

Morphology-driven absorption and emission colour changes in liquid-crystalline, cyclometallated platinum(II) complexes.

Valery N. Kozhevnikov, Bertrand Donnio, Benoît Heinrich and Duncan W. Bruce

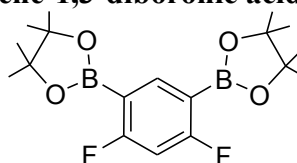
Electronic Supplementary Information

Experimental Section

Materials and Methods. All commercially available reagents were used as received. TLC was carried out on silica gel Si 60-F254. Column chromatography was carried out on silica gel Si 60, mesh size 0.040-0.063 mm (Merck, Darmstadt, Germany). Nuclear magnetic resonance spectra were recorded on a Jeol JNM-EX 270 FT NMR system or Bruker 400 MHz and referenced to TMS or residual solvent resonances. UV-Vis and Infrared spectra were obtained by using a Shimadzu UV-2401 PC and Shimadzu IR Prestige-21 spectrometers, respectively. UV-Vis spectra were obtained using a Shimadzu UV-2401 PC instrument. Microanalyses were performed at the Department of Chemistry, University of York using Exeter Analytical Inc. CE 440 instrument. Hitachi F-4500 fluorescence spectrophotometer was used for recording emission and excitation spectra. The phase transition temperatures were determined using Mettler Toledo DSC-822e differential scanning calorimeter with a heating and cooling rate of $10^{\circ}\text{C min}^{-1}$ (the apparatus was calibrated with indium, 156.6°C). Texture observations were made using Olympus BX50 polarizing microscope in conjunction with a Linkam LTS350 hot stage and Linkam TMS92 control unit.

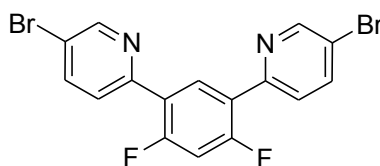
Small-angle X-ray scattering (SAXS) patterns were obtained with two different experimental setups, by using linear $\text{CuK}\alpha_1$ beams ($\lambda = 1.5405 \text{ \AA}$) from a sealed-tube generator (600 W) equipped with bent quartz monochromators. The crude powder was filled in Lindemann capillaries of 1 mm diameter and $10 \mu\text{m}$ wall-thickness, and in each case, exposure times were varied from 1 to 24 h. Patterns at scattering vectors from 0.09 to 2.1 \AA^{-1} were acquired with a curved Inel CPS 120 counter gas-filled detector, by controlling the sample temperature within $\pm 0.01^{\circ}\text{C}$ between 20 to 200°C . Patterns of the pristine sample at room temperature were completed in the 0.05 to 0.10 \AA^{-1} range, by using the other set-up with imaging plate detection (STORM 820 scanner from Molecular Dynamics in $50 \mu\text{m}$ resolution). Exposure times were varied between 1 and 24 h.

4,6-difluorobenzene-1,3-diboronic acid dipinacol ester 1

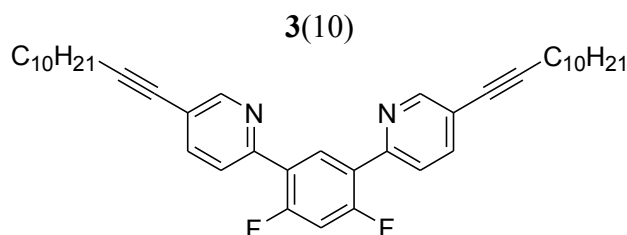


A mixture of 1,5-dibromo-2,4-difluorobenzene (2.72 g, 10 mmol), bispinacolatodiboron (6.6 g, 22 mmol), potassium acetate (4.9 g, 50 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ and dry DMSO (30 cm^3) was degassed by bubbling argon through the mixture for 10 minutes. The reaction mixture was stirred at 80°C for 10 h and filtered. The solid on the filter was washed with chlorophorm ($2 \times 50 \text{ cm}^3$). The filtrate was washed with water ($3 \times 50 \text{ cm}^3$). Organic layer was dried under MgSO_4 and the solvent was removed under reduced pressure. The residue was dissolved in hot petrol ether (50 cm^3) and filtered. The filtrate was evaporated to dryness and the product was purified by column chromatography (silica gel, petrol ether/ethyl acetate, 10/1) to give the title product as colourless solid. Yield 2.6 g, 71%. δ_{H} (270 MHz; CDCl_3 ; solvent): 1.34 (24H, s, 8 x CH_3), 6.71 (1H, t, J 9.8, 5-H), 8.11 (1H, t, J 7.5, 2-H). Elemental analysis calcd for $\text{C}_{18}\text{H}_{26}\text{B}_2\text{F}_2\text{O}_4$: C 59.07, H 7.16; found C 59.07, H 7.34.

