Supporting information for

Liquid crystalline salen manganese(III) complexes. Mesogenic and Catalytic Behavior.

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Experimental

Synthesis of precursors.

Preparation of 4-formyl-5-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate (1). To a mixture of 2,4-dihydroxibenzaldehyde (0.50 g, 3.6 mmol) and DCC (N,N'-dicyclohexylcarbodiimide) (0.82 g, 3.96 mmol) in 100 ml of dichloromethane was added 3,4,5-tris(dodecyloxy) benzoic acid (2.44 g, 3.60 mmol) and DMAP (4-(N,N-dimethylamino)pyridine) (0.044 g, 0.36 mmol). The solution was stirred at room temperature for 24 hours. The precipitated was filtered off and washed with of dichloromethane (2 × 20 ml). The resulting solution was concentrated and the crude product was purified by column chromatography with silica using dichloromethane as

eluent to give a white solid (0.99 g, 35 % yield). IR (KBr/cm^{-1}): ν(C=O, ester): 1727 s, ν(C=O, aldehyde): 1663 s. ^{1}H NMR ($CDCl_3$): δ 0,89 (9H, t, J = 6.7 Hz, CH_3), 1.27-1.82 (m, 60 H, CH_2), 4.06 (t, 6 H, J = 6.6 Hz, CH_2O), 6.87 (d, 1 H, J_1 = 2.1 Hz, H-aryl), 6.91 (dd, 1H, J_1 = 2.1 Hz, J_2 = 8.3 Hz, H-aryl), 7.38 (s, 2H, H-aryl), 7.63 (d, 1H, J_2 = 8.3 Hz, H-aryl), 9.90 (s, 1H, CHO), 11.27 (s, 1H, OH).

Preparation of 3-formyl-5-*tert*-butyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate. To a mixture of 3-*tert*-butyl-2,5-dihydroxybenzaldehyde (0.76 g, 3.9 mmol) and DCC (N,N´-dicyclohexylcarbodiimide) (0.89 g, 4.30 mmol) in 100 mL of dichloromethane was added 3,4,5-tris(dodecyloxy)benzoic acid (2.64 g, 3.90 mmol) and DMAP [4-(N, N-dimethylamino)pyridine] (0,047 g, 0.39 mmol). The solution was stirred at room temperature for 24 hours. The precipitated was filtered off and washed with dichloromethane (2 × 20 ml). The organic fractions were collected and the solution was concentrated and the crude product was purified by column chromatography with silica using dichloromethane as eluent to give a white solid (1.29 g, 45 % yield). IR (KBr/cm^{-1}): n(C=O, ester): 1721 s, ν(C=O, aldehyde): 1662 s. ^{1}H NMR ($CDCl_3$): δ 0.88 (9H, t, J = 6.7 Hz, CH_3), 1.26-1.83 (m, 69 H, CH_3 (*tert*-butyl) and CH_2), 4.05 (m, 6H, CH_2O), 7.27 (d, 1H, J = 2.8 Hz, H-aryl), 7.32 (d, 1H, J = 2.8 Hz, H-aryl), 7.40 (s, 2H, H-aryl), 9.85 (s, 1H, CHO), 11.74 (s, 1H, OH).

Preparation of methyl 3,4,5-tris[(S)-3,7-dimethyloctyloxy]benzoate. Anhydrous K_2CO_3 (3.78 g, 27 mmol) was added to a solution of gallic acid methyl ester (1.25 g, 6.8 mmol) and (S)-3,7-dimethyloctylbromide (5 g, 23 mmol) in 22 mL of dry acetone. The mixture was refluxed under N_2 for 48 hours. After cooling to room temperature, 15 ml of water were added. CH_2Cl_2 was added to this mixture and the organic layer was separated, dried over $MgSO_4$, and filtered. The solvent was evaporated on a rotary evaporator and the residue was purified by column chromatography (silica, hexane/dichloromethane 5/1) to

give a colorless liquid. (3.18 g, 77% yield). $[\alpha]^{25}_{589}$ (M = 1, CH_2Cl_2) = -3º ml/dm g ^{1}H NMR ($CDCl_3$): δ 0.87-0.95 (m, 27H, CH_3), 1.16-1.85 (m, 30H, H-alkyl), 3.89 (s, 3H, CH_3OOC), 4.04 (m, 6H, CH_2O), 7.26 (s, 2H, H-aryl).

Preparation of 3,4,5-tris[(S)-3,7-dimethyloctyloxy]benzoic acid. To a mixture of methyl 3,4,5-tris[(S)-3,7-dimethyloctyloxy]benzoate (3.18g, 5.3 mmol) in 15 mL of ethanol, NaOH (0.34g, 8.4 mmol) was added. The mixture was refluxed for 5 hours. After cooling to room temperature, the reaction mixture was poured into 30 ml of water and acidified with HCl 0.1M. The resulting precipitate was filtered off and recrystallized from acetone to give a white solid. (2.89 g, 93% yield). $[\alpha]^{25}_{589}$ (M = 1, CH_2Cl_2) = -5º ml/dm g ^{1}H NMR ($CDCl_3$): δ 0.77-0.89 (m, 27H, CH_3), 1.16-1.84 (m, 30H, alkyl), 3.81 (m, 6H, CH_2O), 7.09 (s, 2H, H-aryl).

