

Asymmetrical twisted anthracene derivatives as high-efficiency deep-blue emitters for organic light-emitting diodes

Chuanyou He^a, Haoqing Guo^a, Qiming Peng^a, Shengzhi Dong^a, Feng Li^{a*}

^aState Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University Qianjin Avenue, Changchun, 130012, P. R. China

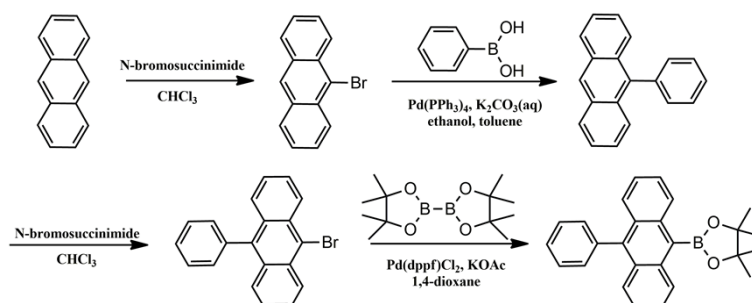
E-mail: lifeng01@jlu.edu.cn

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SI-1. Synthesis

4,4,5,5-Tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane (1a), 1,2-bis(4-bromophenyl)-1H-phenanthro[9,10-d]imidazole (1b), 1,2-bis(4-bromophenyl)-4,5-diphenyl-1H-imidazole (1c), were prepared according to literatures¹.



Scheme S1. The synthesis route of 1a.

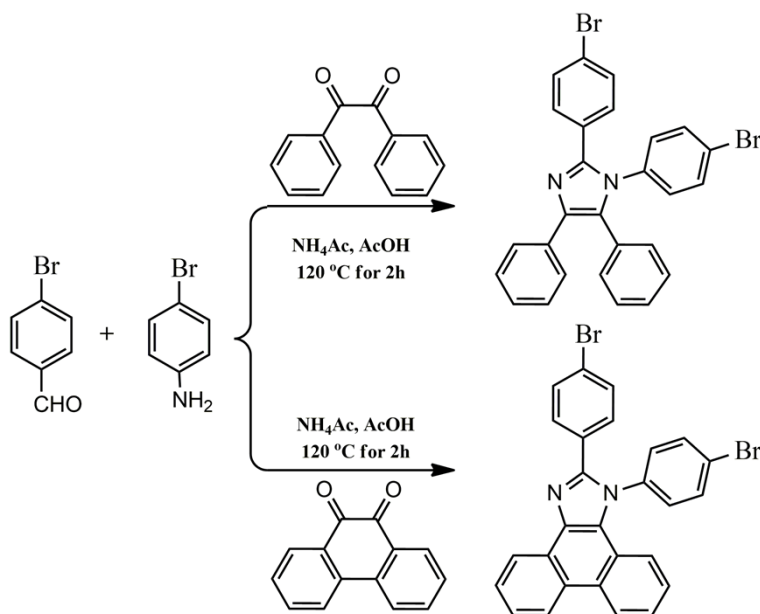
Synthesis of 9-bromoanthracene. Anthracene (5 g, 28.05 mmol) was dissolved in CHCl_3 . Then N-bromosuccinimide (NBS, 4.99 g, 28.05 mmol) was added in batches away from light, and the reaction solution was continuously stirred for 12 h. The resulting mixture was stirred for another 30 min with appropriate water, and extracted with CH_2Cl_2 . The CH_2Cl_2 solution was dried over anhydrous MgSO_4 . After removing CH_2Cl_2 solvent, the residue was recrystallized from anhydrous ethanol to give 4.78 g (66.3 %) of a green-yellow needle solid. ^1H NMR (500 MHz, CDCl_3) δ 8.55 (d, $J = 8.9$ Hz, 2H), 8.48 (s, 1H), 8.03 (d, $J = 8.4$ Hz, 2H), 7.67 – 7.60 (m, 2H), 7.56 – 7.51 (m, 2H). EI-MS (m/z): Calculated for $\text{C}_{14}\text{H}_9\text{Br}$: 257.13. Found [M^+]: 255.96.