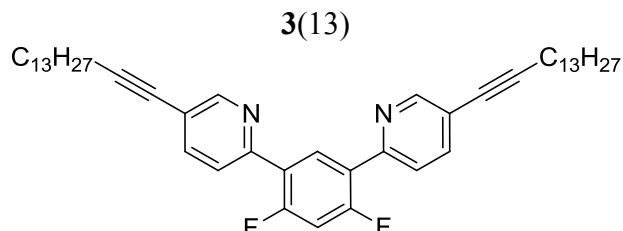
4,6-difluoro-1,3-di(5-bromo-2-pyridyl)benzene 2



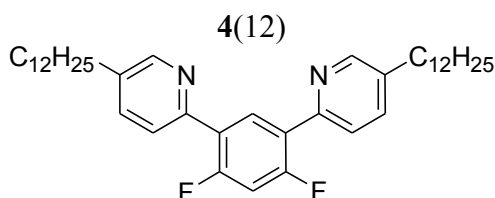
A mixture of 5-bromo-2-iodopyridine (6.81 g, 24 mmol), 4,6-difluorobenzene-1,3-diboronic acid dipinacol ester (3.66 g, 10 mmol), K_3PO_4 (6.36 g, 30 mmol) and dry DMF (150 cm³) was degassed by bubbling argon through the mixture for 10 minutes. $Pd(PPh_3)_4$ (693 mg, 0.6 mmol) was added and the mixture was degassed for additional 15 minutes. The reaction mixture was then stirred at 100°C for 14 hours under argon atmosphere. The solvent was removed under reduced pressure. The residue was treated with methanol (100 cm³) and filtered. The solid was placed in a beaker and stirred with water (100 cm³) for 5 min, filtered, washed with water (50 cm³) and methanol (20 cm³). The solid was then heated to reflux with methanol (100 cm³) cooled to room temperature and filtered to give the titled product. Yield 2.95 g 69%; δ_H (270 MHz; $CDCl_3$; solvent): 6.96 (1H, t, J 10.5.), 7.63 (2H, d, J 8.0), 7.83 (2H, dd, J 8.0, 1.9), 8.59 (1H, t, J 8.9), 8.47 (dd, J 1.9, 0.7, 2H); Elemental analysis calcd for $C_{16}H_8Br_2F_2N_2$: C 45.11, H 1.89, N 6.58; found C 44.93, H 1.90, N 6.43.



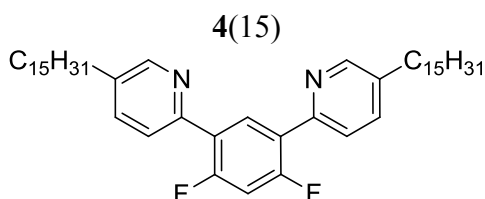
A mixture of bibromo compound **NCN-16** (718 mg, 1.69 mmol), CuI (107 mg, 0.56 mmol), 1-dodecyne (843 mg, 5.07 mmol), dry triethylamine (50 ml) and dry DMF (50 ml) was degassed by bubbling argon through the mixture for 15 min. Catalyst $Pd(Ph_3P)_4$ (196 mg, 0.17 mmol), was added and the reaction mixture was heated under reflux for 12 h. The solvent was removed *in vacuo* and the product was purified by column chromatography (silica gel, petrol ether / ethyl acetate, 10/1). Yield 640 mg, 63%. δ_H (270 MHz; $CDCl_3$; solvent): 0.85 (6H, t, J 7.3), 1.25-1.43 (28H, m), 1.59 (4H, q, J 7.8), 2.42 (4H, t, J 7.8), 6.94 (1H, t, J 8.0), 7.70 (m, 4H), 8.63 (t, 1H, J 9.0), 8.70 (br.s, 2H). Elemental analysis calcd for $C_{40}H_{50}F_2N_2$: C 80.50, H 8.44, N 4.69; found C 80.53, H 8.44, N 4.72.



