

Electronic Supplementary Information

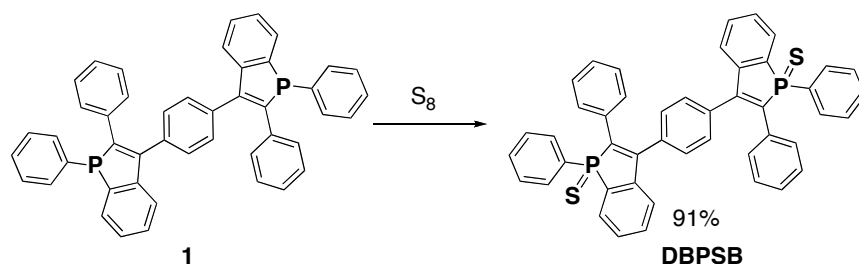
## Benzo[*b*]phosphole Sulfides. Highly Electron-transporting and Thermally Stable Molecular Materials for Organic Semiconductor Devices

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### (1) Synthesis of DBPSB

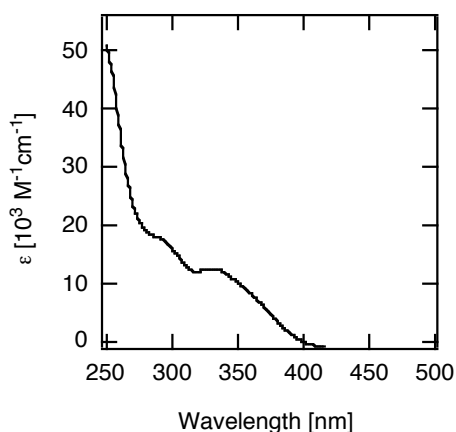
#### Scheme S1



To a solution of 1,4-bis(1,2-diphenylbenzo[*b*]phosphole-3-yl)benzene (**1**, 48.8 mg, 0.0736 mmol) in tetrahydrofuran, hexane, and toluene (0.4 mL each) was added sulfur (20.7 mg, 0.647 mmol) at 0 °C. After the resulting yellow reaction mixture was stirred for 4 h at 80 °C, the solvents were evaporated to obtain a yellow solid. Purification by silica-gel column chromatography afforded the title compound as a white solid (47.4 mg, 0.0667 mmol, 91%). Mp: 298–303 °C (diastereomer mixture, ratio = 1:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ) 7.05–7.20 (m, 10H), 7.31 (dd, *J* = 7.5 Hz, 2.9 Hz, 2H), 7.39–7.54 (m, 14H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.88 (d, *J* = 6.9 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, δ) 124.2 (d, *J*<sub>C,P</sub> = 10.7 Hz), 128.0, 128.8, 128.9, 129.0, 129.4, 129.5, 129.6, 129.9, 130.8, 130.9, 132.0 (d, *J*<sub>C,P</sub> = 2.4 Hz), 132.4, 134.6 (d, *J*<sub>C,P</sub> = 17.9 Hz), 135.6, 136.2, 136.3, 136.8, 137.4, 143.3 (d, *J*<sub>C,P</sub> = 23.0 Hz), 148.4 (d, *J*<sub>C,P</sub> = 23.8 Hz); <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, δ) 48.21; IR (solid): ν = 3056 (s), 1449 (s), 1437 (s) cm<sup>-1</sup>. Anal. calcd for C<sub>46</sub>H<sub>32</sub>P<sub>2</sub>S<sub>2</sub>: C, 77.73; H, 4.54. Found: C, 77.48; H, 4.67.

## (2) UV-vis absorption measurement

UV-vis absorption spectrum is recorded on a JASCO V-570 spectrometer. The measurement was carried out for a  $\text{CH}_2\text{Cl}_2$  solution at a concentration of  $3.4 \times 10^{-5}$  M.



