# Synergistic effects of hydrogen-bonds and hybridized excited-state observed for high efficiency, deep-blue fluorescent emitter with narrow emission in OLED applications

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#### SI-1. Synthesis of TPA-PPI-OH

Starting materials and solvents were purchased from Aldrich Chemical Co., or Energy Chemical Co., China. Tetrahydrofuran (THF) was distilled over metallic sodium and dimethylformamide (DMF) was distilled over calcium hydride before use. They were used without further purification.



Scheme S1 The synthetic route to TPA-PPI-OH.

#### Synthesis of 2-(4-bromophenol)-1-phenyl-1*H*-phenanthro[9,10-*d*]imidazole (M1):

A mixture of 4-bromo-2-hydroxybenzaldehyde (1.00 g, 4.98 mmol), aniline (2.32 g, 24.90 mmol), phenanthrenequinone (1.03 g, 4.98 mmol), and ammonium acetate (1.53 g, 19.92 mmol) with 20 mL acetic acid were added into a clean 100 mL flask and refluxed under argon in a 120 °C oil bath for 2 hours. After cooling down, the solid product was filtrated and washed with 30 mL (water/acetic acid=1/1) and 30 mL water successively, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous magnesium sulphate, purified by thin layer chromatography and the white solid product yield was 1.91 g (yield: 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  13.56 (s, 1H), 8.94 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.4 Hz, 1H), 7.77–7.68 (m, 5H), 7.58 (m, 3H), 7.52 (d, J = 8.4 Hz, 2H), 7.35 (t, J = 7.7 Hz, 1H), 7.09 (d, J = 8.3 Hz, 1H). MS (APCI): m/z: 465.1 [M + 1]<sup>+</sup>.

# Synthesis of *N,N*-Diphenyl-4'-phenol-(1-phenyl-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)biphenyl-4-amine (TPA-PPI-OH):

A mixture of 2-(4-bromophenol)-1-phenyl-1H-phenanthro[9,10-d]imidazole (M1) (1.00 g, 2.15 mmol), 4-(N,N-diphenylamino)-1-phenylboronic acid (0.75 g, 2.58 mmol), potassium carbonate (0.45 g, 3.23 mmol), tetrahydrofuran (20 mL) and deionized water (16 mL), with Pd(PPh<sub>3</sub>)<sub>4</sub> (0.10 g, 0.086 mmol) acting as catalyst was refluxed at 70 °C for 24 hours under argon atmosphere. After

the mixture was cooled down, 40 mL deionized water was added to the resulting solution and the mixture was extracted with dichloromethane for several times. The organic phase was dried over anhydrous magnesium sulphate. After filtration and solvent evaporation, the given residue was purified through silica gel column chromatography using dichloromethane/petroleum ether as eluent to give the product as white solid (1.12 g, 83 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  13.88 (s, 1H), 8.72–8.58 (m, 3H), 7.75–7.63 (m, 4H), 7.63–7.52 (m, 3H), 7.47–7.35 (m, 3H), 7.23–7.13 (m, 6H), 7.09–6.91 (m, 9H), 6.66 (d, J = 1.8 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  159.57, 148.49, 147.67, 147.56, 142.68, 139.14, 134.52, 133.53, 130.93, 130.65, 129.46, 129.32, 129.15, 128.45, 127.57, 127.51, 127.04, 126.54, 126.29, 126.06, 125.79, 125.23, 124.60, 124.20, 123.48, 123.23, 123.10, 122.63, 120.87, 116.39, 115.41, 111.60. MALDI-TOF-MS (m/z): C45H31N3O, 629.2511. Anal. calcd. for C45H31N3O: C, 85.83; H, 4.96; N, 6.67; O, 2.54. Found: C, 85.80; H, 4.97; N, 6.65; O, 2.58.



14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (nom)



Fig. S1 <sup>1</sup>H NMR (top) and <sup>13</sup>C NMR (bottom) spectra of TPA-PPI-OH in CDCl<sub>3</sub>.

## SI-2. Molecular structure and crystal packing of TPA-PPI-OH

Table S1 Crystal data and structural refinement for TPA-PPI-OH crystal.

Compound reference	clear light yellow TPA-PPI-OH crystal
Chemical formula	C45 H31 N3 O
Formula weight	629.73
Crystal system	Triclinic
a/Å	10.6652(3)
<i>b</i> / Å	10.8218(4)
c/ Å	14.7723(6)
α/°	89.128(3)
β/°	76.181(3)
$\gamma^{/\circ}$	73.418(3)
Unit cell volume/ Å3	1584.20(10)
Temperature/K	100.0(8)
Space group	P-1
Ζ	2
Density (calculated) /g cm <sup>-3</sup>	1.320
F(000)	660
Theta range for data collection	3.086 to 67.076 deg.
Index ranges	-6<=h<=12, -12<=k<=12, -17<=l<=17

Reflections measured	14110
Independent reflections	8692
Rint	0.0237
Absorption correction	multi-scan
Refinement method	none
Data / restraints / parameters	5552 / 0 / 443
Goodness-of-fit on $F^2$	1.037
Final $R_l$ values $(l > 2\sigma(l))$	0.0342
Final $wR(F^2)$ values ( $I > 2\sigma(I)$ )	0.0862
Final $R_I$ values (all data)	0.0377
Final $wR(F^2)$ values (all data)	0.0883
CCDC number	1867826

### SI-3. Theoretical calculations



Fig. S2 Energy levels of the first five singlet and triplet excited states in TPA-PPI-OH.

