## **Supporting information**

# Highly efficient violet-blue OLED with Rec.2020 CIEy based on orthogonal phenanthroimidazole-substituted 1,2,4-triazole derivative

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## **Experimental Section**

#### 1. Materials and synthesis

All the reagents and solvents were used as received without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR measurements were recorded by Bruker AVANCE NEO 400 spectrometer with tetramethylsilane (TMS) as the internal standard and CDCl<sub>3</sub> as solvent. MALDI-TOF-MS mass spectra were obtained from High Resolution Quadrupole Time of Flight Tandem Mass Spectrometer (TOF-MS).

### 4-(4-bromophenyl)-3-(4-fluorophenyl)-5-phenyl-4H-1,2,4-triazole (2)

To a stirred solution of benzohydrazide (2.50 g, 18.37 mmol) and trimethylamine (5 mL) in dichloromethane (50 mL) was added 4-fluorbenzoyl chloride (3.19 g, 20.19 mmol) dissolved in dichloromethane (25 mL) slowly. The resulting mixture was stirred for 5 h at room temperature. After stripping off solvent under vacuum, the solid residue was purified by recrystallization using ethanol to afford a compound 1. Then, a mixture of compound 1 (4.35 g, 16.85 mmol), PCl<sub>5</sub> (6.93 g, 33.70 mmol) and toluene (40 mL) was stirred under N<sub>2</sub> at 90 °C for 12 h. Subsequently, 4-bromoaniline (7.20 g, 42.13 mmol) dissolved in DMF (40 mL) was added to the mixture by dropping funnel. The resulting mixture was heated at 150 °C overnight. After adding aqueous of HCl (100 mL, 2 M), the mixture was stirred for an additional 1 h. The precipitated solid was collected by filtration, dried in vacuo, and then recrystallized from ethyl acetate to afford compound 2 (4.70 g, 71.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.52 (m, 2H), 7.44 – 7.29 (m, 7H), 7.07 – 6.98 (m, 4H).

## 4-(4-bromophenyl)-3-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-5-phenyl-4H-1,2,4-triazole (3)

The mixture of compound 2 (2.00 g, 5.09 mmol), 3,6-di-tert-butyl-9H-carbazole (1.43 g, 5.10 mmol), cesium carbonate (3.32 g, 10.18 mmol) and DMF (40 mL) was stirred at 150 °C for 10 h under nitrogen atmosphere. After cooled to room temperature, the mixture was pour into water, extracted with  $CH_2Cl_2$ , separated, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was subject to column chromatography over silica gel using EOA/CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford

a white solid (2.70 g, 81.8%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 – 8.09 (m, 2H), 7.69 – 7.60 (m, 4H), 7.59 – 7.53 (m, 2H), 7.51 – 7.40 (m, 5H), 7.39 – 7.33 (m, 4H), 7.18 – 7.10 (m, 2H), 1.46 (s, 18H). TOF-MS (ESI) m/z calcd for C40H37BrN4: 652.2202; [M + H]<sup>+</sup> found: 653.2200.

## 2-(4'-(3-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-5-phenyl-4H-1,2,4-triazol-4-yl)-[1,1'-biphenyl]-4-yl)-1-phenyl-1H-phenanthro[9,10-d] imidazole (FBITAZtbuCZ)

A mixture of compound 3 (0.90 g, 1.37 mmol), 1-phenyl-2-(4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1H-phenanthro[9,10-d]imidazole (0.75 g, 1.51 mmol), K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 M, 1.5 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.047 g, 0.041 mmol), toluene (50 mL) and ethanol (1.5 mL) was refluxed at 90 °C for 12 h under N2. After being cooled to room temperature, the crude product was concentrated and distilled water was added. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, separated, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/EOA(ethyl acetate/dichloromethane) as eluent to give a white solid (0.80 g, 61.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.91 (d, J = 7.8 Hz, 1H), 8.81 – 8.73 (m, 1H), 8.70 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 1.9 Hz, 2H), 7.78 – 7.42 (m, 22H), 7.42 – 7.22 (m, 8H), 7.17 (dd, J = 8.4, 1.3 Hz, 1H), 1.45 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.01, 154.22, 143.37, 141.57, 139.63, 138.69, 134.48, 130.35, 130.15, 130.01, 129.81, 129.46, 129.12, 128.90, 128.57, 128.49, 128.39, 128.22, 127.45, 126.91, 126.87, 126.41, 126.25, 125.89, 125.09, 124.20, 123.78, 123.67, 123.17, 122.86, 120.89, 116.30, 109.22, 34.76, 31.99. TOF-MS (ESI) m/z calcd for C67H54N6: 942.4410; [M + H]<sup>+</sup> found: 943.4532.

