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Electronic Supplementary Information

Li^+ and K^+ ionic conductivity in ionic nematic liquid crystals based on 18-diaza-crown ether substituted with six decylalkoxy-*p*-cyanobiphenyl chains

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A. Synthesis and characterization of the compounds

*Synthesis of compounds **1** and **2***: Compound 3,4,5-tridecyloxybenzoic acid (0.9 g, 1.52 mmol) was dissolved in 15 mL of dry dichloromethane under argon atmosphere. After addition of oxalyl chloride (1.245 ml, 14 mmol) and DMF (catalytic amount), the mixture was stirred for 3h under reflux. The excess of oxalyl chloride and solvent were removed under vacuum. The acid chloride intermediate was then dried at 60 °C under vacuum for 24 h before being dissolved in 15 mL of dry THF. This solution was dropwise added to a 15 ml THF solution maintained at 0 °C and containing 1,4-diaza-18-crown-6 (0.19 g, 0.72 mmol) and triethylamine (0.3 ml, 2.13 mmol). The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The crude obtained after THF evaporation was purified by column chromatography (silica gel, DCM/MeOH 95:5). The desired product was then dried at 45 °C under vacuum.
Compound **1** was obtained as a waxy orange solid. Yield: 0.807 g, 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56 (4H, s, H_{arom}), 3.94 (12H, t, J = 6.5 Hz, O-CH_2), 3.82-3.71 (m, 8H, CH_2-N), 3.69-3.52 (m, 16H, O-CH_2-CH_2-O) 1.81-1.69 (12H, m, O-CH_2-CH_2), 1.51-1.18 (84H, m, CH_3-(CH_2)$_7$), 0.88 (18H, t, J = 6.7 Hz, CH_3); IR (in solid cm^{-1}): 1634 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{86}H_{154}N_2O_{12}$), $(M + H)^+$ 1408,16; found: 1408,3. Anal. calcd for $C_{86}H_{154}N_2O_{12}$: C 73.35, H 11.02, N 1.99; found C 73.43, H 11.29, N 1.99.

Ligand **1**

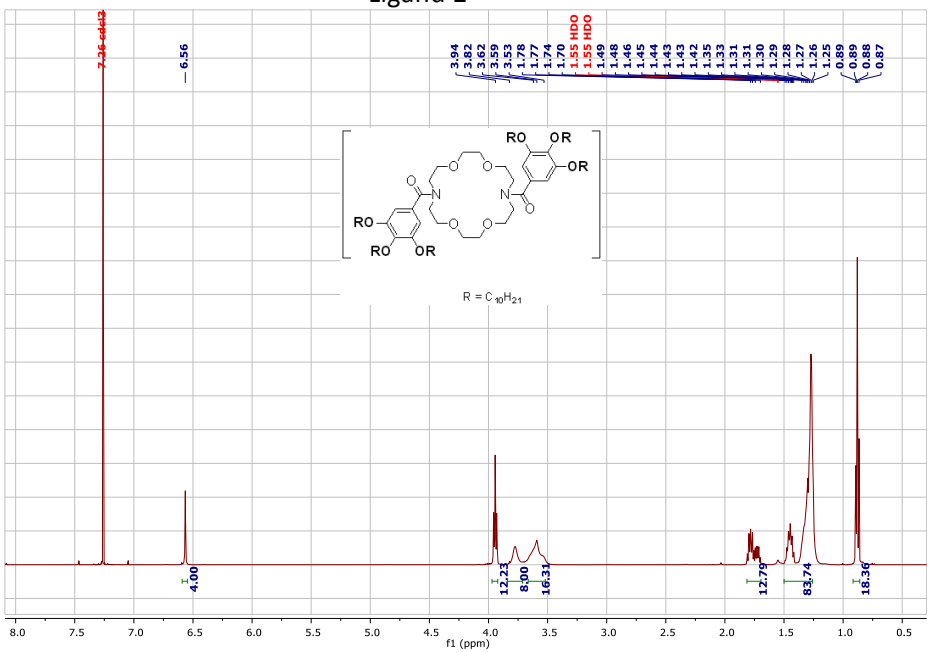

Figure ESI1. ^{1}H NMR spectrum of **1** in $CDCl_3$

*Synthesis of adducts **1a-1b***: KI (4.7 mg, 0.028 mmol) or, respectively, $K_2[PtCl_4]$ (7.4 mg, 0.018 mmol) in 5 ml deoxygenated MeOH was stirred under ultrasound

irradiation during 15 minutes and then added to a solution of macrocycle **1** (for **1a** 40 mg, 0.028 mmol; for **1b** 50 mg, 0.036 mmol in 5 ml diethyl ether under N_2. The mixture was stirred overnight at 35 °C. The solution was filtered over celite and dried in vacuum. The products were obtained as waxy yellow (**1a**) or brown (**1b**) solids.

Yield of **1a**: 40 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (4H, s, H_{arom}), 3.94 (12H, t, J = 6.5 Hz, O-CH_2), 3.823-3.73 (8H, m, -CH_2-N), 3.69-3.51 (16H, m, CH_2-CH_2-O, CH_2-O) 1.82-1.69 (12H, m, O-CH_2-CH_2), 1.50-1.19 (84H, m, CH_3-$(CH_2)_7$), 0.88 (18H, t, J = 6.7 Hz, CH_3); IR (in solid,cm^{-1}): 1634 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calcd.(M = $C_{86}H_{154}N_2O_{12}$ macrocycle **1**), calcd.(M + H)$^+$: 1408,16; found: 1408,3; calcd.(M + Na)$^+$ 1430,14; found: 1430,3; calcd.(M + K)$^+$ 1446,11; found: 1446,1. Anal. calcd. for $C_{86}H_{154}N_2IKO_{12}$: C 65.62, H 9.86, N 1.78; found C 65.36, H 10.07, N 2.02.

Yield of **1b**: 50 mg, 87%: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57 (4H, s, H_{arom}), 3.94 (12H, t, J = 6.5 Hz, O-CH_2), 3.82-3.72 (8H, m, -CH_2-N), 3.68-3.51 (16H, m, CH_2-CH_2-O, CH_2-O) 1.80-1.68 (12H, m, O-CH_2-CH_2), 1.51-1.18 (84H, m, CH_3-$(CH_2)_7$), 0.88 (18H, t, J = 6.6 Hz, CH_3); IR (in solid,cm^{-1}): 1634 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: (M = $C_{86}H_{154}N_2O_{12}$ macrocycle **1**), calcd.(M + H)$^+$: 1408,16; found: 1408,3; calcd.(M + Na)$^+$ 1430,14; found: 1429,4; calcd. (M + K)$^+$ 1446,11; found: 1445,4. Anal. calcd. for $C_{172}H_{308}N_4Cl_4K_2O_{24}Pt$: C 63.93, H 9.61, N 1.73; found C 63.71, H 9.89, N 2.00.

