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Synthesis and thermal properties of mesomorphic 1,1′-bis[ω-(4′-cyano-4-biphenyloxy)alkyl] ferrocenes

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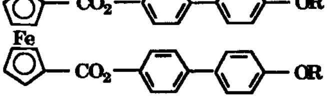
A new series of 1,1′-disubstituted ferrocene compounds of the type $[(\eta^5\text{-}C_5H_4(CH_2)_nOC_6H_4C_6H_4CN]_2Fe$ (**3a–d**, $n = 5, 6, 8, 11$) incorporating a variable length alkyloxy cyanobiphenyl unit has been prepared and their mesomorphic properties have been investigated. Compounds **3b**, **c** and **d** exhibit a thermotropic smectic C phase and **3c** also exhibits a monotropic smectic A phase over a fairly wide range near ambient temperature.

1. Introduction

Research directed towards the synthesis and study of mesomorphic properties of metallo-mesogens has gained tremendous impetus in recent years due to their novel thermal, optical and magnetic properties. Metallo-mesogens of nearly all transition metals have been reported [1–8] and are the subject of a recent review [9]. Whereas much attention has been focused on the study of tetracoordinated square planar complexes of Cu, Pd, Pt, Ir etc., we have concentrated our efforts to incorporate ferrocene as the mesogenic core unit [10–12]. The 1,1′-disubstituted ferrocenyl compounds offer unique structural features for potential twin liquid-crystalline behaviour by connecting the two mesogenic units through the sandwich-shaped ferrocene moiety.

Our initial efforts have demonstrated that 1,1′-disubstituted ferrocene diesters of the type **1** [10] and **2** [12] exhibit liquid-crystalline phases. X-ray diffraction studies in the crystalline form as well as liquid-crystalline state of diester **1** confirmed the S-shaped molecular geometry in both phases [11]. Other examples of the mesomorphic behaviour of monomeric [13] and polymeric [14] 1,1′-disubstituted ferrocenyl



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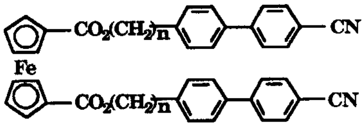

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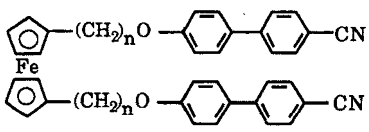
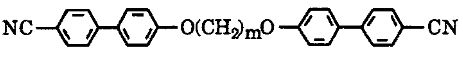


3 a-d



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compounds have been reported recently. In an effort to further elucidate the structure–property relationships of the ferrocene-containing mesogenic compounds, we report herein the synthesis, characterization and thermal properties of a new series of ferrocenyl compounds of the type **3**.

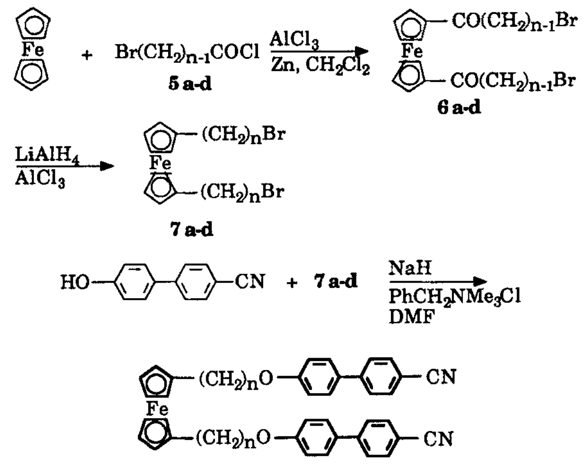
The thermal properties of the ferrocene diesters **2**, which incorporate the cyanobiphenyl unit, were quite surprising and unexpected [12]. The fact that one of the alkyloxy cyanobiphenyl-containing ferrocene diesters did exhibit a thermotropic smectic phase transition from one of its crystalline forms was quite promising [12]. In order for cyanobiphenyl-containing ferrocene compounds to possess the intermolecular interactions favourable for the formation of a liquid-crystalline phase, a further fine tuning of the structure was deemed necessary. The removal of the ester linkage and the introduction of an alkyl chain directly linked to the ferrocenyl unit was the focus of the next target molecules. The replacement of the rigid ester linkage with a flexible alkyl chain directly attached to the ferrocenyl unit was also thought to be better suited to bring the transition temperatures closer to ambient. Compounds **3a–d** also represent the ferrocene analogues of the known organic twin liquid-crystalline compounds **4a–l** [15] and a comparison of the thermal properties of these two series of compounds could provide important information regarding the structure–property relationships of ferrocene-containing liquid-crystalline compounds. Thus efforts were directed towards the synthesis of dialkyl ferrocenyl compounds **3a–d**.

