**Electronic Supplementary Information** 

# Non-doped deep blue emitters based on twisted phenanthroimidazole derivatives for organic light-emitting devices (CIE $y \approx 0.04$ )

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**OLEDs** 

### **SI-1. General Procedures**

<sup>1</sup>HNMR measurements were recorded with a Varian Gemin-400 spectrometer. Mass spectra were performed with a PE SCIEX APIMS spectrometer. Elemental analysis (C, H, N) was performed using a Vario EL III CHNS elemental analyzer. Absorption and photoluminescence spectra were determined with a Perkin-Elmer Lambda 2SUV-Vis spectrophotometer and a Perkin-Elmer LS50B Luminescence spectrophotometer. Density functional theory (DFT) B3LYP/6-31G (d) was used to optimize the structure. Theoretical calculation of the compound was carried out using the Gaussian03 program. Cyclic voltammetry was performed on a BAS 100 B/W electrochemical analyser. The electrolytic cell is constructed a glassy carbon working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel electrode (SCE) as the reference electrode were employed. The ferrocene/ferrocenium couple was used as the internal standard. 0.10 M TBAPF<sub>6</sub> was used as the supporting electrolyte and DCM as the solvent, respectively. Thermal gravity analysis (TGA) and differential scanning calorimetry (DSC) measurements were recorded with a TA Instrument TGAQ50 and a TA Instrument DSC2910 respectively. Diffraction Gemini E equipped with a graphite monochromator and ATLAS CCD detector (CrysAlis CCD, Oxford Diffraction Ltd) at room temperature.

#### SI-2. Synthesis

A one-step synthetic route was showed in **Scheme S1**, and all the compounds have a high yield, the final product chemical structure was fully confirmed by mass spectrometry, <sup>1</sup>HNMR spectrometry. The starting material 1, 2 and 3was prepared as reported previously.<sup>1</sup>

# 2'-methyl-N,N-diphenyl-4'-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1'-biphenyl]-4-amine (4)

The compound 1 (1.48 g, 3.20 mmol), (4-(diphenylamino)phenyl)boronic acid (1.10 g, 3.84 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.17 mmol), and K<sub>2</sub>CO<sub>3</sub> aqueous (2 M, 10 mL) in toluene (20 mL) and ethanol (4 mL) was heated to reflux in a nitrogen atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation. The residue was further purified by column

chromatography (using CH<sub>2</sub>Cl<sub>2</sub>) as fluent to get pure white powder (1.80 g, 90%). 1H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.86 (d, J = 8.5 Hz, 1H), 8.80 (d, J = 8.3 Hz, 1H), 7.87 (s, 1H), 7.83 – 7.68 (m, 4H), 7.64 (d, J = 7.1 Hz, 3H), 7.47 (s, 1H), 7.40 – 7.28 (m, 4H), 7.23 (t, J = 8.8 Hz, 3H), 7.20 – 7.01 (m, 7H), 2.34 (s, 3H). MS (ESI) (m/z): Calculated for C<sub>46</sub>H<sub>33</sub>N<sub>3</sub>: 627.27 Found [M+H]<sup>+</sup> : 628.2743. And calculated for C<sub>46</sub>H<sub>33</sub>N<sub>3</sub>: C, 88.01; H, 5.30; N, 6.69; Found: C, 87.34; H, 4.97; N, 6.56.

## 4'-(1-(4-(tert-butyl)phenyl)-1H-phenanthro[9,10-d]imidazol-2-yl)-2'-methyl-N,N-diphenyl-[1,1'-biphenyl]-4-amine (5)

The compound 2 (1.52 g, 2.93 mmol), (4-(diphenylamino)phenyl)boronic acid (1.00 g, 3.49 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.20 g, 0.28 mmol), and K<sub>2</sub>CO<sub>3</sub> aqueous (2 M, 10 mL) in toluene (20 mL) and ethanol (4 mL) was heated to reflux in a nitrogen atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation. The residue was further purified by column chromatography (using CH<sub>2</sub>Cl<sub>2</sub>) as fluent to get pure white powder (1.80 g, 90%). 1H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.88 (d, J = 8.2 Hz, 1H), 8.83 (d, J = 8.0 Hz, 1H), 7.93 (s, 2H), 7.85 (s, 2H), 7.77 (d, J = 8.5 Hz, 6H), 7.56 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 7.3 Hz, 2H), 7.36 – 7.21 (m, 8H), 7.20 – 7.03 (m, 8H), 2.32 (s, 3H), 1.49 (s, 9H). MS (ESI) (m/z): Calculated for C<sub>50</sub>H<sub>41</sub>N<sub>3</sub>: 683.33 Found [M+H]<sup>+</sup> : 684.3365. And calculated for C<sub>50</sub>H<sub>41</sub>N<sub>3</sub>: C, 87.81; H, 6.04; N, 6.14; Found: C, 85.78; H, 5.76; N, 5.84.

