

Supplementary Information for *Chem. Commun.*

Borazine Materials for Organic Optoelectronic Applications

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General Experimental Procedure

NMR Spectra were obtained on the JOEL JNM-GSX270 FT NMR system. Electrochemical studies were performed using a Princeton Applied Research Potentiostat / Galvanostat 273A. Thermogravimetric studies were carried out using a Perkin Elmer Thermogravimetric Analyzer TGA7. Differential Scanning Calorimetry was performed using a Perkin Elmer Differential Scanning Calorimeter DSC7. Absorption spectra were acquired from HP8453 Spectrometer while emission spectra were from Fluorolog SPEX1680. The charge mobility measurement system involved a Spectra-Physics 337201-01 nitrogen laser and a Tektronix TDS3052B oscilloscope. Quantum Yield of solution samples was measured using Spex-Fluorolog 2 spectrofluorometer. Current density-voltage-luminance data was generated using a Keithley 2400 SourceMeter and a Photo Research SpectraScan650 CCD. Vacuum deposition for OLEDs was carried out in an Edwards Auto 306 system.

Compound 1 was obtained from Aldrich, and purified by vacuum sublimation prior to the studies. Compounds **2**, **3** and **5** were prepared according to modified procedures.¹⁻⁴

Preparation of 2. Freshly distilled aniline (5.0 g, 0.054 mol) was added to borane triethylamine compound (6.1 g, 0.054 mol) under an argon atmosphere. The mixture was heated to 80 °C for 16 hours, and then further to 180 °C. Afterwards, the unreacted reagents removed *in vacuo*. The product was collected upon cooling the reaction mixture to room temperature, and was purified using vacuum sublimation. White solid (3.0 g, 54 % yield) was obtained. ¹H NMR (300 MHz, CDCl₃): δ 7.35 (t, *J* = 6.90 Hz, 6H), 7.25 – 7.18 (m, 9H), 5.00 (bs, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 148.0, 128.8, 125.2, 124.7; FABMS: *m/e* 309 [M⁺]; *T_g*: 118 °C; *T_d*: 238 °C.

Preparation of 3. Freshly distilled acetonitrile (2.0 g, 0.049 mol) was added to calcium chloride-dried chlorobenzene under an argon atmosphere. Boron trichloride gas was then continuously bubbled into the solution until fuming is observed, which indicated that all acetonitrile was consumed. Afterwards, dried ammonium chloride powder (2.8 g) was added and the reaction mixture was refluxed for 3 hours. Upon cooling the reaction mixture to room temperature, the chlorobenzene was removed using a cannula. This was followed by the introduction of 150 mL benzene into the reaction mass, and after that the addition of a benzene solution (100 mL) of diphenylamine (15 g, 0.089 mol) dropwise. The reaction mixture was refluxed for 16 hours. The white product (4.5 g, 47 % yield) was collected with filtration and purified via high vacuum sublimation. FABMS: m/e 582 [M^+]; Anal. Calcd for $C_{36}H_{33}B_3N_6$: C, 74.28; H, 5.71; N, 14.44; Found: C, 74.52; H, 5.74; N, 14.22; T_g : 278 °C; T_d : 340 °C.

Preparation of 4. 4-*tert*-Butylaniline (5 g, 0.04 mol) was added to borane triethylamine compound (4 g, 0.04 mol) under an argon atmosphere. The mixture was heated to 80 °C overnight, and then further to 180 °C. Afterwards, the unreacted reagents were removed *in vacuo*. The product was collected upon cooling the reaction mixture to room temperature and purified using vacuum sublimation. White solid (4 g, 60 % yield) was obtained. 1H NMR (270 MHz, $CDCl_3$): δ 7.36 (d, J = 8.64 Hz, 6H), 7.15 (d, J = 8.37 Hz, 6H), 5.08 (bs, 3H); EIMS: m/e : 477 [M^+], EI-HRMS Calcd for $C_{30}H_{42}B_3N_3$: 477.3658; Found: 477.3669; T_d : 230 °C.

