

SUPPORTING INFORMATION

Supramolecular Metallomesogens: Hydrogen-Bonded Ferrocene-Containing Liquid Crystals which Display Bicontinuous Cubic Phases

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Experimental Section

Materials: Diethyl ether (LiAlH₄, under N₂), CH₂Cl₂ (P₂O₅, under N₂), toluene (NaH, under N₂) and THF (sodium, benzophenone, under N₂) were distilled prior to use. Malonic acid (Fluka), N,N'-dicyclohexylcarbodiimide (Fluka), 4-pyrrolidinopyridine (Aldrich), anhydrous AlCl₃ (Fluka), LiAlH₄ (Fluka), DMF (SDS, analytical grade), POCl₃ (Fluka), decanoyl chloride (Fluka), dodecanoyl chloride (Fluka), 4-hydroxybenzoic acid benzylester (Fluka) and ferrocene (Chemische Betriebe Pluto/Veba Oel) were used as received. Pyridine (Fluka) and piperidine (Fluka) were stored on 4 Å on molecular sieves. Compounds **3a**, **4a**, **5a** and **6a** were synthesized as reported previously.⁴³

Techniques: Column chromatography: silica gel 60 (0.060-0.200 mm, SDS). Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 822 calorimeter, under N₂/He, at a rate of 10°C/min. Optical studies were conducted using a Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N₂. ¹H NMR spectra were recorded on a Varian GEMINI 200 spectrometer or a Bruker AMX 400 spectrometer (solvent as an internal standard). Mass spectra (ESI) were recorded on a Finnigan LCQ. Elemental analyses were done by Mikroelementaranalytisches Laboratorium ETH-Zurich or Laboratoire de chimie pharmaceutique et organique propédeutique, Université de Genève.

X-ray Diffraction studies: Experiments were performed on a rotating anode generator. The copper K α wavelength (0.154 nm) was selected with a OSMIC graded multilayer monochromator and a circular collimator (diameter 1 mm) was used. Detection was performed on a CCD camera (Princeton Instruments) at 460 \pm 5 mm from the sample. The samples were introduced into Lindemann capillaries (diameter 1 mm) sealed at both ends. Capillaries were held inside a home-made oven (not calibrated). In the case of **2a**, a measurement has been performed on an image-plate detector (distance sample-detection : 406 mm) using synchrotron radiation (wavelength 0.145 nm) at the D43 beamline at LURE (Orsay, France).

Abbreviations: N,N'-dicyclohexylcarbodiimide = DCC; 4-pyrrolidinopyridine = 4-PPy; dimethylformamide = DMF; column chromatography = CC.

Syntheses.

Compound 3b: A mixture of AlCl_3 (15.1 g, 113.24 mmol) and decanoyl chloride (20.5 g, 107.5 mmol) was added to a stirred solution of ferrocene (10.0 g, 53.75 mmol) in CH_2Cl_2 (200 mL). The mixture was stirred under reflux for 2h, cooled to room temperature and poured onto ice. The organic layer was separated, dried (MgSO_4) and evaporated to dryness. Purification of the residue by two crystallizations (hexane) gave pure **3b** (21.8 g, 82%). Mp = 69°C . ^1H RMN (200 MHz, acetone- d_6): δ = 0.90 (t, 6H, CH_3), 1.25-1.45 (m, 24H, 12 x CH_2), 1.60-1.75 (m, 4H, $\text{CH}_2\text{CH}_2\text{COCp}$), 2.75 (t, 4H, CH_2COCp), 4.58 (t, 4H, H-Cp), 4.83 (t, 4H, H-Cp). Anal. Calcd for $\text{C}_{30}\text{H}_{46}\text{O}_2\text{Fe}$ (494.53): C, 72.86; H, 9.38. Found: C, 72.79; H, 9.38.

Compound 3c: As for **3b** from dodecanoyl chloride. Purification of the residue by CC (CH_2Cl_2) followed by crystallization (heptane/ AcOEt) gave pure **3c** (77%). Mp = 77°C . ^1H RMN (200 MHz, CDCl_3): δ = 0.89 (t, 6H, CH_3), 1.27-1.33 (m, 32H, 16 x CH_2), 1.65-1.73 (m, 4H, $\text{CH}_2\text{CH}_2\text{COCp}$), 2.65 (t, 4H, CH_2COCp), 4.48 (t, 4H, H-Cp), 4.78 (t, 4H, H-Cp). Anal. Calcd for $\text{C}_{34}\text{H}_{54}\text{O}_2\text{Fe}$ (438.43): C, 74.17; H, 9.88. Found: C, 74.09; H, 9.71.