## 4-(2-(4'-(diphenylamino)-2-methyl-[1,1'-biphenyl]-4-yl)-1H-phenanthro[9,10-d]imidazol-1yl)benzonitrile (6)

The compound 3 (1.51 g, 3.10 mmol), (4-(diphenylamino)phenyl)boronic acid (1.08 g, 3.72 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.18 g, 0.252 mmol), and K<sub>2</sub>CO<sub>3</sub> aqueous (2 M, 10 mL) in toluene (20 mL) and ethanol (4 mL) was heated to reflux in a nitrogen atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporation. The residue was further purified by column chromatography (using CH<sub>2</sub>Cl<sub>2</sub>) as fluent to get pure white powder (1.30 g, 65%). 1H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.85 (dd, J = 28.6, 8.2 Hz, 2H), 8.05 (d, J = 8.2 Hz, 2H), 7.94 – 7.65 (m, 7H), 7.42 (dd, J = 17.4, 9.7 Hz, 3H), 7.32 (dd, J = 15.3, 7.8 Hz, 5H), 7.25 (d, J = 8.5 Hz, 2H), 7.20 – 7.00 (m, 8H), 2.37 (s, 3H).MS (ESI) (m/z): Calculated for C<sub>47</sub>H<sub>32</sub>N<sub>4</sub>: 652.26 Found [M+H]<sup>+</sup>:

653.2692. And calculated for  $C_{47}H_{32}N_4$ : C, 86.48; H, 4.94; N, 8.58; Found: C, 84.65; H, 4.87; N,

8.25.



Scheme S1. Molecular structure and synthetic route of mtp, Tmtp and Cmtp.

## SI-3. Thermal properties



Figure S1. TGA and DSC (the inset) curves of mtp, Tmtp and Cmtp



SI-4. Time-resolved emission decays

Figure S2. Decay profile of mtp, Tmtp and Cmtp in 2-MeTHF.



Figure S3. Decay profile of mtp, Tmtp and Cmtp in thin film.

#### SI-5. Lippert-Mataga calculation

One reliable way to explore the influence of solvent environment on the optical property of our compounds can be understood using the Lippert-Mataga equation,<sup>2</sup> a model that describes the interactions between the solvent and the dipole moment of solute:

$$hc(\upsilon_a - \upsilon_f) = hc(\upsilon_a^o - \upsilon_f^o) + \frac{2(\mu_e - \mu_o)^2}{a^3}f(\varepsilon, n)$$

where  $\Delta f$  is the orientational polarizability of solvents,  $\mu_e$  is the excited-state dipole moment,  $\mu_o$  is the ground-state dipole moment, which could be estimated from a long-range-correction DFT calculation (mtp: 4.4D Tmtp: 5.1D Cmtp: 1.1D);  $\varepsilon$  and n are the solvent dielectric and the solvent refractive index, respectively; *a* is the solvent cavity (Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density ( $d = 1.0 \text{ g/cm}^3$ );  $f(\varepsilon,n)$  and a can be calculated respectively as follows:

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad a = (\frac{3M}{4N\pi d})^{1/3}$$

For mtp, Tmtp and Cmtp in moderately and highly polar solvents, the  $\mu_e$  values were determined to be 19.36D, 18.99D and 20.38D, which is larger than that of the reported LE-emitting BPA-BPI molecule (11 D), <sup>3</sup> but smaller than that of a typical CT molecule such as dimethylaminobenzonitrole (23 D).<sup>2</sup> Obviously, the large  $\mu_e$  should not be treated as the usual LE, suggesting a considerable contribution from the CT component in the emissive state. The result explains the three compounds may be HLCT molecules. **Figure S4** (a), (b) and (c) show the linear Lippert-Mataga plots with the slope values of 17068 cm<sup>-1</sup> (R  $\approx$  0.90) for mtp, 15482 cm<sup>-1</sup> (R  $\approx$ 0.91) for Tmtp, and 18208 cm<sup>-1</sup> (R  $\approx$  0.90) for Cmtp.



