The Effect of Fluorination on the Luminescent Behaviour of 8-Hydroxyquinoline Boron Compounds

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Supporting Information

General

All preparations were carried out using standard Schlenk vacuum/nitrogen and cannula techniques or a conventional nitrogen-filled glove-box, unless stated. Standard ^{1}H, ^{11}B, and ^{19}F NMR spectra and VT ^{19}F NMR were measured on a Bruker AC-250, Bruker AV-400 and JEOL JNM-EX270 spectrometers. ^{1}H NMR chemical shifts are referenced to the protio impurity of the deuterated solvent used. ^{11}B and ^{19}F chemical shifts are referenced to $BF_3{\cdot}OEt_2$, $CFCl_3$ and H_3PO_4 (85%), respectively. Mass spectra were recorded using either a VG Autospec or a VG Platform II spectrometer. Elemental analyses were performed by the Science Technical Support Unit at London Metropolitan University.

All solvents and deuterated solvents used in the preparations were dried over suitable reagents and distilled before use, unless stated. Molecular sieves used are of 4Å, 8 to 12 mesh type. CH_2Cl_2, $CDCl_3$, CH_3CN, pentane and hexane were dried over CaH_2 overnight under nitrogen before distillation. Alternatively, pentane and heptane were dried by passing through a column filled with Q-5 reagent (13 wt % CuO on alumina) and activated alumina pellets (3 mm). Benzene and deuterated benzene were dried by refluxing over sodium or potassium metal with benzophenone ketyl as

indicator. 8-hydroxyquinoline (8-HQ) was used as from commercial sources, without further purification.

*Synthesis of $(4\text{-}FC_6H_4)_2B(8\text{-}OC_9H_6N)$ ($B(4\text{-}FC_6H_4)_2Q$) (**2**).*

$(4\text{-}FC_6H_4)_3B$ (230 mg, 0.777 mmol) and 8-HQ (112 mg, 0.777 mmol) were weighed in a glove-box and placed into a Schlenk flask where they were dissolved by 20 mL of CH_2Cl_2. The resulting solution was bright-yellow. They were stirred under nitrogen overnight, and 16 hours later the solvent was removed under reduced pressure, leaving a yellow solid. Recrystallisation was performed in hexane at -20ºC (yield 56%). EI-MS+ (m/z): 345 ($(4\text{-}FC_6H_4)_2B(8\text{-}OC_9H_6N)$) 250 ($(4\text{-}FC_6H_4)B(8\text{-}OC_9H_6N$) fragment). ^{11}B NMR (δ, $CDCl_3$, 86 MHz): 10.7. ^{19}F NMR (δ, $CDCl_3$, 235 MHz): -116.4 (s). ^{1}H NMR (δ, $CDCl_3$, 250 MHz, *J* in Hz): 8.52 (H, d, $^{3}J_{H\text{-}H}$ 5.1, H_2) 8.44 (H, d, $^{3}J_{H\text{-}H}$ 8.3, H_4) 7.71-7.62 (m, 8-HQ) 7.39-7.29 (m, C_6H_4) 7.18 (H, d, $^{3}J_{H\text{-}H}$ 7.7) 6.99-6.92 (m) 1.58.

*Synthesis of $(C_6F_5)_2B(8\text{-}OC_9H_6N)$ ($B(C_6F_5)_2Q$) via $(C_6F_5)_2BCl$. (**3**)*

$(C_6F_5)_2BCl$ (150 mg, 0.394 mmol) and 8-HQ (57.0 mg, 0.394 mmol) were weighed in a glove-box and placed into a Schlenk flask where they were dissolved by 50 mL of CH_2Cl_2, resulting in a bright-yellow solution. They were stirred under nitrogen for 2 hours, after which the solvent was removed under reduced pressure leaving a yellow solid (yield 91%). CHN elemental analysis (%) (calc. for $(C_6F_5)_2B(8\text{-}OC_9H_6N)$: C, 51.57; H, 1.24; N, 2.86) found: C, 51.53; H, 1.20; N 2.79. EI-MS+ (m/z): 489 ($[M]^+$ 322 ($[M\text{-}C_6F_5]^+$). ^{19}F (δ, $CDCl_3$, 235 MHz, *J* in Hz): -135.4 (2F, d, $^{3}J_{F\text{-}F}$ 25, *o*-F) -156.0 (F, t, $^{3}J_{F\text{-}F}$ 21, *p*-F) -163.3 (2F, m, *m*-F). ^{11}B NMR (δ, $CDCl_3$, 86 MHz): 7.0. ^{1}H NMR (δ, $CDCl_3$, 250 MHz, *J* in Hz): 8.85 (H, d, $^{3}J_{H\text{-}H}$ 5.3, H_2) 8.56 (H, d, $^{3}J_{H\text{-}H}$ 8.2,

H_4), 7.78-7.67 (m), 7.39 (H, d, $^3J_{H\text{-}H}$ 8.2), 7.21 (H, d, $^3J_{H\text{-}H}$ 7.6). Crystals suitable for single crystal X-ray diffraction were obtained in hexane at room temperature.

Figure 5 in the manuscript shows the intermolecular packing interactions present in the crystals of **3**. The π-π stacking interaction (**a**) has mean interplanar and centroid···centroid separations of *ca.* 3.67 and 3.92 Å respectively, the two rings being inclined by *ca.* 11°. The F···π interaction (**b**) has an F···π distance of *ca.* 3.21 Å and a C–F···π angle of *ca.* 156°, and this vector is inclined to ring **B** by *ca.* 78°. Interactions (**a**) and (**b**) subtend an angle of *ca.* 148° at the centroid of ring **B**. The F···π interaction (**c**) has an F···π distance of *ca.* 2.92 Å, a C–F···π angle of *ca.* 147°, and this vector is inclined to ring **C** by *ca.* 75°. The 8-hydroxyquinolate ring system stacks with its centrosymmetrically related counterpart such that ring **C** in one molecule overlays ring **D** in the next with mean interplanar and centroid···centroid separations of *ca.* 3.66 and 4.40 Å respectively. This significant offset means that it is the *para* protons on each ring that actually sit over the ring centroids of the rings in the neighbouring molecule, and these C–H···π interactions have H···π distances of (**d**) *ca.* 3.68 Å, and (**e**) *ca.* 3.70 Å [C–H distances normalised to 0.96 Å]. Interactions (**c**) and (**e**) subtend an angle of *ca.* 167° at the centroid of ring **C**.