Preparation of 3-formyl-4-hydroxyphenyl-3,4,5-tris[(S)-3,7-dimethyloctyloxy]benzoate. To a mixture of 2,5-dihydroxibenzaldehyde (0.67 g, 4.9 mmol) (1.11 g, 5.4 mmol) and DCC (N,N´-dicyclohexylcarbodiimide) (0.059 g, 0.49 mmol) in 100 ml of dichloromethane was added 3,4,5-tris[(S)-3,7-dimethyloctyloxy]benzoic acid (2.89 g, 4.9 mmol) and DMAP [4-(N,N-dimethylamino)pyridine] (0.059 g, 0.49 mmol). The solution was stirred at room temperature for 24 hours. The precipitated was filtered off and washed with dichloromethane (2 × 20 ml). The organic fractions were collected and the solution was concentrated and the crude product was purified by column chromatography with silica using dichloromethane as eluent to give a white solid (0.73 g, 21 % yield). IR (KBr/cm^{-1}): ν(C=O, ester): 1737 s, ν(C=O, aldehyde): 1666 s. $[\alpha]^{25}_{589}$ (M = 1, CH_2Cl_2) = -3º ml/dm g ^{1}H NMR ($CDCl_3$): δ 0.85-0.96 (27H, m, CH_3), 1.16-1.91 (m, 30H, CH_2 and CH), 4.08 (m, 6H, CH_2O), 7.06 (d, 1H, J = 8.6 Hz, H-aryl), 7.39 (dd, 1H, J_1 = 8.6 Hz, J_2 = 2.8 Hz, H-

aryl), 7.40 (s, 2H, H-aryl), 7.44 (d, 1H, J_2 = 2.8 Hz, H-aryl), 9.89 (s, 1H, CHO), 10.95 (s, 1H, OH).

Characterization data for new salen ligands (H_2L).

H_2L^2. Reactives: 3-formyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate **(1)** (1.16 g, 1.5 mmol) and (±)-trans-1,2-diaminocyclohexane (0.083 g, 0.73 mmol). Product: yellow solid (1.26 g, 97 % yield). IR (KBr/cm^{-1}) ν(C=O, ester): 1736 s, ν(C=N, imine): 1637 s. ^{1}H NMR ($CDCl_3$): δ 0.88 (18H, t, J = 6.4 Hz, CH_3), 1.26-1.92 (m, 128 H, CH_2), 3.36 (m, 2H, CHN), 4.04 (m, 12H, CH_2O), 6.93 (d, 2H, J_1 = 8.9 Hz, H-aryl), 7.04 (d, 2H, J_2 = 2.5 Hz, H-aryl), 7.08 (dd, 2H, J_1 = 8.9 Hz, J_2 = 2.5 Hz, H-aryl), 7.37 (s, 4H, H-aryl), 8.27 (s, 2H, HC=N, imine).

H_2L^3. Reactives: **1** (0.30 g, 0.38 mmol) and (1R,2R)-(-)-trans-1,2-diaminocyclohexane (0.023 g, 0.189 mmol). Product: yellow solid (0.33 g, 95 % yield). $[\alpha]^{25}_{589}$ (M = 1, CH_2Cl_2) = -70º ml/dm g. IR (KBr/cm^{-1}): ν(C=O, ester): 1736 s, ν(C=N, imine): 1637 s. ^{1}H NMR ($CDCl_3$): δ 0,88 (18H, t, J = 6.6 Hz, CH_3), 1.26-1.92 (m, 128H, CH_2), 3.38 (m, 2H, CHN), 4.04 (m, 12H, CH_2O), 6.94 (d, 2H, J_1 = 8.8 Hz, H-aryl), 7.04 (d, 2H, J_2 = 2.7 Hz, H-aryl), 7.09 (dd, 2H, J_1 = 8.8 Hz, J_2 = 2.7 Hz, H-aryl), 7.37 (s, 4H, H-aryl), 8.27 (s, 2H, HC=N, imine).