### SI-4. The photophysical properties

The properties of ground state  $(S_0)$  and the lowest singlet excited state  $(S_1)$  can be better understood through solvatochromic experiment. We use the Lippert-Mataga equation to explore the influence of solvent environment on the optical property of our materails, the model can describes the interaction between the solvent and the dipole moment of solute:

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3}f(\varepsilon, n)$$

where f is the orientational polarizability of the solvent,  $v_a^0 - v_f^0$  corresponds to the Stokes shifts when f is zero,  $\mu_e$  is the excited state dipole moment,  $\mu_g$  is the ground-state dipole moment; a is the solvent cavity (Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density (d = 1.0 g cm<sup>-3</sup>);  $\varepsilon$  and n are the solvent dielectric and the solvent refractive index, respectively;  $f(\varepsilon, n)$  and a can be calculated respectively as follows:

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

The relationships between stokes shift and solvent polarity are presented in Fig. 2b, the corresponding  $\mu_e$  was estimated to be 8.3 Debye (Slope = 2790, R = 0.90) and 19.2 Debye (Slope = 14959, R = 0.92) for TPA-PPI-OH. The detailed data are listed in Table S1.



**Fig. S3** UV-vis (a) and PL (b) spectra of TPA-PPI-OH, measured in different solvents with increasing polarity (the orientational polarizability of solvents (*f*) Hexane: 0.0012; Triethylamine: 0.048; Butyl ether: 0.096; Isopropyl ether: 0.145; Ethyl ether: 0.167; Ethyl acetate: 0.200; Tetrahydrofuran: 0.210; Dichloromethane: 0.217; Acetone: 0.284; Acetonitrile: 0.305).

 Table S2 Detailed absorption and emission peak positions and fluorescence quantum efficiency of

 TPA-PPI-OH in different solvents.

Solvents	n	f (ɛ, n)	TPA-PPI-OH				
			$\lambda_{abs}$	$\lambda_{em}$	$v_a$ - $v_f$	$arPhi_{ m F}$	
			(nm)	(nm)	(cm <sup>-1</sup> )	(%)	
Hexane	1.375	0.0012	375	411	2336	78	
Triethylamine	1.401	0.048	375	415	2570	55	
Butyl ether	1.399	0.096	377	417	2544	67	
Isopropyl ether	1.368	0.145	375	418	2743	64	
Ethyl ether	1.352	0.167	375	420	2857	83	
Ethyl acetate	1.372	0.200	376	439	3817	86	
Tetrahydrofuran	1.407	0.210	377	442	3901	89	
Dichloromethane	1.424	0.217	379	453	4310	61	
Acetone	1.359	0.284	376	457	4714	52	
Acetonitrile	1.344	0.305	376	469	5274	50	

 $\lambda_{abs}$  = absorption maximum,  $\lambda_{em}$  = emission maximum,  $\Phi_F$  = fluorescence quantum yield.



Fig. S4 PL spectra of TPA-PPI and TPA-PPI-OH, measured in different solvents with increasing polarity.



Fig. S5 Lifetime measurement of TPA-PPI-OH in three solutions and neat film. (The concentrations of the solutions are  $1 \times 10^{-5}$  mol L<sup>-1</sup>.)



Fig. S6 Fluorescence and phosphorescence of TPA-PPI-OH in THF at 77 K. (The  $\Delta E_{ST}$  of TPA-PPI-OH is calculated to be 0.55 eV.)





Fig. S7 (a) TGA and DSC (the inset) curves of TPA-PPI-OH. (b) Cyclic voltammograms of TPA-

PPI and TPA-PPI-OH.

### SI-6. Device performance



Fig. S8 Normalized EL spectra of the non-doped device from 3 to 7 V.

To further improve the device stability, we have measured the TPA-PPI-OH based device with encapsulation, the maximum efficiency decreased as compared with that in ambient atmosphere, but the roll-off was improved (Fig. S9 and Table S3 in Supporting Information). The reasons for the reduced efficiency may be attributed to the encapsulation, for examples, the encapsulated construction may influence the optical output of the device, the encapsulation adhesive may damage the cathode of the device. Because of the encapsulation, the degradation rate of the device becomes slower, which is beneficial to the device stability.



Fig. S9 External quantum efficiency–luminance curves of devices measured after the encapsulation and in ambient atmosphere.

						EL performance at		e at EL performance at 1000 cd m <sup>-2</sup>	
Emitters	$V_{\text{turn-on}}^{a}$	$CE_{max}^{b}$	EQE <sub>max</sub> <sup>d</sup>	$\lambda_{\text{EL,max}}^{d} \lambda_{\text{EL,max}}^{e} \text{CIE}^{f}$ 100 c		cd m <sup>-2</sup>			
	[V]	[cd A <sup>-1</sup> ]	[%]	[nm]	[x, y]	EQE	CE	EQE	CE
						[%]	[cd A <sup>-1</sup> ]	[%]	[cd A <sup>-1</sup> ]
TPA-PPI-OH	3.0	5.01	5.98	454	(0.15, 0.11)	5.83	4.91	5.42	4.65

4.65

Table S3 EL performance of TPA-PPI-OH measured after the encapsulation.