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Synthesis, Characterization, and Mesomorphic Properties of a Mixed [60]Fullerene−Ferrocene Liquid-Crystalline Dendrimer

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ABSTRACT: Addition reaction of the malonate-based second-generation ferrocene-containing liquid-crystalline dendrimer **16** to [60]fullerene led to the title compound **1**. Molecule **1** showed good solubility in common organic solvents and good thermal stability. Examination of its mesomorphic properties revealed the presence of an enantiotropic smectic A phase, which was identified by polarized optical microscopy from the observation of typical focal−conic and homeotropic textures. The dendritic addend **16** exhibited similar properties as those of the fullerene-based dendrimer. The results described in this report open the way to the elaboration of fullerene-containing liquid-crystalline macromolecules.

Introduction

The search for new mesomorphic materials led us to develop ferrocene-containing thermotropic liquid-crystalline dendrimers,[1] ferrocene-containing thermotropic side-chain liquid-crystalline polymers,[2,3] and [60]fullerene-containing thermotropic liquid crystals.[4] Owing to the presence of either the ferrocene[5] or [60]-fullerene[6] (C_{60}) unit in their structure, such systems represent valuable materials for developing novel molecular devices: for example, the redox activity of the ferrocene was used to prepare switchable liquid crystals.[7] The electrochemical and photophysical properties of C_{60} open the doors to novel investigations within liquid-crystalline organizations. Furthermore, to combine their redox characteristics, we prepared a mixed [60]fullerene (electron acceptor)−ferrocene (electron donor) liquid crystal.[8] The observation of photoinduced electron transfer from ferrocene to C_{60} in [60]fullerene−ferrocene dyads[9] (in solution and for non-mesomorphic compounds) strengthened the idea that such materials are potential candidates for the construction of optical devices.

The incorporation of C_{60} into a ferrocene-based liquid-crystalline dendrimer is of interest as such an architecture would combine the properties of the [60]-fullerene[6] and ferrocene[5] units with the remarkable features (well-defined structure, monodispersity, low viscosity)[10] and properties (encapsulation,[11] catalysis,[12] chiroptical activity[13]) of dendrimers. Furthermore, functionalization of dendrimers with various mesomorphic groups led to liquid-crystalline materials displaying a rich mesomorphism,[14] and modification of C_{60} with dendritic addends[15] has proved to be an elegant concept for the preparation of fullerene-based polymeric materials.

The above mesomorphic C_{60} materials[4,8] were obtained by addition reaction of a liquid-crystalline malonate derivative to C_{60} (leading to [6,6]-closed methanofullerene monoadducts[16]). This synthetic methodology provides the opportunity to elaborate the desired mixed [60]fullerene−ferrocene liquid-crystalline dendrimer: addition reaction of a malonate-containing liquid-crystalline ferrocene dendrimer to C_{60} is expected to furnish the targeted compound.

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We report, herein, the synthesis (via a convergent approach[17]), characterization, and mesomorphic properties of the mixed [60]fullerene−ferrocene liquid-crystalline dendrimer **1** (Chart 1) of second generation (and of its intermediates), which represents the first member of a new family of mesomorphic macromolecular materials.

Results and Discussion

Synthesis. The syntheses that were developed to prepare **1** (Chart 1) are described in Schemes 1−4.

*(a) Synthesis of the Ferrocene Derivative **2** (Scheme 1).* Treatment of ferrocene-1,1′-dicarboxylic acid chloride[19] (**3**) with hydroquinone monobenzyl ether gave, after purification, the acid **4** (conversion of the unreacted carboxylic acid chloride function into the carboxylic acid one is the result of hydrolysis occurring during the purification process which required column chromatography with silica gel), which was transformed with oxalyl chloride into the acid chloride **5**. Condensation of the latter with cholest-5-en-3β-yl 4-(10-hydroxydecyloxy)benzoate[4] gave **6**, which, after removal of the benzyl protecting group, furnished the desired ferrocene derivative **2**.