Figure S4. PL spectra of mtp, Tmtp and Cmtp in solvents of different polarities.

		mtp Tmtp			Cmty			)		
Solvents	$\Delta f$	$\nu_a$	$\nu_{\rm f}$	$\nu_a$ - $\nu_f$	$\nu_a$	$\nu_{\rm f}$	$v_a$ - $v_f$	$\nu_{a}$	$\nu_{\mathrm{f}}$	$\nu_a$ - $\nu_f$
		(nm)	(nm)	(cm <sup>-1</sup> )	(nm)	(nm)	(cm <sup>-1</sup> )	(nm)	(nm)	(cm <sup>-1</sup> )
Hexane	0.0012	335	398	4725.12	335	397	4661.83	344	410	4679.52
Trimethylamine	0.048	337	406	5043.05	338	406	4955.26	344	422	5373.09
Isopropyl ether	0.145	338	408	5252.10	335	407	5280.72	342	425	5710.35
Ether	0.167	333	411	5699.13	333	410	5639.79	330	438	6938.54
Ethyl acetate	0.2	333	422	6333.35	334	422	6187.15	331	445	7484.21
THF	0.21	335	423	6265.84	336	423	6121.24	333	444	7507.51
Dichloromethane	0.217	335	443	7019.70	335	442	6967.45	335	455	8800.11
DMF	0.276	334	452	7816.23	336	450	7539.68	332	479	9199.98
Acetone	0.284	337	442	6997.86	338	440	6858.53	340	466	9200.23
Acetonitrile	0.305	330	455	8373.21	332	454	8094.05	329	483	9430.78

Table S1. Solvatochromic UV-PL data for Lippert-Mataga model.





Figure S5. Solvatochromic Lippert–Mataga models of mtp, Tmtp and Cmtp.

# SI-6. Cyclic voltammetry (CV)



Figure S6. Cyclic voltammograms of mtp, Tmtp and Cmtp in CH<sub>2</sub>Cl<sub>2</sub>

### SI-7. Device fabrication and measurement

Pre-patterned indium tin oxide (ITO) glass substrates with asheet resistance of 15  $\Omega$  per square were cleaned with isopropyl alcohol and Decon 90 solution, then rinsed in deionized waterand dried in an oven. After a 15 min UV-ozone treatment, the ITO substrates were immediately transferred into a deposition chamber with a base pressure of 5 × 10<sup>-7</sup> torr for organic and cathode depositions. Organic materials were deposited viathermal deposition at a rate of 1 Å s<sup>-1</sup>, while the cathodes were completed via deposition of LiF (0.1 – 0.2 Å s<sup>-1</sup>) and Al (5 – 6 Å s<sup>-1</sup>) successively. Electroluminescent spectra and the corresponding (CIE) coordinates were measured with a Spectrascan PR650 photometer. Current–voltage–luminance (*J–V–L*) characteristics were recorded with a Keithley 2400 Sourcemeter under ambient atmosphere without device encapsulation.

#### **SI-8.** Device architectures



Figure S7. The nondoped and doped device architectures



SI-9. The EL spectra of all devices at different voltage

Figure S8. The EL spectra of the nondoped devices.

## SI-10. Luminescence-current density curve of doped device

The EL intensity had a linear relationship with current density (Figure S8), demonstrating the contribution from TTA is insignificant.<sup>1</sup>



Figure S9. Luminescence-current density curve of doped device.

SI-11. EL performance of device based on other high-performance deep blue OLEDs

OLEDs (CIE y < 0.06).											
Emitter	V <sub>on</sub> <sup>a</sup> (V)	EQE <sup>b</sup> (%)	CE <sup>c</sup> (cd/A)	PE <sup>d</sup> (lm/W)	λ <sub>max</sub> e (nm)	CIE (x, y)	Ref				
mtp	3.0	3.89	2.11	2.09	436	(0.15, 0.05)	This work				
Tmtp	3.3	3.00	1.24	1.14	436	(0.15, 0.04)	This work				
mTPA-PPI	3.2	3.33	0.84	0.48	404	(0.161, 0.049)	4				
PPI-F-TPA	4.2	3.03	1.35	1.0	425	(0.16, 0.05)	5				
SIPIM	5.5	2.4	0.8	-	416	(0.157, 0.041)	6				
DPPP	4.0	2.2	0.74	-	396	(0.160, 0.041)	7				
m-PTPAPI	-	2.39	0.78	0.72	-	(0.15, 0.05)	8				

Table S2. EL performance of device based on mtp, Tmtp and other high-performance deep blue

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