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# **Supplementary Material for**

## "Pyrene based materials for exceptionally deep blue OLED's"

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### **S1. Experimental Details**

Commercially available reagents were used without further purification unless otherwise stated. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX250, Bruker DPX300 or Bruker AMX500 spectrometer. Mass spectra were obtained using field desorption ionization (FD) on a VG Instruments ZAB 2 SE-FPD. UV-visible spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature. Cyclovolatammetry was measured on a Princeton Applied Research Parstat 2273 instrument with anhydrous solvents under argon atmosphere.

The OLEDs were fabricated by thermal evaporation in a high vacuum ( $\approx 10^{-8}$  torr). Prior to deposition, the ITO substrates were cleaned with ultrapurified water, acetone, and isopropyl alcohol, and then dried in an oven at 80 °C. We used OLEDs with the structure of glass/ITO (150 nm)/ReO<sub>3</sub>(1 nm)/mCP (25 nm)/mCPPO1(10 nm)/mCPPO1:Py3 5wt%(30 nm)/TSPO1(25-40 nm)/LiF(0.7 nm)/Al (100 nm). All the devices were encapsulated immediately after deposition in a nitrogen atmosphere, using an epoxy glue and cavity glass lids. The active area of each device was 2 mm × 2 mm. The EQE of the OLED was calculated from the current density, luminance, and EL spectra data which were measured using a Keithley 2400 programmable source meter and SpectraScan PR650 (Photo Research).



Figure S2: Synthetic scheme.

### S1. Experimental details, continued

**3,6-Di-(tert-butyl)-9H-carbazole (1):** In a 250 mL flame dried flask, Carbazole (2.0 g, 12.0 mmol) was dissolved in 80 mL Dichloromethane (anhydrous). Tertiarybutylchloride (2.77 ml, 25.1 mmol) is added to the solution. The mixture is cooled to 0°C (ice bath). Aluminiumtrichloride (anhydrous) (1.59 g, 12.00 mmol) is added in Argon counter flow. The mixture is allowed to warm to room temperature and stirred for 16h.

The mixture was poured into ice-water (400 ml), extracted with Dichloromethane (3\*75 mL). The combined organic phases are dried with anhydrous MgSO<sub>4</sub>, after evaporation of the solvent the crude product was obtained. Repeated recrystallization from Hexane afforded the product as a white solid (4.2 g, yield: 66%)

**FD-MS** (8 KV): m/z 279.1 (100%); calcd 279.2.

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub> 300 MHz, ): δ.

<sup>13</sup>C-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 75 MHz):

**9-(3-bromophenyl)-3,6-di-tert-butyl-carbazole (3)**: In a 100 mL flame dried Schlenk-flask, 3,6-Di-(tert-butyl)-9*H*-carbazole (1) (1 g, 3.6 mmol), 1-Bromo-3-iodobenzene (0.55 ml, 4.3 mmol), Potassium carbonate (0.74 g, 5.4 mmol) and Copper iodide (136.3 mg, 0,72 mmol) were suspended in Dimethylformamide (35 ml, water free). The mixture was stirred under argon for 16 h at 150°C. After cooling to room temperature the mixture was poured on 400 mL ammonia solution (1 mol/L). The product was extracted with Dichloromethane (3\*50 ml). The combined organic layers were washed in succession with ammonia solution (300 ml, 1 mol/L), water (200 mL), brine (200 mL) and dried with Magnesium sulphate. After solvent evaporation the crude product was purified by column chromatography (SiO<sub>2</sub>; DCM/Hex 1:3). The product is obtained as a white solid (0.96 g, yield: 62%).

FD-MS (8 KV): m/z 433,14 (100%), calcd 433.3.

<sup>1</sup>**H-NMR** (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.46$  (s, 18H), 7.37 (d, J = 8.7 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.61 – 7.53 (m, 2H), 7.76 (t, J = 1.9 Hz, 1H), 8.16 (d, J = 1.9 Hz, 2H).<sup>1</sup>

<sup>13</sup>**C-NMR** (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 32.3, 35.2, 109.7, 116.9, 123.6, 124.1, 124.4, 125.9, 126.6, 130.2, 130.5, 131.7, 131.8, 136.1, 136.5, 139.5, 140.2, 144.0.