Preparation of 5. 1-Naphthylamine (5.7 g, 0.040 mol) was added to borane triethylamine compound (4.5 g, 0.040 mol) under an argon atmosphere. The mixture was heated to 80 °C overnight, and then further to 180 °C. Afterwards, the unreacted reagents were removed in *vacuo*. The product was collected upon cooling the reaction mixture to room temperature. Pale brown solid (5.0 g, 82 % yield) was obtained. ¹H NMR (270 MHz, CDCl₃) δ 8.24 – 8.00 (m, 3H), 7.89 (d, *J* = 7.83 Hz, 3H), 7.76 (d, *J* = 8.1 Hz, 3H), 7.63 – 7.30 (m, 12H); EIMS: *m/e* 459 [M⁺]; EIHRMS: Calcd for C₃₀H₂₄B₃N₃: 459.2249. Found: 459.2255; *T_d*: 248 °C.

Fabrication of OLED device. ITO glass with sheet resistance of 20 Ω / square was cleaned first with detergent solution and deionized water, and then three times in sequence with ethanol, toluene, acetone and finally with deionized water. Upon fabrication of the device, the ITO was cleaned using an UV-ozone cleaner. The layers of materials were deposited in sequence on the ITO glass substrate at a rate of 0.2 – 0.3 nm s⁻¹ under 5 × 10⁻⁶ torr without breaking the vacuum between different deposition processes. The emissive area was 3 × 3 mm², which was the area where the cathode and the anode overlap. Measurements on the devices were carried out in air without encapsulation.

Reference:

- 1 M. P. Brown, B. G. Mellor, and H. B. Silver, GB Patent 1050434, 1966.
- 2 K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, 1959, **81**, 3561.
- 3 S. J. Groszos and S. F. Stafiej, *J. Am. Chem. Soc.*, 1958, **80**, 1357.
- 4 A. Rizzo and B. Frange, *J. Organomet. Chem.*, 1974, **76**, 1.

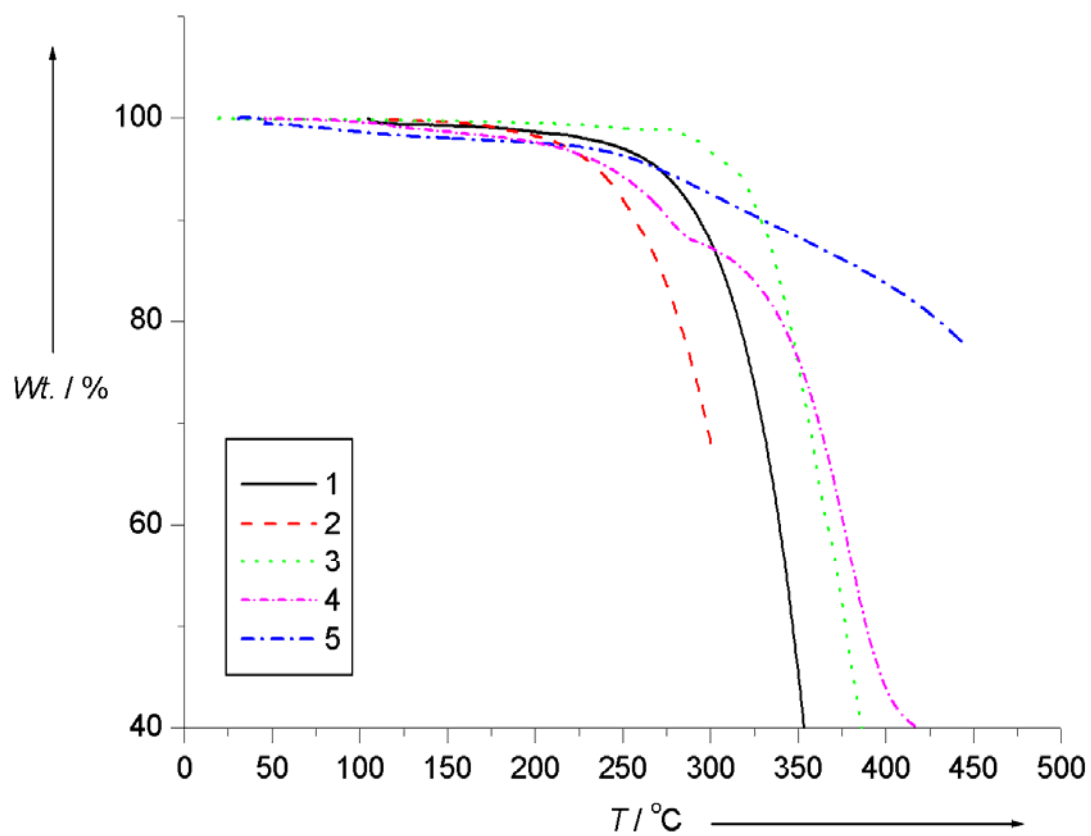


Figure S1 Thermograms of **1** – **5**.