H_2L^4. Reactives: **1** (0.30 g, 0.38 mmol) and 1,2-bis(dodecyloxy)-4,5-diaminobenzene (0.090 g, 0.189 mmol). Product: Orange solid (0.32 g, 85 % yield). IR (KBr/cm^{-1}): ν(C=O, ester): 1735 s, n(C=N, imine): 1618 s. ^{1}H NMR ($CDCl_3$): δ 0.88 (24H, t, J = 6.6 Hz, CH_3), 1.26-1.92 (m, 172 H, CH_2), 4.05 (m, 16 H, CH_2O), 6.80 (s, 2 H, H-aryl), 7.11 (d, 2 H, J_1 = 8.8 Hz, H-aryl), 7.17 (dd, 2 H, J_1 = 8.8 Hz, J_2 = 2.8 Hz, H-aryl), 7.27 (d, 2 H, J_2 = 2.7 Hz, H-aryl), 7.40 (s, 4 H, H-aryl), 8.59 (s, 2 H, HC=N, imine), 13.2 (s, 2H, OH).

H_2L^5. Reactives: 3-formyl-4-hydroxyphenyl-3,4,5-tris[(S)-3,7-dimethyloctyloxi]benzoate (0.68 g, 0.96 mmol) prepared similarly to **1** but starting from 3,4,5-tris[(S)-3,7-

dimethyloctyloxy]benzoic acid,[1] and 1,2-bis(dodecyloxy)-4,5-diaminobenzene (0.23 g, 0.48 mmol). Product: Orange solid (0.72 g, 81 % yield). $[\alpha]^{25}_{589}$ (M = 1, CH_2Cl_2) = -3º ml/dm g. IR (KBr/cm^{-1}): ν(C=O, ester): 1734 s, ν(C=N, imine): 1618 s. ^{1}H NMR ($CDCl_3$): δ 0.86-0.96 (m, 60 H, CH_3), 1.17-1.89 (m, 104 H, CH_2), 4.08 (m, 16 H, CH_2O), 6.81 (s, 2 H, H-aryl), 7.11 (d, 2 H, J_1 = 9.1 Hz, H-aryl), 7.18 (dd, 2H, J_1 = 9.1 Hz, J_2 = 2.5 Hz, H-aryl), 7.28 (d, 2 H, J_2 = 2.5 Hz, H-aryl), 7.42 (s, 4 H, H-aryl), 8.59 (s, 2 H, HC=N, imine), 13.1 (s, 2 H, OH).

H_2L^6. This ligand was not isolated and **[$MnClL^6$]** was prepared one pot starting from 4-formyl-5-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate (0.60 g; 0.76 mmol), ethylenediamine (0.023 g; 0.38 mmol) and manganese (II) diacetate tetrahydrate, as described later.

H_2L^7. Reactives: 3-formyl-5-*tert*-butyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate (2.82 g, 3.31 mmol), (1R,2R)-(-)-trans-1,2-diaminocyclohexane (0.378 g, 1.65mmol). (2.6 g, 88 % yield). $[\alpha]^{25}_{589}$ (M = 1, CH_2Cl_2) = -65º ml/dm g. IR (KBr/cm^{-1}): ν(C=O, ester): 1736 s, ν(C=N, imine): 1637 s. ^{1}H NMR ($CDCl_3$): δ 0,88 (18 H, t, CH_3), 1.26-1.84 (m, 146 H, CH_3 *tert*-butyl and CH_2), 3.37 (m, 2 H, CHN), 4.05 (m, 12 H, CH_2O), 6.87 (d, 2 H, J = 2.8 Hz, H-aryl), 7.05 (d, 2 H, J = 2.8 Hz, H-aryl), 7.37 (s, 4 H, H-aryl), 8.28 (s, 2 H, HC=N, imine).

Characterization data for Salen-Mn(III) complexes ($MnXL^n$).

$MnClL^1$. Yield: 0.28 g, 90%. IR (KBr/cm^{-1}): ν(C=O): 1719 (s), ν(C=N): 1629 (s). Anal. Calcd for $C_{102}H_{166}O_{12}N_2ClMn$: C, 71.96; H, 9.76; N, 1.65; Found C, 71.74; H, 9.59; N, 1.80. UV-Vis (CH_2Cl_2): λ/nm (ε/l $mol^{-1}cm^{-1}$) = 244 (16579), 293 (30965), 433 (4055).

MnClL^{2}. Yield: 0.29 g, 88%. IR (KBr/cm^{-1}): ν(C=O): 1726 (s), ν(C=N): 1629 (s). Anal. Calcd for $C_{106}H_{172}O_{12}N_2ClMn$: C, 72.46; H, 9.87; N, 1.59; Found C, 72.19; H, 9.76; N, 1.69. UV-Vis (CH_2Cl_2): λ/nm (ε/l mol^{-1}cm^{-1}) = 280 (43125), 421 (3542).

MnClL^{3}. Yield: 0.23 g, 71 %. IR (KBr/cm^{-1}): ν(C=O): 1726 (s), ν(C=N): 1627 (s). Anal. Calcd for para $C_{106}H_{172}O_{12}N_2ClMn$: C, 72.46; H, 9.87; N, 1.59; Found C, 72.24; H, 9.66; N, 1.79. UV-Vis (CH_2Cl_2): λ/nm (ε/l mol^{-1}cm^{-1}) = 280 (48974), 416 (3846). $[\alpha]_{589}^{25}$ (M = 1, CH_2Cl_2)) = -25.8.

