

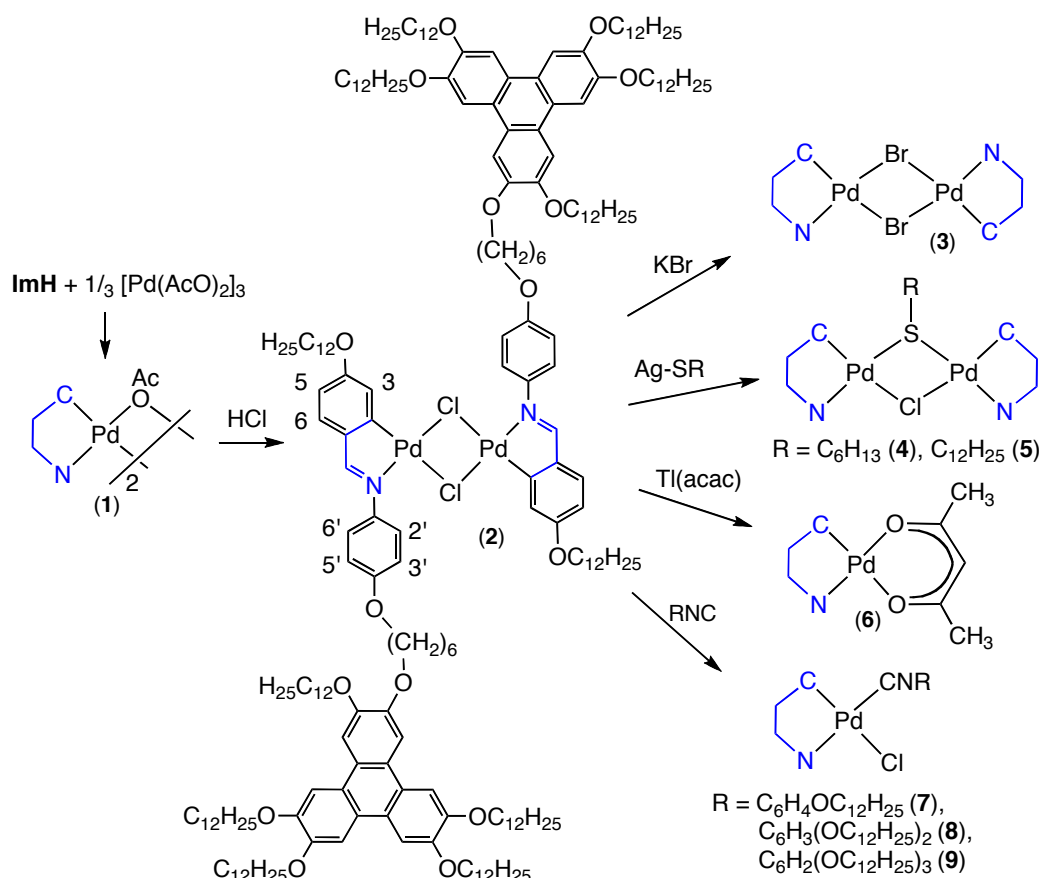
## Supporting Information for

### *Alignment of Palladium Complexes into Columnar Liquid Crystals Driven by Peripheral Triphenylene Substituents*

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**Scheme S1.** Synthesis of palladium orthometallated complexes



## Experimental Section

Combustion analyses were made with a Perkin-Elmer 2400 microanalyzer. IR spectra ( $\text{cm}^{-1}$ ) were recorded on a Perkin-Elmer BX instrument and  $^1\text{H}$  NMR spectra on Bruker AV-400 (400.13 MHz) or Varian 500 (499.73 Hz) instruments in  $\text{CDCl}_3$ . UV/Vis absorption spectra were obtained by means of a Shimadzu UV-2550 spectrophotometer, in dichloromethane ( $\sim 1 \times 10^{-4}$  M). Luminescent data was recorded with a Perkin-Elmer LS-55 luminescence spectrometer. Luminescence quantum yields were obtained at room temperature using the optically dilute method ( $A < 0.1$ ) in degassed dichloromethane (quantum yield standard was quinine sulfate dihydrate in 0.5 M  $\text{H}_2\text{SO}_4$  ( $\Phi_{\text{fl}} = 0.51$ ) using an excitation wavelength of 310 nm).<sup>1</sup>

Microscopy studies were carried out on a Leica DMRB microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . For differential scanning calorimetry (DSC) a Perkin-Elmer DSC7 instrument was used, which was calibrated with water and indium. The scanning rate was  $10\text{ }^\circ\text{C min}^{-1}$ , the samples were sealed in aluminum capsules in the air, and the holder atmosphere was dry nitrogen.

The X-ray studies were carried out in Debye-Scherrer operation mode, using a powder diffractometer with a high temperature implement. For the experiment, Lindemann capillaries of diameter 0.6 mm were utilized. A linear position-sensitive detector (DSP) was employed to measure the diffracted intensity. The angular resolution was better than  $0.01^\circ$ , and the  $2\theta$  interval was  $0.5\text{--}35^\circ$  ( $\theta$  is the Bragg angle). Monochromatic  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 1.5406\text{ \AA}$ ) was used.

Literature methods were used to prepare 2,3,6,7,10,11-hexakis(dodecyloxy)triphenylene,<sup>2</sup> and B-bromocatecholborane.<sup>3</sup>

**Preparation of 4-(6-bromohexyloxy)nitrobenzene (A).** To a solution of 4-nitrophenol (4.6 g, 33.1 mmol) and 1,6-dibromohexane (8.9g, 36.4 mmol) in dry acetone (120 mL) under nitrogen

was added  $K_2CO_3$  (6.1 g, 44.3 mmol). After refluxing for 48 h, water (150 mL) was added, the product was extracted in dichloromethane ( $3 \times 50$  mL) and purified by column chromatography (silica gel, dichloromethane/hexane 1:1 v/v as eluent). The solvent was evaporated to obtain a white solid with a low melting point (4.9 g, 50 % yield).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  8.18 (d, 2H<sub>1</sub>, ArH), 6.93 (d, 2H<sub>2</sub>, ArH), AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 9.3$  Hz,  $J_{A,A'} \approx J_{X,X'}$ ), 4.05 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>), 3.43 (t, 2H,  $J = 6.8$  Hz, OCH<sub>2</sub>), 1.87 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.52 (m, 4H, CH<sub>2</sub>). Anal. Calcd. (%) for  $C_{12}H_{16}BrNO_3$ : C, 47.69; H, 5.34; N, 4.64. Found: C, 47.72; H, 5.38; N, 4.70.