2. Results

2.1. *Synthesis of ferrocene diethers 3a–d*

Compounds **3a–d** were prepared by a three step sequence involving diacylation of ferrocene, followed by complete reduction of the carbonyl group, and subsequent etherification with 4-hydroxy-4′-cyanobiphenyl as shown in the scheme. Each step required a unique synthetic protocol. The diacylation of ferrocene with ω-bromo aliphatic carboxylic acid chlorides and aluminium chloride was initially marred by extensive oxidation of ferrocene, either by the $AlCl_3$ or the acid chloride itself. This is a typical problem encountered whenever strong electrophiles are added to ferrocene because of its ease of oxidation [16]. This recurring problem was overcome by carrying out the reaction in presence of a large excess of granular zinc (20 mol equiv.). The use of zinc to circumvent the oxidation of ferrocene may thus be useful in other similar electrophilic substitutions of ferrocene, where the electrophile may also act as an oxidizing agent. Thus the acylation of ferrocene was affected by stirring (90 h) a mixture of ω-bromo carboxylic acid chloride, aluminium chloride and ferrocene in dichloromethane at room temperature in the presence of zinc. Pure mono and diacylated ferrocene were isolated by flash chromatography. Typically, about 50 per cent of diacylated and about 50 per cent of monoacylated product were obtained. The diacylated products **6a–d** were obtained as orange to red crystalline solids or oils.

Numerous methods for carbonyl to methylene reduction are known and a few have been applied to the reduction of acylferrocenes [17–20]. However, reduction of **6a–d** required a careful choice of reducing agent to prevent potential reductive debromination. Milder methods using sodium borohydride in the presence of trifluoroacetic acid [21], and triethylsilane in the presence of trifluoroacetic acid [22] or trifluoromethane sulfonic acid [23] were attempted on the bis(ω-bromoalkanoyl)-1,1′-ferrocene compounds **6a–d**. The $NaBH_4/CF_3CO_2H$ method gave an uncharacterizable dark red material which was neither the unreacted starting material nor the desired reduction



3 a, n=5; **3 b**, n=6; **3 c**, n=8; **3 d**, n=11

Synthesis of ferrocenyl diethers **3a–d**.

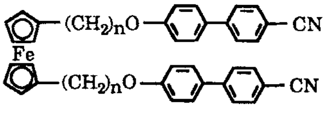
product. Use of triethylsilane resulted in the complete recovery of starting material after 48 h. The complete reduction of the carbonyl group was eventually achieved in quantitative yields using $LiAlH_4/AlCl_3$ as a reducing agent [24]. In a typical reduction, solutions of aluminium chloride and lithium aluminium hydride in diethyl ether were pre-mixed at 0°C to generate the mixed hydride. To this was added a solution of bis(ω-bromoalkanoyl)-1,1′-ferrocene compounds **6a–d** and aluminium chloride in diethyl ether. After stirring at room temperature for 1 h, the reaction was quenched by cautious dropwise addition of ice water. Pure **7a–d** were isolated by flash chromatography. No debromination product was observed.