MnClL^{4}. Yield: 0.33 g, 85 %. IR (KBr/cm^{-1}): ν(C=O): 1720 (s), ν(C=N): 1604 (s). Anal. Calcd. for $C_{130}H_{214}O_{14}N_2ClMn$: C, 72.46; H, 9.87; N, 1.59; Found C, 72.67; H, 10.08; N, 1.42. UV-Vis (CH_2Cl_2): λ/nm (ε/l mol^{-1}cm^{-1}) = 283 (55429), 347 (24143), 485 (13857).

MnBrL^{4}. The synthesis is similar to chloro derivatives but using NaBr instead of NaCl. Yield: 0.35 g, 87 %. IR (KBr/cm^{-1}): ν(C=O): 1720 (s), ν(C=N): 1606 (s). Anal. Calcd. for $C_{130}H_{214}O_{14}N_2BrMn$: C, 72.15; H, 9.97; N, 1.29; Found C, 71.97; H, 9.75; N, 1,52. UV-Vis (CH_2Cl_2): λ/nm (ε/l mol^{-1}cm^{-1}) = 282 (46125), 347 (20938), 486 (8438).

MnClL^{5}. Yield: 0.29 g, 81 %. IR (KBr/cm^{-1}): ν(C=O): 1720 (s), ν(C=N): 1603 (s). Anal. Calcd. for $C_{118}H_{190}O_{14}N_2ClMn$: C, 72.63; H, 9.81; N, 1.43; found C, 72.83; H, 9.57; N, 1.64. UV-Vis (CH_2Cl_2): λ/nm (ε/l mol^{-1}cm^{-1}) = 281 (33320), 343 (13300), 483 (7780). $[\alpha]_{589}^{25}$ (M = 1, CH_2Cl_2) = -9.5 º dm^{-1}cm^{3}g^{-1}.

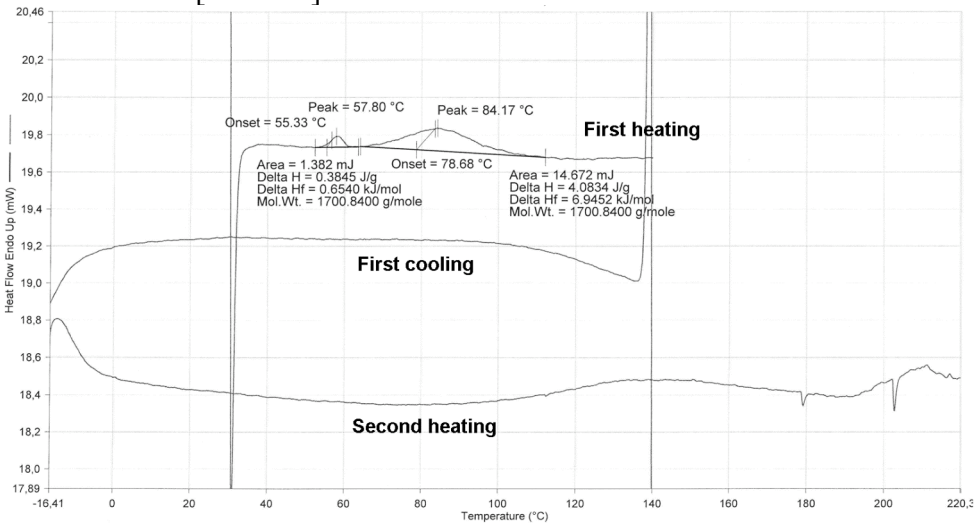
MnClL^{6}. To a mixture of 4-formyl-5-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate **(1)** (0.60 g; 0.76 mmol) in 100 mL under nitrogen was added successively ethylenediamine (0.023 g; 0.38 mmol) and manganese (II) diacetate tetrahydrate (0.093 g; 0.38 mmol). After stirring overnight, air was bubbled through the solution for 4 h. The reaction mixture was concentrated to 40 ml, treated with 50 mL of brine, and extracted with 2 × 80 mL of CH_2Cl_2. The organic layer was washed with 100 ml of H_2O and dried over $MgSO_4$. After evaporation of the solvent and drying under vacuum, 0.54 g, (84% yield) of complex was

obtained as a dark brown solid. Anal. Calcd. for $C_{102}H_{166}O_{12}N_2ClMn$ (%): C, 71.96; H, 9.76; N, 1.65; found C, 71.77; H, 9.29; N, 1.51. IR (KBr/cm^{-1}): 1734 (s, ν(C=O), ester), 1618 (s, νC=N, imine). UV-vis (CH_2Cl_2): λ/nm (ε/l $mol^{-1}cm^{-1}$) = 285 (77305), 408 (9341).

