Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Boron-Nitrogen Analogues of the Fluorenyl Anion

Stephen M. Mansell, Nicholas C. Norman* and Christopher A. Russell*

Preparation of (1): Bipy (1.406 g, 9.0 mmol) was added under a positive pressure of argon to lithium foil (125 mg, 18 mmol) suspended in thf (45 cm^3) and the resulting dark purple mixture was stirred for 16 h forming a dark red/brown solution. The solvent was removed under reduced pressure and toluene was added (45 cm^3). The mixture was then cooled to -78ºC and BCl_3 (1.0 M solution in heptane, 9 cm^3, 9.0 mmol) was added slowly and the black/orange mixture stirred for 16 h at room temperature. After addition of thf (65 cm^3), the solution was filtered (porosity 5 sinter and celite) affording a dark red solution. The solvent was removed by vacuum and analysis by ^{1}H NMR spectroscopy revealed several products. Sublimation (100ºC, 1.0 x 10^{-2} Torr) gave a red oil (141 mg) which contained the desired product **1** but also contained free bipy and ring-opened thf products. Spectroscopic data for **1**: ^{1}H NMR (d^5-pyridine, 300 MHz) 7.78 (m, 2H), 7.54 [br. d, 2H, J(H-H) = 9.18 Hz], 6.38 [qd, 2H, J(H-H) = 6.06 and 0.92 Hz], 6.22 (m, 2H); ^{11}B NMR (d^5-pyridine, 96.13 MHz) 16.8 ppm.

Preparation of (2): Bipy (1.181 g, 7.6 mmol) was added under a positive pressure of argon to lithium foil (105 mg, 15 mmol) suspended in thf (40 cm^3) and the resulting dark purple mixture was stirred for 16 h forming a dark red/brown solution. The solvent was removed under reduced pressure and toluene (40 cm^3) was added. The mixture was cooled to -78ºC and $PhBCl_2$ (0.98 cm^3, 7.6 mmol) was added slowly and the dark red solution stirred for 16 h at room temperature. The solution was filtered (porosity 5 sinter and celite) and then reduced in volume reduced to *ca.* 4 cm^3 affording red crystals upon storage at -78ºC for 48 h (655 mg, 2.7 mmol, 35%). Spectroscopic data for **2**: ^{1}H NMR (C_6D_6, 500 MHz) δ 7.64 [dt, 2H, J(H-H) = 7.21 and 1.22 Hz, bipy H1/H10], 7.49 (m, 2H, Ph H12/H16), 7.30 – 7.23 (m, 3H, Ph H13/H14/H15), 7.19 [dt, 2H, J(H-H) = 9.17 and 1.22 Hz, bipy H4/H7], 6.17 [qd, 2H, J(H-H) = 9.17 and 0.98 Hz, bipy H3/H8], 5.92 [qd, 2H, J(H-H) = 7.21 and 1.22 Hz, bipy H2/H9] ppm. ^{1}H NMR (NOE) irradiated 7.64 (H1/H10), enhanced 7.49 (H12/H16) and 5.92 (H2/H9). ^{13}C-{^{1}H} NMR (C_6D_6, 125.711 MHz) δ 134.2 (Ph, C12/C16), 129.0 (Ph, C13/C15), 128.7, 128.0, 127.6 (bipy, C1/C10), 119.4, 118.9 (bipy, C4/C7), 115.1 (bipy, C3/C8), 111.3(bipy, C2/C9) ppm. ^{13}C-{^{1}H} HMQC δ 134.2 – 7.49, 129.0 – 7.26, 127.6 – 7.64, 118.9 – 7.19, 115.1 – 6.17, 111.3 – 5.92 ppm. ^{11}B NMR (C_6D_6, 96.13 MHz) δ 20.7 ppm. M.S. (E.I.) 244 (M^+). Mp (toluene) 103 – 105 ºC. Sublimed at 60ºC, 4 x 10^{-4} mbar.