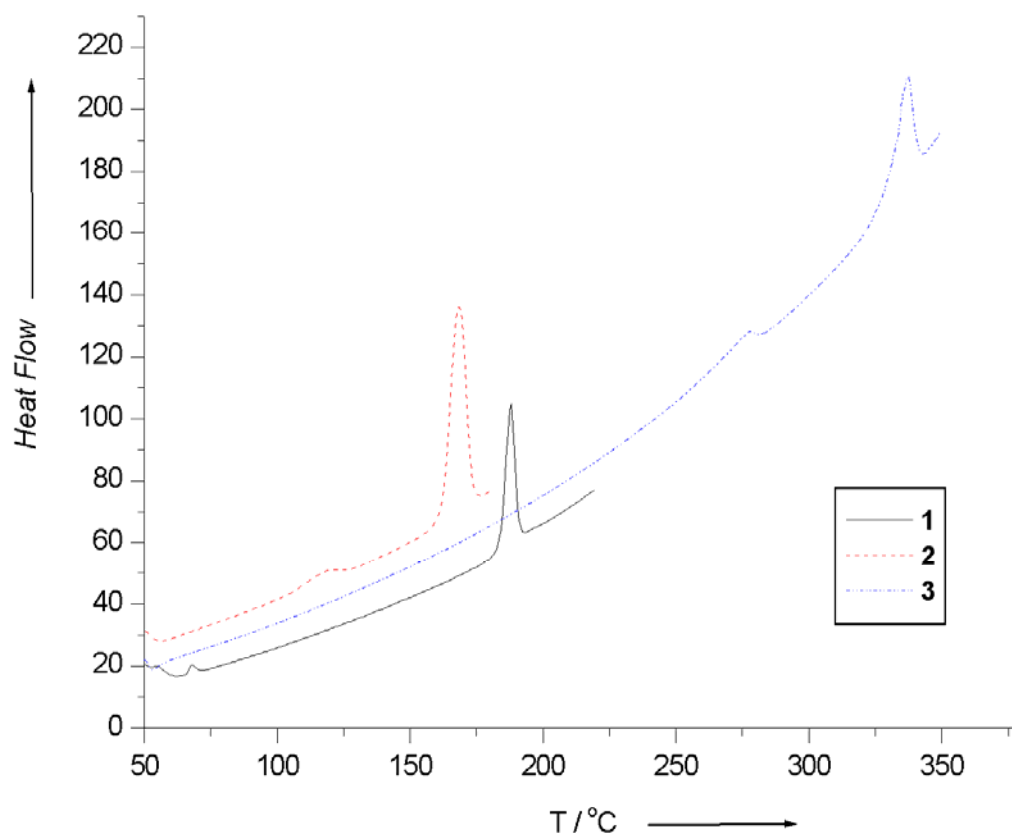


Figure S2 Plots of differential scanning calorimetric (DSC) studies for **1** – **3**.