Synthesis of 9-phenylanthracene. Phenylboronic acid (2.13 g, 17.49 mmol), 9-bromoanthracene (3 g, 11.66 mmol), $\text{Pd(PPh}_3)_4$ (140 mg, 0.12 mmol), K_2CO_3 (16 mL, 2 M), and ethanol (8 mL) were mixed in a 100 mL flask containing anhydrous toluene (32 mL). The mixture was refluxed for 48 h under nitrogen. After cooled to room temperature, the reaction mixture was quenched with dilute hydrochloric acid solution and extracted with CH_2Cl_2 . The organic extracts were dried over anhydrous MgSO_4 and concentrated by rotary evaporation. The crude product was further purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether (1:4,v/v)) to get a white powder (2.43 g, 81.9 %). ^1H NMR (500 MHz, CDCl_3) δ 8.53 (s, 1H), 8.08 (d, $J = 8.5$ Hz, 2H), 7.70 – 7.67 (m, 2H), 7.63 – 7.54 (m, 3H), 7.50 – 7.45 (m, 4H), 7.37 (ddd, $J = 8.7, 6.5, 1.2$ Hz, 2H). EI-MS (m/z): Calculated for $\text{C}_{20}\text{H}_{14}$: 254.33. Found [M^+]: 253.02.

Synthesis of 9-bromo-10-phenylanthracene. 9-Phenylanthracene (2.5g, 9.83mmol) and NBS (2.1g, 11.8mmol) were dissolved in 80mL CHCl_3 . Then the mixture was heated to 60°C for 2h under N_2 . After cooled to room temperature, 20 mL water was added. And the mixture was extracted with CH_2Cl_2 . The organic extracts were dried over anhydrous MgSO_4 and concentrated by rotary evaporation.

The crude product was recrystallized from methanol to get a green-yellow powder (2g, 61.2%). ^1H NMR (500 MHz, CDCl_3) δ 8.67 – 8.61 (m, 2H), 7.71 – 7.65 (m, 2H), 7.64 – 7.56 (m, 5H), 7.45 – 7.37 (m, 4H). EI-MS (m/z): Calculated for $\text{C}_{20}\text{H}_{13}\text{Br}$: 333.22. Found [M^+]: 332.30.

Synthesis of 4,4,5,5-Tetramethyl-2-(10-phenylanthracen-9-yl)-1,3,2-dioxaborolane (1a). 9-Bromo-10-phenylanthracene (5.8g, 17.4mmol), bis(pinacolato)diboron (6.63 g, 26.1 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (710 mg, 0.87 mmol), and KOAc (10.23 g, 104.4 mmol) were mixed in a 250mL flask containing 1,4-dioxane (60 mL). The reaction mixture was refluxed for 24h under nitrogen. After it was cooled to room temperature, a dilute hydrochloric acid solution quenched. The mixture was extracted with CH_2Cl_2 and dried over anhydrous MgSO_4 . The crude product was concentrated by rotary evaporation and further purified by silica gel column chromatography (CH_2Cl_2 / petroleum ether (1:1,v/v)) to afford a light yellow powder (4.0 g, 60.4 %). ^1H NMR (500 MHz, CDCl_3) δ 8.46 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.57 (dq, J = 14.2, 7.0 Hz, 3H), 7.51 – 7.46 (m, 2H), 7.41 (d, J = 7.0 Hz, 2H), 7.34 (dd, J = 8.1, 7.1 Hz, 2H), 1.63 (s, 12H). EI-MS (m/z): Calculated for $\text{C}_{26}\text{H}_{25}\text{BO}_2$: 380.29. Found [M^+]: 379.92.



Scheme S1. The synthesis route of 1b and 1c.

Synthesis of 1,2-Bis(4-bromophenyl)-1H-phenanthro[9,10-d]imidazole (1b). A mixture of phenanthrenequinone (4.5 g, 21.6 mmol), 4-Bromoaniline (1.84g, 10.8 mmol), 4-bromobenzaldehyde (2 g, 10.8 mmol), ammonium acetate (5.0 g, 64.8 mmol), and acetic acid (30 mL) was refluxed for 2 h under nitrogen. When the mixture was cooled to room temperature, the precipitation was collected by vacuum filtration. The crude product was further purified by silica gel column

chromatography (CH_2Cl_2 / petroleum ether (4:1,v/v)) to afford a light yellow powder (4.1 g, 71.9 %). ^1H NMR (500 MHz, CDCl_3) δ 8.89 (d, J = 7.7 Hz, 1H), 8.79 (d, J = 8.3 Hz, 1H), 8.73 (d, J = 8.3 Hz, 1H), 7.78 (t, J = 7.4 Hz, 1H), 7.67 (ddd, J = 19.7, 12.0, 4.0 Hz, 5H), 7.59 – 7.41 (m, 7H), 7.19 (d, J = 8.2 Hz, 1H). m/z : 448.71 [M^+] (calcd: 449.34). ^1H NMR (500 MHz, DMSO) δ 8.95 (d, J = 8.3 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.79 (t, J = 7.4 Hz, 1H), 7.71 (t, J = 8.9 Hz, 3H), 7.61 (dd, J = 17.7, 8.3 Hz, 3H), 7.52 (d, J = 8.5 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 7.15 (d, J = 8.3 Hz, 1H). EI-MS (m/z): Calculated for $\text{C}_{27}\text{H}_{16}\text{Br}_2\text{N}_2$: 528.24. Found [M^+]: 528.08.