The commonly used procedures for the etherification of 4-hydroxy-4′-cyanobiphenyls involve refluxing an ethanolic solution of the alkyl halide and the 4′-cyanobiphenyl-4-ol in the presence of a weak base, for example, potassium carbonate, for more than 36 h [25]. Problems regarding the solubility of 1,1′-bis(ω-bromoalkyl) ferrocene compounds **7a–d** in ethanol were recognized and hence this procedure was totally avoided. A new procedure was devised in which the etherification was carried out under non-aqueous conditions using DMF/NaH with catalytic amounts of $PhCH_2NMe_3^+Cl^-$. Thus 4-hydroxy-4′-cyanobiphenyl dissolved in a miniumum amount of DMF was treated with NaH. A small pinch of $PhCH_2NMe_3^+Cl^-$ was then added followed by the addition of **7** dissolved in a minimum amount of DMF. The reaction was quenched after 6 h by dropwise addition of water; the air dried solid precipitate was then purified by flash chromatography to obtain **3a–d** as bright yellow crystalline solids (yield 80–90 per cent). The compounds were further purified by another chromatographic treatment before carrying out thermal analysis. Because of limited availability of the starting bromoacids **5**, only compounds with $n = 5, 6, 8$ and 11 were studied.

2.2. *Thermal properties of ferrocenyl ethers 3a–d*

The thermal properties of ferrocene diethers **3a–d** were studied under a polarizing microscope. Whenever liquid-crystalline phases were observed, the phases were identified by comparing the patterns with those of previously observed phases [10] or the ones available in two excellent monographs [26, 27]. Compound **3a** exhibited

Melting Properties of ferrocenyl diethers **3a–d**.



3 a-d

Compound	n	Transition temperatures/ °C	$\Delta T_S = T_{SI} - T_{CS}$/ °C
3a	5	C 155 I	—
		I 138 C	—
3b	6	C 109·5 S_C 118·2 I	8·7
		I 67 S_C ~30 C	37
3c	8	C 102·5 S_C 108·5 I	6·0
		I 71 S_A ~33 C	38
3d	11	C 104·5 S_C 109·3 I	4·8
		I 85 S_C ~81 C	4·0

normal melting behaviour with a melting point of 155°C, considerably higher than that of the other homologues. During the cooling cycle, the isotropic melt supercooled somewhat, forming the crystalline solid at 138°C.

Compound **3b** exhibited a solid to liquid-crystalline phase transition at 109·5°C. Upon further heating, a transition from liquid crystal to isotropic was observed at 118·2°C. Closer examination of the liquid-crystalline phase formed by **3b** indicated that it was a smectic C phase as demonstrated by the typical schlieren texture. Upon cooling, the isotropic melt again supercooled and reformed the same smectic phase at 67°C. Once formed, this liquid-crystalline phase supercooled considerably. A small portion of the liquid-crystalline phase started to crystallize at 45°C; complete crystallization occurred at about 30°C.

Compound **3c** displayed a crystal to smectic C transition at 102·5°C and changed to isotropic at 108·5°C. When the isotropic melt was cooled, a monotropic smectic A phase showing the typical focal conic fan texture was formed at 71°C. The smectic A phase once formed supercooled considerably, crystallizing to a solid only at about 33°C.

When observed under the polarizing microscope during the heating cycle, compound **3d** exhibited a crystal to smectic C phase transition at 104·5°C and smectic C to isotropic at 109·3°C. During the cooling cycle, the same smectic C phase was reformed at about 85°C but it was found to be quite unstable as rapid crystallization of this phase occurred at about 83°C. In fact, the liquid-crystalline phase could only be observed when the cooling rate was rapid (20°C min^{-1}). The table summarizes the transition temperatures of the compounds **3a–d**.

3. Discussion

In this series of 1,1′-disubstituted ferrocenyl compounds three of the four compounds exhibit a thermotropic smectic C phase. Although the number of compounds studied is not large enough to show the typical odd-even effect in the transition temperatures, the characteristic decrease in clearing temperature with increasing number of methylene units in the flexible core is evident. It is to be noted that the clearing temperatures of these dialkyl-substituted ferrocenyl compounds are slightly higher than those of analogous ferrocenyl diesters reported earlier [12]. The removal of the fairly rigid diester linkage does not alter the clearing temperatures significantly. The thermotropic smectic C phases formed by **3b, c** and **d** are stable and in the case of **3b** and **c**, the liquid-crystalline phases reformed during the cooling cycle supercool to the extent that they exhibit a wide monotropic range compared to the previously prepared mesogenic ferrocenyl compounds.