**Preparation of monohydroxy-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (C).** The monohydroxy derivative C was synthesized as reported for similar systems.<sup>4</sup> To an ice-cooled solution of 2,3,6,7,10,11-hexakis(dodecyloxy)triphenylene (0.5 g, 0.37 mmol) in dichloromethane (15 mL) was added B-bromocatecholborane (0.6 mL, 0.44 mmol, 0.74 M in dichloromethane). The solution was stirred at room temperature for 24 h. Then it was poured on ice water (50 mL) and extracted with dichloromethane ( $2 \times 30$  mL). The combined organic phases were dried over  $MgSO_4$  and the solvent removed under vacuum. The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate 50:1 v/v as eluent) to yield an off-white solid (0.14 g, 31 % yield).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.96 (s, 1H, ArH), 7.82 (m, 4H, ArH), 7.77 (s, 1H, ArH), 5.90 (s, 1H, OH), 4.30-4.19 (m, 10H, OCH<sub>2</sub>), 1.93 (m, 10H, OCH<sub>2</sub>CH<sub>2</sub>), 1.55-1.27 (m, 90H, CH<sub>2</sub>), 0.88 (t, 15H,  $J = 7.1$  Hz, CH<sub>3</sub>). Anal. Calcd. (%) for  $C_{78}H_{132}O_6$ : C, 80.35; H, 11.41; Found: C, 80.37; H, 11.45.

**Preparation of 2-(6-(4-nitrophenoxy)hexyloxy)-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (D).** To a solution of monohydroxy-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (2 g, 1.75 mmol) and 4-(6-bromohexyloxy)nitrobenzene (4.3 g, 14.2 mmol) in dry 2-butanone (30 mL), under nitrogen, was added  $K_2CO_3$  (1.45 g, 10.5 mmol). The mixture was heated at 100 °C for 16 h. Then water (50 mL) was added and the mixture was extracted with dichloromethane ( $2 \times 50$

mL). The combined organic layers were dried over  $\text{MgSO}_4$  and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, hexane/dichloromethane 2:1 v/v as eluent) to give a yellow waxy solid (2.11 g, 87 % yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.17 (d, 2H,  $\text{O}_2\text{N-C}_6\text{H}_4^-$ , AA' part of AA'XX' spin system,  $N_{\text{A,X}} = J_{\text{A,X}} + J_{\text{A,X}'} = 9.3$  Hz,  $J_{\text{A,A}} \approx J_{\text{X,X}'}$ ), 7.83 (s, 6H, ArH-triphenylene), 6.93 (d, 2H,  $\text{O}_2\text{N-C}_6\text{H}_4^-$ , XX' part of AA'XX' spin system,  $J_{\text{A,X}} + J_{\text{A,X}'} = 9.3$  Hz,  $J_{\text{A,A}} \approx J_{\text{X,X}'}$ ), 4.22 (m, 12H,  $\text{OCH}_2$ ), 4.07 (t, 2H,  $J = 6.6$  Hz,  $\text{OCH}_2$ ), 1.92 (m, 14H,  $\text{OCH}_2\text{CH}_2$ ), 1.70-1.26 (m, 94H,  $\text{CH}_2$ ), 0.88 (m, 15H,  $\text{CH}_3$ ). Anal. Calcd. (%) for  $\text{C}_{90}\text{H}_{147}\text{NO}_9$ : C, 77.93; H, 10.68; N, 1.01. Found: C, 78.02; H, 10.73; N, 1.15.

**Preparation of 2-(6-(4-acetilaminophenoxy)hexyloxy)-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (E).** To a mixture of 2-(6-(4-nitrophenoxy)hexyloxy)-3,6,7,10,11-pentakisdodecyloxytriphenylene (2 g, 1.44 mmol) in glacial acetic acid (100 ml), powder tin (1.26 g) was added. The mixture was refluxed for 4 h. After reaching room temperature, water (200 ml) was added and the mixture was extracted with dichloromethane ( $2 \times 100$  ml). The combined organic layers were dried over  $\text{MgSO}_4$  and the solvent was evaporated under vacuum to give a white solid (1.84 g, 92 % yield).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.83 (s, 6H, ArH-triphenylene), 7.35 (d, 2H, ArH, AA' part of AA'XX' spin system,  $N_{\text{A,X}} = J_{\text{A,X}} + J_{\text{A,X}'} = 9.0$  Hz), 7.06 (s, 1H, NH), 6.85 (d, 2H, ArH, XX' part of AA'XX' spin system,  $N_{\text{A,X}} = J_{\text{A,X}} + J_{\text{A,X}'} = 9.0$  Hz), 4.22 (m, 12H,  $\text{OCH}_2$ ), 4.07 (t, 2H,  $J = 6.5$  Hz,  $\text{OCH}_2$ ), 2.14 (s, 3H,  $\text{COCH}_3$ ), 1.92 (m, 14H,  $\text{OCH}_2\text{CH}_2$ ), 1.70-1.26 (m, 94H,  $\text{CH}_2$ ), 0.88 (m, 15H,  $\text{CH}_3$ ). Anal. Calcd. (%) for  $\text{C}_{92}\text{H}_{151}\text{NO}_8$ : C, 78.97; H, 10.88; N, 1.00. Found: C, 79.01; H, 10.95; N, 1.19.

