# **Supplementary Information**

# Orthogonal Anthracene and Pyrene Derivatives for Efficient

## **Pure Deep-Blue Organic Light-Emitting Diodes**

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### 1. Materials and Synthesis

**Materials:** All materials and reagents, unless otherwise specified, were purchased from commercial suppliers and used without further purification.

Structure characterization instruments: <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ultra Shield Plus 400 MHz instrument (400 MHz for <sup>1</sup>H and 101 MHz for <sup>13</sup>C, respectively) with dimethyl sulfoxide (DMSO)- $d_6$  or chloroform-d (CDCl<sub>3</sub>) as the solvent and tetramethylsilane (TMS,  $\delta = 0.00$  ppm) as the internal standards. Molecular mass was determined by Bruker Ultraflextreme MALDI-TOF mass spectrometer.

#### Synthesis of 1-pyrenylboronic acid (1)

To a freshly distilled tetrahydrofuran (THF) (40 mL) solution of 1-bromopyrene (2.00 g, 7.11 mmol) at -78 °C under a nitrogen atmosphere, *n*-butyl lithium (5.3 mL, 8.53 mmol, 1.6 M in hexane) was added dropwise. After lithiation at -78 °C for 1 h, trimethyl borate (1.33 g, 12.80 mmol) was added dropwise into the reaction mixture. After this, the reaction mixture was allowed to warm to room temperature and stirred overnight, followed by adding 2 N hydrogen chloride solution (15 mL) under ice cooling, and further stirring for 24 h. The reaction mixture was extracted with ethyl acetate (EA) and then the organic layers were collected and dried with anhydrous sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>). The organic solvents were removed under reduced pressure and the residue was crystallized from *n*-hexane to afford 1.43 g of the yellow solid.<sup>[11]</sup> Yield: 81%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  (ppm): 8.72 (d, *J* = 9.2 Hz, 1H), 8.55 (s, 2H), 8.31-8.25 (m, 4H), 8.21-8.16 (m, 3H) 8.09-8.05 (t, *J* = 7.6 Hz, 1H).

#### Synthesis of 9,10-dibromo-2,6-di-tert-butylanthracene (2)

Compound **2** was synthesized by the following two steps. Firstly, anthracene (2.00 g, 11.22 mmol), *tert*-butyl alcohol (3.3 mL, 33.66 mmol), and trifluoroacetic acid (15 mL) were heated at reflux for 16 h. After cooling to the room temperature, the black crude mixture was treated with solid sodium bicarbonate. Then, the reaction was quenched with water and extracted with hexane. The organic layer was collected and dichloromethane (DCM) was added to obtain a clear solution which was then dried with

Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was removed under vacuum and the residue was treated with hexane in refrigeration. The white solid was filtered and washed with a small amount of cold hexane. Without further purification, the white solid was dissolved in chloroform (40 mL) and acetic acid (12 mL), and then *N*-bromosuccinimide (3.53 g, 19.85 mmol) was added to react for 5 h at room temperature. After that, the mixture was poured into a water bath and extracted with DCM. The organic layer was collected and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel to afford 3.85 g of compound **2** (yellow solid).<sup>[2]</sup> Yield: 77%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.54 (s, 1H), 8.52 (s, 1H), 8.48 (d, *J* = 1.6 Hz, 2H), 7.73 (dd, *J* = 9.2, 1.8 Hz, 1H), 1.51 (s, 1H).

#### Synthesis of 9,10-di(pyren-1-yl)anthracene (PyAnPy)

To a solution of compound 1 (2.20 g, 8.94 mmol), 9,10-dibromoanthracene (1.00 g, 2.98 mmol) and tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.35 g, 0.30 mmol) in toluene (70 mL), aqueous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (15 mL, 2 M) and ethanol (15 mL) were added. The reaction mixture was stirred at 90 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with water and extracted with EA. The organic layers were collected and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the organic solvents were removed under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel to afford the product as a yellow solid. Yield: 52%.<sup>[3-5]</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.48 (d, J = 7.7Hz, 2H), 8.33-8.30 (m, 4H), 8.27-8.20 (m, 6H), 8.09 (t, J = 7.6 Hz, 2H), 7.97 (d, J = 9.2 Hz, 2H), 7.61 (d, J = 9.1 Hz, 2H), 7.51 (dd, J = 6.8, 3.3 Hz, 4H), 7.23 (dd, J = 6.9, 4H).  ${}^{13}C{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  (ppm): 135.93, 134.19, 131.52, 3.2 Hz, 131.18, 131.05, 130.95, 129.52, 127.93, 127.76, 127.56, 127.33, 126.19, 125.87, 125.44, 125.36, 125.29, 125.00, 124.82. MALDI-TOF: m/z calcd for C<sub>46</sub>H<sub>26</sub> [M]+: 578.2035, found: 578.1314.