Typically, it has been found that liquid-crystalline compounds have a rigid core which serves as the mesogenic unit and flexible alkyl chain(s) at the terminal end(s) [28]. This feature has been considered to be of prime importance in the design and synthesis of new liquid-crystalline compounds. The observation of thermotropic liquid-crystalline behaviour by main chain polymers in which rigid groups and flexible cores alternate along the main chain of the polymer [29, 30] has prompted attention towards the synthesis of new liquid-crystalline materials with a flexible core linking two rigid mesogenic groups [31]. These are the so-called twin liquid crystals [30]. A number of organic twin liquid-crystalline compounds have been reported [15, 31–33]. The ferrocenyl compounds **3a–d** represent the first known ferrocene-containing twin liquid-crystalline compounds with a stable thermotropic liquid crystalline phase. Compared with analogous organic twin liquid-crystalline α,ω-bis(4-cyanobiphenyl-4′-oxy)alkanes **4** having $m=2n$ [15], the ferrocenyl twin liquid-crystalline compounds **3** have lower clearing temperatures and smaller mesomorphic ranges. This is most likely due to the ‘kinked’ structure with some rotational freedom introduced by the ferrocene unit. Thus the comparison does not support a recent suggestion that the ferrocene unit enhances the mesogenic properties of liquid-crystalline compounds [13].

The ferrocene diethers incorporating the alkyloxy cyanobiphenyl unit represent the first series of stable thermotropic twin liquid crystals with the ferrocenyl unit in the core of the molecule. All the disubstituted ferrocenyl compounds reported thus far have smectic mesophases. This suggests that an interdigitated layer packing arrangement having strong intermolecular interactions (dipolar, π–π or van der Waals type) in the S-conformation of ferrocenyl compounds may be favoured. The stable thermotropic liquid-crystalline phases exhibited by the present series of ferrocenyl compounds suggest that a careful choice of mesogenic group, terminal group and flexible chain can overcome the undesirable ‘kinking’ effect of the ferrocene unit on the otherwise linear molecular geometry. Dating from the first ferrocenyl liquid crystal [34] to a recent example of liquid crystals incorporating a butadiene iron tricarbonyl unit [35], this strategy has been used by investigators in the synthesis of organometallic liquid crystals. Systematic studies which consider how much deviation from core linearity can be tolerated before loss of liquid-crystalline behaviour for purely organic compounds have also been reported recently [36]. The results indicate that decreasing core angle (linear = 180°) certainly destabilizes the mesophase but liquid-crystalline properties are retained up to a core angle of 148°. Studies of this type certainly enhance our understanding of the structural factors contributing to the formation of liquid crystals.

4. Experimental

High resolution ^1H and ^{13}C NMR spectra were obtained at 300 MHz and 75·4 MHz respectively on a Varian XL-300 spectrometer equipped with a VXR-4000 data station. Generally chloroform-d was used as a solvent for NMR spectra unless otherwise specified. IR spectra were recorded either as KBr pellets or as solutions in chloromethane on a Perkin–Elmer 1420 Ratio-recording IR spectrophotometer.

Elemental analysis for compounds **3a–d** were carried out by Midwest Microlabs, Ltd. Melting points are uncorrected. The polarizing microscope studies were performed using an Olympus BH-2 polarizing microscope equipped with a Linkam TH600 heating stage and PR600 temperature programmer. Samples were typically made by melting a small quantity of the material between two thin glass microscope cover slips so as to obtain a uniform coating. Samples were heated and cooled at 5°C min^{-1}. Photographs were taken using an Olympus OM-2S camera using either Kodak 1000 ASA 35 mm film or Ektachrome 160 slide film. Glassware was oven dried at 130°C overnight followed by flame drying of the reaction apparatus. All reactions were carried out under a nitrogen atmosphere. Dichloromethane, chloroform, hexane, and pyridine were freshly distilled over calcium hydride just prior to use. Flash column chromatography was carried out with E. Merck silica gel (230–400 mesh) under nitrogen pressure (10–15 psi). TLC aluminium plates with 0·2 mm silica gel 60 F_{254} coating were obtained from EM Science. 4-Hydroxy-4′-cyanobiphenyl (B.D.H. Chemicals), ω-halo-1-carboxylic acids, thionyl chloride (Aldrich Chemical Co.) and ferrocene (Pressure Chemical Co.) were used without further purification.

