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Erratum

Erratum to "Synthesis and characterisation of rod-like metallomesogens of Mn(I) based on Schiff base ligands" [J. Organomet. Chem. 551 (1998) 235–246]☆,☆☆

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The Publisher regrets that in the above article the Experimental section was incorrectly printed. The correct Experimental section is as follows:

1. Experimental

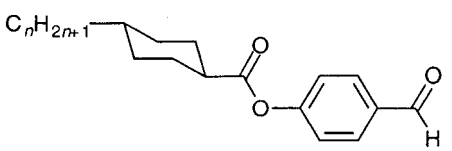
Apparatus and general techniques of microscopy and calorimetry are as described elsewhere [23].

1.1. 4′-(4-Octyloxybenzoyloxy)benzaldehyde

Dicyclohexylcarbodiimide (5.94 g, 28.8 mmol) and *N*,*N*-dimethylaminopyridine (0.15 g) were added to a stirred solution of 4-octyloxybenzoic acid (6.0 g, 24 mmol) and hydroxybenzaldehyde (3.0 g, 24.0 mmol) in dry dichloromethane (DCM, 100 cm^3). The reaction mixture was stirred at room temperature for 6 h. The dicyclohexylurea was filtered off and the solvent from the filtrate was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM). A colourless product was obtained.

Yield: 7.35 g (87%). M.p.: 103°C. ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.34–1.85 (m, 12H, $6CH_2$), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.98 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.4 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.12 (d, 2H, $J = 9.0$ Hz, AA′XX′), 10.02 (s, 1H, CHO) ppm.

For the next two aldehydes ($n = 5$, 7), the synthesis was performed in an analogous manner—one set of NMR data is given—the other is similar.



^{1}H-NMR (250 MHz, $CDCl_3$, ppm) $n = 5$ δ: 0.9 (t, 3H, CH_3), 1.0 (m, 2H, H_{3ax}–H_{5ax}), 1.25 (m, 9H, $4CH_2 + H_4$), 1.55 (qd, 2H, $H_{2ax} + H_{6ax}$), 1.85 (dd, 2H, $H_{3eq} + H_{5eq}$), 2.1 (dd, 2H, $H_{2eq} + H_{6eq}$), 2.45 (tt, 1H, H_1), 7.23 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.94 (d, 2H, $J = 9.0$ Hz, AA′XX′), 10.0 (s, 1H, CHO).

1.2. 4′-(4-Octyloxybenzoyloxy)nitrobenzene

DCC (34.61 g, 168 mmol) and DMAP (0.3 g) were added to a stirred solution of 4-octyloxybenzoic acid (35 g, 140 mmol) and hydroxybenzaldehyde (29 g, 210 mmol) in dry DCM (400 cm^3). The reaction mixture was stirred at room temperature for 6 h. The dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. The crude product was crystallised from ethanol to give a colourless solid.

Yield: 46.2 g (89%). ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.25–1.45 (m, 10H, $5CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.98 (d, 2H, $J = 9$ Hz, AA′XX′), 7.4 (d, 2H, $J = 9$ Hz, AA′XX′), 8.1 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.13 (d, 2H, $J = 9$ Hz, AA′XX′) ppm. Elemental analysis (%): Found: C, 68.0; H, 6.8; N, 3.9; $C_{21}H_{25}NO_5$ requires: C, 67.9; H, 6.8; N, 3.8.

☆ PII of original article S0022-328X(97)00437-3.

☆☆ Dedicated to Peter Maitlis on the occasion of his 65th birthday.

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PII: S0022-328X(98)01023-7

1.3. 4′-(4-Octyloxybenzoyloxy)aniline

A mixture of 4′-(4-octyloxybenzoyloxy)nitrobenzene (**25**) (5 g, 13 mmol) and five equivalents of $SnCl_2 \cdot 2H_2O$ (15.2 g, 65 mmol) was refluxed in ethanol (100 cm^3) for 6 h. After cooling, the mixture was poured into ice and the pH value was adjusted to 7 ~ 8 using sodium hydroxide. The mixture was extracted with ethyl acetate. The ethyl acetate solution was washed three times with brine and was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The brownish solid was purified by column chromatography (silica gel: DCM and 1% triethylamine) and then crystallised from ethanol to give a whitish solid.

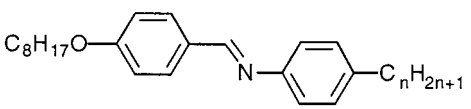
Yield: 3.24 g (70.4%). M.p. 94°C. ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.17 ~ 1.55 (m, 10H, $5CH_2$), 1.82 (qn, 2H, OCH_2CH_2), 3.64 (s, 2H, NH_2), 4.03 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.7 (d, 2H, $J = 9$ Hz, AA′XX′), 6.95 (d, 4H, $J = 9$ Hz, 2AA′XX′, overlapped), 8.1 (d, 2H, $J = 9$ Hz, AA′XX′) ppm. Elemental analysis (%): Found: C, 73.6; H, 7.8; N, 4.1; $C_{21}H_{27}NO_3$ requires: C, 73.9; H, 8.0; N, 4.1.