#### Synthesis of 1,1'-(2,6-di-*tert*-butylanthracene-9,10-diyl)dipyrene (PyTAnPy)

PyTAnPy was prepared in an identical synthetic procedure as for PyAnPy, except

that compound **2** (1.34 g, 2.98 mmol) was adopted instead of 9,10-dibromoanthracene. Yield: 59%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.38 (d, *J* = 7.7 Hz, 3H), 8.28 (d, *J* = 7.6 Hz, 3H), 8.22 (d, *J* = 6.6 Hz, 4H), 8.18 (d, *J* = 8.0 Hz, 6H), 8.07 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 9.3 Hz, 3H), 7.69 (d, *J* = 9.2 Hz, 3H), 1.57 (s, 18H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  (ppm): 136.30, 131.51, 131.01, 130.95, 130.06, 128.84, 127.62, 127.60, 127.50, 126.11, 125.80, 125.27, 125.08, 124.82, 124.54, 30.67, 25.61. MALDI-TOF: m/z calcd for C<sub>54</sub>H<sub>42</sub> [*M*]<sup>+</sup>: 690.329, found: 690.422.

### 2. Thermal Stabilities

Thermal properties of the deep-blue emitters were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA measurements were performed using a Perkin Elmer Pyris 6 under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup> from 34-800 °C. DSC analyses were performed on a Perkin Elmer Pyris Diamond DSC instrument under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>. Temperature at 5% weight loss was used as the decomposition temperature ( $T_d$ ). As shown in **Figure S1**, both materials showed good thermal stabilities with  $T_d$ s of 498 °C and 381 °C for **PyAnPy** and **PyTAnPy**, respectively. Meanwhile, **PyTAnPy** showed a high melting point of up to 339 °C.



Figure S1. (a) TGA and (b) DSC curves of PyAnPy and PyTAnPy.

## 3. Photophysical Properties

Ultraviolet-visible (UV-Vis) spectra were recorded on a Varian Cary 4000 UV-Visible spectrophotometer, while photoluminescent (PL) spectra were obtained on an Fluoromax-4 spectrophotometer. Transient PL decay curves were collected using an Edinburgh FLS 980 fluorescence spectrophotometer with a picosecond pulsed LED at room temperature under the excitation wavelength of 375 nm. The absolute photoluminescence quantum yield (PLQY) was obtained on an Edinburgh FLS980 fluorescence spectrophotometer with an integrating sphere. The lifetimes of the luminescence were figured out by fitting the luminescent intensity decay curve (I(t)) with a multi-exponential decay function in **Equation S1**:

$$I(t) = \sum_{i} A_{i} e^{\frac{t}{\tau_{i}}}$$
(S1)

The radiative  $(k_r)$  and non-radiative  $(k_{nr})$  decay rates were calculated from the **Equations S2 and S3**:

$$k_{\rm r} = 1 / \tau \qquad (S2)$$

$$k_{\rm nr} = \frac{1 - \emptyset_{\rm PL}}{\emptyset_{\rm PL}} k_{\rm r} \qquad (S3)$$

where  $\tau$  represents the fluorescent lifetime, which can be determined from the transient PL spectra.



Figure S2. UV-vis absorption and PL spectra of anthracene in 10<sup>-5</sup> M in toluene.



Figure S3. PL spectra of PyAnPy and PyTAnPy in solvents with different polarities. The concentration is  $\sim 10^{-5}$  M.



Figure S4. Lippert-Mataga diagrams of PyAnPy and PyTAnPy.

	$f(\varepsilon, \mathbf{n})^{\mathrm{a}}$	PyAnPy			PyTAnPy		
Solvents		$\lambda_a (nm)^b$	$\lambda_{f}(nm)^{c}$	$v_{\rm a} - v_{\rm f} ({\rm cm}^{-1})$	$\lambda_{a} (nm)^{b}$	$\lambda_{f}(nm)^{c}$	$v_{a^{-}r_{f}}(cm^{-1})$
Hexane	0.0012	396	431	2051	345	421	5233
Toluene	0.014	401	438	2107	348	427	5905
Dioxane	0.022	398	431	1924	348	433	5641
Triethylamine	0.048	397	431	1987	347	438	5987
Chlorobenzene	0.143	400	437	2117	350	437	5688
Chloroform	0.149	400	441	2324	349	435	5978
Diethyl Ether	0.167	397	427	1770	345	426	5511
Ethyl Acetate	0.200	397	431	1987	346	430	5646
Dichloromethane	0.217	400	442	2376	348	432	5587

**Table S1.** Solvatochromic UV-PL data of **PyAnPy** and **PyTAnPy** for Lippert-Matagamodel.

<sup>a</sup>  $f(\varepsilon, n)$ : solvent orientation polarizability. <sup>b</sup>  $\lambda_a$ : absorption onset. <sup>c</sup>  $\lambda_f$ : maximum emission peak.