Compound **2** was obtained as a yellow solid in a similar way to compound **1**. Yield: 1.34 g, 61%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.58 (24H, m, H^1+H^2), 7.53-7.47 (12H, m, H^3), 7.01-6.93 (12H, m, H^4), 6.57 (4H, s, -CH_{ar}), 4.06-3.92 (24H, m, O-CH_2), 3.82-3.70 (8H, m, CH_2-N-) 3.69-3.52 (16H, m, O-C*H*$_2$-C*H*$_2$-O), 1.85-1.70 (24H, m, O-CH_2-C*H*$_2$), 1.51-1.25 (72H, m, (-CH_2-)$_6$). IR (in solid cm^{-1}): 2223 ($\nu_{C\equiv N}$), 1623 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$), (M + H)$^+$ 2566,47; found: 2566,5. Anal. calcd for $C_{164}H_{196}N_8O_{18}$: C 76.72, H 7.69, N 4.36; found C 76.44, H 7.9, N 4.23.

Ligand **2**

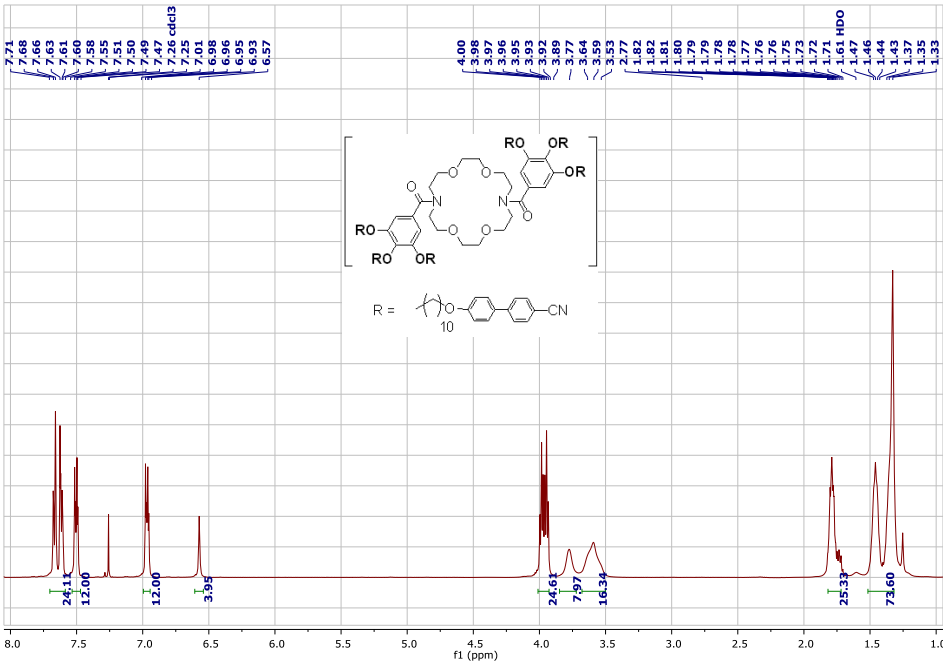

Figure ESI2. ^{1}H NMR spectrum of **2** in $CDCl_3$.