1.4. Ligands **1** (4′-octyloxybenzylidene)-4-hexylaniline

4-Hexylaniline (3.79 g, 19.2 mmol) was dissolved in toluene (25 cm^3) and then acetic acid (two drops) was added into the solution. 4-Octyloxybenzadehyde (4.5 g, 19.2 mmol) was added to the solution, and stirred for a few minutes then left unstirred overnight. The crude product was filtered and recrystallised in ethanol to give a colourless crystalline solid.

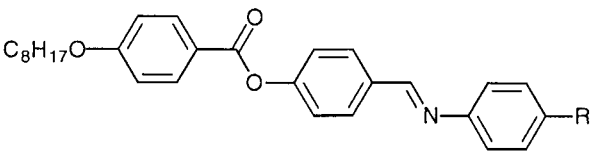
Yield: 6.45 g (85.4%). ^{1}H-NMR ($CDCl_3$) δ: 0.9 (m, 6H, $2CH_3$), 1.2–1.6 (m, 18H, $9CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 2.6 (t, 2H, Ph–CH_2), 4.0 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.1 (dd, 2H, $J = 9.0$ Hz, AA′XX′), 7.85 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.4 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 81.9; H, 10.0; N, 3.4; $C_{27}H_{39}NO$ requires: C, 82.4; H, 9.9; N, 3.6.

For the homologous Schiff base ligands ($n = 7$, 10, 12), the synthesis was performed in an analogous manner; the alkylanilines were commercially available. NMR data were effectively identical and satisfactory analytical data were obtained.



1.5. Ligands **3**

For the ligands **3**, the synthesis was performed in an analogous manner starting from the corresponding alkoxybenzoyloxybenzaldehyde; the aniline derivatives were commercially available.



R = C_6H_{13} (**3a**)

Yield: 67%. ^{1}H-NMR ($CDCl_3$) δ: 0.9 (m, 6H, $2CH_3$), 1.2–1.6 (m, 18H, $9CH_2$), 1.85 (qn, 2H, OCH_2CH_2), 2.6 (t, 2H, Ph–CH_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.98 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.12 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.18 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.3 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 79.4; H, 8.6; N, 2.6; $C_{34}H_{43}NO_3$ requires: C, 79.5; H, 8.4; N, 2.7.

R = F (**3b**)

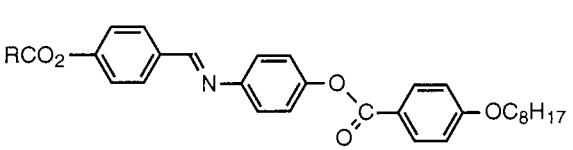
Yield: 70%. ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.28–1.55 (m, 10H, $5CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.05 (dd, 2H, AA′XX′), 7.2 (m, 2H, AA′XX′), 7.3 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.94 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.17 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 74.9 H, 6.9; N, 3.0; $C_{28}H_{30}NFO_3$ requires: C, 75.1; H, 6.8; N, 3.1.

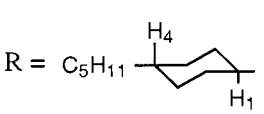
R = CN (**3c**)

Yield: 78%. ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.17–1.55 (m, 10H, $5CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 4.0 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.3 (d, 2H, AA′XX′), 7.6 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.92 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.1 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.35 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 76.3 H, 6.6; N, 6.3; $C_{29}H_{30}N_2O_3$ requires: C, 76.6; H, 6.7; N, 6.2.

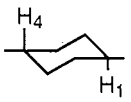
1.6. Ligands **9**

Four-ring imine ligands (**9**) were synthesised similarly to the two-ring imines, **1**, except the final products were purified by crystallisation from DCM/methanol.

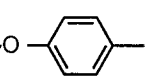




Yield: 81.4%. ^{1}H-NMR ($CDCl_3$) δ: 0.85–1.1 (m 8H, $2CH_3 + H_{3ax}–H_{5ax}$), 1.2–1.65 (m, 21H, $9CH_2 + H_4 + H_{2ax} + H_{6ax}$), 1.85 (m, 4H, $H_{3eq} + H_{5eq} + OCH_2CH_2$), 2.15 (dd, 2H, $H_{2eq} + H_{6eq}$), 2.5 (tt, 1H, H_1), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.2 (m, 6H, AA′XX′, overlapped), 7.9 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 77.0 H, 8.5; N, 2.3; $C_{40}H_{51}Nos_5$ requires: C, 76.8; H, 8.2; N, 2.2.