**Preparation of 2-(6-(4-aminophenoxy)hexyloxy)-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (F).** To a mixture of 2-(6-(4-acetilaminophenoxy)hexyloxy)-3,6,7,10,11-pentakisdodecyloxytriphenylene (1 g, 0.74 mmol) in ethanol (40 ml), KOH (1.26 g) was added. The mixture was refluxed for 5 h and then the solvent was evaporated under vacuum. The residue was extracted with toluene ( $3 \times 50$  ml) and the solution obtained was washed with

water until neutral pH. The combined organic solution was dried over MgSO<sub>4</sub> and the solvent was evaporated under vacuum to give a red solid (0.73 g, 78 % yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.83 (s, 6H, ArH-triphenylene), 6.75 (d, 2H, ArH), 6.63 (d, 2H, ArH), AA'XX' spin system (N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 4.22 (m, 12H, OCH<sub>2</sub>), 4.07 (t, 2H, J = 6.5 Hz, OCH<sub>2</sub>), 3.40 (s, 2H, NH<sub>2</sub>), 1.92 (m, 14H, OCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.26 (m, 94H, CH<sub>2</sub>), 0.88 (m, 15H, CH<sub>3</sub>). Anal. Calcd. (%) for C<sub>90</sub>H<sub>149</sub>NO<sub>7</sub>: C, 79.65; H, 11.07; N, 1.03. Found: C, 79.72; H, 11.15; N, 1.12.

**Preparation of the Imine ligand (ImH).** The imine was synthesized by acetic acid condensation of the 4-octyloxy-benzaldehyde and 2-(6-(4-aminophenoxy)hexyloxy)-3,6,7,10,11-pentakisdodecyloxytriphenylene (0.200 g, 0.15 mmol) in toluene, as described for similar Schiff's bases.<sup>5</sup> The imine was isolated as a cream solid (0.148 g, 71 % yield). IR (KBr): 1627 [ν(C=N)] cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.38 (s, 1H, HCN), 7.83 (s, 6H, ArH-triphenylene), 7.81 (d, 2H<sup>2,6</sup>, ArH, AA' part of AA'XX' spin system (N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 7.19 (d, 2H<sup>3,5</sup>, ArH, AA' part of AA'XX' sytem, N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 6.96 (d, 2H<sup>3,5'</sup>, ArH, XX' part of AA'XX' spin system ((N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 6.91 (d, 2H<sup>2,6'</sup>, ArH), XX' part of AA'XX' spin system (N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 4.22 (m, 12H, OCH<sub>2</sub>), 4.00 (m, 4H, OCH<sub>2</sub>), 1.92-0.8 (138H, alkylic protons). Anal. Calcd. (%) for C<sub>105</sub>H<sub>169</sub>NO<sub>8</sub>: C, 80.15; H, 10.83; N, 0.89. Found: C, 80.25; H, 10.94; N, 0.92.

**Preparation of (μ-OAc)<sub>2</sub>[Pd<sub>2</sub>Im<sub>2</sub>] (1).** A mixture of palladium acetate (0.021 g, 0.031 mmol) and imine (0.147 g, 0.094 mmol) in glacial acetic acid was stirred at 50 °C for 14 h. The solvent was removed and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through silica. The complex was crystallized as a yellow solid by concentration of the solution and addition of acetone (0.148 g, 91% yield). IR/KBr: ν(C=N): 1609 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.83 (s, 12H, ArH-triphenylene), 7.44 (s, 2H, HC=N), 7.10 (d, J = 8.3 Hz, 2H<sup>6</sup>, ArH), 6.68 (d, 4H<sup>2,6</sup>, ArH), 6.65 (d, 4H<sup>3,5'</sup>, ArH), AA'XX' spin system (N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 6.53 (dd, J<sub>5,6</sub> = 8.3 Hz, J<sub>5,3</sub> = 2.4 Hz, 2H<sup>5</sup>, ArH), 6.05 (d, J = 2.4 Hz, 2H<sup>3</sup>, ArH), 4.22 (m, 24H, OCH<sub>2</sub>), 4.13-3.49 (m, 8H, OCH<sub>2</sub>);

1.92-0.8 (282H, alkylic protons + CH<sub>3</sub>COO). Anal. Calcd. (%) for C<sub>214</sub>H<sub>342</sub>Pd<sub>2</sub>N<sub>2</sub>O<sub>20</sub>: C, 73.95; H, 9.92; N, 0.81. Found: C, 73.83; H, 9.80; N, 0.85.

**Preparation of (μ-Cl)<sub>2</sub>[Pd<sub>2</sub>Im<sub>2</sub>] (2).** To a stirred solution of (μ-OAc)<sub>2</sub>[Pd<sub>2</sub>Im<sub>2</sub>] (0.079g, 0.027 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added dropwise a stoichiometric amount of a HCl solution in methanol (0.024 M, 2 ml). After stirring at room temperature for 1 hour the solution was evaporated to dryness. Addition of acetone (10 ml) afforded the chloro-bridged complex as a yellow solid which was purified by column chromatography (silica gel, dichloromethane as eluent) (0.054 g, 55 % yield). IR IR/KBr: ν(C=N): 1609 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.83 (s, 12H, ArH-triphenylene), 7.75 (s, 2H, HCN), 7.28 (d, J = 8.3 Hz, 2H<sup>6</sup>, ArH), 7.19 (d, 4H<sup>2',6'</sup>, ArH), 6.88 (d, 4H<sup>3',5'</sup>, ArH), AA'XX' spin system (N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 6.83 (d, J = 2.3 Hz, 2H<sup>3</sup>, ArH), 6.54 (dd, J<sub>5,6</sub> = 8.3 Hz, J<sub>5,3</sub> = 2.3 Hz, 2H<sup>5</sup>, ArH), 4.22 (m, 24H, OCH<sub>2</sub>), 4.01 (t, 4H, OCH<sub>2</sub>), 3.93 (t, 4H, OCH<sub>2</sub>), 1.92-0.8 (276H, alkylic protons). Anal. Calcd. (%) for C<sub>210</sub>H<sub>336</sub>Pd<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>16</sub>: C, 73.56; H, 9.88; N, 0.82. Found: C, 73.71; H, 9.63; N, 1.02.