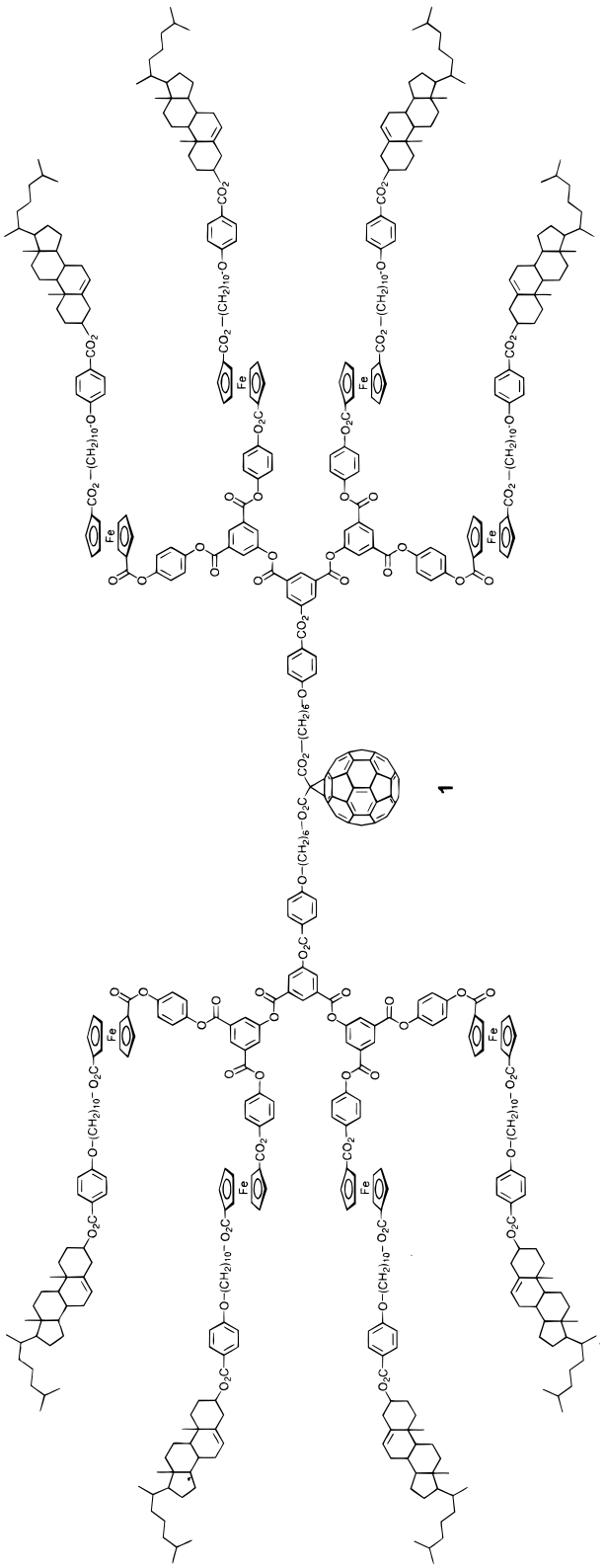
*(b) Synthesis of the Ramified Unit **7** (Scheme 2).* Esterification of 5-(benzyloxy)isophthalic acid[20] (**8**) with **2** gave the bis-ferrocene intermediate **9**, which was deprotected into the phenol derivative **10**. Condensation of the latter with 5-(benzyloxy)isophthaloyl dichloride (**11**) furnished the dendritic compound **12**, the deprotection of which led to **7**.

*(c) Synthesis of the Malonate Derivative **13** (Scheme 3).* Condensation of 4-[6-(hydroxyhexyl)oxy]benzoic acid[21] (**14**) with malonyl chloride furnished the diacid **15**, the treatment of which with oxalyl chloride led to the bis-acid chloride **13**.

*(d) Synthesis of the Malonate-Derived Dendrimer **16** and Mixed Fullerene−Ferrocene Dendrimer **1** (Scheme 4).* Condensation of the phenol derivative **7** with the diacid chloride **13** gave the dendrimer of second-generation **16**, the addition reaction of which to C_{60} furnished the targeted mixed [60]fullerene−ferrocene dendrimer **1**.