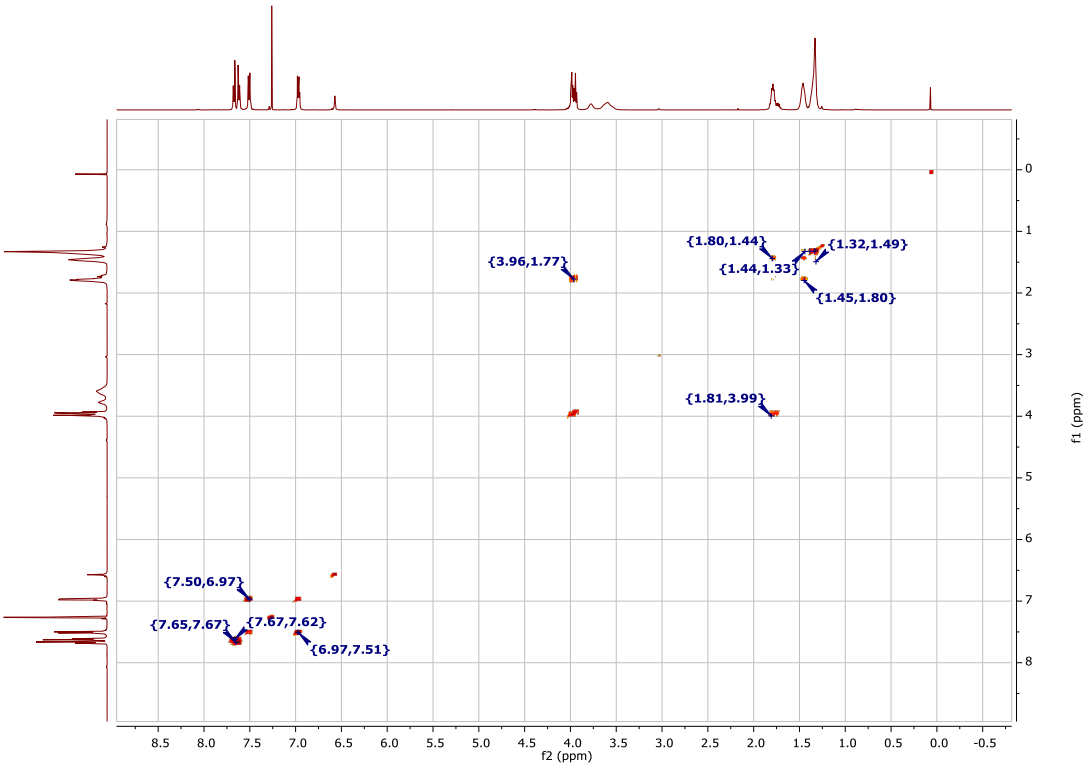

Figure ESI3. COSY spectrum of **2**

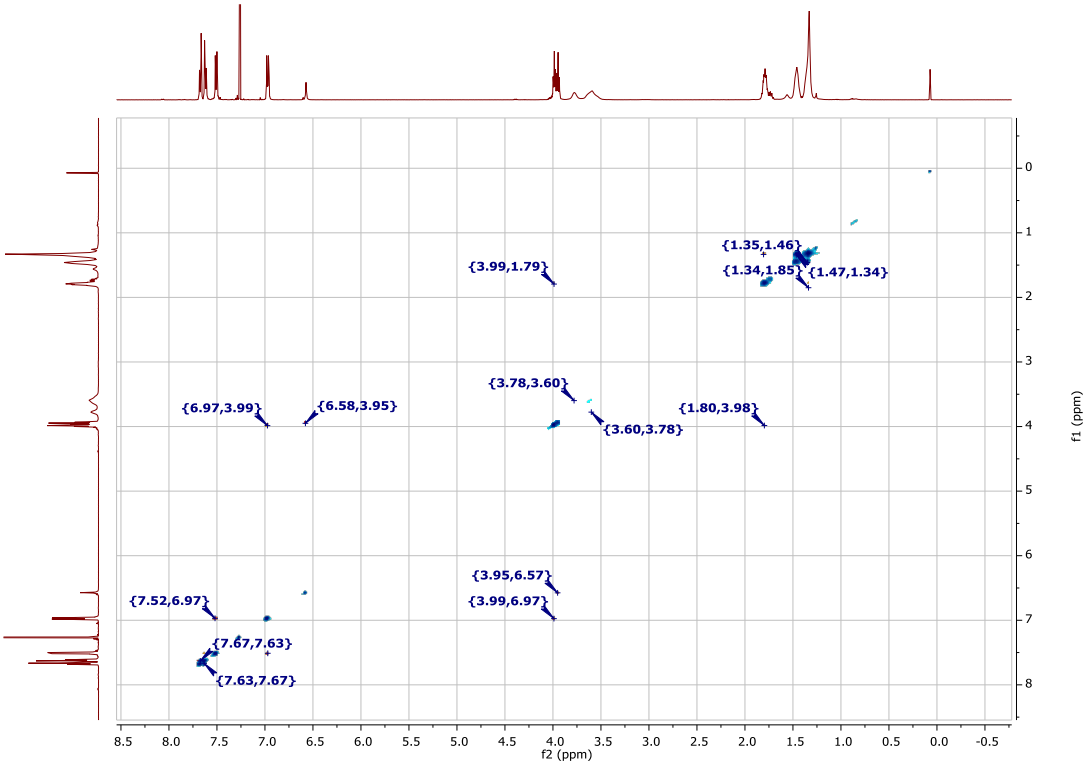

Figure ESI4. ROESY spectrum of **2**

*Synthesis of adducts **2a-2f***: M_nA (KI 4.8 mg, 0.029 mmol, $K_2[PtCl_4]$ 7.0 mg, 0.017 mmol, $K[AuCl_4]$ 10.5 mg, 0.028 mmol, $K[AuCl_4]$ 5.3 mg, 0.014 mmol, $K_4[Fe(CN)_6]$ 3.0 mg, 0.007 mmol, or LiI 3.4 mg, 0.025 mmol), respectively, in 5 ml dry dichloromethane was stirred under ultrasound irradiation during 15 minutes and then added to a solution of macrocycle **2** (for **2a** 75 mg, 0.029 mmol; for **2b** 86.6 mg, 0.034 mmol; for **2c**-**2d**-**2e** 72 mg, 0.028 mmol; for **2f** 64 mg, 0.025 mmol) in 3 ml dichloromethane under N_2. The mixture was stirred overnight at 35 °C. The solution was filtered over celite and dried in vacuum. The products were obtained as beige (**2a**), ligth yellow (**2b**, **2e**) grey (**2c**, **2d**) or yellow (**2f**) solids.

Yield of **2a**: 73 mg, 92%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.59 (24H, m, H_1, H_2), 7.54-7.48 (12H, m, H_3), 7.00-6.94 (12H, m, H_4), 6.57 (4H, s, $-CH_{ar}$), 4.06-3.92 (24H, m, O-CH_2), 3.82-3.71 (8H, m, $-CH_2$-N-), 3.69-3.52 (16H, m, O-C*H*$_2$-C*H*$_2$-O), 1.85-1.70 (24H, m, O-CH_2-C*H*$_2$-), 1.51-1.25 (72H, m, $(-CH_2-)_6$). IR (in solid cm^{-1}): 2224 ($\nu_{C\equiv N}$), 1631 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$ macrocycle **2**), calc (M + H)$^+$ 2566,47; found: 2566,5; calc (M + Na)$^+$: 2588,46; found: 2588,5; calc (M + K)$^+$: 2604,43; found: 2604,5. Anal. calcd for $C_{164}H_{196}N_8KIO_{18}$: C 72.06, H 7.23, N 4.10; found C 71.87, H 7.14, N 4.02.

Yield of **2b**: 80 mg, 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71-7.58 (24H, m, H_1, H_2), 7.54-7.48 (12H, m, H_3), 7.00-6.93 (12H, m, H_4), 6.57 (4H, s, $-CH_{ar}$), 4.03-3.91 (24H, m, O-CH_2), 3.83-3.71 (8H, m, $-CH_2$-N-) 3.69-3.52 (16H, m, O-C*H*$_2$-C*H*$_2$-O), 1.84-1.68 (24H, m, O-CH_2-C*H*$_2$-), 1.51-1.18 (36H, m, $(-CH_2-)_6$). IR (in solid cm^{-1}): 2224 ($\nu_{C\equiv N}$), 1628 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$ macrocycle **2**), calc (M + H)$^+$ 2566,47; found: 2566,5; calc (M + Na)$^+$: 2588,46; found: 2588,5; calc (M + K)$^+$: 2604,43; found: 2604,5. Anal. calcd for $C_{328}H_{392}Cl_4K_2N_{16}O_{36}Pt$: C 70.99, H 7.12, N 4.04; found C 70.83, H 7.17, N 3.90.

Yield of **2c**: 80 mg, 98%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.58 (24H, m, H_1, H_2), 7.57-7.44 (12H, m, H_3), 7.03-6.91 (12H, m, H_4), 6.57 (4H, s, $-CH_{ar}$), 4.09-3.88 (24H, m, O-CH_2), 3.82-3.71 (8H, m, $-CH_2$-N-) 3.67-3.48 (16H, m, O-C*H*$_2$-C*H*$_2$-O), 1.83-1.69 (24H, m, O-CH_2-C*H*$_2$-), 1.60-1.22 (72H, m, $(-CH_2-)_6$). IR (in solid cm^{-1}): 2223 ($\nu_{C\equiv N}$), 1628 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$ macrocycle **2**), calc (M + H)$^+$ 2566,47; found: 2566,5; calc (M+Na)$^+$: 2588,46; found: 2588.5; calc (M+K)$^+$: 2604,43: found 2604,5; calc ($AuCl_4^-$): 338.83; found: 338.9. Anal. calcd $C_{164}H_{196}AuCl_4KN_8O_{18}$: C 66.88, H 6.71, N 3.80; found C 67.11, H 7.00, N 3.69.

