF_6) as supporting electrolyte. The onset potential was determined from the
112	intersection of two tangents drawn at the rising and background current of the cyclic
113	voltammogram. The solutions were purged with a nitrogen stream for 10 min before
114	measurements.
115	2.2. Preparation of compounds
116	2.2.1. Synthesis of
117	1-(4-(tert-butyl)phenyl)-2-(4-(9,9-diphenylacridin-10(9H)-yl)phenyl)-1H-phen
118	anthro[9,10-d]imidazole (DPACTPI)
119	A mixture of
120	2-(4-bromophenyl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazole (1.515)
121	g, 3 mmol), 9,9-diphenyl-9,10-dihydroacridine (1 g, 3 mmol), t-BuONa (0.576 g, 6
122	mmol), tri-tert-butylphosphonium tetrafluoroborate (52 mg, 0.18 mmol) and
123	palladium acetate (20 mg, 0.09 mmol) was dissolved in dry toluene (50 mL), and
124	purged three times by nitrogen/vacuum cycle. And then, the reaction mixture was
125	refluxed for 12 hours. After cooling to room temperature, the solution was extracted
126	with dichloromethane. The organic layer was dried by anhydrous $MgSO_4$ and
127	concentrated. Then the crude product was purified by silica gel chromatography. The
128	desired product was obtained as white powder (2.1 g, yield: 92%). ¹ H NMR (400
129	MHz, CDCl ₃) δ [ppm]: 8.93 (s, 1H), 8.79 (d, <i>J</i> = 8.4 Hz, 1H), 8.73 (d, <i>J</i> = 8.4 Hz, 1H),
130	7.78-7.52 (m, 8H), 7.47 (d, J = 8.0 Hz, 2H), 7.31-7.20 (m, 6H), 7.04-6.97 (m, 9H),
131	6.89-6.88 (m, 4H), 6.40 (d, $J = 8.0$ Hz, 2H), 1.45 (s, 9H); ¹³ C NMR (100 MHz, CDCl ₃)

132	δ [ppm]: 146.35, 141.88, 131.65, 130.95, 130.36, 130.08, 128.44, 127.62, 127.21,
133	126.82, 126.46, 126.26, 124.16, 123.14, 120.99, 120.37, 114.16, 56.74, 35.10, 31.39;
134	MS (APCI): calculated for $C_{56}H_{43}N_3$, 757.35; found, 758.4, $[M+H]^+$; Elemental
135	analysis calculated (%) C ₅₆ H ₄₃ N ₃ : C 88.74, H 5.72, N 5.54; found: C 88.53, H 5.87, N
136	5.51.
137	2.2.2. Synthesis of 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde (1)
138	A mixture of (4-formylphenyl)boronic acid (0.6 g, 4 mmol),
139	1-bromo-4-iodobenzene (1.3 g, 4.3 mmol), $Pd(PPh_3)_4$ (46 mg, 0.04 mmol), K_2CO_3
140	(2.0 M aqueous solution, 60 mL), toluene (60 mL) and ethanol (30 mL) were stirred
141	under nitrogen at 90 °C for 12 h. After cooling to room temperature, the reaction
142	mixture was extracted with dichloromethane and further purified by column
143	chromatography to obtain a white solid (1 g, yield: 95%). ¹ H NMR (400 MHz, CDCl ₃)
144	δ [ppm]: 10.06 (s, 1H), 7.96 (d, <i>J</i> = 8.0 Hz, 2H), 7.72 (d, <i>J</i> = 8.0 Hz, 2H), 7.61 (d, <i>J</i> =
145	8.0 Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H).