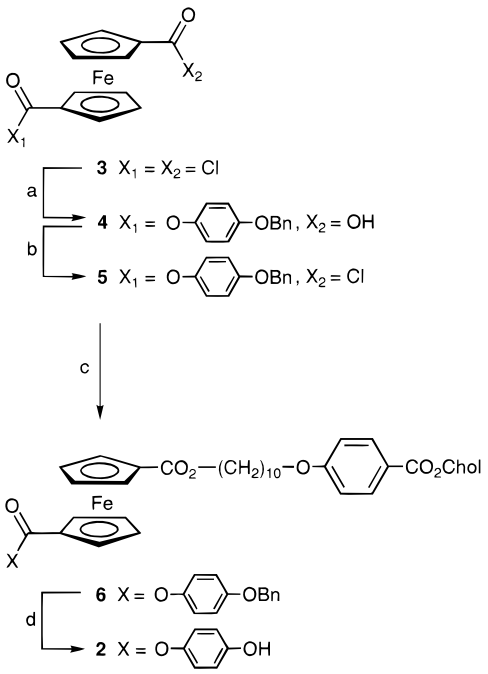
Compound **1** was purified by column chromatography and precipitation. The low yield (12%) obtained for the formation of **1** is probably the consequence of the

Chart 1



1

Scheme 1[a]



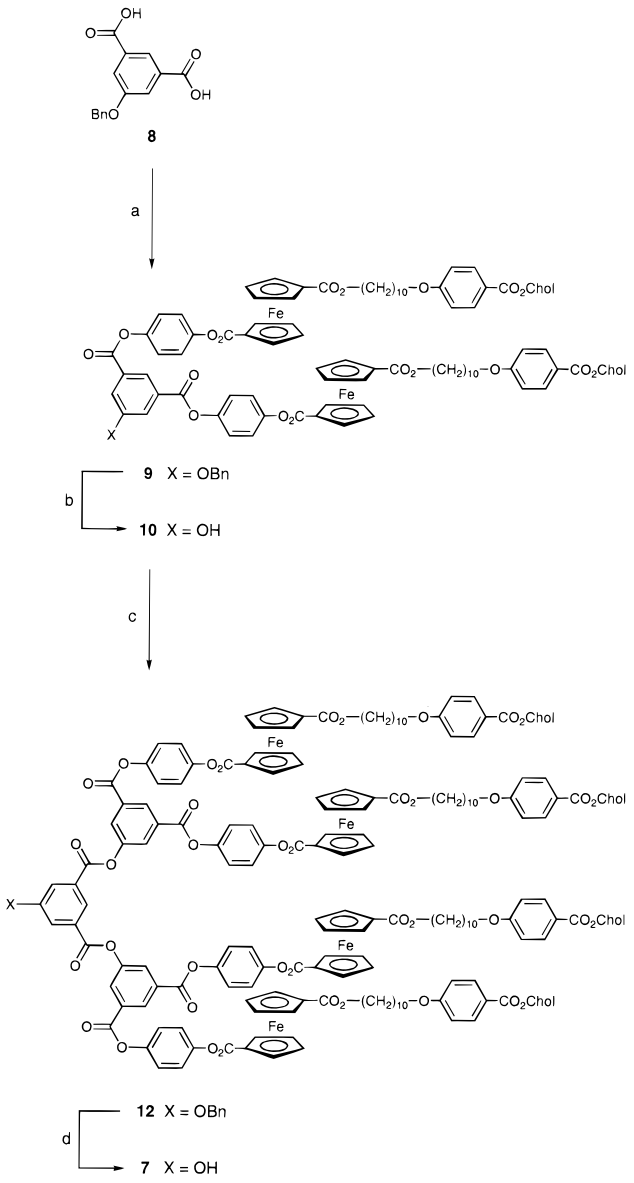
[a] Key: (a) hydroquinone monobenzyl ether, triethylamine, CH_2Cl_2, reflux, 67%; (b) oxalyl chloride, pyridine, CH_2Cl_2, reflux, 81%; (c) cholest-5-en-3β-yl 4-(10-hydroxydecyloxy)benzoate,[4] triethylamine, CH_2Cl_2, reflux, 90%; (d) H_2, Pd/C, CH_2Cl_2/EtOH, room temperature, 87%. Chol: see Chart 2.[18]