**Preparation of (μ-Br)<sub>2</sub>[Pd<sub>2</sub>Im<sub>2</sub>] (3).** A mixture of (μ-Cl)<sub>2</sub>[Pd<sub>2</sub>Im<sub>2</sub>] (0.100 g, 0.029 mmol), potassium bromide (0.138g, 1.16 mmol) in dichloromethane/acetone (20 ml/10 ml) was refluxed for 5 hours. The resulting suspension was evaporated to dryness. The complex was extracted in dichloromethane (25 ml) and the insoluble potassium chloride was filtered off. Evaporation of the dichloromethane solution and addition of acetone (20 ml) afforded the complex as a yellow solid, which was filtered, washed with acetone and dried (0.076 g, 75% yield). IR/KBr: ν(C=N): 1609 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.83 (s, 12H, ArH-triphenylene), 7.77 (s, 2H, HCN), 7.26 (d, J<sub>6,5</sub> = 8.3 Hz, 2H<sup>6</sup>, ArH), 7.21 (d, 4H<sup>2',6'</sup>, ArH), 7.02 (d, 4H<sup>3',5'</sup>, ArH), AA'XX' spin system (N<sub>A,X</sub> = J<sub>A,X</sub> + J<sub>A,X'</sub> = 8.8 Hz, J<sub>A,A'</sub> ≈ J<sub>X,X'</sub>), 6.89 (d, J<sub>3,5</sub> = 2.2 Hz, 2H<sup>3</sup>, ArH), 6.53 (dd, J<sub>5,6</sub> = 8.3 Hz, J<sub>5,3</sub> = 2.2 Hz, 2H<sup>5</sup>, ArH), 4.22 (m, 24H, OCH<sub>2</sub>), 4.00 (t, 4H, OCH<sub>2</sub>), 3.92 (t, 4H, OCH<sub>2</sub>), 1.92-0.8 (276H, alkylic protons). Anal. Calcd. (%) for C<sub>210</sub>H<sub>336</sub>Pd<sub>2</sub>Br<sub>2</sub> N<sub>2</sub>O<sub>16</sub>: C, 71.70; H, 9.63; N, 0.80. Found: C, 71.54; H, 9.49; N, 0.99.

**Preparation of  $(\mu\text{-Cl})(\mu\text{-SC}_n\text{H}_{2n+1})[\text{Pd}_2\text{Im}_2]$ ,  $n = 6$  (**4**), **12** (**5**).** To a solution of  $(\mu\text{-Cl})_2[\text{Pd}_2\text{Im}_2]$  (0.03 mmol) in 20 mL of dichloromethane was added  $[\text{AgSC}_n\text{H}_{2n+1}]$  (0.04 mmol). The mixture was stirred in the dark for 5 h at room temperature. After filtering off the AgCl precipitate, ethanol (20 mL) was added. The resulting solution was concentrated to a small volume affording the complex as a yellow solid, which was filtered, washed with ethanol and dried.

**$n = 6$ :** 0.077g, 73% yield. IR/KBr:  $\nu(\text{C}=\text{N})$ : 1610  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.91 (s, 2H, HCN), 7.83 (s, 12H, ArH-triphenylene), 7.39 (d,  $J_{3,5} = 2.3$  Hz,  $2\text{H}^3$ , ArH), 7.27 (d,  $J = 8.3$  Hz,  $2\text{H}^6$ , ArH), 7.19 (d,  $4\text{H}^{2',6'}$ , ArH), 6.77 (d,  $4\text{H}^{3',5'}$ , ArH), AA'XX' spin system ( $N_{\text{A,X}} = J_{\text{A,X}} + J_{\text{A,X}'} = 8.8$  Hz,  $J_{\text{A,A}} \approx J_{\text{X,X}'}$ ), 6.56 (dd,  $J_{5,6} = 8.3$  Hz,  $J_{5,3} = 2.3$  Hz,  $2\text{H}^5$ , ArH), 4.22 (m, 24H,  $\text{OCH}_2$ ), 4.01 (t, 4H,  $\text{OCH}_2$ ), 3.96 (t, 4H,  $\text{OCH}_2$ ), 2.97 (t, 2H,  $\text{SCH}_2$ ); 1.92-0.8 (287H, alkylic protons). Anal. Calcd. (%) for  $\text{C}_{216}\text{H}_{349}\text{Pd}_2\text{ClN}_2\text{O}_{16}\text{S}$ : C, 73.89; H, 10.04; N, 0.80. Found: C, 73.57; H, 9.91; N, 0.84.

**$n = 12$ :** 0.084g, 71% yield. IR/KBr:  $\nu(\text{C}=\text{N})$ : 1610  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.91 (s, 2H, HCN), 7.83 (s, 12H, ArH-triphenylene), 7.40 (d,  $J_{3,5} = 2.3$  Hz,  $2\text{H}^3$ , ArH), 7.27 (d,  $J = 8.3$  Hz,  $2\text{H}^6$ , ArH), 7.20 (d,  $4\text{H}^{2',6'}$ , ArH), 6.77 (d,  $4\text{H}^{3',5'}$ , ArH), AA'XX' spin system ( $N_{\text{A,X}} = J_{\text{A,X}} + J_{\text{A,X}'} = 8.8$  Hz,  $J_{\text{A,A}} \approx J_{\text{X,X}'}$ ), 6.56 (dd,  $J_{5,6} = 8.3$  Hz,  $J_{5,3} = 2.3$  Hz,  $2\text{H}^5$ , ArH), 4.22 (m, 24H,  $\text{OCH}_2$ ), 4.05 (t, 4H,  $\text{OCH}_2$ ), 3.97 (t, 4H,  $\text{OCH}_2$ ), 2.96 (t, 2H,  $\text{SCH}_2$ ); 1.92-0.8 (299H, alkylic protons). Anal. Calcd. (%) for  $\text{C}_{222}\text{H}_{361}\text{Pd}_2\text{ClN}_2\text{O}_{16}\text{S}$ : C, 74.16; H, 10.14; N, 0.78. Found: C, 74.16; H, 10.05; N, 0.92.