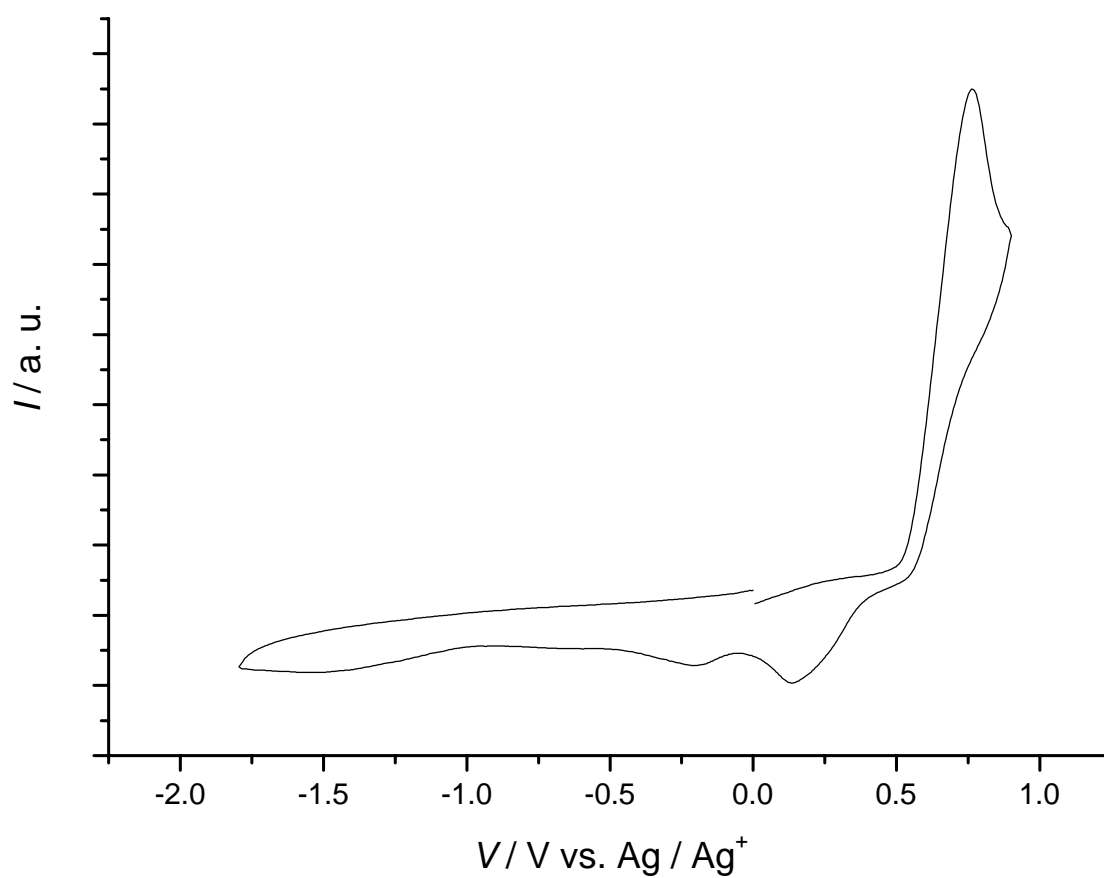


Figure S3 Cyclic voltammogram of **4** in *N,N*-dimethylformamide (DMF) solution.

