Electronic Supplementary Material (ESI) for Chemical Communications

Polarised Phosphorescent Emission in an Organoplatinum(II)-based Liquid-crystalline Polymer

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Supplementary Information

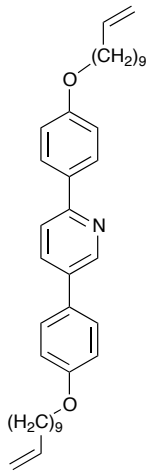
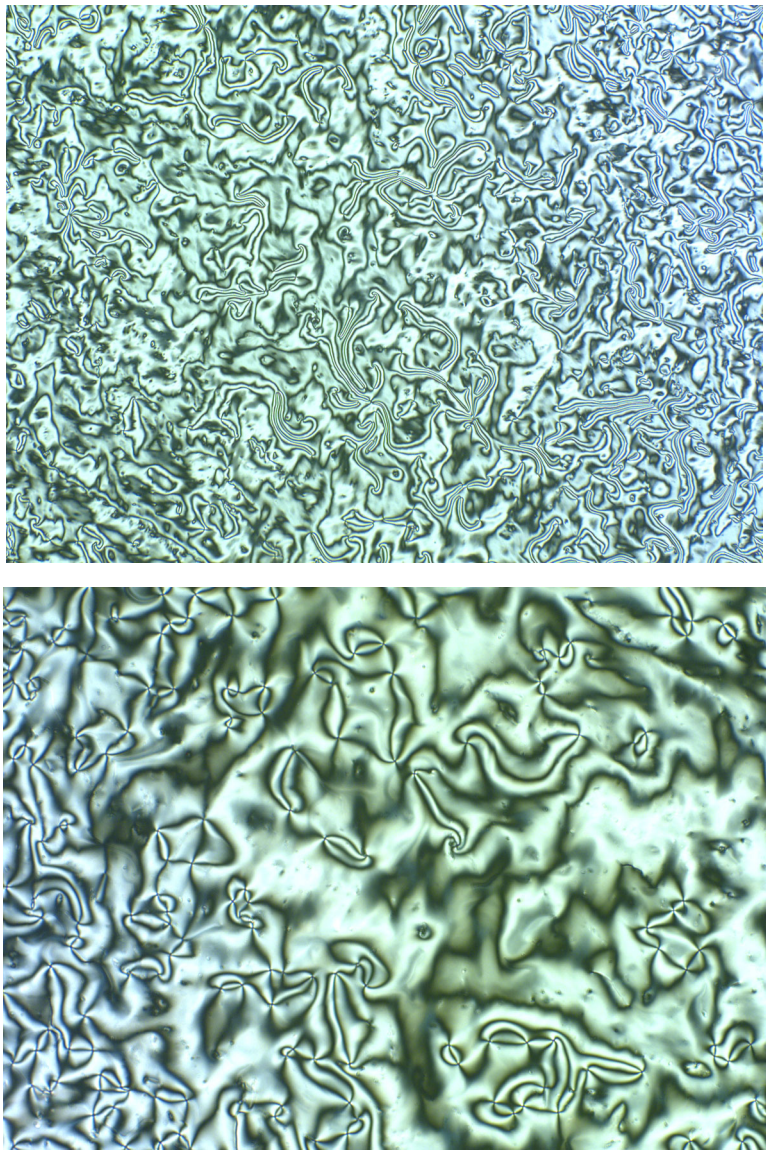


Figure S1 Analogue of **2** *without* the fused C_5 ring



(a)

(b)

Figure S2 (a) SmC phase (204 °C on cooling) and (b) SmI phase (167 °C on cooling) of the compound in Fig. S1.

Synthesis

2,5-Di{4-(undec-10-enyloxyphenyl)}cyclopentenopyridine (**1**).

2,5-Di(4-hydroxyphenyl)cyclopentenopyridine (0.400 g, 1.32 mmol) was added to a solution of 11-bromo-1-undecene (0.7 cm^3, 3.18 mmol) and potassium carbonate (1.83 g, 13.2 mmol) in DMF (60 cm^3). The dark solution was stirred and heated at 95 °C for 12 h. After cooling to room temperature, the mixture was dropped into H_2O (50 cm^3) and the resultant precipitate was filtered and washed with EtOH (2 × 5 cm^3) and acetone (4 cm^3). **1** was obtained as a brown solid (0.550 g, 68%).

^{1}H NMR δ_H (399.78 MHz, $CDCl_3$): 8.49 (1H, s, H^6), 7.73 (2H, d, J(H-H) = 8.8 Hz, AAXX'), 7.40 (2H, d, J(H-H) = 8.7 Hz, AA'XX'), 6.98 (4H, dd, ^3J(H-H) = 8.8 Hz, ^4J(H-H) = 2.2 Hz, AA'XX'), 5.81 (2H, m, C*H*=CH_2), 4.96 (4H, m, CH=C*H*$_2$), 4.00 (4H, m, OCH_2), 3.14 (2H, t, CH_2 cyclopent), 3.01 (2H, t, CH_2 cyclopent), 2.04 (6H, m, 2H cyclopent + 4H CH_2), 1.80 (4H, m, CH_2), 1.48 (4H, m, CH_2), 1.30 (20H, br m, CH_2). MS(ESI+) *m/z* (%): 608.4 (100) [M^+]. Calcd. for $C_{42}H_{57}NO_2$ (607.44): C 82.97, H 9.46, N 2.30; found C 83.07, H 9.29, N 2.36.