## 2. Experimental measurements

Thermal gravimetric analysis (TGA) was performed on a a Netzsch (209F1) thermogravimetric analyzer at a heating rate of 20 °C/minute under  $N_2$  protection. Differential scanning calorimetry (DSC) measurement was obtained on a Netzsch DSC (204F1) instrument. Cyclic voltammetry (CV) was measured by a CHI760D electrochemical workstation with standard three-electrode system (a glassy carbon

electrode as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgNO<sub>3</sub> electrode as the pseudo-reference electrode with Fc/Fc+ as the internal standard, which has an absolute HOMO level of -4.80 eV). The potential relative to Ag/AgNO<sub>3</sub> electrode obtained from CV measurement was eventually referenced against Fc+/Fc to calculate HOMO levels. Absorption and photoluminescence spectra were determined with Hitachi U-4100 absorption spectrometer and Hitachi F-4600 spectrophotometer, respectively. The absolute fluorescence quantum yield of neat film was measured by Hamamatsu C11347-11. The fluorescence and phosphorescence spectra were measured in dichloromethane via using liquid nitrogen after delay time of 0 and 1 ms on the Edinburgh FLS-980 with an EPL-340 optical laser at 77 K. The PL lifetime was measured on an FLS1000 spectrophotometer. Density functional theory (DFT) calculations were performed to predicate HOMO and LUMO energy levels by the Gaussian 09 program package. The ground state structure and the excited state energies were optimized and calculated with the B3LYP/6-31G (d) basis set.

## 3. Device fabrication and measurement

ITO coated glasses with a sheet resistance of 20  $\Omega$  m<sup>-2</sup> were used as the substrate and cleaned by detergents and deionized water, then dried for 30 min in an oven at 120 °C. The ITO glasses were irradiated in UV-zone for 7 min and transferred into a deposition chamber. When the pressure is less than 2 × 10<sup>-4</sup> Pa, the devices were fabricated. The evaporation rates were detected by a frequency counter and calibrated by a Dektak 6 M profiler (Veeco). The evaporating rates of organic layers, lithium fluoride, and aluminum are 1-1.5, 0.2, and 5-10 Å s<sup>-1</sup>, respectively. A mask with an array of 3 mm × 3 mm openings was used to define the cathode. The electroluminescent (EL) spectra were measured with an optical analyzer FIAME-S-VIS-NIR photometer, and the current-voltage characteristics were recorded with a constant source of Keithley 2450 source meter and LS160 luminance meter. Supposing the light emitted by OLEDs accord with the Lambertian distribution, the EQEs can be calculated from the EL spectra, luminance, and current density. All the results were measured in the forwardviewing direction.



Fig. S1-1. <sup>1</sup>H NMR of compound 2 (CDCl<sub>3</sub>, 400 MHz).



Fig. S1-2. <sup>1</sup>H NMR of compound 3 (CDCl<sub>3</sub>, 400 MHz).



Fig. S1-3. <sup>1</sup>H NMR of compound PI-TAZ-tbuCZ (CDCl<sub>3</sub>, 400 MHz).



**Fig. S1-4.** <sup>13</sup>C NMR of compound **PI-TAZ-tbuCZ** (CDCl<sub>3</sub>, 101 MHz).

Compound	λ <sub>abs</sub> (nm) sol <sup>a</sup> /film <sup>b</sup>	λ <sub>PL</sub> (nm) solª/film <sup>b</sup>	PLQY° (%)	HOMO/LUMO <sup>d</sup> (eV)	E <sup>e</sup> (eV)	$\frac{E_{S1}^{f}}{E_{T1}^{g}}$ (eV)	Т <sub>d</sub> <sup>h</sup> (°С)
PI-TAZ- tbuCZ	333/336	428/434	59.7	-5.46/-2.36	3.10	3.02/2.41	459

Table S1. Photophysical, electrochemical and thermal properties of PI-TAZ-tbuCZ.