Yield of **2d**: 71 mg, 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72-7.58 (24H, m, H_1, H_2), 7.55-7.48 (12H, m, H_3), 7.01-6.92 (12H, m, H_4), 6.57 (4H, s, $-CH_{ar}$), 4.05-3.89 (24H, m, O-CH_2), 3.86-3.72 (8H, m, $-CH_2$-N-) 3.71-3.49 (16H, m, O-C*H*$_2$-C*H*$_2$-O), 1.84-1.69 (24H, m, O-CH_2-CH_2-), 1.65-1.20 (72H, m, $(-CH_2-)_6$). IR (in solid cm^{-1}): 2221 ($\nu_{C\equiv N}$), 1631 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$ macrocycle **2**), calc (M+H)$^+$ 2566,47; found: 2567,5; calc (M+Na)$^+$: 2588,46; found: 2588.5; calc (M+K)$^+$: 2604,43; found: 2604,5. Anal. calcd for $C_{164}H_{196}Au_{0.5}Cl_2K_{0.5}N_8O_{18}$: C 71.46, H 7.17, N 4.07; found C 71.66, H 7.26, N 3.98.

Yield of **2e**: 70 mg, 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.57 (24H, m, H_1, H_2), 7.57-7.46 (12H, m, H_3), 7.06-6.90 (12H, m, H_4), 6.57 (4H, s, $-CH_{ar}$), 4.11-3.88 (24H, m, O-CH_2), 3.86-3.68 (8H, m, $-CH_2$-N-) 3.68-3.48 (16H, m, O-C*H*$_2$-C*H*$_2$-O), 1.91-1.68 (24H, m, O-CH_2-C*H*$_2$-), 1.66-1.17 (72H, m, $(-CH_2-)_6$). IR (in solid cm^{-1}): 2224, 2060 ($\nu_{C\equiv N}$), 1628 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$ macrocycle **2**), calc (M + H)$^+$ 2566,47; found: 2566,5; calc (M+Na)$^+$: 2589,46; found: 2588,5; calc (M + K)$^+$: 2604,43; found: 2604,4. Anal. calcd for $C_{662}H_{784}FeK_4N_{38}O_{72}$: C 74.74, H 7.43, N 5.00; found C 74.52, H 7.60, N 4.84.

Yield of **2f**: 67 mg, 97%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72-7.56 (24H, m, H_1, H_2), 7.54-7.45 (12H, m, H_3), 7.02-6.89 (12H, m, H_4), 6.57 (4H, s, $-CH_{ar}$), 4.03-3.89 (24H,

m, O-CH_2), 3.88-3.75 (8H, m, -CH_2-N-) 3.73-3.51 (16H, m, O-CH_2-CH_2-O), 1.86-1.69 (24H, m, O-CH_2-CH_2-), 1.64-1.23 (72H, m, (-CH_2-)$_6$). IR (in solid cm^{-1}): 2223 ($\nu_{C\equiv N}$), 1628 ($\nu_{c=o}$); MS (MALDI-TOF): *m/z*: calc (M = $C_{164}H_{196}N_8O_{18}$ macrocycle **2**), calc $(M + H)^+$ 2566,47; found: 2566,5; calc $(M + Li)^+$: 2572,48; found: 2572,6; calc $(M+Na)^+$: 2589,46; found: 2588.6. Anal. calcd for $C_{164}H_{196}N_8ILiO_{18}$: C 72.92, H 7.31, N 4.15; found C 72.63, H 7.44, N 4.13.