146 2.2.3. Synthesis

of

147 2-(4'-bromo-[1,1'-biphenyl]-4-yl)-1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,1
 148 0-d]imidazole (2)

149 mixture of 9,10-phenanthrenequinone (0.8 3.83 mmol), А g, 4'-bromo-[1,1'-biphenyl]-4-carbaldehyde (1 g, 3.83 mmol), 4-(tert-butyl)aniline (0.57 150 g, 3.83 mmol) and ammonium acetate(1.8 g, 23 mmol) was dissolved in acetic acid 151 (50 mL), and was heated to reflux for 8 h under nitrogen atmosphere. After cooling to 152 153 room temperature, the mixture was poured into water. The solid product was filtered,

154	washed with methanol and dried under vacuum to afford a pale-yellow solid (1.8 g,
155	yield: 80%). The crude product was used in the next step without further purification.
156	¹ H NMR (400 MHz, CDCl ₃) δ [ppm]: 8.92 (s, 1H), 8.77 (d, $J = 8.4$ Hz, 1H), 8.71 (d, J
157	= 8.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.70-7.62 (m, 5H), 7.56-7.43 (m, 9H),
158	7.29-7.25 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 1.46 (s, 9H); HRMS (APCI): calculated
159	for $C_{37}H_{29}BrN_2$, 582.1494; found, 583.1540, $[M+H]^+$.
160	2.2.4. Synthesis of
161	1-(4-(tert-butyl)phenyl)-2-(4'-(9,9-diphenylacridin-10(9H)-yl)-[1,1'-biphenyl]-
162	4-yl)-1H-phenanthro[9,10-d]imidazole (DPACPhTPI)
163	DPACPhTPI was prepared with the similar procedure as that of DPACTPI . ¹ H
164	NMR (400 MHz, CDCl ₃) δ [ppm]: 8.99 (s, 1H), 8.78 (d, <i>J</i> = 8.4 Hz, 1H), 8.72 (d, <i>J</i> =
165	8.4 Hz, 1H), 7.79-7.48 (m, 13H), 7.30-7.19 (m, 8H), 7.13 (d, $J = 8.0$ Hz, 2H),
166	7.08-7.00 (m, 6H), 6.91-6.86 (m, 4H), 6.48 (d, $J = 8.0$ Hz, 2H), 1.47 (s, 9H); ¹³ C
167	NMR (100 MHz, CDCl ₃) δ [ppm]: 146.46, 142.13, 140.33, 140.00, 131.65, 130.41,
168	130.05, 129.59, 129.45, 129.05, 128.52, 128.40, 127.62, 127.23, 126.86, 126.38,
169	126.26, 125.94, 125.10, 124.13, 123.12, 120.97, 120.20, 114.04, 56.76, 35.11, 31.45;
170	MS (APCI): calculated for $C_{62}H_{47}N_3$, 833.38; found, 834.8, $[M+H]^+$; Elemental
171	analysis calculated (%) C ₆₂ H ₄₇ N ₃ : C 89.28, H 5.68, N 5.04; found: C 89.03, H 5.81, N
172	5.01.
173	2.2.5. Synthesis of
174	2-(4-bromophenyl)-1-(4-(trifluoromethyl)phenyl)-1H-phenanthro[9,10-d]imid
175	azole (3)