difficulty for the two constituents (C_{60} and **16**) to interact because of the steric hindrance caused by the dendritic structure of **16** and the purification process which required several purifications by column chromatography (35−40% yields were obtained from less bulky malonates[4,8]). Compounds **1** and **16** showed similar ^{1}H NMR spectra (see Experimental Section); as expected, **16** gave an additional signal (3.39 ppm) arising from the malonate protons ($RO_2C-CH_2-CO_2R$). The UV−vis spectrum of **1** (see Experimental Section) is in agreement with the [6,6]-closed methanofullerene structure.[22] Dendrimer **1** retained the solubility characteristics of the precursor **16** (and of the ferrocene-containing liquid-crystalline dendrimer we previously reported[1]) and was found to be soluble in common organic solvents, such as toluene, chloroform, and dichloromethane.

Liquid-Crystalline Properties. The mesomorphic and thermal properties of the mixed [60]fullerene−ferrocene dendrimer **1**, malonate based-dendrimer **16**, and intermediates **6, 2, 9**, and **12** were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The data are reported in Table 1.

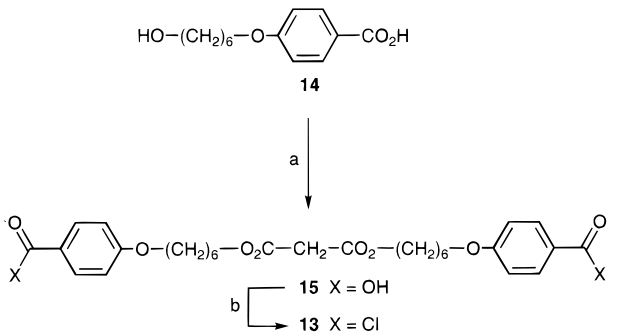
All the investigated compounds showed enantiotropic smectic A phases. An additional enantiotropic chiral nematic (cholesteric) phase was observed for **6**. The mesophases were identified by POM from the observation of typical textures: the smectic A phase gave a focal−conic texture and homeotropic areas; a plane texture was observed for the chiral nematic phase. For the compounds containing either four (**12**) or eight (**16** and **1**) cholesterol units, the focal−conic texture developed only when the samples were slowly cooled (0.1−0.2 °C min^{-1}) from the isotropic melt. This result was attributed to a higher viscosity resulting from enhanced interactions between the cholesterol frameworks com-

Scheme 2[a]



[a] Key: (a) **2**, *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine, THF/CH_2Cl_2, 0 °C and then room temperature, 66%; (b) H_2, Pd/C, CH_2Cl_2/EtOH, room temperature, 77%; (c) 5-(benzyloxy)isophthaloyl dichloride (**11**), triethylamine, CH_2Cl_2, reflux, 87%; (d) H_2, Pd/C, CH_2Cl_2/EtOH, room temperature, 78%. Chol: see Chart 2[18]

Scheme 3[a]



[a] Key: (a) malonyl chloride, triethylamine, THF, reflux, 50%; (b) thionyl chloride, DMF, CH_2Cl_2, reflux, 98%.

pared to the structures containing either one (**6** and **2**) or two (**9**) cholesterol units.

By DSC, a melting point was obtained only for **6** and **2** and during the first heating run exclusively. The ramified compounds **9** and **12** gave a glass transition (T_g). No T_g could be clearly detected for the dendrimers **1** and **16**: though a change of the baseline was observed in the 50−60 °C temperature range, the baseline deflection was too small to certify that this event corresponded to the T_g. The low enthalpy value associated with the melting point of **6** and **2** could be the consequence of a semicrystalline character of the samples that were precipitated during the purification process. During the cooling run, none of these materials presented an exothermic transition corresponding to crystallization. No decomposition was detected either by POM or by DSC: this result was expected in view of our recent investigations conducted on a ferrocene-containing liquid-crystalline dendrimer which revealed to be thermally stable up to ca. 250 °C.[1]