B. Differential Scanning Calorimetry (DSC) thermograms for compounds 2-2f

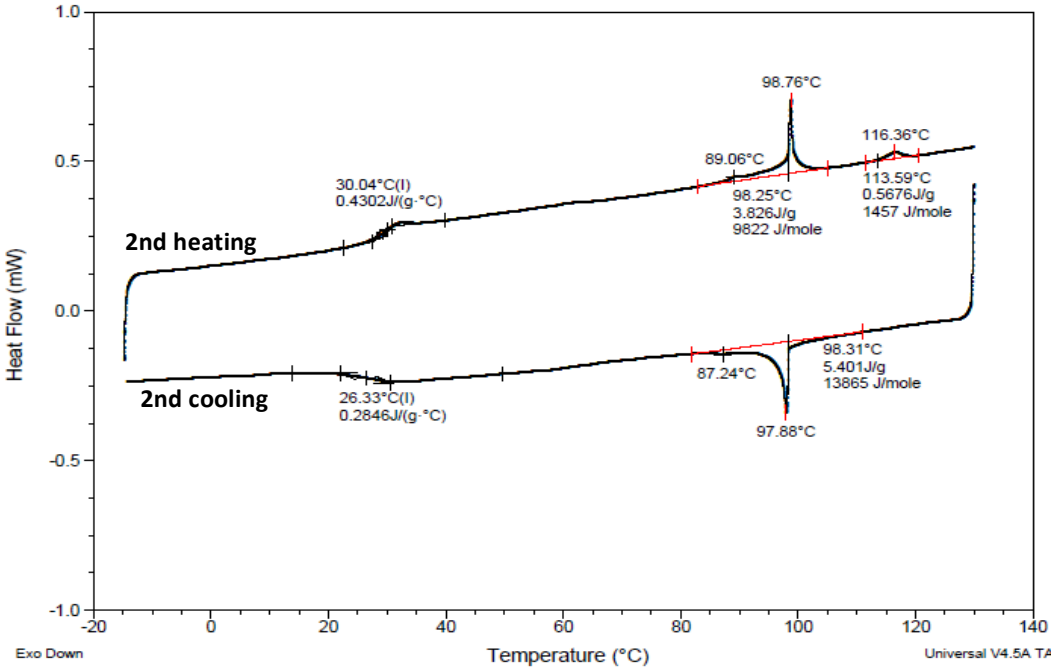

Figure ESI5. DSC thermograms for **2**

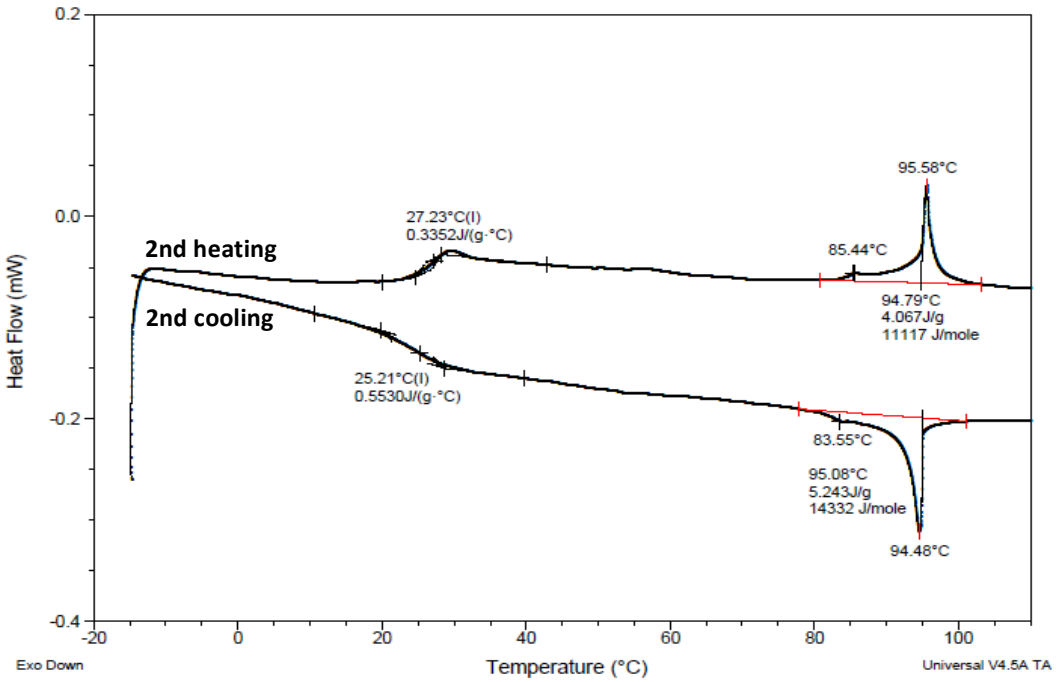

Figure ESI6. DSC thermograms for **2a**

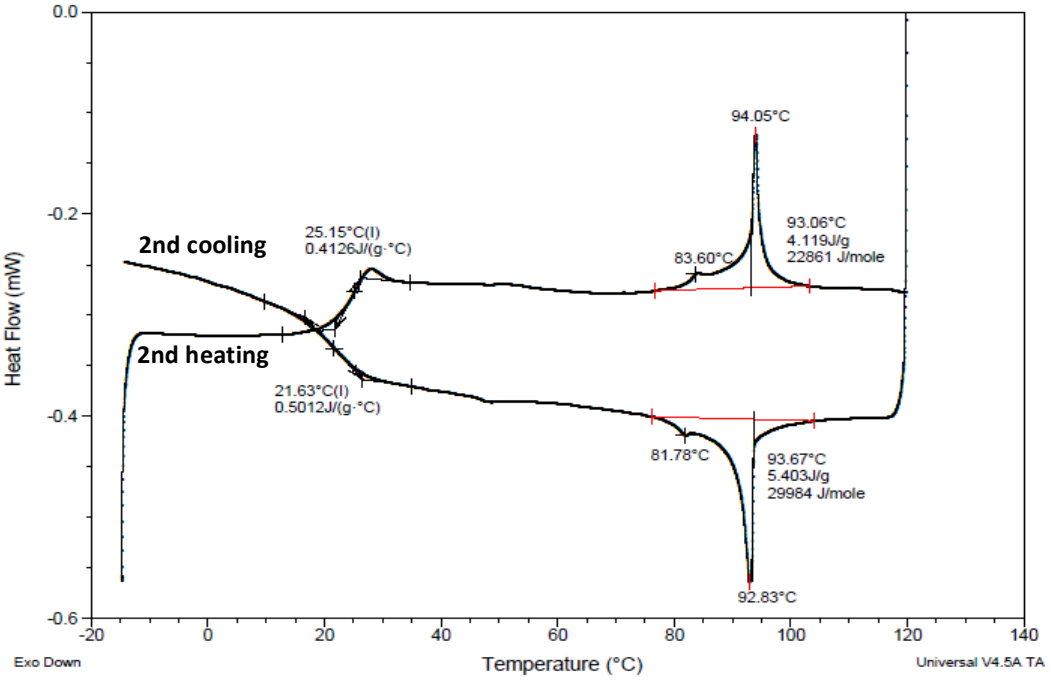

Figure ESI7. DSC thermograms for **2b**

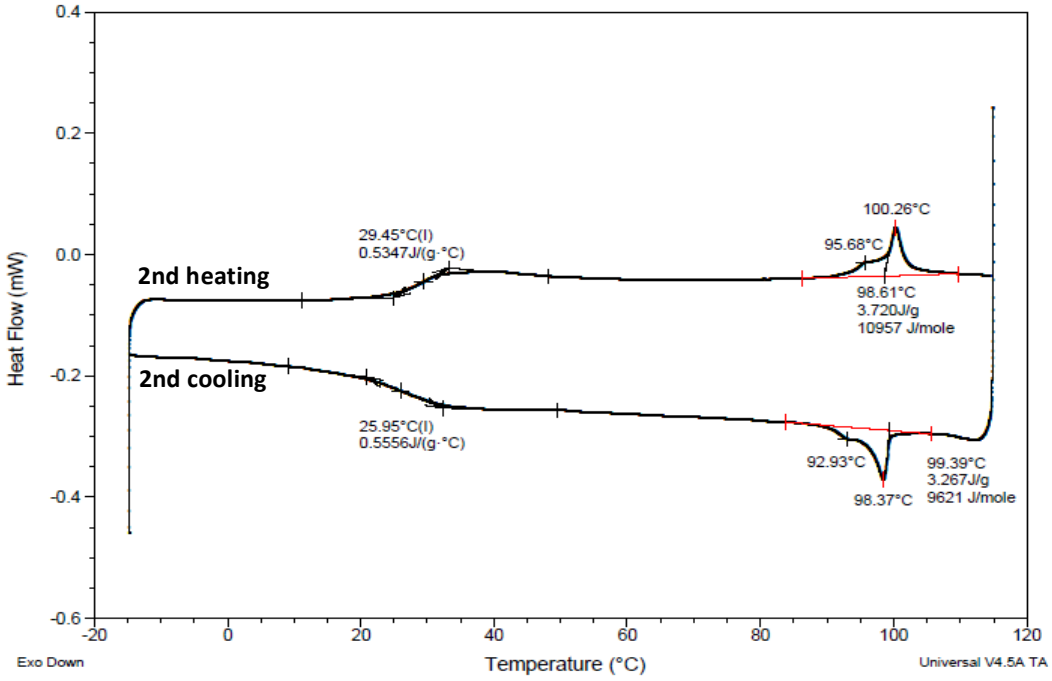