176	3 was prepared with the similar procedure as that of 2. Yield: 88% . ¹ H NMR
177	(400 MHz, CDCl ₃) δ [ppm]: 8.85 (d, J = 7.6 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H), 8.69 (d, J
178	<i>J</i> = 8.0 Hz, 1H), 7.88 (d, <i>J</i> = 8.0 Hz, 2H), 7.74 (t, <i>J</i> = 7.6 Hz, 1H), 7.69-7.63 (m, 3H),
179	7.54 (t, $J = 7.6$ Hz, 1H), 7.45-7.28 (m, 5H), 7.09 (d, $J = 8.0$ Hz, 1H); MS (APCI):
180	calculated for $C_{28}H_{16}BrF_{3}N_{2}$, 516.04; found, 517.1, $[M+H]^{+}$.
181	2.2.6. Synthesis of
182	2-(4-(9,9-diphenylacridin-10(9H)-yl)phenyl)-1-(4-(trifluoromethyl)phenyl)-1H
183	-phenanthro[9,10-d]imidazole (DPACFPPI)
184	DPACFPPI was prepared with the similar procedure as that of DPACTPI . ¹ H
185	NMR (400 MHz, CDCl ₃) δ [ppm]: 9.00 (s, 1H), 8.81 (d, <i>J</i> = 8.0 Hz, 1H), 8.73 (d, <i>J</i> =
186	8.0 Hz, 1H), 7.92 (d, J = 6.8 Hz, 2H), 7.81-7.71 (m, 6H), 7.58 (t, J = 7.6 Hz, 1H),
187	7.35-7.23 (m, 7H), 7.12-7.03 (m, 5H), 6.98-6.96 (m, 4H), 6.90-6.89 (m, 4H), 6.39 (d,
188	$J = 8.0$ Hz, 2H); ¹³ C NMR (100 MHz, CDCl ₃) δ [ppm]: 146.26, 141.79, 131.74,
189	131.07, 130.35, 130.13, 129.72, 128.55, 127.65, 127.53, 126.86, 126.70, 126.31,
190	124.44, 123.19, 120.60, 120.56, 114.27, 56.77; HRMS (APCI): calculated for
191	$C_{53}H_{34}F_3N_3$, 769.2705; found, 770.2785, $[M+H]^+$; Elemental analysis calculated (%)
192	C ₅₃ H ₃₄ F ₃ N ₃ : C 82.69, H 4.45, N 5.46; found: C 82.37, H 4.63, N 5.41.
193	2.3. Computational Details
194	The geometrical and electronic properties were computed using the Gaussian 09

194 The geometrical and electronic properties were computed using the Gaussian 09 195 program package. The ground-state geometry was optimized using density functional 196 theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31G(d). The 197 excited-state geometry was optimized by time-dependent density functional theory

(TD-DFT) with the B3LYP functional at the same basis set level. To get a better
insight into the nature of the excited state, the natural transition orbitals (NTOs)
analyses were also carried out by TD-DFT calculations. Molecular orbitals were
visualized using Gauss view 5.0 program.

202 2.4. Device Fabrication and Measurement

The carrier-injection material MoO_3 , lithium fluoride (LiF), 203 and carrier-transporting material 4,4'-(cyclohexane-1,1-diyl)bis(*N*,*N*-di-*p*-tolylaniline) 204 3,3'-(5'-(3-(pyridin-3-yl)phenyl)-[1,1':3',1"-terphenyl]-3,3"-diyl)dipyridine 205 (TAPC), 1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene 206 (TmPvPB) (TPBi) were commercially available. Commercial ITO coated glass with a sheet resistance of 20 Ω 207 per square was used as the substrate. Before device fabrication, the ITO glass 208 substrates were pre-cleaned carefully and treated with oxygen plasma for 5 min. 209 MoO₃ was firstly deposited on the ITO substrate, followed by TAPC, the emission 210 layer, and TmPyPB. Finally, a cathode composed of LiF and aluminum was 211 sequentially deposited onto the substrate in the vacuum of 2×10^{-6} Torr. For all of the 212 OLEDs, the emitting areas were determined by the overlap of two electrodes as 0.09 213 cm². The EL spectra, CIE coordinates and J-V-L curves of the devices were measured 214 using a PHOTO RESEARCH SpectraScan PR655 photometer and a KEITHLEY 215 2400 SourceMeter constant current source. The efficiency values were calculated 216 according to previously reported methods. All measurements were carried out at room 217 218 temperature under ambient conditions.

219 **3. Results and discussion**

220 *3.1. Synthesis*

The synthetic routes and molecular structures are depicted in Scheme 1. 221 2-(4-bromophenyl)-1-(4-(*tert*-butyl)phenyl)-1*H*-phenanthro[9,10-*d*]imidazole 222 and 9.9-diphenyl-9.10-dihydroacridine were synthesized according to the literature [25, 223 35]. The intermediate compound 1 was prepared through the palladium-catalyzed 224 Suzuki coupling reaction in high yield. The intermediate compound 2 and 3 were 225 synthesized in a one-pot reaction. The target products were prepared through the 226 palladium-catalyzed **Buchwald-Hartwig** 227 reaction between 228 9,9-diphenyl-9,10-dihydroacridine and the corresponding phenanthroimidazole intermediates, then purified by column chromatography on silica gel. The chemical 229 structures of the compounds were confirmed by ¹H-NMR, ¹³C-NMR, elemental 230 analysis and mass spectrometry. Before fabrication of the OLED device, the three 231 new compounds were further purified by repeated temperature-gradient vacuum 232 sublimation. 233