Compound 4b: To a suspension of LiAlH_4 (3.63 g, 95.64 mmol) and diethyl ether (200 mL) cooled to 0°C and kept under N_2 , was added portionwise AlCl_3 (12.78 g, 95.84 mmol). A solution of **3b** (21.53 g, 43.53 mmol) in diethyl ether (500 mL) was added. The mixture was stirred for 15 min and cautiously poured onto ice. The organic layer was separated and the aqueous phase extracted with diethyl ether. The organic layers were combined, washed successively with a saturated aqueous NaHCO_3 solution and a saturated aqueous NaCl solution, dried (MgSO_4) and evaporated to dryness. Purification of the residue by CC (diethyl ether) gave pure **4b** (19.66 g, 97%, oil). ^1H RMN (400 MHz, acetone- d_6): δ = 0.90 (t, 6H, CH_3); 1.20-1.35 (m, 28H, 14 x CH_2); 1.48-1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{Cp}$); 2.35 (m, 4H, CH_2Cp); 3.98 (m, 8H, H-Cp). Anal. Calcd for $\text{C}_{30}\text{H}_{50}\text{Fe}$ (466.57): C, 77.23; H, 10.80. Found: C, 77.18; H, 10.79.

Compound 4c: As for **4b** from **3c** in toluene. Purification of the residue by CC (diethyl ether) gave pure **4c** (97%, oil). ^1H RMN (400 MHz, acetone- d_6): δ = 0.89 (t, 6H, CH_3), 1.20-1.35 (m, 36H, 18 x CH_2), 1.48-1.54 (m, 4H, $\text{CH}_2\text{CH}_2\text{Cp}$), 2.29 (m, 4H, CH_2Cp), 3.98 (m, 8H, H-Cp).

Compound 5b: To a solution of **4b** (19.43 g, 41.64 mmol) in CH_2Cl_2 (200 mL) heated under reflux, was added dropwise a solution of POCl_3 (14.11 g, 92.02 mmol) and DMF (12.23 g, 167.32 mmol) in CH_2Cl_2 (50 mL). The solution was stirred under reflux for 18h, cooled to room temperature and poured onto ice. K_2CO_3 (60 g) was added portionwise and the mixture was stirred for 1h. CH_2Cl_2 (100 mL) was added and the organic layer separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL). The organic layers were combined, washed with water, dried (MgSO_4) and evaporated to dryness. Purification of the residue by CC (CH_2Cl_2) gave pure **5b** (7.73 g, 38%, oil). ^1H RMN (400 MHz, acetone- d_6): δ = 0.88 (t, 6H, CH_3), 1.20-1.35 (m, 28H, 14 x CH_2), 1.45-1.57 (m, 4H, $\text{CH}_2\text{CH}_2\text{Cp}$), 2.28 (m, 2H, CH_2Cp), 2.40-2.45 (m, 2H, $\text{CH}_2\text{Cp}(\text{CHO})$), 4.11 (m, 4H, H-Cp), 4.51 (m, 1H, H-Cp), 4.62-4.64 (m, 2H, H-Cp), 9.86 (s, 1H, CHO).

Compound 5c: As for **5b** from **4c**. Purification of the residue by CC (CH₂Cl₂) gave pure **5c** (38%, oil). ¹H RMN (200 MHz, CDCl₃): δ = 0.88 (t, 6H, CH₃), 1.26-1.56 (m, 40H, 20 x CH₂), 2.23 (t, 2H, CH₂Cp), 2.37 (t, 2H, CH₂Cp(CHO)), 4.08 (m, 4H, H-Cp), 4.43 (s, 1H, H-Cp), 4.58 (s, 1H, H-Cp), 4.61 (s, 1H, H-Cp), 9.88 (s, 1H, CHO).

