Electronic Supplementary Information

Fused-seven-ring Anthracene Derivative with Two Sulfur Bridges for High Performance Red Organic Light-emitting Diodes

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1. Materials Synthesis.

Toluene was distilled before use. Other Chemicals and solvents were purchased from Aldrich, Alfa Aesar and used without further purification; Alq_3, Ni-GD2 and BAlq were purchased from Nichem Fine Technology Co. Ltd.

Compound 1. Into a mixture of 9,10-dibromo-anthracene (1.34 g, 4 mmol) and 2-methylsulfanyl-benzeneboronic acid (1.34 g, 8 mmol) in freshly distilled toluene (20 ml), 2 M K_2CO_3 solution (15 ml) were added , then $Pd(PPh_3)_4$ (100 mg) was added in one portion under argon. The mixture was refluxed for 24 hours, and then was cooled to room temperature then extracted with dichloromethane. The organic layers were dried, evaporated in vacuum. The residue was purified with column chromatography on silica gel with petroleum ether as the eluent to give pure compound 1 (1 g, 57.5 %) as yellow solid. EI-MS: *m*/*z*: 422 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 6H), 7.26–7.28 (d, 2H), 7.36–7.46 (m, 4H), 7.55–7.63 (m, 8H), 8.64–8.66 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.56, 123.68, 124.86, 124.91, 126.12, 127.00, 127.25, 128.27, 129.02, 130.58, 131.09, 131.67, 135.62, 136.51, and 139.92.

Compound 2. Compound 1 (2.3 mmol, 1 g) was dissolved in glacial acetic acid (10 ml). Hydrogen peroxide (35%, 0.56 g) dissolved in glacial acetic acid (10 ml) was added dropwise to the solution. The mixture was allowed to stir at room temperature for 12 h. The acetic acid was removed by evaporation under reduced pressure, giving crude product **2** about 0.95 g (90%) as yellow solid was used without further purification. EI-MS: *m*/*z*: 454 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (s, 6H), 7.38–7.40 (m, 4H), 7.51–7.52 (m, 4H), 7.63–7.64 (d, 2H), 7.89–7.91 (d, 4H), 8.00–8.01 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.3, 122.5, 125.6, 128.7, 129.0, 130.9, 131.6, 133.1, 145.0.

Compound 3, (BTA**).** Compound 2 (0.78 g, 2 mmol) was added to trifluoromethanesulfonic acid (4.5 ml). The solution was stirred at room temperature for 24 h and then poured slowly into a water–pyridine mixture (90 ml, 8:1). Demethylation was achieved by heating the mixture to reflux for 30 minutes. Upon cooling, the dark red precipitate was collected and washed with water and ethanol. The final compound BTA was purified by vapor sublimation as deep-red solid. EI-MS: *m*/*z*: 390 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.40 (m, 6H), 7.49–7.51 (d, 2H), 7.56–7.58 (d, 2H), 7.76–7.78 (d, 2H), 8.06–8.08 (d, 2H). Elemental analysis calcd (%) for $C_{26}H_{14}S_2$: C, 79.96; H, 3.61; Found: C, 79.76; H, 3.65.

2. Instruments and measurement

^{1}H-NMR (400 MHz) spectra were obtained on a Bruker DMX-400 NMR Spectrometer using tetramethylsilane as internal standard. High-resolution mass spectra (HRMS) and EI MS were both recorded on Micromass GCT-MS spectrometer. Elemental analyses were performed on a Carlo Erba model 1160 elemental analyzer. Electronic absorption spectra were measured on a Jasco V570 UV–vis spectrophotometer. TGA-DTA measurements were carried out on a TA SDT 2960 instruments under a dry nitrogen flow, heating from room temperature (R.T.) to 500°C, with a heating rate of 10 °C/min. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using Pt disk working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled CHI660C instruments at R.T.

OLED Fabrication and Characterization: All OLEDs were fabricated on bare indium tin oxide (ITO) substrates that were cleaned with detergent, deionized water, acetone, and ethanol. A mixture of Alq_3 or Ni-GD2 and guest materials (x %) were vapour cast. A Newport 2835-C multifunction optical meter was used to measure luminance output. Current–Voltage characteristics were measured with a Hewlett-Packard 4140B semiconductor parameter analyzer. Commission International de L' Eclairage (CIE) coordinates were measured with a PhotoResearch PR–650 spectrophotometer.