234 3.2. Thermal properties

The thermal properties of the three compounds were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. As presented in **Fig. 1** and **Table 1**, compounds **DPACTPI**, **DPACPhTPI** and **DPACFPPI** exhibit high decomposition temperatures (T_d , corresponding to 5% weight loss) of 439 \Box , 476 \Box and 419 \Box , respectively. The three new compounds did not show any glass transition temperatures up to 250 \Box . It is most likely due to their highly rigid and twisted structures which might mitigate the intermolecular interactions of these molecules in the solid state [28]. These results
reveal that the three materials are suitable for vacuum thermal evaporation
technology.

245 *3.3. Theoretical calculations*

To gain a better insight into the electronic structures of the three compounds, the 246 molecular configuration and frontier molecular orbitals were optimized using DFT at 247 the B3LYP/6-31G(d) level in the Gaussian 09 software. Fig. 2 shows the highest 248 occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital 249 250 (LUMO) distribution of the three compounds. The HOMO is mainly distributed on the donor DPAC moiety. The LUMO of DPACTPI and DPACPhTPI are localised 251 on the phenanthroimidazole and the adjacent phenyl or biphenyl rings, while the 252 253 LUMO of DPACFPPI is mostly spread over the acceptor benzotrifluoride and extended to phenanthroimidazole. It is obviously found that the HOMO and the 254 LUMO are almost completely spatially separated for the three compounds, which can 255 provide hole- and electron-transporting channels for intermolecular hole and electron 256 hopping along their respective conducting pathways, improving the device 257 performance. In the optimized configurations of the three compounds as shown in Fig. 258 2, very large dihedral angles of 84.5°, 83.9° and 83.3° were found between DPAC and 259 the phenyl ring connected to the phenanthroimidazole, which might effectively 260 prevent intramolecular extending of π -electron and suppress molecular packing in the 261 262 solid state. In addition, these molecules also show the large dihedral angles between the N-substituted benzene and phenanthroimidazole planes. 263

264 3.4. Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of the three 265 compounds are measured in dilute CH₂Cl₂, as shown in Fig. 3a. The fluorescence 266 spectra of compounds in solid film at room temperature is showed in Fig. 3b. Key 267 optical parameters are summarized in Table 1. All compounds show a strong 268 absorption band at around 260 nm, which may originate from the π - π * transition of 269 the benzene ring. The weaker absorption band at around 300-360 nm were assigned to 270 the π - π * transition of the phenanthroimidazole moiety. The absorption spectrum of 271 DPACTPI and DPACFPPI is very similar. While DPACPhTPI shows higher 272 absorption intensity between 300 and 360 nm, which could be assigned to the 273 extended π -conjugation for the phenanthroimidazole moiety. The maximum emission 274 wavelengths of **DPACTPI**, **DPACPhTPI** and **DPACFPPI** in CH₂Cl₂ were observed 275 at 435, 451 and 447 nm, respectively. Compared with **DPACTPI**, the redshift of 12 276 and 16 nm for **DPACFPPI** and **DPACPhTPI** could be attributed to the introduction 277 of the trifluoromethyl group and the increased conjugation by the insert of the 278 benzene ring. It is noteworthy that the emission peaks of the three compounds in the 279 film state show a large blue-shift of more than 20 nm, revealing little intermolecular 280 interactions in the film state. The blue-shift could be explained by the large dihedral 281 angle between DPAC and the phenyl ring connected to the phenanthroimidazole. 282 Using 9,10-diphenylanthracene as a standard, the PL quantum yields (Φ) in CH₂Cl₂ 283 were determined as high as 0.359, 0.352 and 0.287, respectively. Additionally, optical 284 band-gap (Eg) of **DPACTPI**, **DPACPhTPI** and **DPACFPPI** were calculated to be 285

286 3.26 eV, 3.18 eV and 3.22 eV from its absorption edge in solution, respectively.