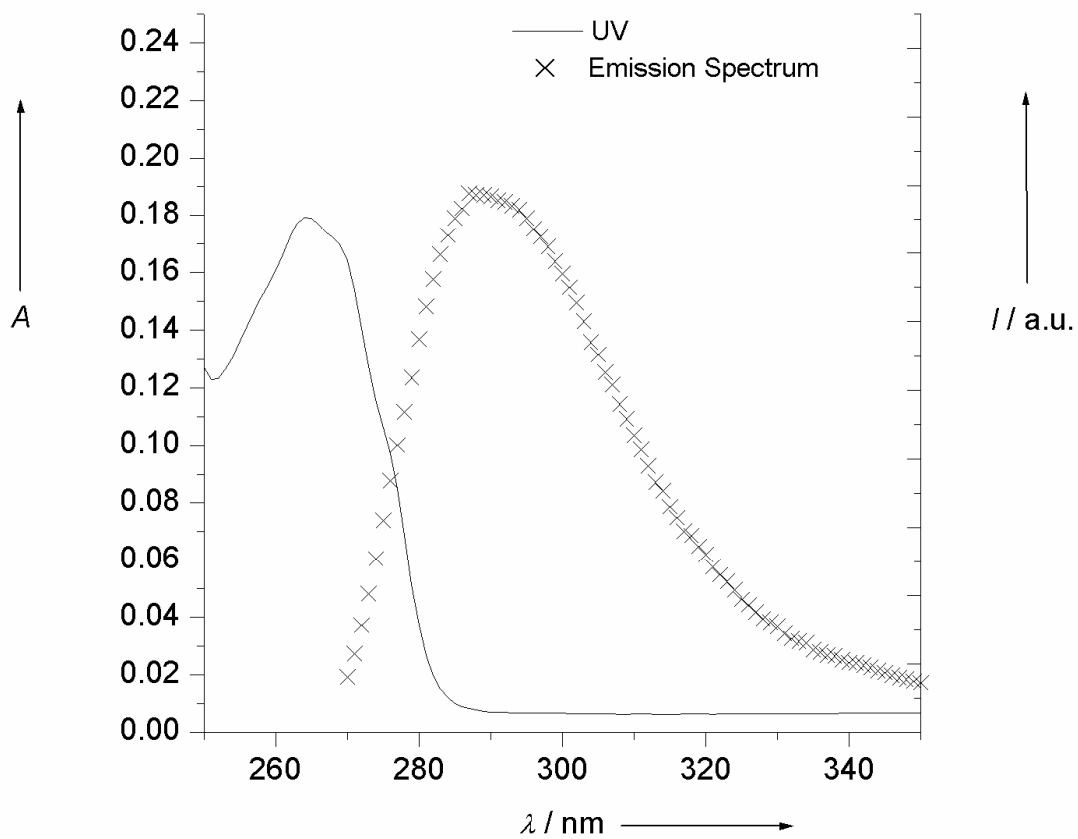


Figure S4 The absorption (UV) and emission spectra of **1** in dichloromethane.

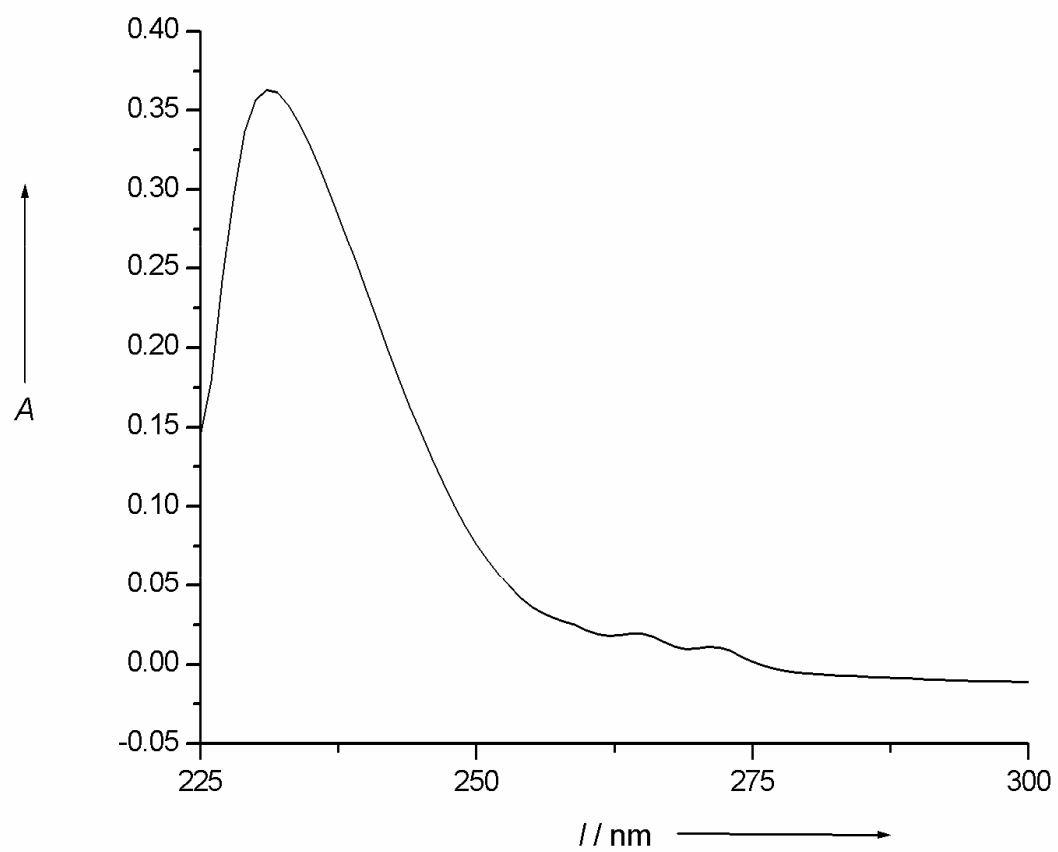


Figure S5 The absorption spectra of **2** in dichloromethane.