<sup>a</sup> Measured in solution of dichloromethane. <sup>b</sup> Measured in thin film. <sup>c</sup> The fluorescent quantum yield in film. <sup>d</sup> HOMO level energy measured by cyclic voltammetry method; LUMO calculated from the equation: LUMO = HOMO + optical band gap ( $E_g$ ). <sup>e</sup> Optical energy gap measured from the absorption onset in film. <sup>f</sup> Calculated by the highest energy peak of low temperature fluorescence spectrum in dichloromethane at 77 K. <sup>g</sup> Calculated by the highest energy peak of low temperature phosphorescence spectrum in dichloromethane at 77 K with 1 ms of delaying. <sup>h</sup> Decomposition temperature ( $T_d$ ) at 5% weight reduction.



Fig. S2. Frontier molecular orbitals and energy levels of the compound PI-TAZ-tbuCZ.



Fig. S3. The natural transition orbitals (NTOs) of  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow S_2$ , and  $S_0 \rightarrow S_3$  of **PI-TAZ-tbuCZ**. The molecular geometry is optimized using B3LYP/6-31g (d) method, and the excited state properties are calculated using B3LYP /6-31g (d) method.

	Singlet	<b>Triplet States</b>		
	Energy Level (eV)	Oscillator Strength	Energy Level (eV)	
1	3.148	0.0024	2.559	
2	3.292	0.8506	2.847	
3	3.449	0.5026	2.967	
4	3.693	0.0000	3.137	
5	3.742	0.0025	3.145	
6	3.798	0.0007	3.257	
7	3.840	0.0222	3.287	
8	3.875	0.0010	3.358	
9	3.884	0.0001	3.373	
10	3.894	0.0289	3.575	

Table S2. Calculated vertical excitation energy of the first ten excited-states of PI-TAZ-tbuCZ.



Fig. S4. Normalized Absorption spectra of PI-TAZ-tbuCZ in different solvents.

## Lippert-Mataga equation

The properties of ground state  $(S_0)$  and the lowest singlet excited state  $(S_1)$  can be better understood through solvatochromic experiment. One reliable way to explore the influence of solvent environment on the optical property of our sample is by using the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of solute:

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

where *f* is the orientational polarizability of solvents,  $\mu_e$  is the dipole moment of excited state,  $\mu_g$  is the dipole moment of ground state; a is the solvent cavity (Onsager) radius;  $\epsilon$  and n are the solvent dielectric and the solvent refractive index, respectively.  $f(\epsilon,n)$  and a can be calculated respectively as follows:

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

Solvents	3	n	<i>f</i> (ε, n)	$\lambda_{abs}$	$\lambda_{PL}$	$v_{a-f}$
Hexane	1.9	1.375	0.0012	335	417	5869.93092
Toluene	2.38	1.494	0.014	337	424	6088.684844
Triethylamine	2.42	1.401	0.048	335	420	6041.222459
<b>Butyl ether</b>	3.08	1.399	0.096	335	422	6154.063804
Isopropyl ether	3.88	1.368	0.145	333	419	6163.681581
Ethyl ether	4.34	1.352	0.167	333	419	6163.681581
Ethyl acetate	6.02	1.372	0.2	332	420	6310.958118
Tetrahydrofuran	7.58	1.407	0.21	333	423	6389.368091
Dichloromethane	8.93	1.424	0.217	333	428	6665.544049
Dimethylformamide	37	1.427	0.276	331	434	7170.005708
Acetone	20.7	1.359	0.284	326	427	7255.642879
Acetonitrile	37.5	1.344	0.305	326	431	7472.990477

 Table S3. The data about absorption and emission peak positions of PI-TAZ-tbuCZ

 in different solvents.



**Fig. S5.** The fluorescence and phosphorescence spectra of **PI-TAZ-tbuCZ** in dilute dichloromethane at 77 K.



**Fig. S6.** The electrochemical CV curve for **PI-TAZ-tbuCZ**. The oxidation potential was measured in dichloromethane solution.



**Fig. S7.** The schematic diagram of the structure of OLEDs (ITO/HATCN (20 nm)/ TAPC (50 nm)/TCTA (10 nm)/EML (20 nm)/TmPyPb (40 nm)/LiF (1 nm)/Al) and the energy levels of the materials.



**Fig. S8.** The Normalized UV–vis spectrum of **PI-TAZ-tbuCZ** and the PL spectrum of CBP in films.



Fig. S9. Measured p-polarized PL apectra of CBP: 3wt% PI-TAZ-tbuC in film as a function of the emission angle and simulated curves with different  $\Theta_{//}$ .



Fig. S10. Luminance-current density characteristic of PI-TAZ-tbuCZ based OLED.



Fig. S11. The Transient EL decay curves of PI-TAZ-tbuCZ based OLED at different

voltages.