287 *3.5. Electrochemical properties*

288 The electrochemical properties and energy levels of the three compounds were investigated by cyclic voltammetry. As shown in Fig. 4, the onset oxidation peaks 289 (E_{ox}) for DPACTPI, DPACPhTPI and DPACFPPI are 0.54, 0.53, and 0.53 eV 290 versus the Ag/Ag^+ redox couple, respectively. With the same DPAC donor unit, all 291 show a similar oxidation potential and HOMO level, which is in accordance with the 292 computed result. The HOMO energy levels of DPACTPI, DPACPhTPI and 293 DPACFPPI are estimated to be 5.44 eV, 5.43 eV and 5.43 eV with regard to 294 ferrocene. The LUMO energy levels were calculated from $E_{g}\xspace$ and HOMO values, 295 which were listed in Table 1. 296

297 Table 1

298 Physical properties of DPACTPI, DPACPhTPI and DPACFPPI.

299 *3.6. Carrier transporting characteristics*

Before characterizing the performance of these blue emitters in OLEDs, 300 hole-only and electron-only devices were fabricated to investigate the charge 301 transporting properties. The device configurations are shown as follows: ITO/MoO₃ 302 (10 nm)/TAPC (20 nm)/DPACTPI, DPACPhTPI or DPACFPPI (30 nm)/TAPC (20 303 nm)/MoO₃ (10 nm)/Al (100 nm) and ITO/LiF (1 nm)/TPBi (20 nm)/DPACTPI, 304 DPACPhTPI or DPACFPPI (30 nm)/TPBi (20 nm)/LiF (1 nm)/Al (100 nm). MoO₃ 305 and LiF performed as the hole injection layer (HIL) and the electron injection layer 306 (EIL), respectively. TAPC was used as the electron-blocking material, whereas the 307 TPBi layer was used to prevent hole injection from the anode. Fig. 5 shows the 308

current density versus voltage (J-V) curves of these single-carrier devices. The J-V 309 characteristics of single-carrier devices demonstrated the good bipolar transport 310 311 property of the three compounds. All of the compounds show higher and similar hole current density due to the good hole-transporting mobility of DPAC donor unit [36]. 312 Besides, the barrier of carrier injection from TAPC layer (~0.13 eV) is smaller than 313 TPBi layer (>0.45 eV), which also resulted in higher hole current density in a 314 hole-only device. The introduction of strong electron-withdrawing trifluoromethyl 315 group endow **DPACFPPI**-based device with higher electron current density at low 316 voltage (<9 V), while the poor electron-transporting mobility at high voltage (>10 V) 317 could be ascribed to the poor stability of the trifluoromethyl unit [30, 37]. The 318 superior bipolar transporting characteristic of **DPACPhTPI** indicate a better 319 320 electroluminescence performance.

321 *3.7. Electroluminescence*

To evaluate the EL performances of **DPACTPI**, **DPACPhTPI** and **DPACFPPI** 322 as blue emitters, we initially fabricated nondoped devices I-III with a multilayer 323 structure: ITO/MoO₃ (10 nm)/TAPC (40 nm)/EML (30 nm)/TmPyPB (20 nm)/LiF (1 324 nm)/Al (100 nm). In these devices, indium tin oxide (ITO) was used as the anode, 325 MoO₃ was used as hole injection layer, TAPC was used as hole transporting layer 326 (HTL), TmPyPB was used as electron transporting layer (ETL), LiF was used as 327 electron injecting layer, and Al was used as cathode. The relative HOMO/LUMO 328 energy levels of the materials are illustrated in Scheme 2, and detailed structures and 329 key performance of these devices are summarized in Table 2. 330