3. Physicochemical properties of compound BTA.

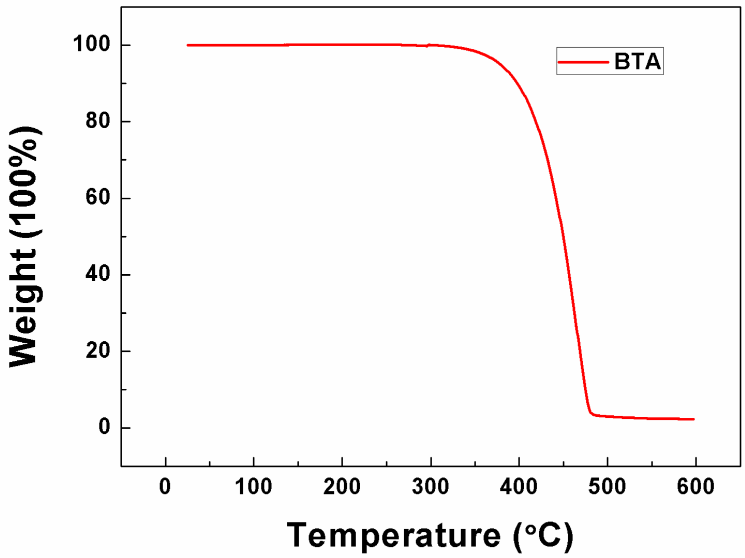

Figure S1. Thermogravimetric analysis (TGA) property of compound BTA.

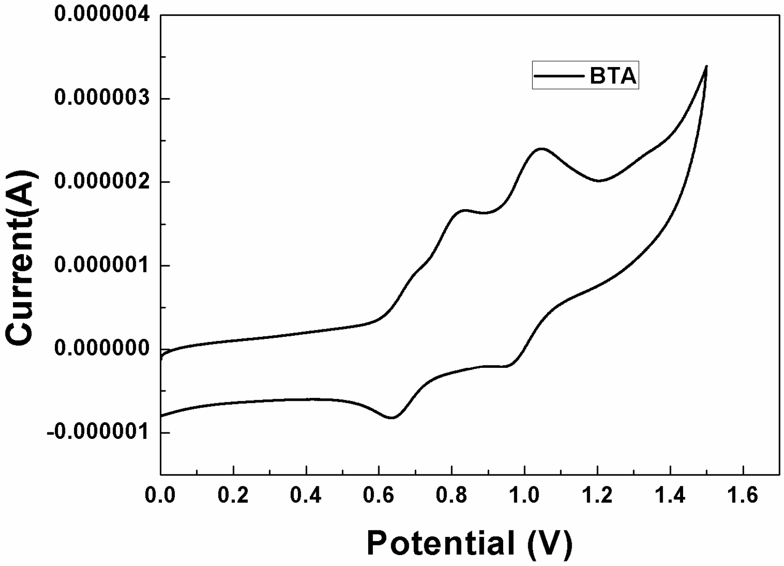

Figure S2. Cyclic voltammetry spectrum of BTA in CH_2Cl_2 solution.

4. The structures and performances list of non-doped devices and doped devices.

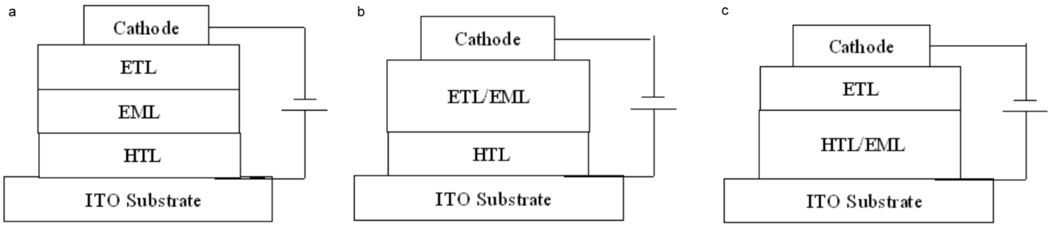

Figure S3. The structures of three kinds of devices used in our experiments.

Table S1. Device performance of non-doped red fluorescent OLEDs in the configuration of ITO/NPB (40 nm)/BTA (X nm)/ETL/cathode, for which Device A1 and A2, X = 10; A3 and A4, X = 20 nm; device A1 and A3, ETL = Alq_3; device A2 and A4, ETL = BAlq.