**Preparation of  $[\text{PdIm}(\text{acac})]$  (**6**).** To a solution of  $(\mu\text{-Cl})_2[\text{Pd}_2\text{Im}_2]$  (0.095 g, 0.028 mmol) in 30 mL of dichloromethane,  $[\text{Tl}(\text{acac})]$  (0.017 g, 0.055 mmol) was added. The mixture was stirred for 1 h at room temperature. After filtering off the  $\text{TlCl}$  precipitate, ethanol (30 mL) was added. The resulting solution was concentrated to a small volume affording the complex as a pale yellow solid, which was filtered, washed with ethanol and dried (0.079 g, 72% yield). IR/KBr:  $\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{O}) + \nu(\text{C}=\text{C})$ : 1585  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.93 (s, 1H, HCN), 7.83 (s, 6H, ArH-triphenylene), 7.33 (d,  $2\text{H}^{2',6'}$ , ArH, AA' part of AA'XX' spin system ( $N_{\text{A,X}} = J_{\text{A,X}} + J_{\text{A,X}'} = 8.8$

Hz,  $J_{A,A} \approx J_{X,X'}$ ), 7.27 (d,  $J_{6,5} = 8.3$  Hz,  $1H^6$ , ArH), 7.10 (d,  $J_{3,5} = 2.4$  Hz,  $1H^3$ , ArH), 6.87 (d,  $2H^{3',5'}$ , ArH, XX' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.8$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.59 (dd,  $J_{5,6} = 8.3$  Hz,  $J_{5,3} = 2.4$  Hz,  $1H^5$ , ArH), 5.33 (s, 1H, CH-acac), 2.08 (s, 3H, CH<sub>3</sub>-acac), 1.87 (s, 3H, CH<sub>3</sub>-acac), 4.22 (m, 12H, OCH<sub>2</sub>), 4.00 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>), 3.92 (t, 2H,  $J = 6.5$  Hz, OCH<sub>2</sub>), 1.92-0.8 (138H, alkylic protons). Anal. Calcd. (%) for C<sub>110</sub>H<sub>175</sub>PdNO<sub>10</sub>: C, 74.29; H, 9.94; N, 0.79. Found: C, 73.98; H, 9.78; N, 0.81.

**Preparation of [PdImCl(CNR)].** To a solution of  $(\mu\text{-Cl})_2[\text{Pd}_2\text{Im}_2]$  (0.027 mmol) in 20 mL of dichloromethane, the corresponding CNR (0.054 mmol) was added. After stirring for 15 minutes, the resulting solution was concentrated and addition of acetone afforded the complexes as yellow solids, which were filtered and dried.

**[PdImCl(CNC<sub>6</sub>H<sub>4</sub>OC<sub>12</sub>H<sub>25</sub>)] (7):** 0.066 g, 62 % yield. IR/KBr:  $\nu(\text{C}\equiv\text{N})$ : 2198 cm<sup>-1</sup> (2200 cm<sup>-1</sup>/CH<sub>2</sub>Cl<sub>2</sub>);  $\nu(\text{C}=\text{N})$ : 1610 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.98 (s, 1H, HCN), 7.83 (s, 6H, ArH-triphenylene), 7.47 (d, 2H, ArH-isocyanide, AA' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 9.1$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 7.36 (d,  $J_{6,5} = 8.4$  Hz,  $1H^6$ , ArH), 7.28 (d,  $2H^{2',6'}$ , ArH, AA' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.9$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.92 (d,  $J_{3,5} = 2.3$  Hz,  $1H^3$ , ArH), 6.91 (d, 2H, ArH-isocyanide, XX' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 9.1$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.87 (d,  $2H^{3',5'}$ , ArH, XX' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.9$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.63 (dd,  $J_{5,6} = 8.4$  Hz,  $J_{5,3} = 2.3$  Hz,  $1H^5$ , ArH), 4.22 (m, 12H, OCH<sub>2</sub>), 3.96 (m, 6H, OCH<sub>2</sub>), 1.92-0.8 (161H, alkylic protons). Anal. Calcd. (%) for C<sub>124</sub>H<sub>197</sub>PdClN<sub>2</sub>O<sub>9</sub>: C, 74.38; H, 9.94; N, 1.40. Found: C, 74.65; H, 9.89; N, 1.41.

**[PdImCl(CNC<sub>6</sub>H<sub>3</sub>(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>)] (8):** 0.078 g, 67 % yield. IR/KBr:  $\nu(\text{C}\equiv\text{N})$ : 2198 cm<sup>-1</sup> (2201 cm<sup>-1</sup>/CH<sub>2</sub>Cl<sub>2</sub>);  $\nu(\text{C}=\text{N})$ : 1610 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.99 (s, 1H, HCN), 7.83 (s, 6H, ArH-triphenylene), 7.36 (d,  $J_{6,5} = 8.4$  Hz,  $1H^6$ , ArH), 7.28 (d,  $2H^{2',6'}$ , ArH, AA' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.8$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 7.10 (dd,  $J = 2.3$  Hz,  $J = 8.6$  Hz, 1H, ArH-isocyanide), 7.02 (d,  $J = 2.3$  Hz, 1H, ArH-isocyanide), 6.93 (d,  $J_{3,5} = 2.3$  Hz,  $1H^3$ , ArH), 6.88 (d,



$2H^{3,5}$ , ArH, XX' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.8$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.83 (d,  $J = 8.6$  Hz, 1H, ArH-isocyanide), 6.63 (dd,  $J_{5,6} = 8.4$  Hz,  $J_{5,3} = 2.3$  Hz,  $1H^5$ , ArH), 4.22 (m, 12H, OCH<sub>2</sub>), 3.96 (m, 8H, OCH<sub>2</sub>), 1.94-0.8 (184H, alkylic protons). Anal. Calcd. (%) for C<sub>136</sub>H<sub>221</sub>PdClN<sub>2</sub>O<sub>10</sub>: C, 74.72; H, 10.19; N, 1.28. Found: C, 74.90; H, 10.22; N, 1.39.