331	The current density-voltage-luminance (I-V-L) and current density-current
332	efficiency-power efficiency characteristics are shown in Fig. 6. As can be seen in Fig.
333	6 (a), the turn-on voltages of three devices were 3.6 V, 3.3 V and 3.6 V, respectively.
334	The lower turn-on voltage of DPACPhTPI-based device II should result from a
335	relatively smaller injection barrier from TmPyPB. All the three non-doped devices
336	show deep-blue emission with the maximum emission wavelengths of 428 nm, 436
337	nm and 424 nm, respectively. Compared with the fluorescence spectra in films, the
338	EL emission peaks showed a small redshift, which may be caused by the
339	intermolecular interactions and the electrical field polarization in the excited states.
340	The DPACTPI-based nondoped device I achieves a maximum current efficiency
341	(CE _{max}) of 1.85cd/A, a maximum power efficiency (PE _{max}) of 1.76 lm/W and a
342	maximum external quantum efficiency (EQE _{max}) of 2.31%. DPACPhTPI exhibits the
343	best EL performance with a CE _{max} of 3.84 cd/A, a PE _{max} of 4.02 lm/W and a EQE _{max}
344	of 3.51%. DPACFPPI displays a CE _{max} of 1.51 cd/A, a PE _{max} of 1.40 lm/W and a
345	EQE_{max} of 3.03%. However, because of the poor electron mobility at high voltage,
346	DPACFPPI shows the lowest luminance and a large efficiency roll-off.
347	Inspired by the relatively better device performance of DPACPhTPI, the blue

electroluminescent device based on **DPACPhTPI** was further optimized with the device configuration **IV-VIII** as follows: ITO/MoO₃ (10 nm)/TAPC (x nm) /**DPACPhTPI** (20 nm)/TmPyPB (y nm)/LiF (1 nm)/Al (100 nm). The detailed device structures, current density-voltage-luminance (I-V-L) and current density-current efficiency-power efficiency characteristics are shown in **Fig. 7**. Devices **IV-VII** show

353	the same turn-on voltage of 3.0 V. While, device VIII exhibits a higher turn-on
354	voltage of 3.3V. By changing the thickness of HTL and ETL, the EL spectra of the
355	devices vary from 420 nm to 444 nm. With the increasing of the thickness of HTL or
356	ETL, the emission peak is shifted gradually bathochromically, which could be
357	induced by the movement of exciton formation zone. The microcavity effect arising
358	from the change of the thickness may also contribute to this bathochromic
359	shift [38-39]. Device VII showed outstanding performance with the CIE coordinates
360	of (0.156, 0.047) and a maximum EQE of 3.50%, which was among the best results
361	for OLEDs with similar color (Table 2).

362 The EQE for OLEDs can be calculated by the following equation:

363 EQE =
$$\gamma \times \Phi_{PL} \times \eta_r \times \eta_{out}$$
,

where EQE is the maximum external quantum efficiency; γ is the carrier 364 recombination efficiency, which is assumed to be 100%; Φ_{PL} is the PLQY of the 365 emission layer; η_r is the radiative exciton yield; and η_{out} is light out-coupling 366 efficiency, which is 20~25% for glass substrates if there are not any out-coupling 367 enhancing structures in the device. Considering Φ_{PL} of **DPACPhTPI** is 35.2% and 368 the maximum EQE is 3.51%, the calculated radiative exciton yield is near 50%. This 369 result breaks the 25% theoretical limit of spin statistics for conventional fluorescence 370 OLEDs. The possibility of the triplet-triplet annihilation (TTA) seem to be excluded 371 because the brightness increases linearly with the increase of the current density at 372 low current injection and less than linearly at higher current injection [40], as shown 373 in Fig. S1. TADF is unlikely to take place due to the large ΔE_{ST} (0.72 eV, Fig. 374