Devices	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
A1	2.6	6013.9	0.89	1.23	0.4	0.86	0.83
A2	3.0	11227.9	1.02	0.77	0.6	0.95	0.42
A3	3.0	5281.0	0.92	0.43	0.5	0.75	0.41
A4	4.0	5428.0	0.63	0.49	0.4	0.60	0.21

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S2. Device performance of red fluorescent OLED in the configuration of ITO/NPB (40 nm)/Alq_3: x % BTA (30 nm)/BAlq (15 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
B1, 0.3%	2.4	41763.0	4.2	2.4	2.7	3.5	2.4
B2, 0.5%	2.8	39469.8	3.8	2.4	2.5	2.9	2.3
B3, 1.0%	2.6	37867.3	3.8	2.2	2.5	3.3	1.9
B4, 1.9%	2.4	23899.0	3.8	3.7	2.5	3.7	2.5

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S3. Device performance of red fluorescent OLED in the configuration of ITO/NPB (50 nm)/Alq_3: x % BTA (30 nm)/Alq_3 (15 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
C1, 0.5%	3.0	29698.2	4.0	3.0	2.6	4.0	2.0
C2, 1.8%	2.9	19573.0	3.9	3.0	2.5	3.8	2.1
C3, 2.3%	3.3	19536.0	4.0	3.7	2.6	3.7	1.5
C4, 5.2%	3.3	16060.9	3.4	2.4	2.2	3.4	1.3

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S4. Device performance of red fluorescent OLED in the configuration of ITO/NPB (50 nm)/Ni-GD2: x % BTA (30 nm)/Alq_3 (15 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
D1, 0.4%	6.7	14887.0	2.2	0.63	0.9	1.8	0.55
D2, 1.6%	5.2	10863.6	1.3	0.31	0.3	0.4	0.14
D3, 2.4%	5.8	10618.1	1.6	0.41	0.5	1.2	0.36
D4, 5.3%	6.3	9382.6	1.4	0.38	0.4	1.2	0.35

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S5. Device performance of red fluorescent OLED in the configuration of ITO/NPB (50 nm)/Ni-GD2: x % BTA (30 nm)/BAlq (15 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
E1, 0.5%	4.9	14439.0	3.1	1.28	1.8	3.0	1.20
E2, 1.0%	5.4	17579.8	3.5	1.36	2.2	3.4	1.32
E3, 1.7%	4.4	14226.1	3.0	1.14	1.7	2.7	1.10
E4, 4.0%	4.6	14397.7	2.4	0.85	1.0	2.2	0.83

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S6. Device performance of red fluorescent OLED in the configuration of ITO/NPB (15 nm)/Ni-GD2: x % BTA (40 nm)/Alq_3 (50 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})

F1, 0.2%	4.4	19481.4	3.5	1.7	2.1	3.0	1.5
F2, 0.8%	4.3	22991.8	3.1	1.4	1.7	1.4	1.3
F3, 1.1%	4.4	19386.4	2.6	1.2	1.3	2.1	1.0
F4, 4.0%	4.4	10561.8	2.1	1.1	0.8	2.1	1.0

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S7. Device performance of red fluorescent OLED in the configuration of ITO/NPB (15 nm)/Ni-GD2: x % BTA (40 nm)/BAlq (50 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
G1, 0.7%	3.5	20610.5	3.4	1.7	2.0	3.0	1.6
G2, 1.2%	4.0	23066.6	3.6	1.8	2.2	3.4	1.8
G3, 3.0%	3.7	12339.4	3.3	2.0	2.0	2.1	1.5
G4, 3.6%	4.0	13334.6	3.2	1.6	1.8	3.1	1.5

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.

Table S8. Device performance of red fluorescent OLED in the configuration of ITO/Ni-GD2: x % BTA (40 nm)/BAlq (50 nm)/cathode.

Doping levels	V_{on}[a] (V)	L_{max} (cd m^{-2})	Max. L.E. (cd A^{-1})	Max.P.E. (lm W^{-1})	η_{ex} (%)	L.E.[b] (cd A^{-1})	P.E.[b] (lm W^{-1})
H1, 0.5%	2.4	40752.8	4.1	3.1	2.7	3.8	3.1
H2, 0.7%	2.5	37464.2	4.2	3.3	2.8	4.2	3.0
H3, 1.0%	2.4	35730.6	4.4	3.6	2.9	4.3	3.4
H4, 1.6%	2.5	40323.4	4.2	3.6	2.8	2.7	3.2

[a] Recorded at 1 cd m^{-2}. [b] Obtained at a brightness of 100 cd m^{-2}.