[PdImCl(CNC<sub>6</sub>H<sub>2</sub>(OC<sub>12</sub>H<sub>25</sub>)<sub>3</sub>)] (**9**): 0.090 g, 63 % yield. IR/KBr:  $\nu(C\equiv N)$ : 2197 cm<sup>-1</sup> (2199 cm<sup>-1</sup>/CH<sub>2</sub>Cl<sub>2</sub>);  $\nu(C=N)$ : 1610 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.99 (s, 1H, HCN), 7.83 (s, 6H, ArH-triphenylene), 7.37 (d,  $J_{6,5} = 8.4$  Hz,  $1H^6$ , ArH), 7.28 (d,  $2H^{2,6}$ , ArH, AA' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.8$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.93 (d,  $J_{3,5} = 2.3$  Hz,  $1H^3$ , ArH), 6.88 (d,  $2H^{3,5}$ , ArH, XX' part of AA'XX' spin system ( $N_{A,X} = J_{A,X} + J_{A,X'} = 8.8$  Hz,  $J_{A,A} \approx J_{X,X'}$ ), 6.74 (s, 2H, ArH-isocyanide), 6.63 (dd,  $J_{5,6} = 8.4$  Hz,  $J_{5,3} = 2.3$  Hz,  $1H^5$ , ArH), 4.22 (m, 12H, OCH<sub>2</sub>), 3.96 (m, 10H, OCH<sub>2</sub>), 1.94-0.8 (207H, alkylic protons). Anal. Calcd. (%) for C<sub>148</sub>H<sub>245</sub>PdClO<sub>11</sub>N<sub>2</sub>: C, 74.99; H, 10.42; N, 1.18. Found: C, 74.87; H, 10.21; N, 1.14.