**Pyrene-2,7-bis(pinacolatoboronate)** (4).<sup>2</sup> Pyrene (8.0 g, 39.6 mmol), Bispinacolatodiborane (21.1 g, 83.0 mmol) [Ir(OMe)COD]<sub>2</sub> (1.0 g, 2,0 mmol) and 4,4'-di-tert-butyl-2,2'-bipyridine (1.1 g, 4 mmol) are placed in a 250 ml flame dried Schlenk flask. Cyclohexane (160 ml, water free) is added. The solution is stirred at 60°C, over night under an argon atmosphere. After cooling to room temperature the mixture is filtered through a silica plug (the plug is flushed with Dichloromethane). The solvent is evaporated; the crude product is purified by column-chromatography (SiO<sub>2</sub>; gradient DCM/Hex 1:2 to DCM). 4 is obtained as a white solid (9.7g, yield: 54%)

FD-MS (8 KV): m/z 454.4 (100%), calcd 454.2.

<sup>1</sup>**H-NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 250 MHz):  $\delta = 4.18$  (s, 12H), 8.55 (s, 4H).

<sup>13</sup>**C-NMR** (CD<sub>2</sub>Cl<sub>2</sub>, 175 MHz): δ = 111.8, 119.3, 120.8, 121.5, 123.5, 162.2.

**2,7-bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)pyrene (5).** In a 50 mL flame-dried Schlenk-flask 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (0.50 g, 1.1 mmol), 9-(3-bromophenyl)-3,6-di-tert-butyl-9H-carbazole (1.00 g, 2.31 mmol) were dissolved in a mixture of 20 ml toluene, 10 ml  $2 N \text{Na}_2\text{CO}_3$  solution and 0.05 ml Aliquat 336 and degassed by freeze, pump, thaw (three cycles). Tetrakis(triphenylphosphine)palladium (101.8 mg, 88.1 µmol) was added and the mixture was stirred at 100 °C for 16 h. The cooled mixture was poured on 50 ml of water and filtered. The crude product was washed with water (300 ml), methanol (200 ml), hexane (200 ml) and cool CH<sub>2</sub>Cl<sub>2</sub> (150 ml), filtered through a plug of silica (CH<sub>2</sub>Cl<sub>2</sub>), recrystallized from toluene (three times) and dried under high vacuum to give 2,7-bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)pyrene as a white solid (0.72 g, 73%).

**Mp:** 225-226°C

**FD-MS** (8 KV): m/z 909.3 (100%), 909.5 calcd.

<sup>1</sup>**H-NMR** (500 MHz, 373 K, C<sub>2</sub>D2Cl<sub>4</sub>)  $\delta$  1.56 (s, 36H), 7.50 – 7.59 (m, 8H), 7.67 – 7.75 (m, 2H), 7.83 (t, *J* = 7.8 Hz, 2H), 8.02 (d, *J* = 8.1 Hz, 2H), 8.17 (t, *J* = 1.9 Hz, 2H), 8.22 (d, *J* = 2.4 Hz, 8H), 8.52 (d, *J* = 3.2 Hz, 4H). <sup>13</sup>**C-NMR** (126 MHz, 373 K, C<sub>2</sub>D2Cl<sub>4</sub>)  $\delta$  31.9, 34.5, 73.8, 109.3, 116.1, 123.4, 123.6, 123.7, 123.9, 125.5, 126.0, 126.3,

127.9, 128.8, 130.1, 131.6, 138.1, 139.0, 139.4, 143.1.

Elemental Analysis (%) found C, 89.77; H, 7.12; N, 3.11 calculated C68H64N2 C, 89.82; H, 7.09; N, 3.08.

### S2. Solution UV/Vis absorption and Fluorescence spectra of 5 (in DMF)



**Figure S2:** Solution UV/Vis absorption and Fluorescence spectra of **5**. Spectra recorded in DMF at  $c = 1*10^5$  mol/l,  $\lambda_{(exc.),PL} = 300$  nm

### S3. Concentration dependent fluorescence spectra of 5 (in DMF)



**Figure S3:** Concentration dependent fluorescence spectra of **5** in DMF ( $\lambda_{(exc.),PL} = 300$  nm). For comparison the film PL spectrum of **5** is included (squares). Increasing the concentration affects the relative intensities of the fluorescence features at  $\lambda = 414$  nm and  $\lambda = 436$  nm. The latter peak gains in intensity at higher concentrations. In the film the relative intensities are inverted and a bathochromic shift takes place as a consequence of aggregation. A

In contrast, a pyrene excimer feature is expected as a broad absorption at l > 475 nm (<sup>3-6</sup> and references there in). Even at high concentrations no excimer emission is observed.