Supplementary Information

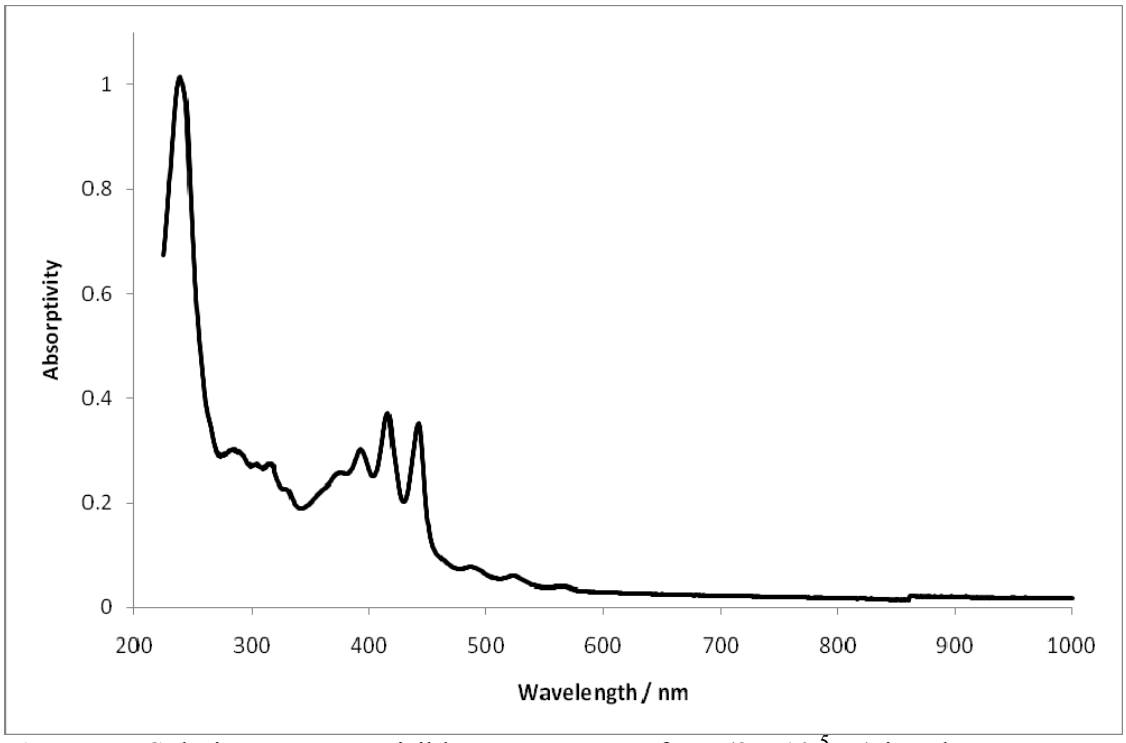

Figure S1. Solution state UV-visible measurements for **2** (2 x 10^{-5} M) in *n*-hexane.

Table S1 UV-visible peaks for compound **2**

λ_{max} / nm	Absorptivity
565	0.041009
523.5	0.060727
486.5	0.077557
442.5	0.350133
416	0.370483
392.5	0.302031
239	1.013842

Supplementary Information

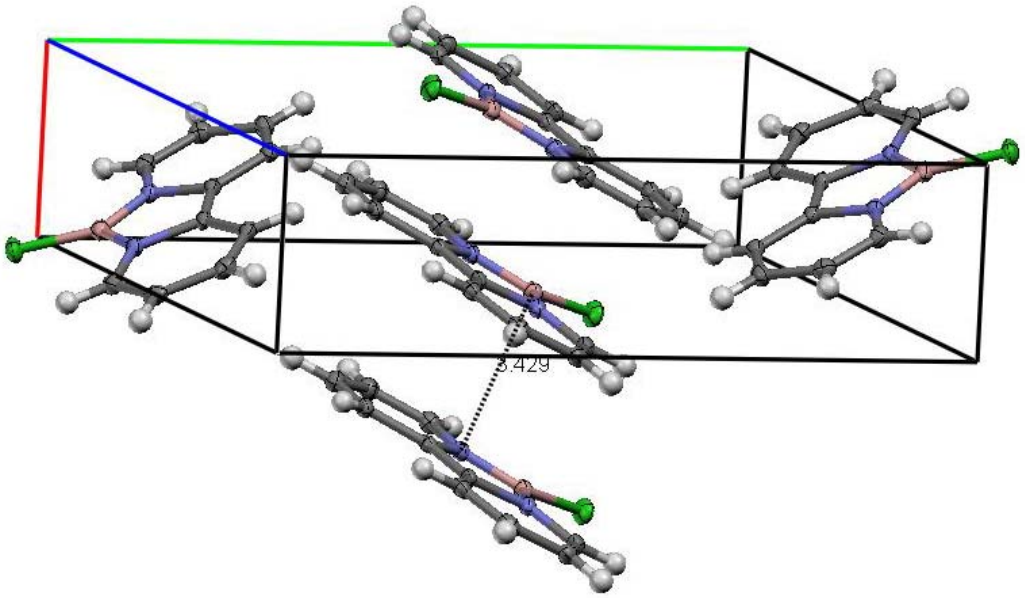

Figure S2. A view of the packing in the crystal structure of **1**.

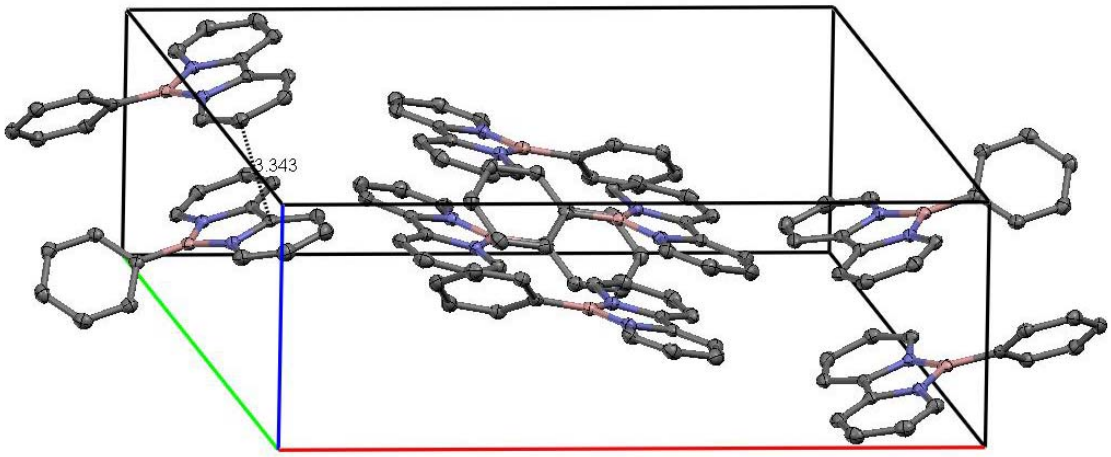

Figure S3. A view of the packing in the crystal structure of **2**.