## Representative DSC scans

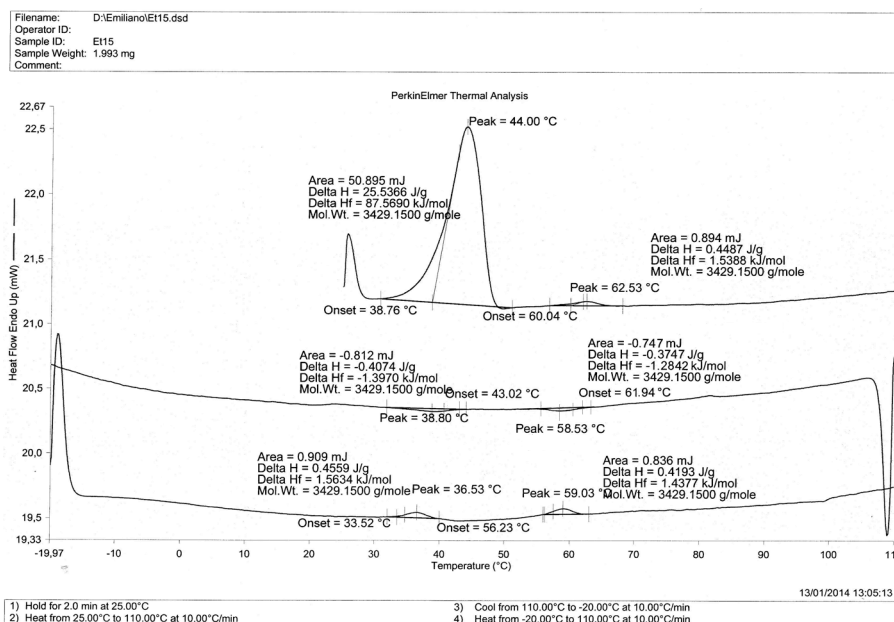


Figure S1. DSC scans for  $(\mu\text{-Cl})_2[\text{Pd}_2\text{Im}_2]$

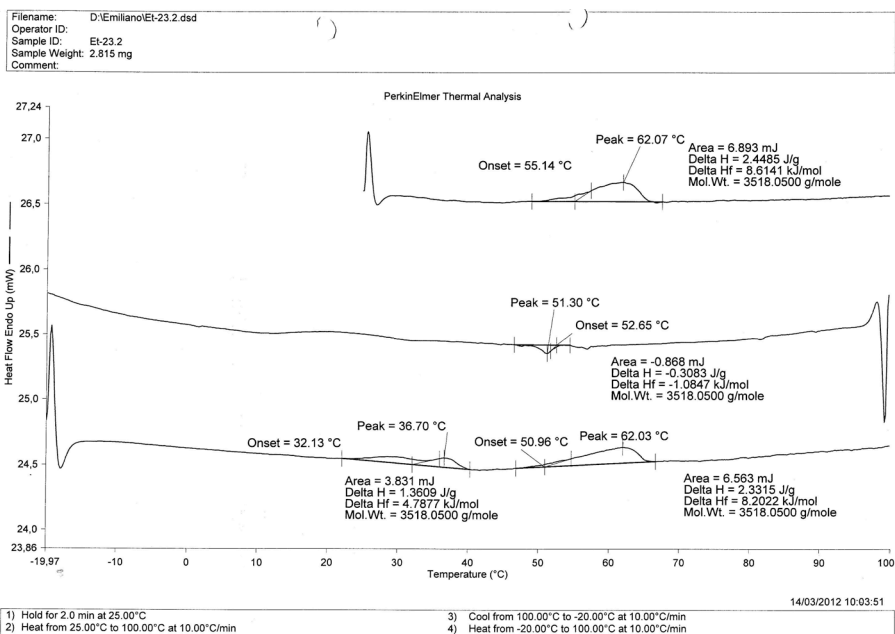


Figure S2. DSC scans for  $(\mu\text{-Br})_2[\text{Pd}_2\text{Im}_2]$

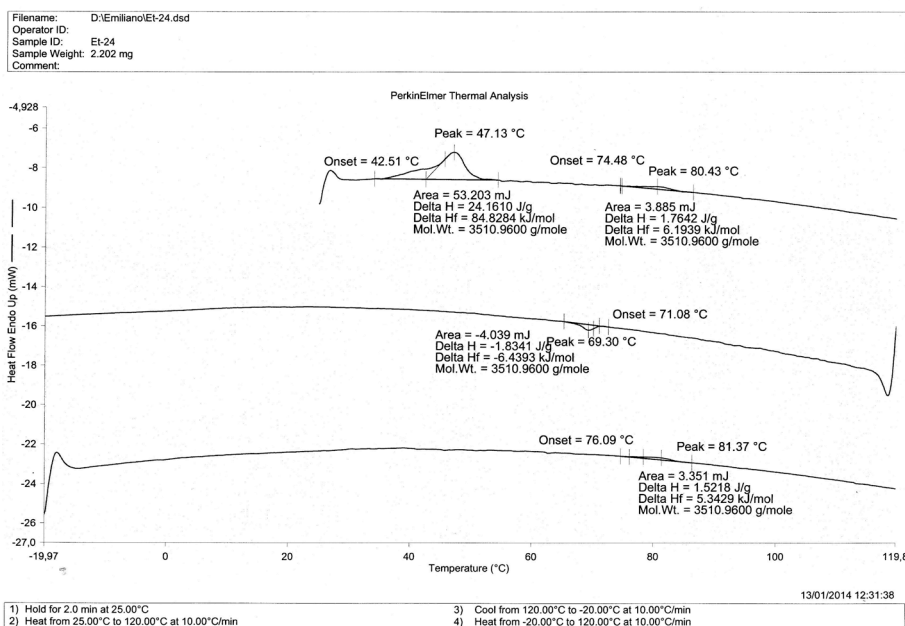
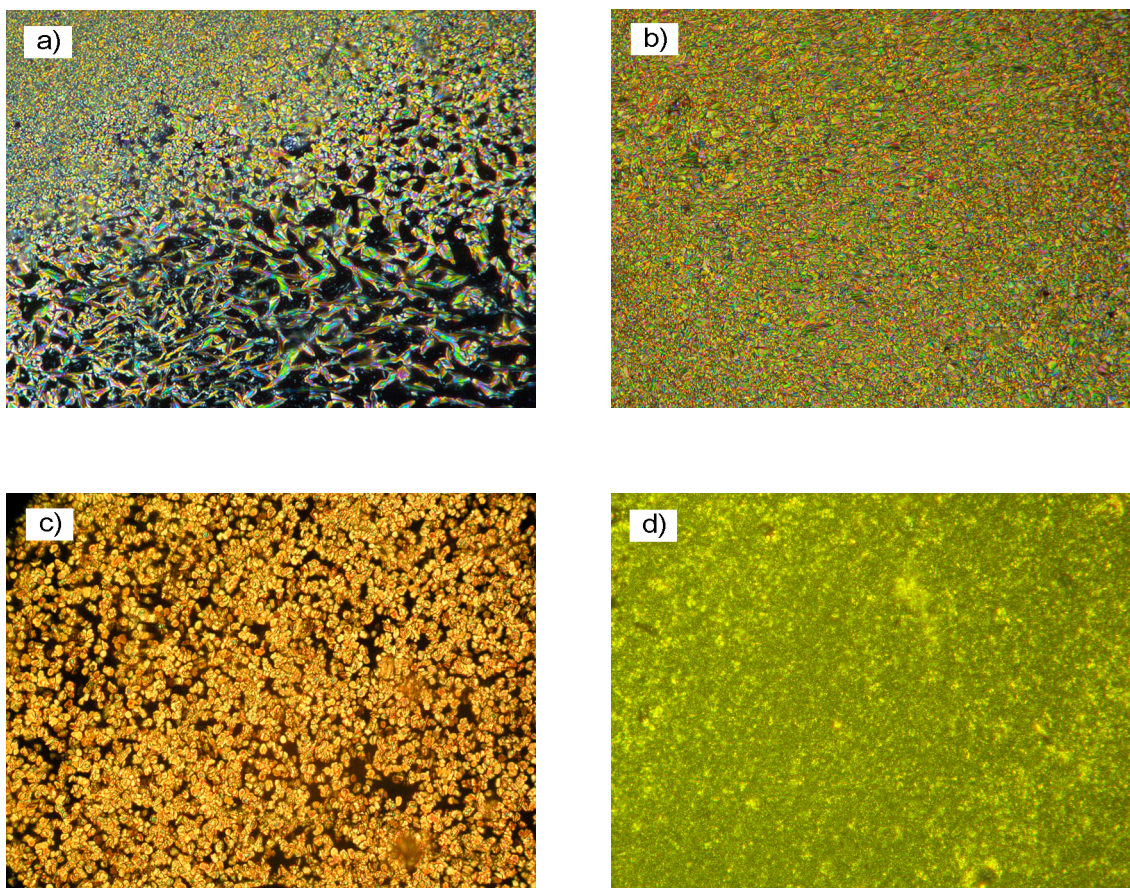
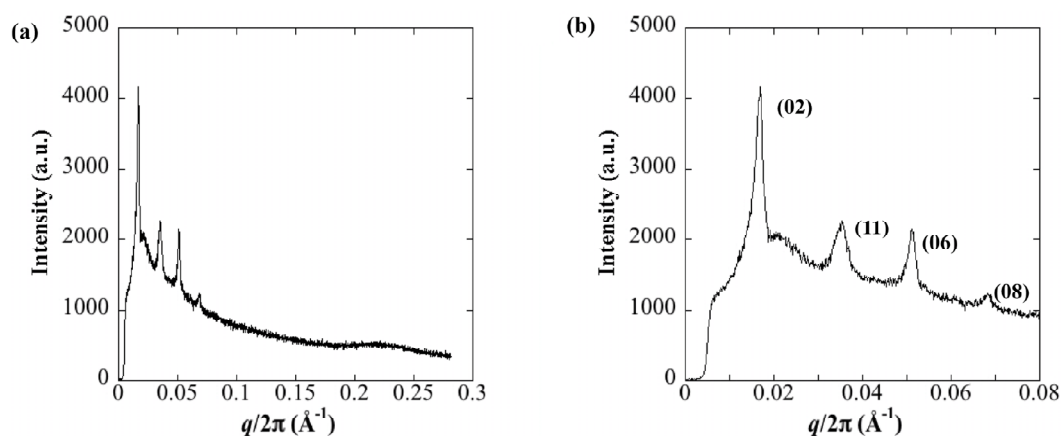