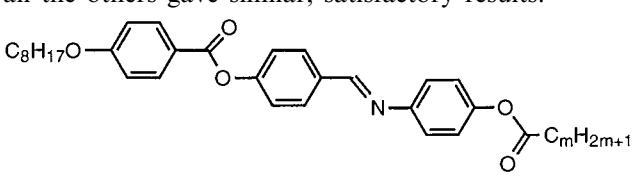
R = C_7H_{15} 

Yield: 90%. ^{1}H-NMR ($CDCl_3$) δ: 0.85–1.1 (m, 8H, $2CH_3 + H_{3ax}–H_{5ax}$), 1.2–1.65 (m, 25H, $9CH_2 + H_4 + H_{2ax} + H_{6ax}$), 1.85 (m, 4H, $H_{3eq} + H_{5eq} + OCH_2CH_2$), 2.15 (dd, 2H, $H_{2eq} + H_{6eq}$), 2.5 (tt, 1H, H_1), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.2 (m, 6H, AA′XX′, overlapped), 7.9 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 76.9; H, 8.5; N, 2.1; $C_{42}H_{55}NO_5$ requires: C, 77.1; H, 8.5; N, 2.1.

R = $C_8H_{17}O$ 

Yield: 86.3%. ^{1}H-NMR ($CDCl_3$) δ: 0.9 (t, 6H, $2CH_3$), 1.25–1.5 (m, 22H, $11CH_2$), 1.85 (m, 4H, OCH_2CH_2), 4.05 (t, 4H, $J = 9.0$ Hz, $2OCH_2$), 6.95 (d, 4H, $J = 9.0$ Hz, AA′XX′), 7.2–7.35 (m, 6H, AA′XX′), 7.9 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 4H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH=N) ppm. ^{13}C{^{1}H}-NMR (250 MHz, $CDCl_3$) δ: 14.11, 22.66, 25.99, 29.11, 29.23, 29.33, 31.8, 68.36, 114.3, 114.4, 121.2, 121.5, 121.8, 122.2, 122.4, 130.0, 132.3, 132.4, 133.7, 149.3, 149.4, 153.6, 159.3, 163.6, 163.7, 164.6, 165.0 ppm. Elemental analysis (%): Found: C, 75.9; H, 7.7; N, 2.0; $C_{43}H_{51}NO_6$ requires: C, 76.2; H, 7.6; N, 2.1.

Three ring Schiff base ligands which have alkanoyloxy terminal groups were synthesised as described below. Analytical and NMR data are given for one example—all the others gave similar, satisfactory results.



$m = 7$ (**5a**)

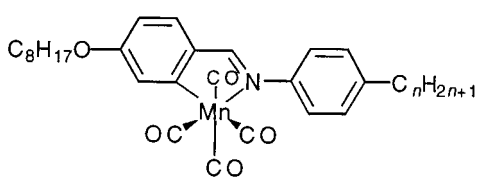
DCC (0.33 g, 1.6 mmol) and DMAP (0.05 g) were added to a stirred solution of octanoic acid (0.2 g, 1.3 mmol) and compound **33** (0.6 g, 1.3 mmol) in dry DCM (30 cm^3). The reaction mixture was stirred at room temperature for 12 h. The dicyclohexylurea was filtered and the solvent was removed under reduced pressure. The crude product was crystallised from DCM/methanol to give a colourless solid.

Yield: 0.54 g (69%). ^{1}H-NMR ($CDCl_3$) δ: 0.9 (6H, $2CH_3$, two overlapped triplets), 1.25–1.5 (m, 18H, $9CH_2$), 1.8 (m, 4H, $CH_2CH_2CO_2 + OCH_2CH_2$), 2.55 (t, 2H, CH_2CO_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.1 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.2 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.33 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 75.4; H, 7.7; N, 2.4; $C_{36}H_{45}NO_5$ requires: C, 75.7; H, 7.9; N, 2.5.

1.7. Manganese complexes

All Mn^I complexes were synthesised in an analogous manner by using the method now described. When the number of rings in the ligands were increased from two to four, the reaction time was increased from 4 to 8 h.

Under a nitrogen atmosphere, an equimolar amount of the Schiff base and [$MnMe(CO)_5$] were dissolved in dry toluene and heated at reflux for between 4 and 8 h, depending on the ligand. The solvent was removed in vacuo and passed through a column of neutral alumina eluting with DCM. The yellow band from the column gave, on removal of the solvent, a yellow solid which was crystallised from DCM/methanol to give the product.



Details are given for $n = 6$. All other complexes gave satisfactory elemental analyses, and related NMR and IR data.

$n = 6$—Yield: 91.2%. M.p.: 38–40°C. IR (DCM solution) ν_{CO} cm^{-1}: 2073(w), 1986(vs), 1938(s). ^{1}H-NMR (CD_2Cl_2) δ: 0.9 (6H, $2CH_3$, two overlapped triplets), 1.2–1.6 (m, 18H, $9CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 2.6 (t, 2H, Ph–CH_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.63 (dd, 1H, $J = 8.4$, 2.4 Hz), 7.12 (d, 2H, $J = 8.4$ Hz, AA′XX′), 7.23 (d, 2H, $J = 8.4$ Hz, AA′XX′), 7.52 (d, 1H, $J = 2.4$ Hz), 7.62 (d, 1H, $J = 8.4$ Hz), 8.17 (s, 1H, CH=N) ppm. Elemental analysis (%): Found: C, 66.4; H, 6.4; N, 2.4; $C_{31}H_{38}NO_5Mn$ requires: C, 66.5; H, 6.8; N, 2.5.

Acknowledgements

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