Compound 6b: A solution of **5b** (7.73 g, 15.63 mmol), malonic acid (3.12 g, 30.0 mmol) and piperidine (20 drops) in pyridine (20 mL) was stirred at 55°C for 4h and at 115°C for 2h. The solution was poured onto ice and water and acidified with HCl (2 N). Diethyl ether was added. The organic layer was separated, washed with water, dried (MgSO₄) and evaporated to dryness. Purification of the residue by CC (heptane/diethyl ether 2:1) gave pure **6b** (5.85 g, 70%). Mp = 45°C. ¹H RMN (200 MHz, acetone-d₆): δ = 0.90 (t, 6H, CH₃), 1.20-1.40 (m, 28H, 14 x CH₂), 1.43-1.62 (m, 4H, CH₂CH₂Cp), 2.26-2.33 (m, 2H, CH₂Cp), 2.38-2.46 (m, 2H, CH₂Cp(substituted by the vinylic function)), 3.98-4.07 (m, 4H, H-Cp), 4.34-4.36 (m, 1H, H-Cp), 4.47-4.50 (m, 2H, H-Cp), 6.02 (d, 1H, vinylic proton), 7.50 (d, 1H, vinylic proton). Anal. Calcd for C₃₃H₅₂O₂Fe (536.62): C, 73.86; H, 9.77. Found: C, 74.07; H, 9.79.

Compound 6c: As for **6b** from **5c**. Purification of the residue by CC (heptane/diethyl ether 1:1) gave pure **6b** (97%). Mp = 57°C. ¹H RMN (200 MHz, CDCl₃): δ = 0.88 (t, 6H, CH₃), 1.26-1.56 (m, 40H, 20 x CH₂), 2.21 (t, 2H, CH₂Cp), 2.34 (t, 2H, CH₂Cp(substituted by the vinylic function)), 3.96-4.01 (m, 4H, H-Cp), 4.29-4.32 (m, 3H, H-Cp), 5.96 (d, 1H, vinylic proton), 7.62 (d, 1H, vinylic proton). Anal. Calcd for C₃₇H₆₀O₂Fe (592.72): C, 74.98; H, 10.20. Found: C, 74.89; H, 10.01.

Compound 7b: A solution of **6b** (1.75 g, 3.26 mmol), 4-hydroxybenzoic acid benzylester (0.75 g, 3.29 mmol), DCC (1.01 g, 4.9 mmol) and 4-ppy (50 mg, 0.34 mmol) in CH₂Cl₂ (40 mL) was stirred at room temperature for 3h. Purification of the residue by CC (CH₂Cl₂/AcOEt 40:1) gave pure **7b** (1.73 g, 74%, oil). ¹H RMN (200 MHz, acetone-d₆): δ = 0.88 (t, 3H, CH₃), 0.90 (t, 3H, CH₃), 1.20-1.60 (m, 32H, 16 x CH₂), 2.27-2.35 (m, 2H, CH₂Cp), 2.41-2.49 (m, 2H, CH₂Cp(substituted by the vinylic function)), 4.02-4.13 (m, 4H, H-Cp), 4.44-4.46 (m, 1H, H-Cp), 4.60-4.62 (m, 2H, H-Cp), 5.42 (s, 2H, CO₂CH₂), 6.25 (d, 1H, vinylic proton), 7.36 (d, 2 arom H), 7.39-7.57 (m, 5 arom H), 7.76 (d, 1H, vinylic proton), 8.15 (d, 2 arom H).

Compound 7a: As for **7b** from **6a**. Purification of the residue by CC (CH₂Cl₂) gave pure **7a** (95%, oil). ¹H RMN (200 MHz, acetone-d₆): δ = 0.85 (t, 3H, CH₃), 0.89 (t, 3H, CH₃), 1.20-1.70 (m, 24H, 12 x CH₂), 2.29 (t, 2H, CH₂Cp), 2.43 (t, 2H, CH₂Cp(substituted by the vinylic function)), 3.98-4.11 (m, 4H, H-Cp), 4.43 (m, 1H, H-Cp), 4.59 (m, 2H, H-Cp), 5.40 (s, 2H, CO₂CH₂), 6.23 (d, 1H, vinylic proton), 7.34 (d, 2 arom H), 7.35-7.55 (m, 5 arom H), 7.74 (d, 1H, vinylic proton), 8.13 (d, 2 arom H).

Compound 7c: As for **7b** from **6c**. Purification of the residue by CC (CH₂Cl₂/AcOEt 40:1) gave pure **7c** (66%, oil). ¹H RMN (200 MHz, acetone-d₆): δ = 0.89 (t, 3H, CH₃), 0.90 (t, 3H, CH₃), 1.20-1.45 (m, 36H, 18 x CH₂), 1.45-1.65 (m, 4H, CH₂CH₂Cp), 2.27-2.35 (m, 2H, CH₂Cp), 2.41-2.48 (m, 2H, CH₂Cp(substituted by the vinylic function)), 4.01-4.13 (m, 4H, H-Cp), 4.45-4.47 (m, 1H, H-Cp), 4.60-4.61 (m, 2H, H-Cp), 5.42 (s, 2H, CO₂CH₂), 6.25 (d, 1H, vinylic proton), 7.36 (d, 2 arom H), 7.40-7.57 (m, 5 arom H), 7.76 (d, 1H, vinylic proton), 8.15 (d, 2 arom H).