4.1. *ω-Bromo aliphatic-1,1′-diacyl ferrocenes* (***6a–d***)

In a typical acylation reaction, the ω-bromo aliphatic carboxylic acid (4·0 mmol) was refluxed with thionyl chloride (6 ml) for 6–8 h under a nitrogen atmosphere. The mixture was cooled; excess thionyl chloride was removed either under reduced pressure at room temperature or distilled off after adding 1,2-dichloroethane (5 ml) (in case of compounds with $n=5$ and 6, the acid chloride itself was purchased). The crude acid chloride was dissolved in CH_2Cl_2 (5 ml) and treated with anhydrous aluminium chloride (0·43 g; 3·2 mmol). After 10 min of stirring, zinc (3·3 g; 51·2 mmol) was added (reactions in absence of zinc resulted in the formation of little acylation products and complete oxidation of ferrocene). Ferrocene (0·30 g; 1·6 mmol) dissolved in CH_2Cl_2 (5 ml) was added dropwise over a period of 3 h. The reaction mixture was then stirred under nitrogen for 48 h after which the reaction was quenched by dropwise addition of water (25 ml). The organic products were extracted into CH_2Cl_2, dried over Na_2SO_4 and then dried *in vacuo*. The mono and diacyl ferrocenes were isolated by flash chromatography using CH_2Cl_2 and CH_2Cl_2: ethyl acetate (20 : 1) as orange-red solids (monoacyl about 30–60 per cent; diacyl about 30–60 per cent).

4.1.1. *1,1′-Bis(5-bromopentanoyl) ferrocene* (***6a***)

Yield 71 per cent; $R_f(CH_2Cl_2)$ 0·4; ^1H NMR ($CDCl_3$) δ4·78 (s, 4 H), 4·50 (s, 4 H), 3·48 (t, 4 H, $J=6·4$ Hz), 2·68 (t, 4 H, $J=7·2$ Hz), 1·97–1·84 (m, 8 H); MS 70 eV (relative intensity) 509·9 (14·6), 512·0 (29·1), 514·0 (14·0).

4.1.2. *1-(5-Bromopentanoyl) ferrocene*

Yield 25 per cent; $R_f(CH_2Cl_2)$ 0·65; ^1H NMR ($CDCl_3$) δ4·79 (s, 2 H), 4·51 (s, 2 H), 4·20 (s, 5 H), 3·47 (t, 2 H, $J=6·6$ Hz), 2·75 (t, 2 H, $J=6·9$ Hz), 1·97–1·89 (m, 4 H); MS 70 eV (relative intensity) 348 (54·3), 349·9 (50·3).

4.1.3. *1,1′-Bis(6-bromohexanoyl) ferrocene* (***6b***)

Yield 66 per cent; $R_f(CH_2Cl_2)$ 0·45; ^1H NMR ($CDCl_3$) δ4·76 (s, 4 H), 4·50 (s, 4 H), 3·44 (t, 4 H, $J=6·4$ Hz), 2·66 (t, 4 H, $J=7·2$ Hz), 1·97–1·81 (m, 12 H); MS 70 eV (relative intensity) 538 (51·6), 540 (97·8), 542 (46·3).

4.1.4. *1-(6-Bromohexanoyl) ferrocene*

Yield 25 per cent; $R_f(CH_2Cl_2)$ 0·66; ^1H NMR ($CDCl_3$) δ4·81 (s, 2 H), 4·50 (s, 2 H), 4·19 (s, 5 H), 3·45 (t, 2 H, $J=6·8$ Hz), 2·73 (t, 2 H, $J=7·3$ Hz), 1·93 (q, 2 H, $J=7·1$ Hz), 1·54 (m, 4 H); MS 70 eV (relative intensity) 362 (100), 364 (87·8).