Figure S5. Transient PL decay curves of PyAnPy and PyTAnPy in toluene.

## 4. Electrochemical Properties

Cyclic voltammetry (CV) measurements were performed at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag<sup>+</sup>, referenced against ferrocene/ferrocenium (FOC), and a counter electrode (Pt wire) in acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) (0.1 M) at a sweeping rate of 100 mV s<sup>-1</sup>. Highest occupied molecular orbital (HOMO) energy level ( $E_{HOMO}$ ) of the compound was estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum) according to **Equation S4**:

$$E_{\text{HOMO}} = -\left(E_{\text{onset}}^{\text{Ox}} - E_{(\text{Fc/Fc}^+)} + 4.8\right) \text{eV}$$
(S4)

where  $E_{(Fc/Fc^+)}$  is the onset potential of oxidation wave of ferrocene (Fc) vs Ag/Ag<sup>+</sup> and  $E_{onset}^{Ox}$  is the onset potential of the oxidation wave of the materials deposited as thin films on the surface of the working electrode. Lowest unoccupied molecular orbital energy level ( $E_{LUMO}$ ) was estimated by adding the optical bandgap ( $E_g$ ) to the corresponding HOMO energy level as in **Equation S5**:



$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm g} \tag{S5}$$

Figure S6. Cyclic voltammograms of PyAnPy and PyTAnPy.

## 5. Device Fabrication and Measurements

Device Fabrication: Glass precoated with a 180 nm thick layer of indium tin oxide (ITO) was used as the device substrate, which has a sheet resistance of 10  $\Omega$  sq<sup>-1</sup>. The ITO substrates were first ultrasonicated for 50 min and then cleaned with detergents

and deionized water. Subsequently, all the substrates were dried in an oven at 120 °C for 20 min, treated with UV-ozone for 4 min, and finally transferred into a high-vacuum evaporator ( $<1\times10^{-5}$  Pa). All the organic materials were thermally evaporated onto the ITO substrates without breaking the vacuum.

Device Measurements: The current density-luminance-voltage properties were tested using a complete measurement system including a Keithley 2400 source meter and a LS-110 luminance meter. The EL spectra were collected using a Spectrascan PR650 spectrophotometer. The EQEs were calculated using the luminance intensity, current density, and EL spectra of the devices according to **Equation S6**.

$$EQE = \frac{\pi e \eta_{cd/A} \int \lambda p(\lambda) d\lambda}{hc K_m \int p(\lambda) \Phi(\lambda) d\lambda}$$
(S6)

where  $\eta_{cd/A}$  is the current efficiency (cd/A); *h* is the Planck constant; *c* is the speed of light in vacuum;  $\lambda$  is the wavelength (nm); *e* is the electron charge;  $p(\lambda)$  is relative electroluminescent intensity at each wavelength;  $\Phi(\lambda)$  is the Commission International del'Eclairage chromaticity (CIE) standard photopic luminous efficiency function; and  $K_{\rm m}$  is a constant of 683 lm/W.



**Figure S7**. The molecular structures of the materials used in the deep-blue devices based on **PyAnPy** and **PyTAnPy** emitters.



**Figure S8**. Comparison of EL spectra and PL spectra of 3 wt% and 5 wt% doped film for (a) **PyAnPy** and (b) **PyTAnPy** emitters.



Figure S9. EL spectra of PyAnPy- and PyTAnPy-doped devices at different voltages.



Figure S10. Luminance-current density curves of the deep-blue devices based on **PyAnPy** and **PyTAnPy** emitters. (a) High injection current. (b) Low injection current.

## 6. References

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## 7. NMR Spectra



Figure S11. <sup>1</sup>H NMR spectrum of compound 1 in DMSO-*d*<sub>6</sub>.



Figure S12. <sup>1</sup>H NMR spectrum of compound 2 in CDCl<sub>3</sub>.



Figure S14. <sup>13</sup>C NMR spectrum of PyAnPy in CDCl<sub>3</sub>.







Figure S16. <sup>13</sup>C NMR spectrum of PyTAnPy in CDCl<sub>3</sub>.