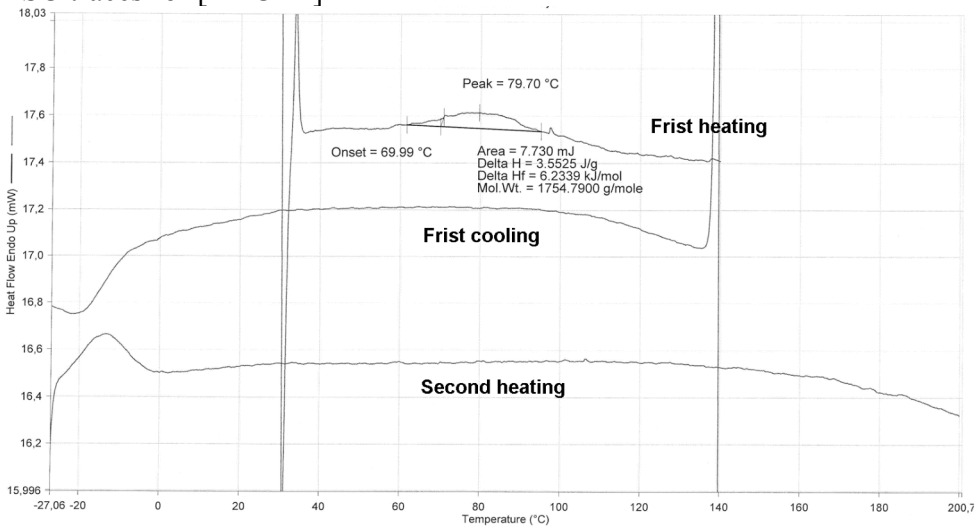
MnClL[7]. (0.251 g, 84 % yield). IR (KBr/cm^{-1}): 1721 ν(C=O), 1626 ν(C=N). Anal. Calculated for $C_{114}H_{188}N_2O_{12}ClMn$ (%): C, 73.26; H, 10.14; N, 1.50; found C, 73.31; H, 9.34; N, 1.85. UV-vis (CH_2Cl_2): λ/nm (ε/l $mol^{-1}cm^{-1}$) = 273 (52480), 437 (5000). $[\alpha]_{589}^{25}$ (M = 1, CH_2Cl_2) = -21º ml/dm g.

Representative DSC traces.

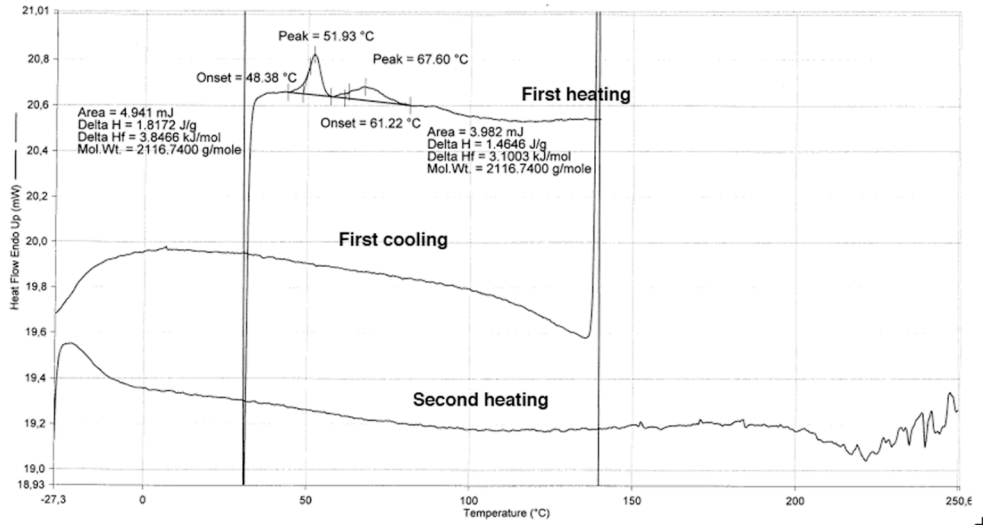
DSC traces for [MnClL[1]]