4.1.5. *1,1′-Bis(8-bromooctanoyl) ferrocene* (**6c**)

Yield 40 per cent; $R_f(CH_2Cl_2)$ 0·4; ^1H NMR ($CDCl_3$) δ4·76 (s, 4 H), 4·49 (s, 4 H), 3·42 (t, 4 H, $J=6·8$ Hz), 2·65 (t, 4 H, $J=7·3$ Hz), 1·88 (q, 4 H, $J=7·1$ Hz), 1·72–1·39 (m, 16 H); MS 70 eV (relative intensity) 594·2 (26·5), 596·2 (47), 598·2 (23).

4.1.6. *1-(8-Bromooctanoyl) ferrocene*

Yield 56 per cent; $R_f(CH_2Cl_2)$ 0·66; ^1H NMR ($CDCl_3$) δ4·78 (t, 2 H, $J=1·9$ Hz), 4·50 (t, 2 H, $J=1·9$ Hz), 4·20 (s, 5 H), 3·42 (t, 2 H, $J=6·8$ Hz), 2·71 (t, 2 H, $J=7·4$ Hz), 1·88 (q, 2 H, $J=7·2$ Hz), 1·72 (q, 2 H, $J=7·3$ Hz), 1·50–1·38 (m, 6 H); MS 70 eV (relative intensity) 390 (66·6), 392 (64·8).

4.1.7. *1,1′-Bis(11-bromoundecanoyl) ferrocene* (**6d**)

Yield 38 per cent; $R_f(CH_2Cl_2)$ 0·46; ^1H NMR ($CDCl_3$) δ4·77 (s, 4 H), 4·48 (s, 4 H), 3·41 (t, 4 H, $J=6·9$ Hz), 2·64 (t, 4 H, $J=7·4$ Hz), 1·85 (q, 4 H, $J=7·3$ Hz), 1·68–1·28 (m, 28 H); MS 70 eV (relative intensity) 678·3 (6·4), 680·3 (12·3), 682·3 (5·6).

4.1.8. *1-(11-Bromoundecanoyl ferrocene*

Yield 54 per cent; $R_f(CH_2Cl_2)$ 0·7; ^1H NMR ($CDCl_3$) δ4·77 (s, 2 H), 4·49 (s, 2 H), 4·19 (s, 5 H), 3·40 (t, 2 H, $J=6·8$ Hz), 2·69 (t, 2 H, $J=7·4$ Hz), 1·85 (q, 2 H, $J=7·6$ Hz), 1·71–1·30 (m, 14 H); MS 70 eV (relative intensity) 432·1 (100), 434·1 (88·7).

4.2. *1,1′-Bis(ω-bromoalkyl) ferrocenes* (**7a–d**)

In a typical reduction procedure, a mixture of anhydrous aluminium chloride (2·1 mmol) in diethyl ether (5 ml) was slowly added to a stirred solution of lithium aluminium hydride (2·1 mmol) also in ether and maintained at 0°C. The evolution of hydrogen was observed. Similarly, a solution of anhydrous aluminium chloride (2·1 mmol) in ether (5 ml) was added to a solution of the diacyl ferrocene (1·0 mmol) in ether (5 ml). The $AlCl_3$-complexed diacyl ferrocene solution was then slowly added to the reducing mixture. An immediate colour change from purple to pale yellow was observed. The mixture was further stirred for half an hour after which the reaction was quenched by slow and cautious addition of ice water. The organic material was extracted in ether, washed twice with water, dried over sodium sulfate, and the solvent evaporated *in vacuo*. Pure **7a–d** were isolated as yellow oils by flash chromatography using 95 per cent pentane: 5 per cent ether as eluant.

4.2.1. *1,1′-Bis(5-bromopentyl) ferrocene* (**7a**)

Yield 92 per cent; ^1H NMR ($CDCl_3$) δ4·05 (s, 4 H), 4·04 (s, 4 H), 3·49 (t, 4 H, $J=6·8$ Hz), 2·41 (t, 4 H, $J=7·2$ Hz), 1·95 (q, 4 H, $J=6·9$ Hz), 1·59–1·34 (m, 8 H); MS 70 eV (relative intensity) 482 (53·4), 484 (100), 486 (43·9).