Figure ESI8. DSC thermograms for **2c**

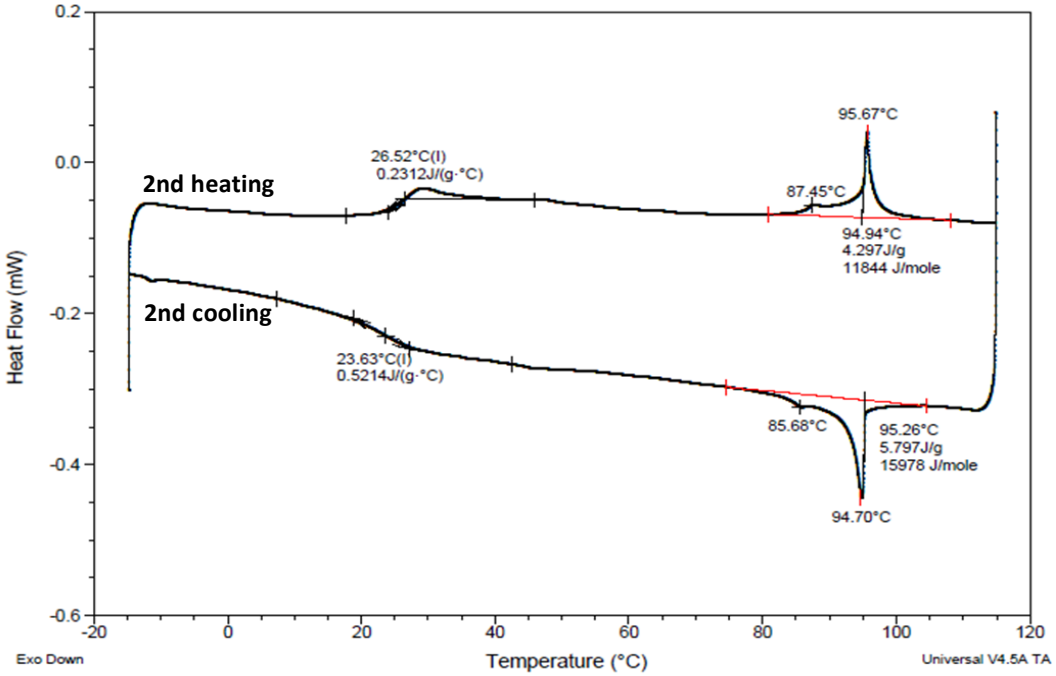

Figure ESI9. DSC thermograms for **2d**

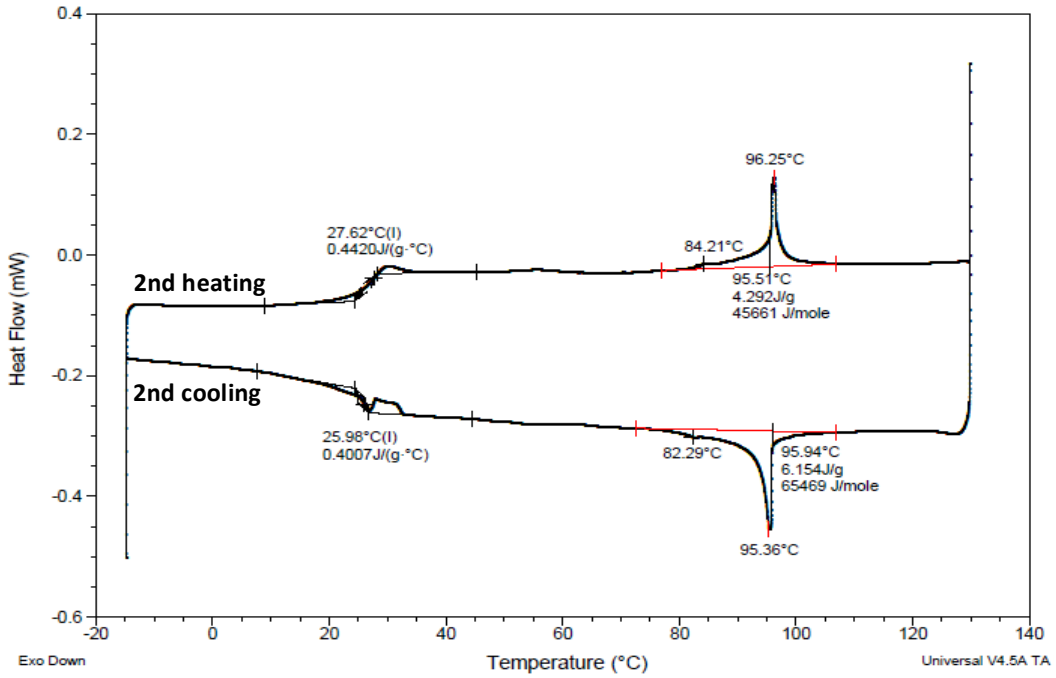

Figure ESI10. DSC thermograms for **2e**

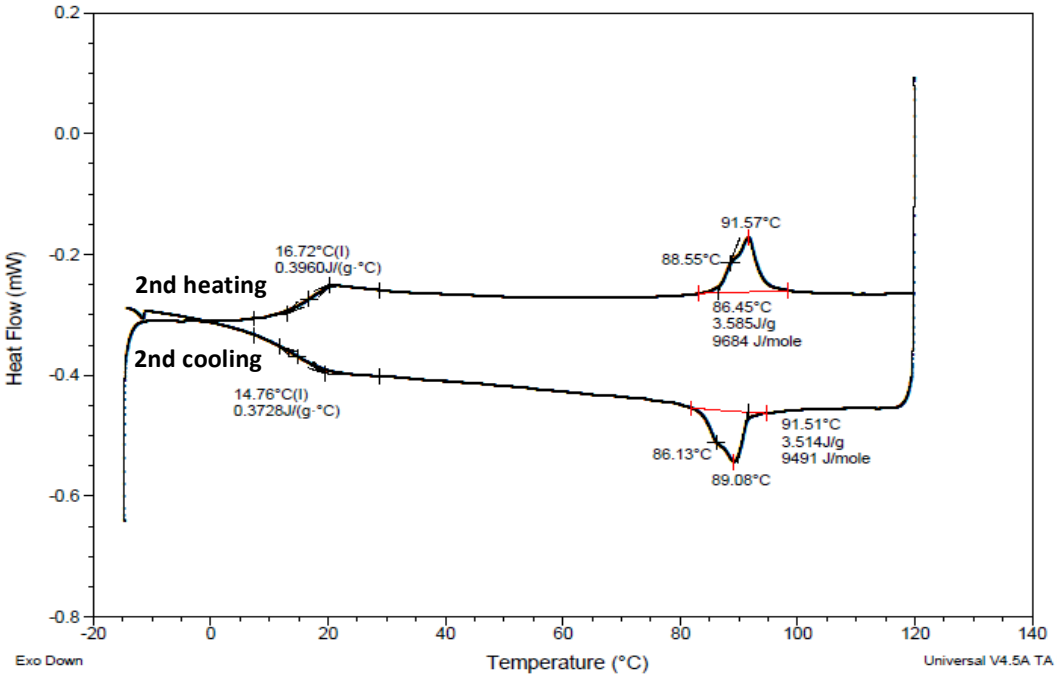

Figure ESI11. DSC thermograms for **2f**

C. X-ray Powder Diffraction (XRD) patterns

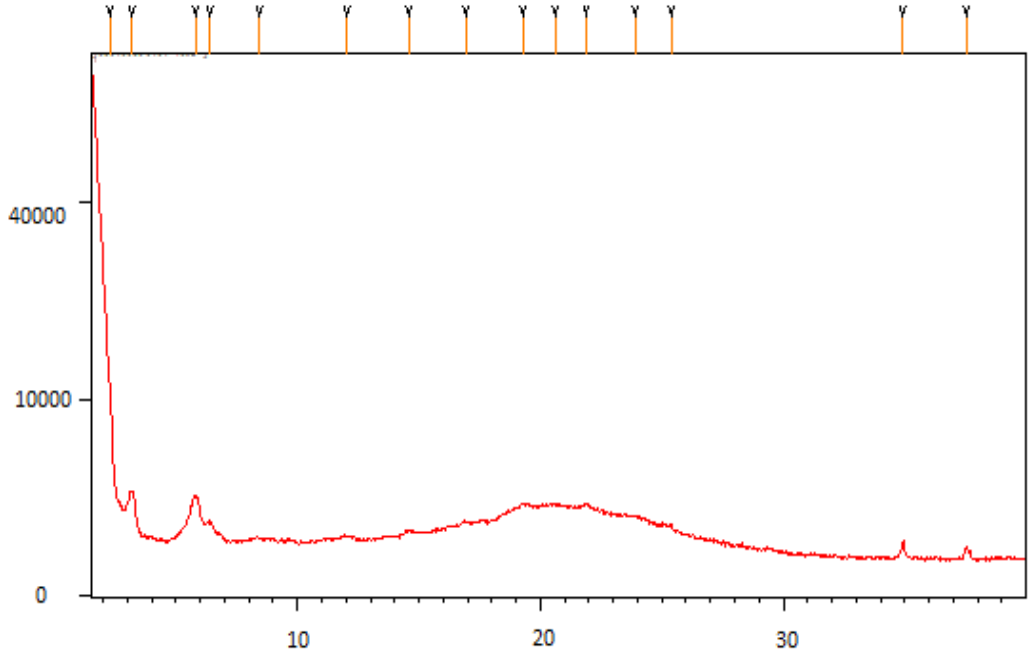