#### S4. Solvent dependent fluorescence spectra of 5



**Figure S4:** Solution fluorescence spectra of **5** in various solvents ( $c = 5*10^5 \text{ mol/l}$ ,  $\lambda_{(exc.),PL} = 300 \text{ nm}$ ). Asterisk \* indicates solutions with  $c < 5*10^5 \text{ mol/l}$  due to insufficient solubility of **5** in the respective solvent. Only minimal solvatochromic shifts of the fluorescence maximum (l = 4 nm Hexane to DMF) are observed. Even in poor solvents (hexane, DMSO) excimer formation does not occur.

## **S5.** Cyclic voltammetry of target structure



**Figure S5:** Cyclic voltammograms of **5** in THF; [n-Bu<sub>4</sub>NClO<sub>4</sub>] = 0.1 M, 100 mV/s. N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) was used as an internal standard. On-set of oxidations peak was used to determine LUMO and HOMO energy (see table 1). HOMO = (Eox – E<sub>NPB/NPB+</sub>) + 5.4 eV. E<sub>HOMO,NMP</sub> according to the literature.<sup>7</sup>











<sup>145</sup> <sup>140</sup> <sup>135</sup> <sup>130</sup> <sup>125</sup> <sup>120</sup> <sup>115</sup> <sup>110</sup> <sup>105</sup> <sup>100</sup> <sup>95</sup> <sup>90</sup> <sup>85</sup> <sup>80</sup> <sup>75</sup> <sup>70</sup> <sup>75</sup> <sup>70</sup> <sup>65</sup> <sup>60</sup> <sup>55</sup> <sup>50</sup> <sup>45</sup> <sup>40</sup> <sup>35</sup> <sup>30</sup> <sup>25</sup> <sup>20</sup> <sup>15</sup> <sup>10</sup> <sup>5</sup> <sup>2,7</sup> <sup>2,</sup>

## **S7.** Calculated Frontier Orbital Distributions

# Frontier orbital densities of Material 5



HOMO -1

HOMO



LUMO

Frontier orbital densities of the p-phenyl isomer of 5



HOMO -1

HOMO



LUMO

<sup>a</sup> The density functional theory (DFT) calculations have been performed using the Gaussian 03 program (Frisch, M. J. et al.) with the B3LYP hybrid functional (Becke 3-Parameter, Lee, Yang and Parr), and a basis set 6-31G\* for the ground state geometry optimization.

### **S8.** Device structure

a) OLED Device



b) Comparison of triplet energy levels.



The triplet energy level of **5** was determined to be around  $E_{t,5} = 2.9 \text{ eV}$  to 3.0 eV. In order to confine the triplet energy within the active layer (mCPPO1 : **5**), ETL- (TSPO1  $E_{t,TSPO1} = 3.4 \text{ eV}$ ) and blocking layer- (mCPPO,  $E_{t,mCPPO} = 3.0 \text{ eV}$ ) materials are chosen that have higher triplet energy levels than Material **5**.

## **S9. "Emitter-only" EML devices.**

OLED device structures for emitter-only OLEDs.



Device properties of emitter-only OLEDs. Left: EL spectra. Center: U/I curve. Right: EQE.



The EL spectrum for these devices is broader, the shoulder at  $\lambda = 460$  nm is more pronounced. Thus, the colour purity is diminished compared to the host:guest OLED. The turn-on voltage is much higher (6.3 V vs. 3.3 V), while a maximum EQE of only 1.89 % is reached (40 nm ETL).

### S10. Literature

- 1. H.-Y. Chen, C.-T. Chen and C.-T. Chen, *Macromolecules*, 2010, 43, 3613-3623.
- 2. D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder and R. N. Perutz, *Chem. Commun.*, 2005, 16, 2172-2174.
- 3. Y. Nagata, T. Nishikawa and M. Suginome, *Chem. Commun.*, 2012, 48, 11193-11195.
- 4. J. B. Birks and L. G. Christophorou, *Spectrochim. Acta*, 1963, 19, 401-410.
- 5. E. M. S. Castanheira and J. M. G. Martinho, *Chem. Phys. Lett.*, 1991, 185, 319-323.
- 6. E. M. S. Castanheira and J. M. G. Martinho, *Journal of Photochemistry and Photobiology A: Chemistry*, 1994, 80, 151-156.
- 7. V. K. Rai, M. Nishiura, M. Takimoto and Z. Hou, *Chem. Commun.*, 2011, 47, 5726-5728.