Figure S3. DSC scans for  $(\mu\text{-Cl})(\mu\text{-SC}_6\text{H}_{13})[\text{Pd}_2\text{Im}_2]$

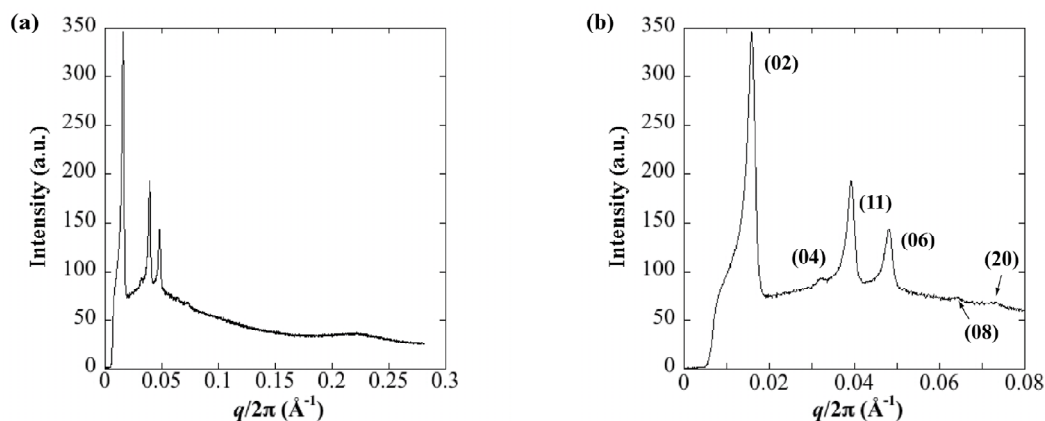


**Figure S4. POM textures** (x 100) on cooling from the isotropic liquid. a)  $(\mu\text{-Cl})_2[\text{Pd}_2\text{Im}_2]$  (**2**) at 49 °C; b)  $(\mu\text{-Br})_2[\text{Pd}_2\text{Im}_2]$  (**3**) at 45 °C; c)  $(\mu\text{-Cl})(\mu\text{-SC}_6\text{H}_{13})[\text{Pd}_2\text{Im}_2]$  (**4**) at 50 °C; d)  $[\text{PdImCl}(\text{CNC}_6\text{H}_2(\text{OC}_{12}\text{H}_{25})_3)]$  (**9**) at 58 °C.

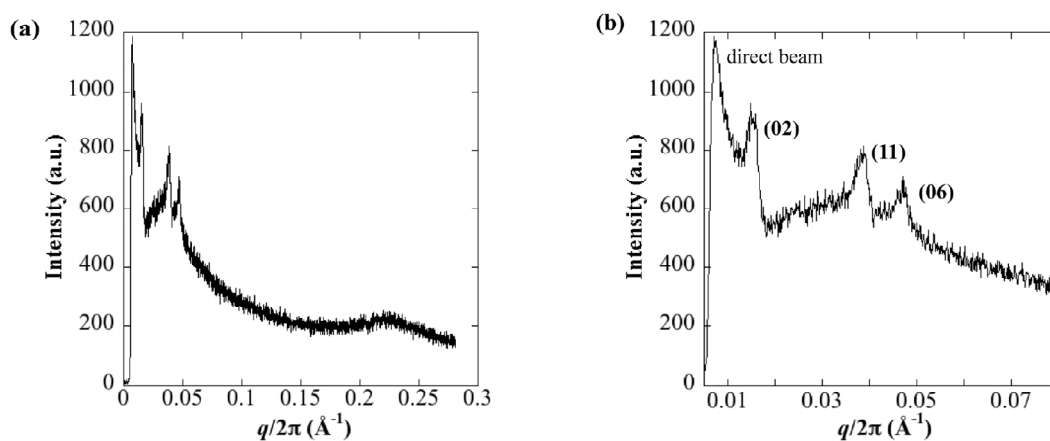
### X-ray diffraction studies



**Figure S5.** (a) X-ray diffraction pattern of compound **3** at 45°C.  $q$  is the diffraction vector. (b) Small angle region with the corresponding indexation scheme.



**Figure S6.** (a) X-ray diffraction pattern of compound **4** at 50°C.  $q$  is the diffraction vector. (b) Small angle region with the corresponding indexation scheme.



**Figure S7.** (a) X-ray diffraction pattern of compound **5** at 50°C.  $q$  is the diffraction vector. (b) Small angle region with the corresponding indexation scheme.

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