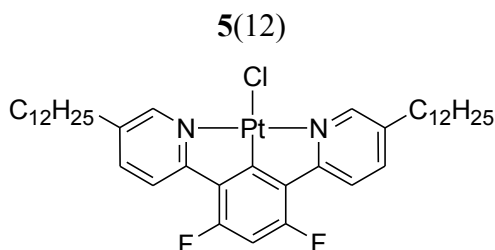
A mixture of bibromo compound **NCN-16** (426 mg, 1 mmol), CuI (70 mg), 1-tetradecyne (624 mg, 3 mmol), dry triethylamine (30 ml) and dry DMF (30 ml) was degassed by bubbling argon through the mixture for 15 min. Catalyst $Pd(Ph_3P)_4$ (116 mg, 0.045 mmol), was added and the reaction mixture was heated under reflux for 12 h. The solvent was removed *in vacuo* and the product was purified by column chromatography (silica gel, petrol ether / ethyl acetate, 5/1). Yield 120 mg, 45%. δ_H (270 MHz; $CDCl_3$; solvent): 0.81 (6H, t, J 7.3), 1.15-1.45 (40H, m), 1.55 (4H, q, J 7.4), 2.38 (4H, t, J 7.2), 6.94 (1H, t, J 10.7), 7.68 (m, 4H), 8.59 (t, 1H, J 9.1), 8.65 (br.s, 2H).



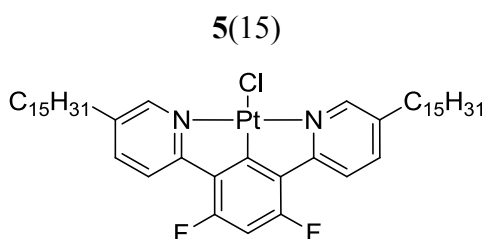
The starting material (120 mg, 0.2 mmol) was dissolved in ethylacetate (10 cm³), Pd/C (10%, 50 mg) was added. Hydrogen was bubbled through the mixture for 10 min and then reaction mixture was stirred for 2 days at room temperature under hydrogen atmosphere. The reaction mixture was then filtered and the filtrate was evaporated under reduced pressure. Yield 108 mg, 89%. mp 40.2-40.7°C. δ_{H} (270 MHz; CDCl₃; solvent): 0.81 (6H, t, *J* 7.3), 1.17-1.37 (36H, m), 1.53-1.68 (4H, m), 2.58 (4H, t, *J* 7.3), 6.93 (1H, t, *J* 10.5.), 7.50 (2H, dd, *J* 8.0, 1.9), 7.61 (2H, d, *J* 8.0), 8.47 (br.s, 2H), 8.48 (1H, t, *J* 8.9).



The starting material (520 mg, 0.76 mmol) was dissolved in ethylacetate (30 cm³), Pd/C (10%, 250 mg) was added. Hydrogen was bubbled through the mixture for 10 min and then reaction mixture was stirred for 7 days at room temperature under hydrogen atmosphere. The reaction mixture was then filtered and the filtrate was evaporated under reduced pressure. Yield 484 mg, 92%. δ_{H} (270 MHz; CDCl₃; solvent): 0.80 (6H, t, *J* 7.3), 1.1-1.7 (52H, m), 2.58 (4H, t, *J* 7.3), 6.92 (1H, t, *J* 10.5.), 7.50 (2H, dd, *J* 8.0, 1.9), 7.61 (2H, d, *J* 8.0), 8.47 (br.s, 2H), 8.48 (1H, t, *J* 8.9).



A mixture of the ligand (300 mg, 0.5 mmol), K₂PtCl₄ (206 mg, 0.5 mmol) and acetic acid was (50 cm³) heated under reflux for 24 hours. Precipitated upon cooling solid was filtered off, washed on filter with acetone (20 cm³), dissolved in chloroform (10 cm³) and filtered. Acetone 30 (cm³) was added to the filtrate, and precipitated solid was filtered off to give the product. Yield 292 mg, 59%. δ_{H} (270 MHz; CDCl₃; solvent): 0.85 (6H, t, *J* 7.3), 1.1-1.7 (40H, m), 2.64 (4H, t, *J* 7.2), 6.55 (1H, t, *J* 11.1.), 7.70 (4H, m), 9.05 (br.s, 2H). Elemental analysis calculated for C₄₀H₅₇ClF₂N₂Pt: C 57.58, H 6.89, N 3.36; found C 57.55, H 6.86, N 3.31.