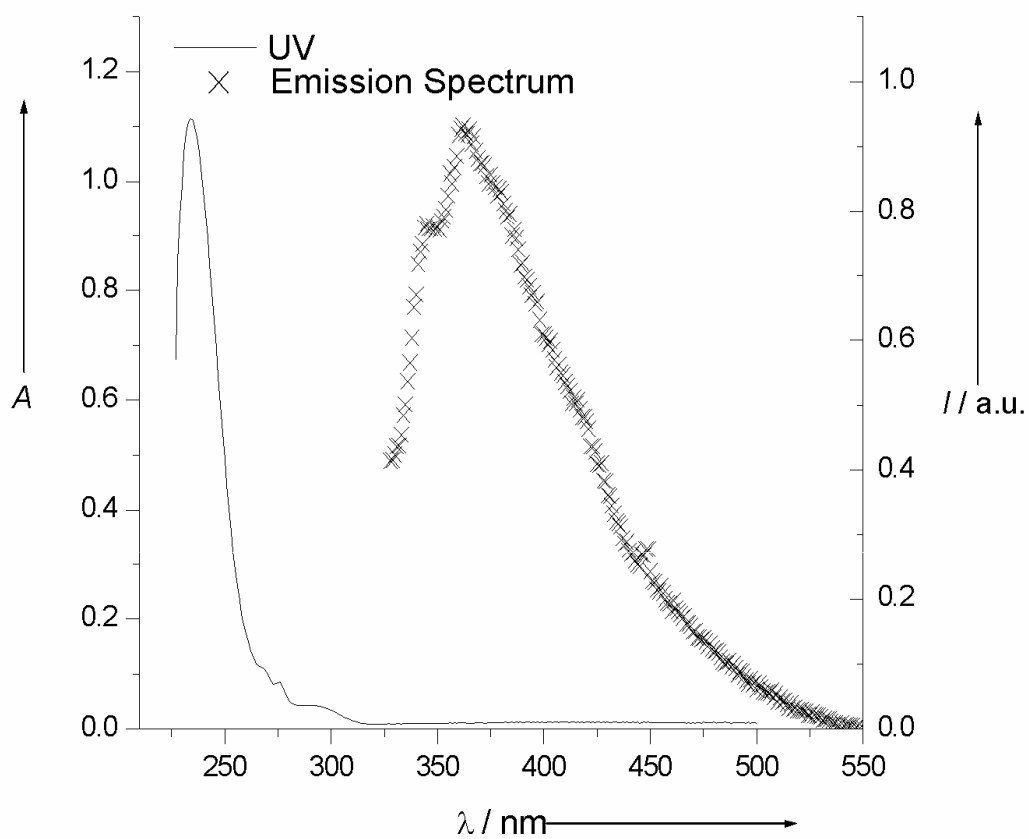


Figure S6 The absorption (UV) and emission spectra of **4** in dichloromethane.