4.2.2. *1,1′-Bis(6-bromohexyl) ferrocene* (**7b**)

Yield 88 per cent; ^1H NMR ($CDCl_3$) δ3·99 (s, 4 H), 3·98 (s, 4 H), 3·42 (t, 4 H, $J=6·8$ Hz), 2·32 (t, 4 H, $J=7·5$ Hz), 1·87 (q, 4 H, $J=7·2$ Hz), 1·53–1·35 (m, 12 H);

^{13}C NMR (CDCl$_3$) δ91·0, 70·6, 69·7, 35·8, 34·6, 32·9, 31·1, 30·5, 29·8; MS 70 eV (relative intensity) 510 (48·9), 512 (100), 514 (46·4).

4.2.3. *1,1′-Bis(8-bromooctyl) ferrocene* (*7c*)

Yield 94 per cent; ^{1}H NMR (CDCl$_3$) δ3·96 (bm, 8 H), 3·41 (t, 4 H, J = 6·8 Hz), 2·30 (t, 4 H, J = 7·7 Hz), 1·85 (q, 4 H, J = 6·9 Hz), 1·45–1·31 (m, 20 H); MS 70 eV (relative intensity) 566·1 (51·1), 568·1 (96·4), 570·1 (45·2).

4.2.4. *1,1′-Bis(11-bromoundecyl) ferrocene* (*7d*)

Yield 88 per cent; ^{1}H NMR (CDCl$_3$) δ4·06 (bm, 8 H), 3·49 (t, 4 H, J = 6·9 Hz), 2·38 (t, 4 H, J = 7·7 Hz), 1·94 (q, 4 H, J = 7·3 Hz), 1·57–1·28 (m, 32 H); MS 70 eV (relative intensity).

4.3. *Synthesis of 1,1′-bis[ω-(4′-cyano-4-biphenyloxy)alkyl] ferrocenes* (*3a–d*)

In a typical etherification reaction, 4-hydroxy-4′-cyanobiphenyl (0·30 mmol) dissolved in dimethyl formamide (5 ml) was treated with sodium hydride (0·30 mmol; 50 per cent oil emulsion) to obtain a greenish-yellow fluorescent mixture. A pinch of benzyl trimethyl ammonium chloride was added after 5 min. The dibromoferrocene derivative (0·15 mmol) dissolved in a minimum amount of DMF was then added after another 5 min. The mixture was stirred for 4–6 h after which the product precipated. The reaction was quenched by slow, cautious addition of ice water. The precipitated product was filtered, washed first with water and then with pentane. The dried residue was further purified by flash chromatography using dichloromethane as eluant (80–95 per cent).

4.3.1. *1,1′-Bis[5-(4′-cyano-4-biphenyloxy)pentyl] ferrocene* (*3a*)

Yield 86 per cent; mp 155°C; R_f 0·50 (dichloromethane); ^{1}H NMR (CDCl$_3$) δ7·69 (d, 4 H, J = 8·3 Hz), 7·63 (d, 4 H, J = 8·5 Hz), 7·52 (d, 4 H, J = 8·6 Hz), 6·99 (d, 4 H, J = 8·6 Hz), 4·05–4·0 (m, 12 H), 2·31 (bs, 4 H), 1·82 (t, 4 H, J = 6·4 Hz), 1·57–1·52 (m, 8 H); ^{13}C NMR (CDCl$_3$) δ159·7, 145·2, 132·5, 131·2, 128·2, 126·9, 119·0, 115·0, 110·0, 89·1, 68·8, 68·0, 67·9, 31·0, 29·3, 29·1, 25·9; IR (KBr pellet), 3100–3060, 2950, 2890, 2220, 1600, 1495, 1250 cm^{-1}; HRMS m/e calculated for C$_{46}$H$_{44}$N$_2$O$_2$Fe: 712·2752, found 712·2766.