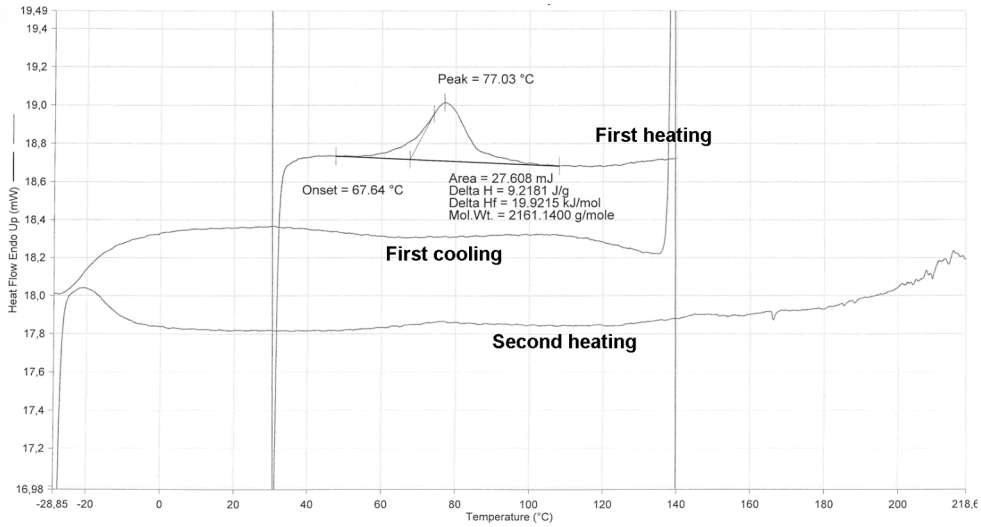
DSC traces for [MnClL^3]



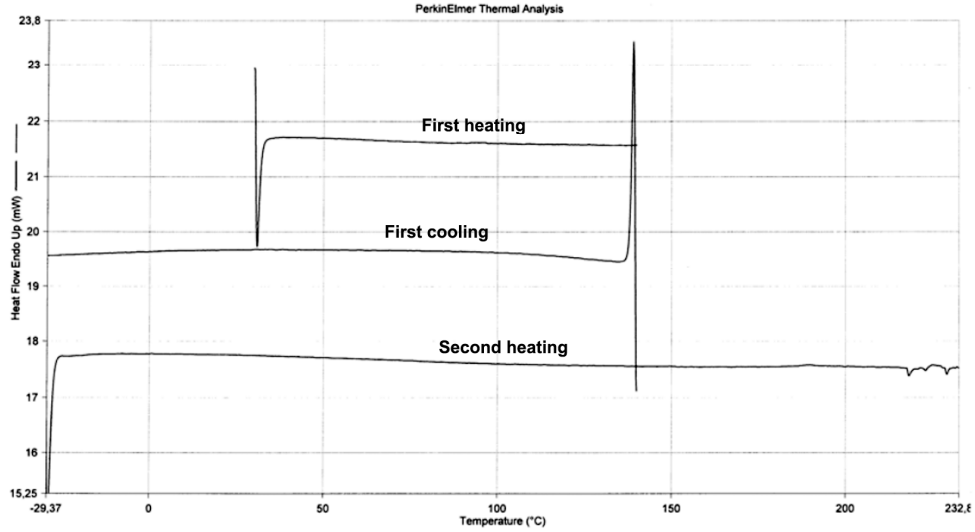
DSC traces for [MnClL^4]



DSC traces for [MnBrL^4]



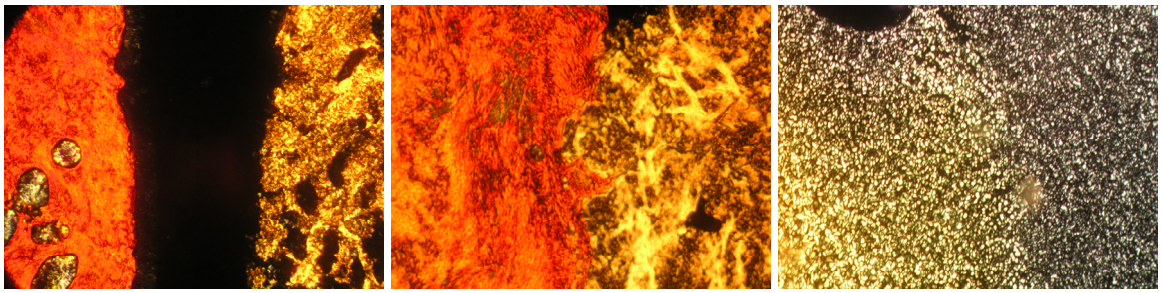
DSC traces for [MnClL^5]



Miscibility experiments

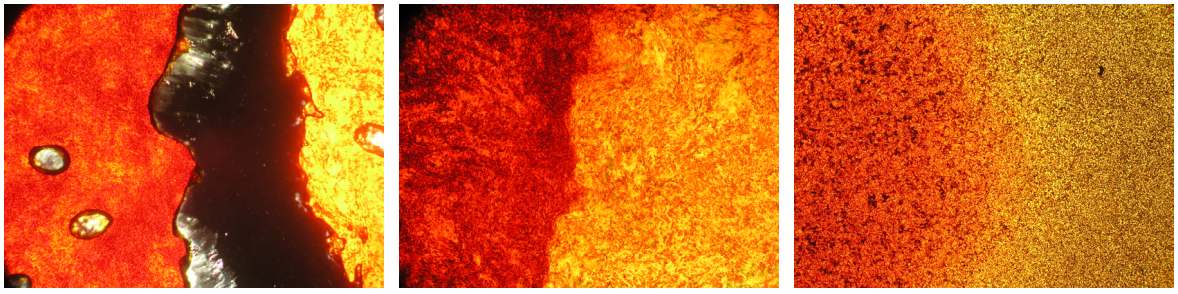
The miscibility tests were carried out by the contact method.[2] In all cases, the photographs display the evolution of phase separation through the contact method: a) the two separate mesophases, b) the mesophases in contact and c) mesophases in contact after cooling from the isotropic liquid. Only for [MnClL^4] + [MnClL^6] and [MnClL^4] + [MnClL^6] inmiscibility lines are observed.