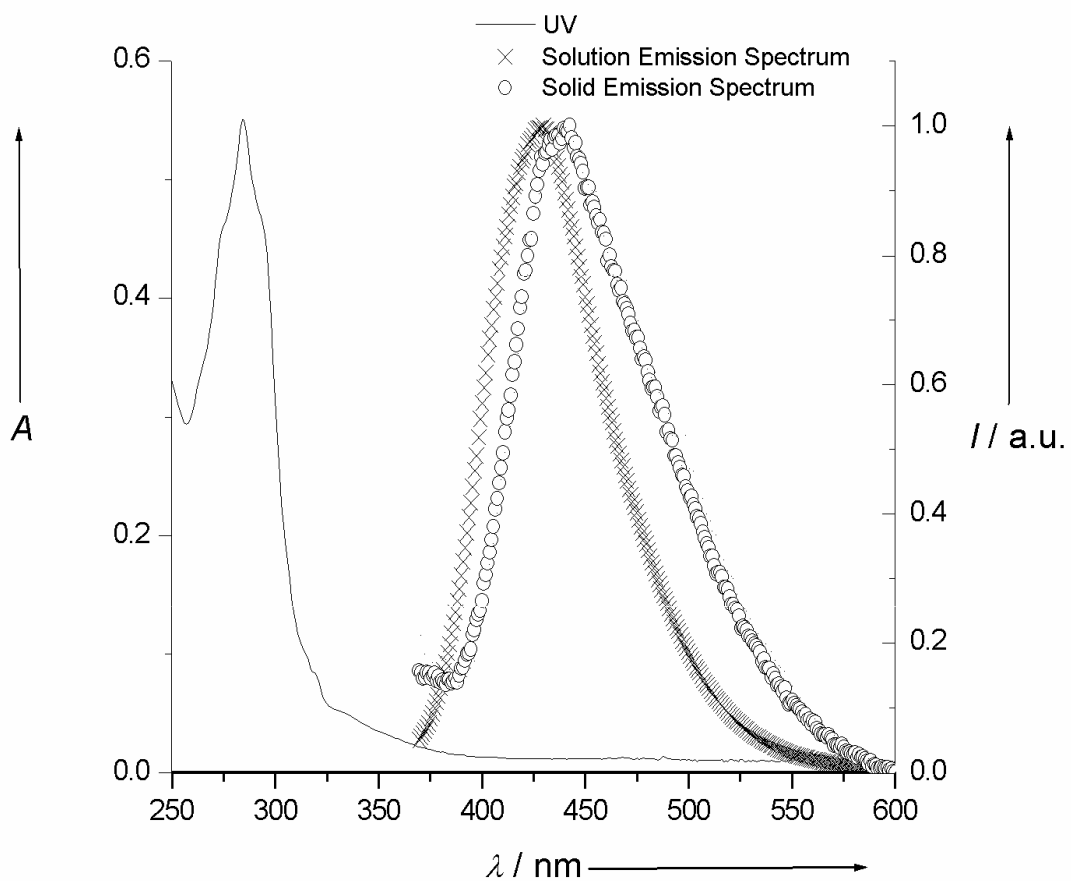


Figure S7 The absorption (UV) and emission spectra of **5** in dichloromethane solution, and the emission spectrum of **5** in solid state.