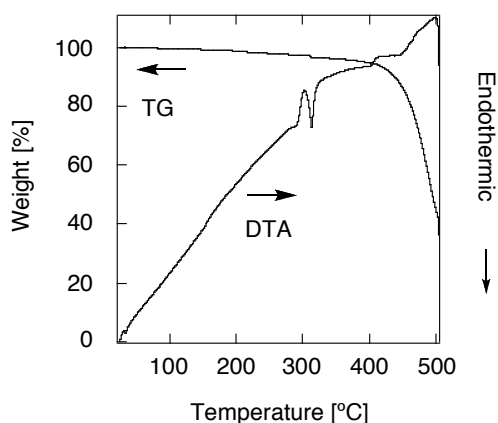
**Fig S1.** UV-vis absorption spectrum of **DBPSB** in  $\text{CH}_2\text{Cl}_2$ .

## (3) Time-of-flight carrier drift mobility measurement

Films of the benzophosphole derivatives were prepared on indium tin oxide (ITO, 145 nm) coated glass substrates. The vacuum deposition was performed on ULVAC KIKO (VPC-260). The film of **DBPSB** was deposited by vacuum sublimation at  $5 \times 10^{-4}$  Pa, under heating with an average deposition rate of 96 nm/s. The ITO-coated glass substrate was spaced at 100 mm from the sample, and it was kept at 25 °C. The thickness of the film obtained was 2.7  $\mu\text{m}$ . The TOF measurement was performed at Sumitomo Heavy Industries Advanced Machinery, TOF-401. The transient photocurrent signals showed dispersive behavior.

## (4) TG-DTA (Thermogravimetry analysis, Differential thermalgravimetric analysis)

TG-DTA was performed on a Rigaku Thermo plus 2 thermal analyzer (TG 8120). Sample (4.69 mg) was placed in aluminum pan and heated to 500 °C at the rate of 10 K/min, under  $\text{N}_2$  purge at a flow rate of 10 mL/min.  $\text{Al}_2\text{O}_3$  was used as reference material.

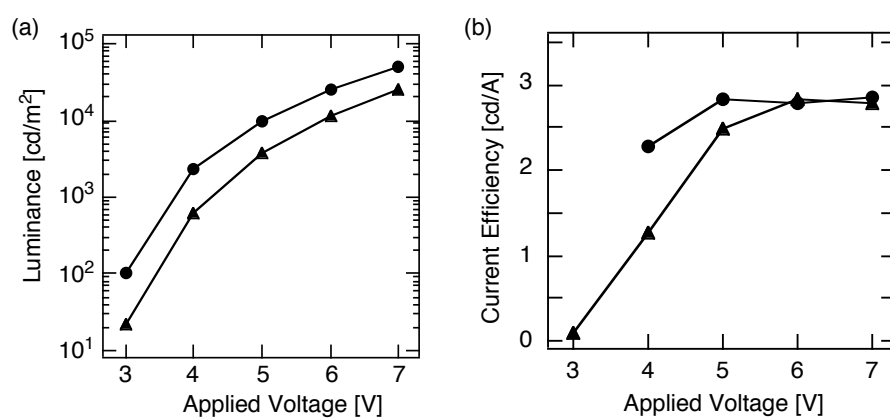


**Fig S2.** TG-DTA traces of **DBPSB**.

### (5) Fabrication and evaluation of OLED devices

To fabricate the OLED devices, a clean glass substrate pre-coated with 145-nm-thick indium-tin-oxide (ITO) layer with a sheet resistance of 8.4  $\Omega/\text{sq}$  was used as anode electrode. On the ITO coated glass substrate, PEDOT:PSS with a sheet resistance of 100,000  $\Omega/\text{sq}$  was spin coated as hole-injection layer. Secondly,  $\alpha$ -NPD was deposited with 45-nm thickness as hole-transporting layer. Then, Alq<sub>3</sub> was deposited with 40-nm thickness onto the HTL. Finally, **DBPSB** or **DBPOB** was co-deposited with Cs, with 20-nm thickness as electron-transporting layer followed by deposition of Al with 80-nm thickness as cathode electrode.

The luminance-voltage and current-voltage characteristics of OLED devices were measured by PRECISE GAUGES, EL 1003. All the measurements were carried out under an ambient atmosphere.



**Fig S3.** OLED characteristics. (a)  $L$ - $V$  and (b)  $L/J$ - $V$  characteristics of the OLED devices using **DBPSB** (circle) or **DBPOB** (triangle) as electron-transporting material