375	S2) [12]. Therefore, the high radiative exciton yield may have possibly resulted from
376	hybridized local and charge transfer (HLCT) [41]. TD-DFT calculations and NTOs
377	analyses were performed for DPACPhTPI, as shown in Fig. 8. According to the
378	NTOs analyses of S_1 excited state, DPACPhTPI exhibits HLCT characteristic and
379	CT state is dominant in the emission, which also explains the moderate PLQY of
380	DPACPhTPI. The solvatochromism behavior of DPACPhTPI agrees well with the
381	NTOs calculations as shown in Fig. S4. Fig. 8 also shows that the T_3 excited state of
382	DPACPhTPI is similar to the S_1 excited state and the energy difference between T_3
383	and S_1 is estimated to be of only 0.011 eV, which suggests the possibility of the
384	reverse intersystem crossing (RISC) from T_3 to S_1 . These results further show that
385	DPACPhTPI should be HLCT emitter instead of others.

386 Table 2

387 Key characteristics of devices based on **DPACTPI**, **DPACPhTPI** and **DPACFPPI** and other 388 recently reported non-doped blue emitting devices with $CIE_y < 0.08$

389 4. Conclusions

In conclusion, we have designed and synthesized three bipolar, fluorescent 390 391 emitters, DPACTPI, **DPACPhTPI** and **DPACFPPI**, incorporating 9,9-diphenyl-9,10-dihydroacridine as electron-donor and phenanthroimidazole as 392 electron-acceptor. The three compounds exhibit strong blue PL emissions, good 393 thermal stability, good film-forming property, together with appropriate energy levels. 394 These molecules showed large intramolecular torsion angles, which avoided π - π 395 stacking in the solid state. The experimental results were well supported by DFT 396 397 theoretical calculations. The nondoped OLED device based on **DPACPhTPI** showed a good performance with maximum EL peak at 436 nm, EQE of 3.51%, CE of 3.84 398

399	cd/A, PE of 4.02 lm/W and CIE coordinate of (0.160, 0.078). What's r	nore, with
400	optimized device structure, DPACPhTPI-based nondoped device also e	xhibited a
401	near ultraviolet emission, a high maximum EQE of 3.50% with a CIE coo	ordinate of
402	(0.156, 0.047).	~

403

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410

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Physical properties of DPACIPI, DPACPHIPI and DPACFPPI.											
Compound	Abs ^a (nm)	PL ^{a/b} (nm)	Φ^{c}	$E_{g}^{d}(eV)$	E _{ox} (V)	HOMO/ LUMO(eV) ^e	HOMO/ LUMO(eV) ^f	$T_d^{g}(\Box)$			
DPACTPI	261, 287, 306, 361	435/412	0.359	3.26	0.54	-5.44/-2.18	-5.03/-1.20	439			
DPACPhTPI	262, 326, 360	451/428	0.352	3.18	0.53	-5.43/-2.25	-5.04/-1.37	476			
DPACFPPI	259, 286, 306, 358	447/422	0.287	3.22	0.53	-5.43/-2.21	-5.10/-1.52	419			

Table 1 Physical properties of DPACTPI, DPACPhTPI and DPACFPPI.

a Measured in dilute CH₂Cl₂ solution at room temperature.

b Solid state thin-film samples on quartz substrate.

c Measured in CH_2Cl_2 using 9,10-diphenylanthracene as a standard (Φ =0.90 in cyclohexane).

d Measured by the onset absorption wavelength of solution state.

e HOMO was determined from the onset of oxidation potentials with ferrocene as reference; LUMO was determined from E_g and HOMO level.

f Values obtained using Gaussian 09 at the B3LYP/6-31G(d) level.

g Measured from TGA.

Table 2

Key characteristics of devices based on **DPACTPI**, **DPACPhTPI** and **DPACFPPI** and other recently reported non-doped blue emitting devices with $CIE_y < 0.08$