Compound 8b: A mixture of **7b** (2.45 g, 3.41 mmol), Pd(10%)/C (0.25 g) and CH₂Cl₂ (100 mL) was stirred at room temperature under 4 bar of H₂ for 5h. The mixture was filtered through celite and the solvent evaporated to dryness. Purification of the residue by

crystallization (methanol) gave pure **8b** (2.03 g, 90%). Mp = 64°C. ¹H RMN (200 MHz, acetone-d₆): δ = 0.90 (t, 6H, CH₃), 1.20-1.35 (m, 28H, 14 x CH₂), 1.45-1.62 (m, 4H, CH₂CH₂Cp), 2.31-2.43 (m, 4H, CH₂Cp), 2.72-2.92 (m, 4H, CpCH₂CH₂CO₂), 3.96-4.03 (m, 7H, H-Cp), 7.27 (d, 2 arom H), 8.11 (d, 2 arom H). Anal. Calcd for C₄₀H₅₈O₄Fe (658.73) : C, 72.93; H, 8.87. Found: C, 72.94; H, 8.90.

Compound 8a: As for **8b** from **7a**. Purification of the residue by CC (CH₂Cl₂/MeOH 100:1) gave pure **8a** (89%). Mp = 48°C. ¹H RMN (400 MHz, acetone-d₆): δ = 0.89 (t, 6H, CH₃), 1.25-1.45 (m, 20H, 10 x CH₂), 1.63 (m, 4H, CH₂CH₂Cp), 2.40-2.49 (m, 4H, CH₂Cp), 2.80-3.00 (m, 4H, CpCH₂CH₂CO₂), 4.09-4.16 (m, 7H, H-Cp), 7.36 (d, 2 arom H), 8.20 (d, 2 arom H). Anal. Calcd for C₃₆H₅₀O₄Fe (602.64) : C, 71.75; H, 8.36. Found: C, 71.87; H, 8.48.

Compound 8c: As for **8b** from **7c**. Purification of the residue by crystallization (methanol) gave pure **8c** (92%). Mp = 53°C. ¹H RMN (200 MHz, acetone-d₆): δ = 0.90 (t, 6H, CH₃), 1.25-1.45 (m, 36H, 18 x CH₂), 1.45-1.62 (m, 4H, CH₂CH₂Cp), 2.31-2.43 (m, 4H, CH₂Cp), 2.72-2.92 (m, 4H, CpCH₂CH₂CO₂), 3.97-4.03 (m, 7H, H-Cp), 7.27 (d, 2 arom H), 8.11 (d, 2 arom H). Anal. Calcd for C₄₄H₆₆O₄Fe (714.84) : C, 73.93; H, 9.31. Found: C, 73.90; H, 9.30.

Compounds 1a-c and 2a-c: A solution of the corresponding acid (30 mmol) and stilbazole (30 mmol) in THF (4 mL) was stirred at room temperature for 30 min. The solvent was then slowly evaporated under vacuum and the residue dried for 24h under vacuum. Anal. Calcd for C₅₅H₇₃FeNO₅ (884.03) (**1a**): C, 74.73; H, 8.32; N, 1.58. Found: C, 74.75; H, 8.44; N, 1.63. Anal. Calcd for C₅₉H₈₁FeNO₅ (940.14) (**1b**): C, 75.38; H, 8.68; N, 1.49. Found: C, 75.16; H, 8.72; N, 1.46. Anal. Calcd for C₆₃H₈₉FeNO₅ (996.25) (**1c**): C, 75.95; H, 9.00; N, 1.41. Found: C, 76.10; H, 8.89; N, 1.49. Anal. Calcd for C₅₉H₈₁FeNO₅ (940.14) (**2a**): C, 75.38; H, 8.68; N, 1.49. Found: C, 75.31; H, 8.77; N, 1.56. Anal. Calcd for C₆₃H₈₉FeNO₅ (996.25) (**2b**): C, 75.95; H, 9.00; N, 1.41. Found: C, 75.80; H, 8.83; N, 1.46. Anal. Calcd for C₆₇H₉₇FeNO₅ (1052.35) (**2c**): C, 76.47; H, 9.29; N, 1.33. Found: C, 76.50; H, 9.21; N, 1.44.