[MnClL^4] + [MnClL^1]



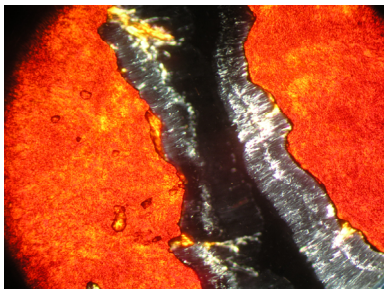
a) 130 ºC on heating b) 130 ºC on heating c) 150 ºC on cooling from isotropic liquid

[MnClL^4] + [MnClL^2]

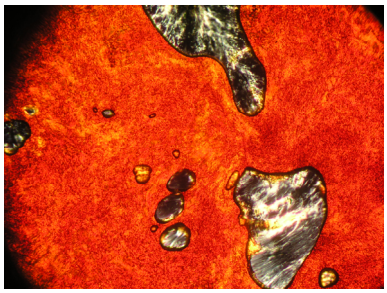


a) 140 ºC on heating b) 140 ºC on heating c) 140 ºC on cooling from isotropic liquid

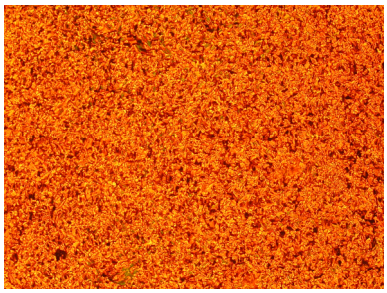
[$MnClL^4$] + [$MnBrL^4$]



a) 130 ºC on heating

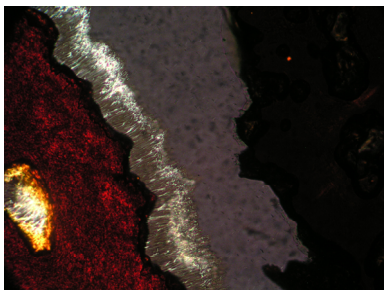


b) 130 ºC on heating

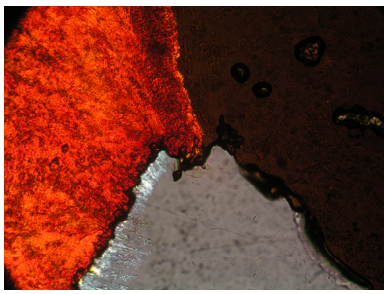


c) 145 ºC on cooling from isotropic liquid

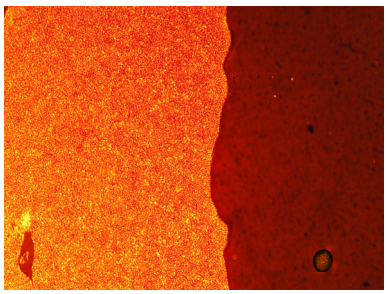
[$MnClL^4$] + [$MnClL^6$]



a) 90 ºC on heating

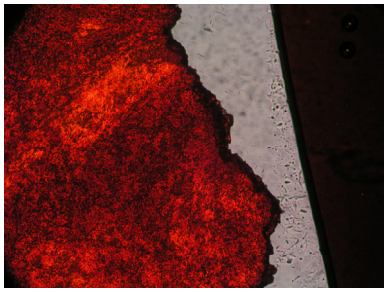


b) 90 ºC on heating

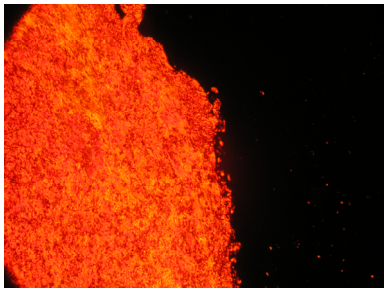


c) 130 ºC on cooling from isotropic liquid (polarizer and analyzer at about 60º)