Emitters	$\lambda_{EL}{}^a\!(nm)$	V _{on} ^b (V)	CE ^c (cd/A)	PE ^d (lm/w)	EQE ^e (%)	CIE (x, y)	Ref
DPACTPI	428	3.6	1.848	1.758	2.31	$(0.165, 0.068)^{\rm f}$	Device I
DPACPhTPI	436	3.3	3.842	4.022	3.51	$(0.160, 0.078)^{\rm f}$	Device II
DPACFPPI	424	3.6	1.506	1.403	3.03	$(0.162, 0.057)^{\rm f}$	Device III
DPACPhTPI	428	3.0	1.379	1.403	3.50	(0.156, 0.047) ^f	Device VII
BPA-BPI	428	3.1	0.65	0.68	1.37	(0.15, 0.05)	[25]
TPAXAN	428	3.4	-	-	4.62	(0.155, 0.049)	[29]
mTPA-PPI	404	3.2	0.84	0.48	3.33	(0.161, 0.049)	[42]
CPhBzIm	426	2.5	1.6	1.07	3	(0.16, 0.05)	[43]
PIBCz	414	2.7	1.28	1.12	2.74	(0.15, 0.05)	[44]
CzS1	426	3.5	1.89	1.58	4.21	(0.157,0.055)	[45]
DPPP	396	4.0	0.74	-	2.2	(0.160, 0.041)	[46]
CzB-S	-	5.5	0.75	-	2.03	(0.160, 0.054)	[47]
CzB-PIM	420	4.75	2.30	1.52	-)	(0.166, 0.064)	[48]
TPA-PIM	420	-	1.14	0.79	3.28	(0.161, 0.046)	[49]
m-BBTPI	428	3.2	1.99	1.81	3.63	(0.16, 0.06)	[50]
PPI-F-TPA	425	4.2	1.35	1.0	3.11	(0.16, 0.05)	[51]

a λ_{EL} is the emission wavelength at 20 mA/cm².

b V_{on} is the voltage at 1 cd/m².

c Maximum current efficiency.

d Maximum power efficiency.

e Maximum external quantum efficiency.

f CIE at 20 mA/cm².



Fig. 1. (a) TGA curves of DPACTPI, DPACPhTPI and DPACFPPI; (b) DSC curves of DPACTPI, DPACPhTPI and DPACFPPI.

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Scheme 1. Synthetic routes and Chemical Structures of the Materials: (a) $Pd(OAc)_2$, $[(t-Bu)_3PH]BF_4$, *t*-BuONa, toluene, 110 ; (b) toluene, ethanol, $Pd(PPh_3)_4$, $K_2CO_3(2.0 \text{ M})$, 100 ; (c) NH₄OAc, AcOH, 120 .



Fig. 2. Optimized molecular geometries and calculated spatial distributions of the HOMO and LUMO of **DPACTPI**, **DPACPhTPI** and **DPACFPPI**.

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Scheme 2. Energy-level diagram of the materials used in the devices.



Fig. 3. (a) Room-temperature UV-Vis absorption spectra and PL spectra in dilute CH₂Cl₂ solution and (b) PL spectra in neat films for **DPACTPI**, **DPACPhTPI** and **DPACFPPI**.



Fig. 4. Cyclic voltammograms of **DPACTPI**, **DPACPhTPI** and **DPACFPPI** at room temperature with a scan rate of 100 mV/s.



Fig. 5. Current density versus voltage characteristic of the hole-only and electron-only devices for DPACTPI, DPACPhTPI and DPACFPPI.



Fig. 6. (a) The current density-voltage-luminance (I-V-L), (b) EL spectra at 20 mA/cm², (c) current density-current efficiency-power efficiency and (d) EQE-current density characteristics for blue devices **I**, **II** and **III**.



Fig. 7. (a) The current density-voltage-luminance (I-V-L), (b) EL spectra at 20 mA/cm², (c) current density-current efficiency-power efficiency and (d) EQE-current density characteristics for blue devices **IV**, **V**, **VI**, **VII** and **VIII**.



Fig. 8. NTOs analyses and TDDFT calculated energy levels of DPACPhTPI.

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Highlights

Three new deep-blue emitters were designed and synthesized.

The highly twisted conformation inhibits π - π intermolecular interactions and results in a large blueshift in solid state.

Nondoped OLED based on **DPACPhTPI** achieves a maximum EQE of 3.50% with a CIE coordinate of (0.156, 0.047).

A MARINE CERTIFICATION OF THE SECOND