Synthesis of 1,2-bis(4-bromophenyl)-4,5-diphenyl-1H-imidazole (1c). The procedure was analogous to that described for 1b (62.3%, white powder). ^1H NMR (500 MHz, DMSO) δ 7.55 (dd, J = 8.4, 4.3 Hz, 4H), 7.50 (d, J = 7.9 Hz, 2H), 7.34 (d, J = 8.6 Hz, 5H), 7.26 (dd, J = 9.8, 5.4 Hz, 6H), 7.19 (t, J = 7.3 Hz, 1H). EI-MS (m/z): Calculated for $\text{C}_{27}\text{H}_{16}\text{Br}_2\text{N}_2$: 530.25. Found [M^+]: 530.15.

SI-2.The PL spectra in cycle-hexane, toluene, dichloromethane solution.

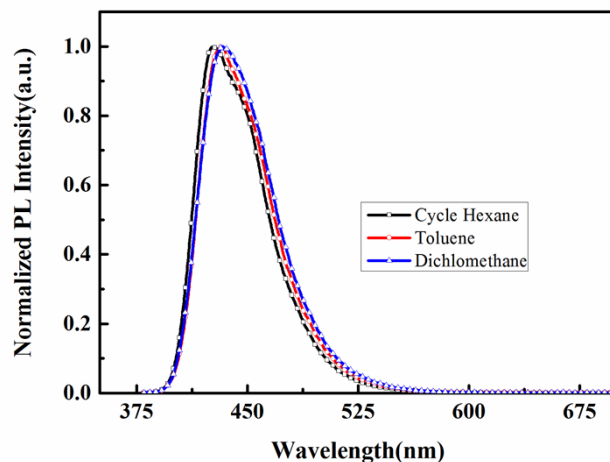


Figure S1. The PL spectra of DPA-PPI in different solvent.

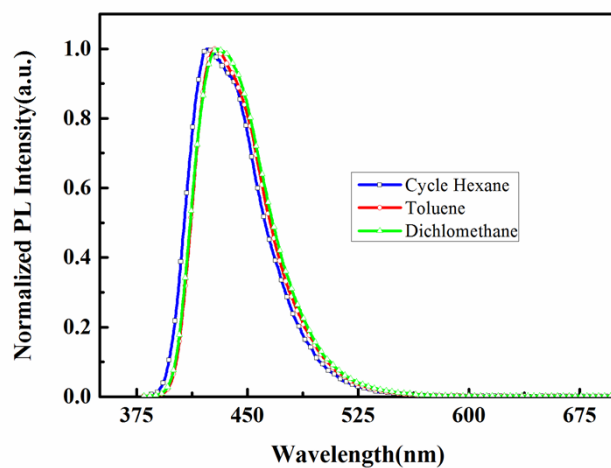


Figure S2. The PL spectra of DPA-PIM in different solvent.

SI-3. The EL spectra of the DPA-PPI-based OLEDs and DPA-PIM-based OLEDs at different voltages.

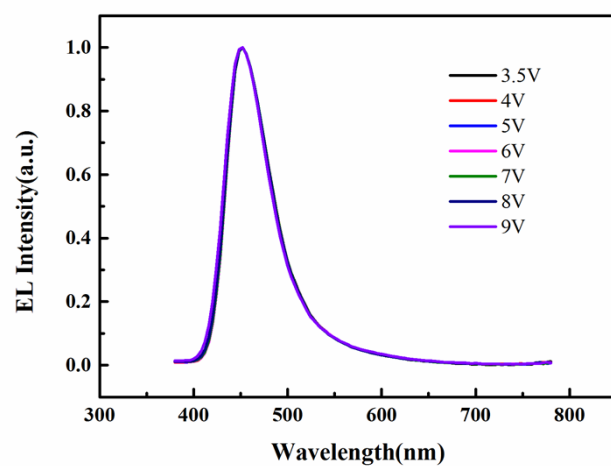


Figure S3. The EL spectra of the Device I under different voltages with the structure of ITO / MoO_3 (5 nm) / NPB (25nm) / TCTA (10nm) / DPA-PPI (20 nm) / TPBI (50 nm) / LiF (0.7 nm) / Al (100 nm), they barely change with the driving voltage.