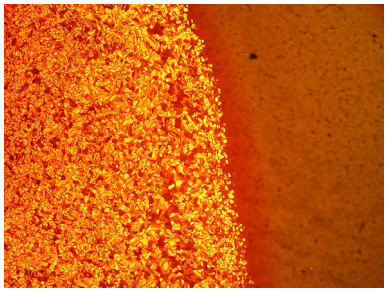
[$MnClL^4$] + [$MnClL^7$]



a) 90 ºC on heating



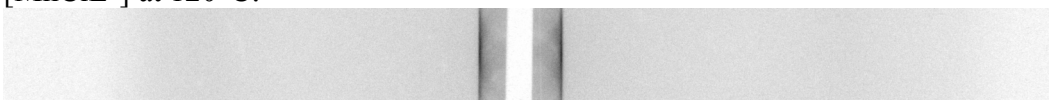
b) 90 ºC on heating



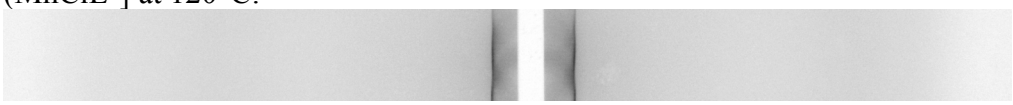
c) 130 ºC on cooling from isotropic liquid (polarizer and analyzer at about 60º)

Small-angle diffraction patterns of the Mn complexes:

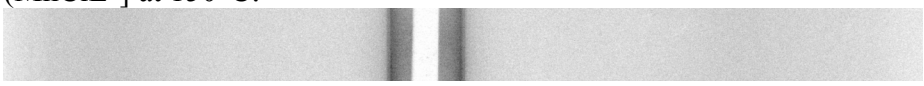
[MnClL[1]] at 120°C:



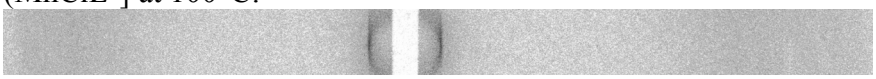
(MnClL[2]] at 120°C:

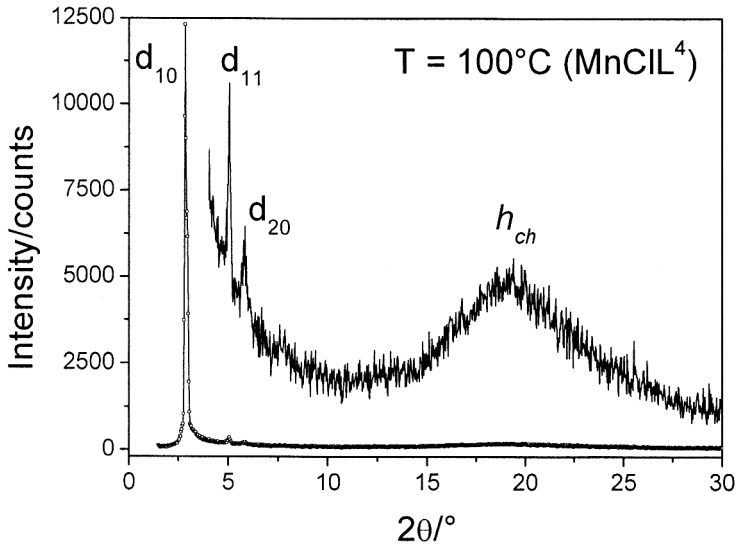


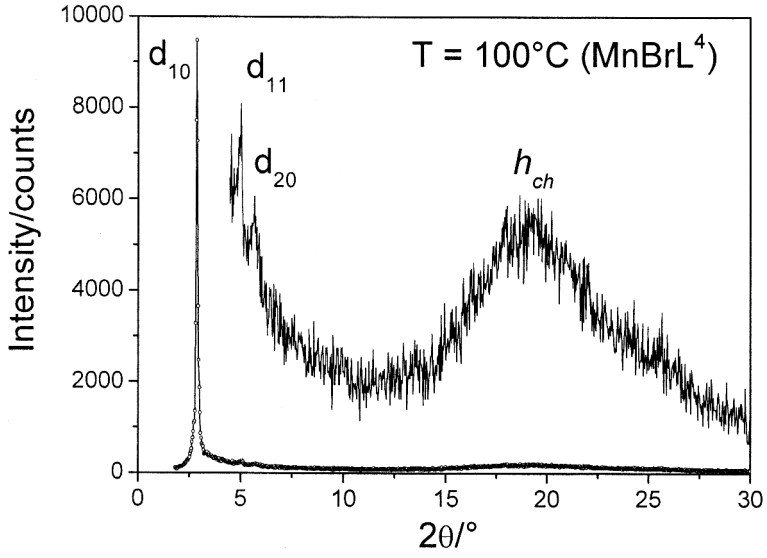
(MnClL[6]] at 150°C:



(MnClL[7]] at 100°C:







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[2] G.Sigaud, M. F. Achad, F. Hardouin, M. Mauzac, H. Richard, H. Gaspaoux, *Macromolecules*, **1987**, *20*, 578-585.