Complex **4**.

Compound **2** (0.500 g, 0.822 mmol) was added over a yellow-pink suspension of [$PtCl_2(dms)_2$] (0.321 g, 0.822 mmol) in deoxygenated ethoxyethanol (70 cm^3). The mixture was heated to reflux (125 ºC) and stirred overnight. The solvent was then removed and the intermediate dms complex, [Pt(L)Cl(dms)] (**3**) was collected by addition of EtOH as a dark solid (0.560 g, 0.622 mmol, 76%). Without further purification, Na(acac) (0.087 g, 0.622 mmol) in a mixture of acetone/CH_2Cl_2 (2:1, 45 cm^3), was added to the dark solid obtained. The resultant suspension was stirred overnight at room temperature and then the solvent was removed, CH_2Cl_2 was added and the suspension filtered through celite. Complex **4** was obtained as a yellow solid after evaporation of the solvent and purification by column chromatography on silica using $CHCl_3$ as eluent (0.213 g, 38%).

^{1}H NMR δ_H (399.78 MHz, $CDCl_3$): 8.82 (1H, d, ^3J(Pt-H) = 36.0 Hz, H^6), 7.51 (1H, d, ^3J(H-H) = 7.51 Hz, Ar), 7.37 (2H, d, J = 8.7 Hz, AA'XX'), 7.18 (1H, d, ^3J(H-H) = 2.6 Hz, H^x),

6.99 (2H, d, J = 8.7 Hz, AA'XX'), 6.66 (1H, dd, ^{3}J(H-H) = 8.6 Hz, ^{4}J(H-H) = 2.6 Hz, Ar), 5.81 (2H, m, CH=), 5.44 (1H, s, CH acac), 4.97 (4H, m, =CH_2), 4.08 (2H, t, ^{3}J(H-H) = 6.6 Hz, OCH_2), 4.01 (2H, t, ^{3}J(H-H) = 6.5 Hz, OCH_2), 3.36 (2H, t, ^{3}J(H-H) = 7.3 Hz, CH_2 cyclopenten), 3.02 (2H, t, ^{3}J(H-H) = 7.6 Hz, CH_2 cyclopenten), 2.18 (2H, m, CH_2 cyclopenten), 2.04 (4H, m, CH_2), 1.99 (3H, s, CH_3 acac), 1.94 (3H, s CH_3 acac), 1.81 (4H, m, CH_2), 1.48 (4H, m, CH_2), 1.31 (20H, br m, CH_2). MS(MALDI+) *m/z* (%): 801.4 (100) [(M – acac)$^{+}$], 900.4 (18) [M^{+}]. Calcd. for $C_{47}H_{63}NO_4Pt$ (900.44): C 62.64, H 7.05, N 1.56; found C 62.55, H 7.04, N 1.65.

Polymer **5**.

Over a pale yellow suspension of complex **4** (0.15 g, 0.166 mmol) in dry toluene (1.5 cm^3), 1,1,3,3-tetramethyldisiloxane (42 µl, 0.166 mmol) and a solution of [$PtCl_2$(COD)] in dichloromethane (1% w/w, 30 µl) were added. The temperature was increased to 50 °C and the resultant solution was stirred overnight. The polymer **4** was then isolated as a pale yellow solid by precipitation in methanol, before being purified by successive precipitations from methanol and air dried (0.169 g, 91%).

^{1}H NMR δ_H (399.78 MHz, $CDCl_3$): 8.76 (1H, br s, H^6), 7.43 (1H, br s, Ar), 7.35 (2H, br s, AA'XX'), 7.15 (1H, br s, H^x), 6.96 (2H, br s, AA'XX'), 6.60 (1H, br s, Ar), 5.43 (1H, s, CH acac), 4.01 (4H, m, OCH_2), 3.29 (2H, br s, CH_2 cyclopenten), 2.98 (2H, br s, CH_2 cyclopenten), 2.13 (2H, m, CH_2 cyclopenten), 1.98 (3H, s, CH_3 acac), 1.93 (3H, s CH_3 acac), 1.81 (4H, m, CH_2), 1.47 (4H, m, CH_2), 1.28 (28H, br m, CH_2), 0.53 (4H, m, CH_2-Si), 0.06 (12H, s, CH_3, siloxane), 0.02 (6H, s, CH_3, siloxane). Calcd. for $C_{53}H_{83}NO_6PtSi_3$ (1108.52): C 57.37, H 7.55, N 1.26; found C 57.66, H 7.29, N 1.28.