Figure ESI12. Powder XRD diffraction patterns for **2a** at 40 °C (on heating at 2°C/min).

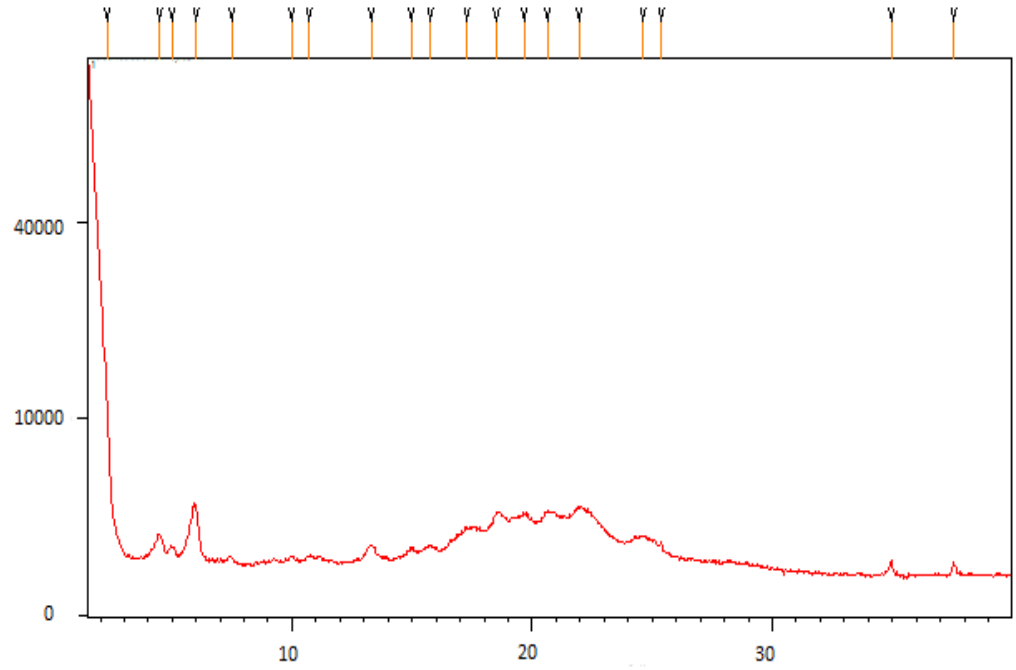

Figure ESI13. Powder XRD diffraction patterns for compound **2a** at 90 °C (on heating at 2 °C/min).

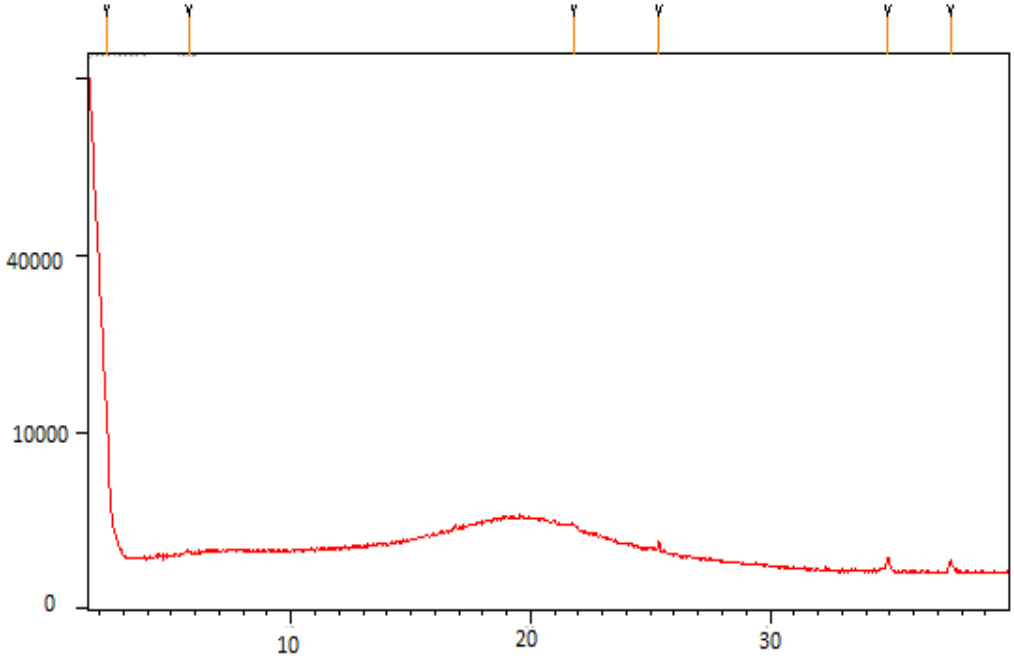

Figure ESI14. Powder XRD diffraction patterns for compound **2a** at 110 °C on heating at 2 °C/min (isotropic liquid).