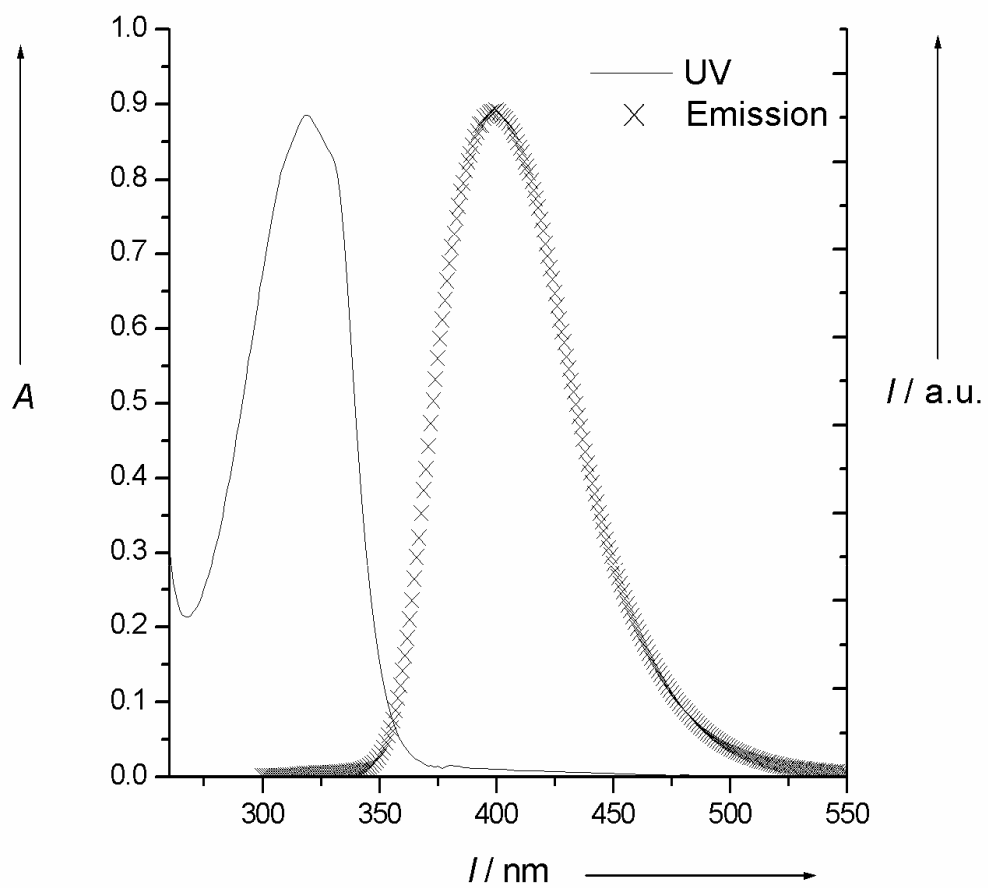


Figure S8 The absorption (UV) and emission spectra of 1-naphthylamine in dichloromethane.

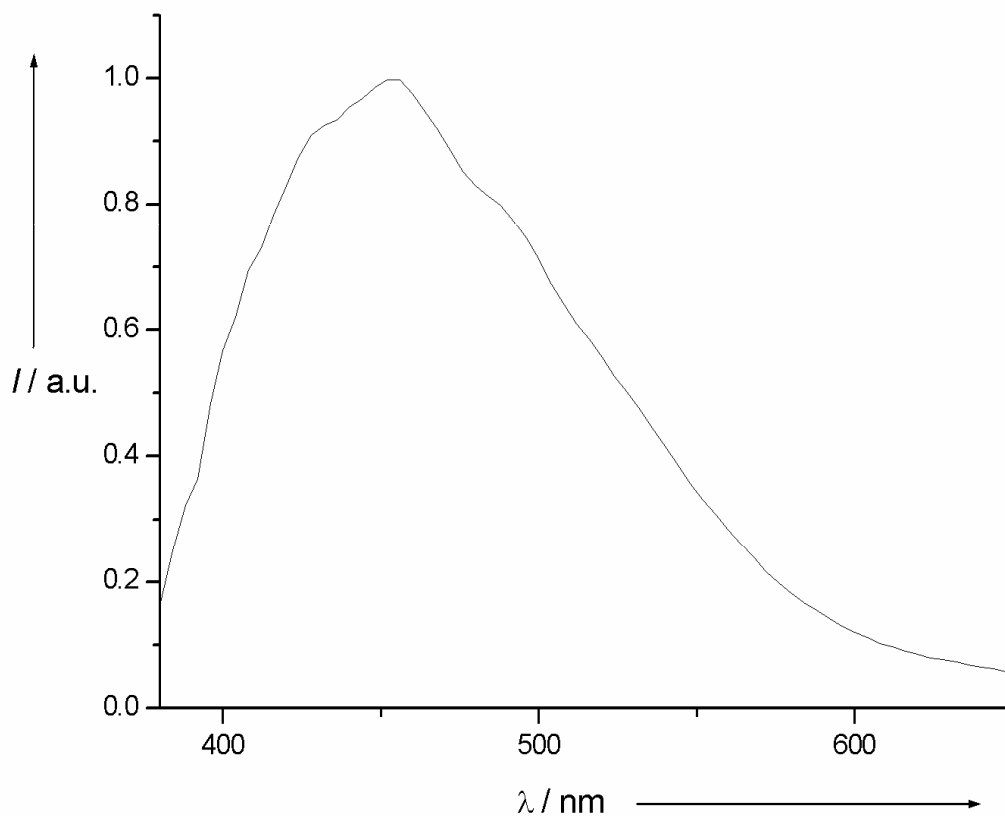


Figure S9 EL spectrum blue device C (ITO / **4** (30 nm) / **4** : [Zn₄OL₆] (L = 7-azaindolate, 5 %, 20 nm) / BCP (10 nm) / Alq₃ (30 nm) / LiF (0.5 nm) / Al (100 nm)) with CIE₁₉₃₁ coordinates of (0.19, 0.22) at 20V.

Table S1 CIE coordinates of the white-light emitting device **B** at different applied voltages.

Voltage (V)	x	y
9	0.34	0.44
10	0.35	0.44
11	0.34	0.44
12	0.35	0.43
13	0.35	0.43
14	0.36	0.43
15	0.36	0.43
16	0.36	0.44
17	0.37	0.44
18	0.37	0.44
19	0.37	0.43
20	0.37	0.43
21	0.36	0.43