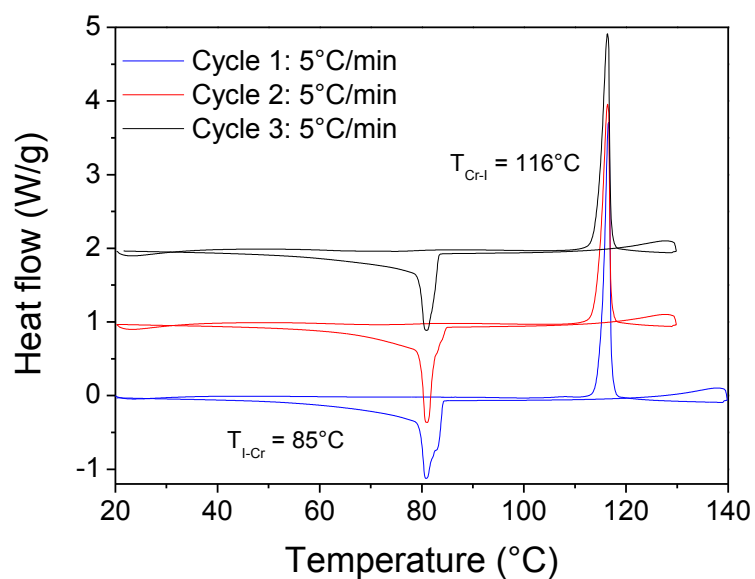


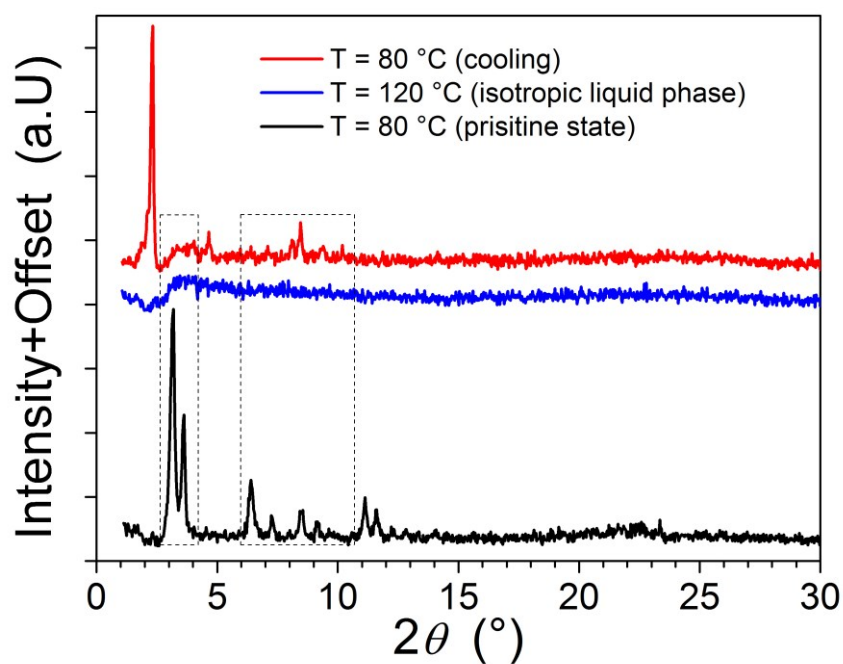
A mixture of the ligand (220 mg, 0.32 mmol), K₂PtCl₄ (132 mg, 0.32 mmol) and acetic acid was (50 cm³) heated under reflux for 24 hours. Precipitated upon cooling solid was filtered off, washed

on filter with acetone (20 cm³), dissolved in chloroform (10 cm³) and filtered. Acetone 20 (cm³) was added to the filtrate, and precipitated solid was filtered off to give the product. Yield 187 mg, 64%. δ_{H} (270 MHz; CDCl₃; solvent): 0.85 (6H, br.t, *J* 7.5), 1.1-1.7 (52H, m), 2.66 (4H, t, *J* 7.2), 6.69 (1H, t, *J* 11.1), 7.74 (4H, m), 9.11 (br.s, 2H). Elemental analysis calculated for C₄₆H₆₉ClF₂N₂Pt: C 60.15, H 7.57, N 3.05; found C 60.33, H 7.54, N 3.01.

DSC of **5**(12)

Same pan, three consecutive identical cycles





SAXS diffractogram of a mixture of **5**(12) and **5**(15) at 83 °C in crystalline (black), isotropic (blue) and liquid crystalline states (red).

The mixture of **5**(12) and **5**(15) was prepared by dissolving 30 mg of each compound in 20 mL of dichloromethane, followed by evaporation in vacuum.