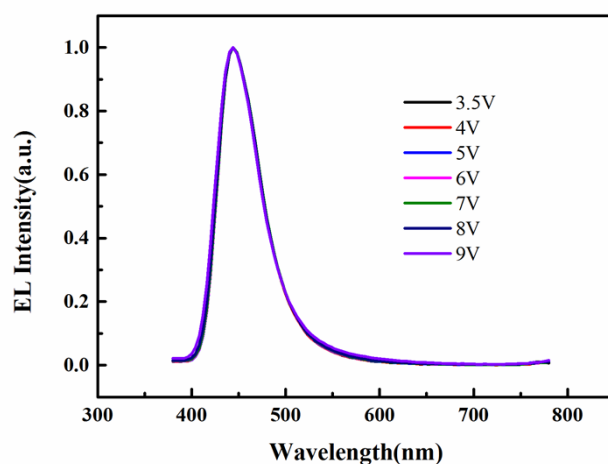


Figure S4. The EL spectra of the Device II under different voltages with the structure of ITO / MoO₃ (5 nm) / NPB (25nm) / TCTA (10nm) / DPA-PIM (20 nm) / TPBI (50 nm) / LiF (0.7 nm) / Al (100 nm), they barely change with the driving voltage.

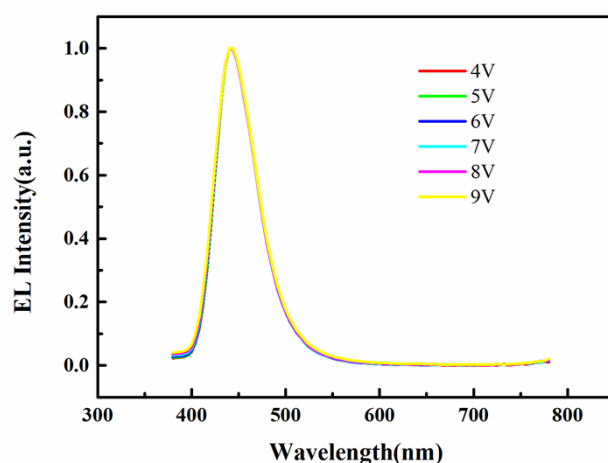


Figure S5. The EL spectra of the Device III under different voltages with the structure of ITO / MoO₃ (5 nm) / TCTA (40nm) / DPA-PPI : CBP (6 wt%, 20 nm) / TPBI (50 nm) / LiF (0.7 nm) / Al (100 nm), they barely change with the driving voltage.

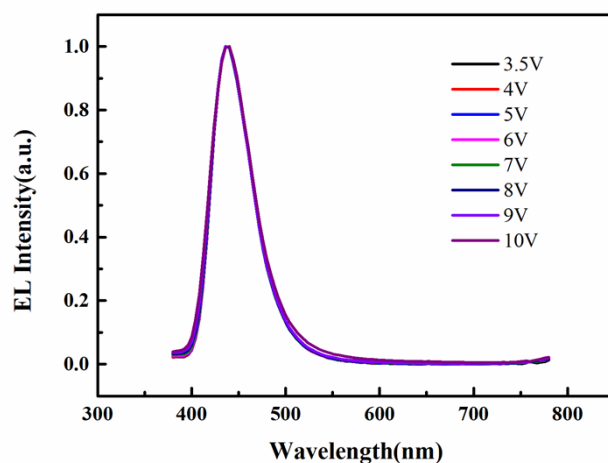


Figure S6. The EL spectra of the Device IV under different voltages with the structure of ITO / MoO₃ (5 nm) / TCTA (40nm) / DPA-PIM : CBP (6 wt%, 20 nm) / TPBI (50 nm) / LiF (0.7 nm) / Al (100 nm), they barely change with the driving voltage.

SI-4. The energy diagram of compounds utilized in OLEDs

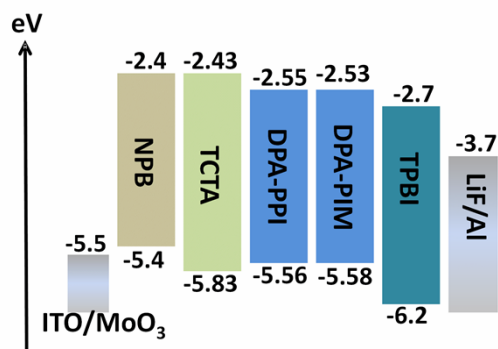


Figure S7. The energy level of compounds used in non-doped devices.

Reference

- 1 (a) J.-Y. Hu, Y.-J. Pu, Y. Yamashita, F. Satoh, S. Kawata, H. Katagiri, H. Sasabe and J. Kido, *J. Mater. Chem. C*, 2013, **1**, 3871; (b) Z. M. Wang, P. Lu, S. Chen, Z. Gao, F. Shen, W. Zhang, Y. Xu, H. S. Kwok and Y. Ma, *J. Mater. Chem.*, 2011, **21**, 5451–5456.