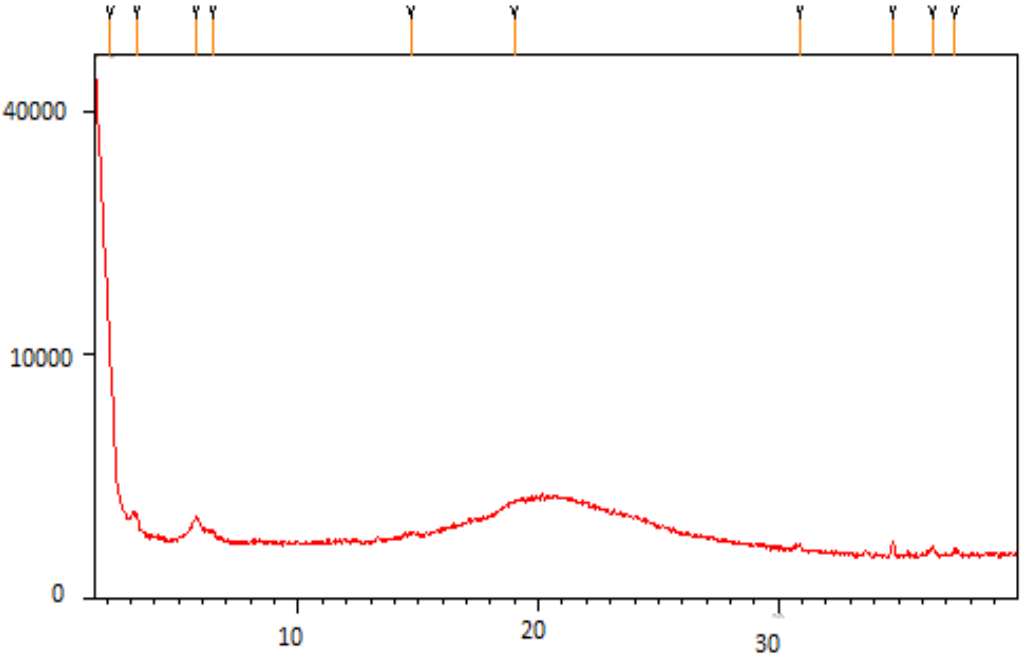

Figure ESI15. Powder XRD diffraction patterns for **2f** at 40 °C (on heating at 10 °C/min).

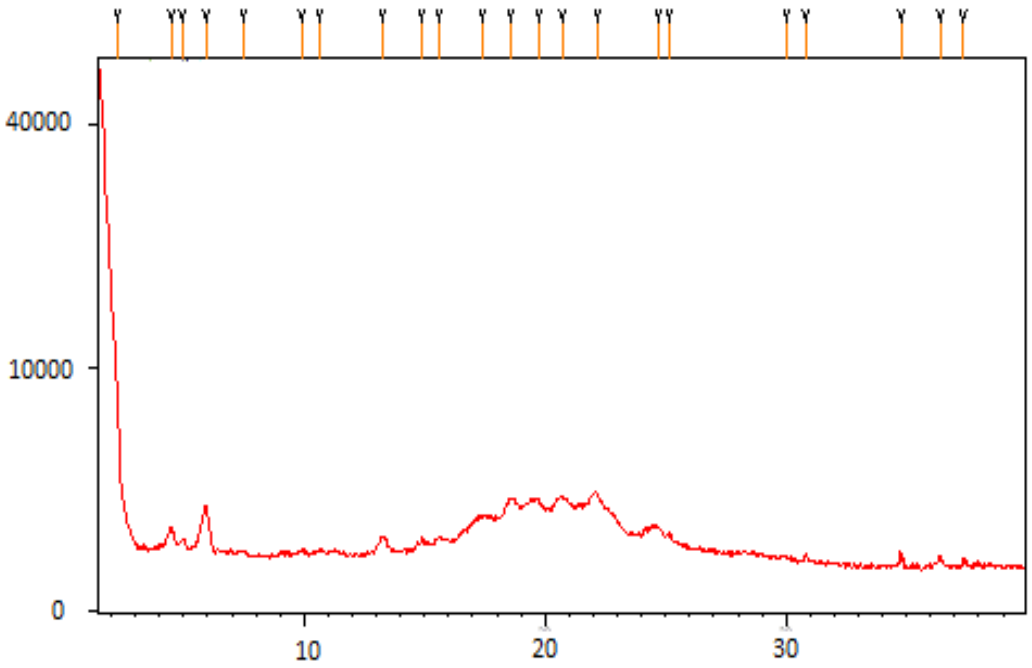

Figure ESI16. Powder XRD diffraction patterns for compound **2f** at 90 °C (on heating at 10 °C/min).

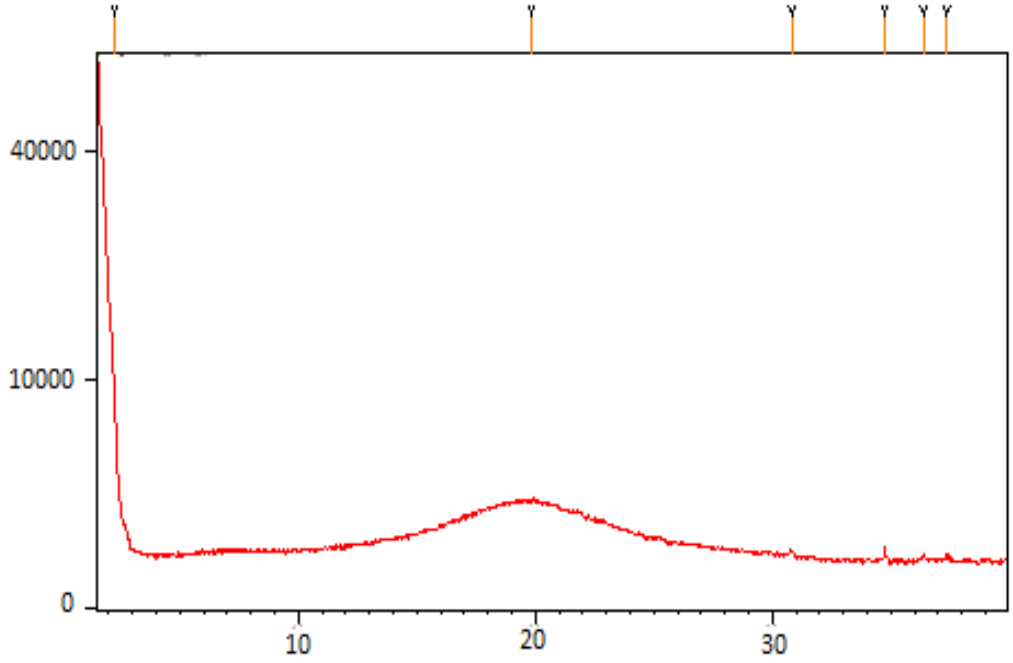

Figure ESI17. Powder XRD diffraction patterns for compound **2f** at 120 °C on heating at 10 °C/min (isotropic liquid).