4.3.2. *1,1′-Bis[6-(4′-cyano-4-biphenyloxy)hexyl] ferrocene* (*3b*)

Yield 90 per cent; mp 118·2°C; R_f 0·50 (dichloromethane); ^{1}H NMR (CDCl$_3$) δ7·69 (d, 4 H, J = 8·5 Hz), 7·64 (d, 4 H, J = 8·5 Hz), 7·53 (d, 4 H, J = 8·6 Hz), 6·99 (d, 4 H, J = 8·7 Hz), 4·03–3·99 (m, 12 H), 2·32 (t, 4 H, J = 7·3 Hz), 1·82 (q, 4 H, J = 7·1 Hz), 1·51–1·38 (m, 12 H); ^{13}C NMR (CDCl$_3$) δ159·8, 145·2, 132·5, 131·3, 128·3, 127·0, 119·1, 115·1, 110·0, 89·2, 68·7, 68·1, 67·8, 31·2, 29·4, 29·3, 29·2, 25·9; IR (KBr pellet), 3100–3050, 2940, 2860, 2230, 1605, 1495, 1250 cm^{-1}; HRMS m/e calculated for C$_{48}$H$_{48}$N$_2$O$_2$Fe: 740·3065, found 740·3081; Elemental Analysis: calculated (found) C 77·84 per cent (77·80 per cent), H 6·49 per cent (6·74 per cent), N 3·78 per cent (3·74 per cent).

4.3.3. *1,1′-Bis[8-(4′-cyano-4-biphenyloxy)octyl] ferrocene* (*3c*)

Yield 85 per cent; mp 108·5°C; R_f 0·54 (dichloromethane); ^{1}H NMR (CDCl$_3$) δ7·69 (d, 4 H, J = 8·3 Hz), 7·63 (d, 4 H, J = 8·4 Hz), 7·52 (d, 4 H, J = 8·3 Hz), 6·99 (d, 4 H, J = 8·4 Hz), 4·19 (bs, 8 H), 4·0 (t, 4 H, J = 6·4 Hz), 2·15 (bs, 4 H), 1·78 (t, 4 H, J = 7·1 Hz), 1·61–1·24 (m, 20 H); ^{13}C NMR (CDCl$_3$) δ159·6, 145·0, 132·4, 131·0, 128·1, 126·9, 119·0, 114·9, 109·8, 89·4, 68·7, 68·0, 67·7, 31·1, 29·4, 29·3, 29·2, 29·1, 25·9; IR (KBr pellet), 3100–3040, 2930, 2860, 2230, 1605, 1495, 1250 cm^{-1}; HRMS *m/e* calculated for $C_{52}H_{56}N_2O_2Fe$: 796·3691, found 796·3611; Elemental Analysis: calculated (found) C 78·39 per cent (77·72 per cent), H 7·04 per cent (7·18 per cent), N 3·52 per cent (3·42 per cent).

4.3.4. *1,1'-Bis[11-(4'-cyano-4-biphenyloxy)undecyl] ferrocene* (*3d*)

Yield 88 per cent; mp 109·3°C; R_f 0·54 (dichloromethane); ^{1}H NMR (CDCl$_3$) δ7·68 (d, 4 H, $J = 8·3$ Hz), 7·63 (d, 4 H, $J = 8·6$ Hz), 7·52 (d, 4 H, $J = 8·5$ Hz), 6·99 (d, 4 H, $J = 8·5$ Hz), 4·01–3·97 (m, 12 H), 2·12 (bs, 4 H), 1·80 (t, 4 H, $J = 7·1$ Hz), 1·60–1·30 (m, 32 H); ^{13}C NMR (CDCl$_3$) δ159·7, 145·2, 132·5, 131·1, 128·2, 127·0, 119·0, 115·0, 109·9, 89·7, 68·8, 68·1, 67·8, 31·2, 29·5, 29·3, 29·2, 26·0; IR (KBr pellet), 3080–3040, 2930, 2860, 2230, 1605, 1500, 1255 cm^{-1}; HRMS *m/e* calculated for $C_{58}H_{68}N_2O_2Fe$: 880·4630, found 880·4643; Elemental Analysis: calculated (found) C 79·09 per cent (79·01 per cent), H 7·73 per cent (8·00 per cent), N 3·18 per cent (3·23 per cent).

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