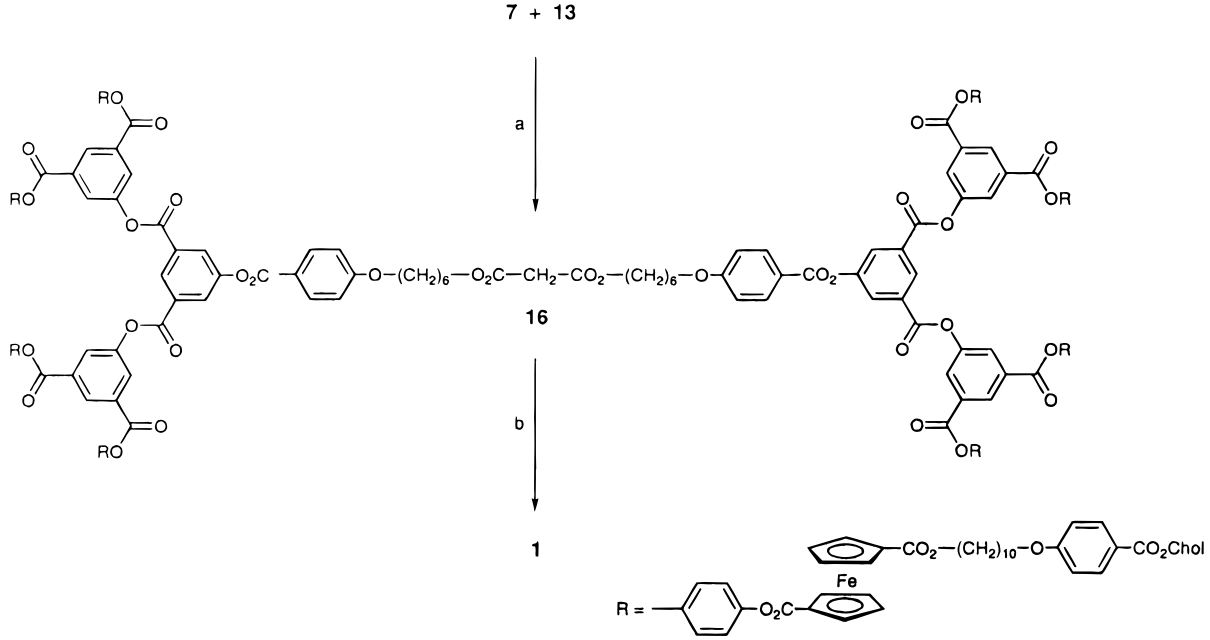
The mixed [60]fullerene−ferrocene dendrimer **1** and the addend **16** showed similar mesomorphic and thermal properties: both compounds gave rise to a smectic A phase, and a moderate difference was noticed between their clearing temperatures (157 °C for **1** and 169 °C for **16**). Taking into account their respective size, it is understandable that the C_{60} unit has only little influence on the thermal properties of the dendrimer **16**. As for the nature of the liquid-crystalline phase exhibited by **1** and **16**, this result is in agreement with literature data reported for other cholesterol-based dendrimers which also generated smectic A phases.[1,23] To understand the organization of fullerene-based liquid-crystalline dendrimers within the mesomorphic state, further compounds will be prepared and their liquid-crystalline properties investigated by X-ray diffraction.

Incorporation of C_{60} into a ferrocene-based liquid-crystalline dendrimer led to a material showing good solubility in common organic solvents, good thermal stability, and enantiotropic liquid-crystalline behavior. This collection of properties further confirms, in association with our initial investigations,[4,8] that functionalization of C_{60} with a mesomorphic malonate derivative is a valuable conceptual approach to design [60]fullerene-containing thermotropic liquid crystals. The fact that C_{60} does not modify markedly the thermal and liquid-crystalline properties of the mesomorphic addend **16** is an important result which shows that, owing to its size, the dendrimer can thwart the unfavorable interactions generated by the bulky, nonmesogenic, C_{60} unit. Therefore, the thermal and liquid-crystalline properties of such materials could be controlled and, most likely, tuned through synthetic engineering at the dendrimer level. The use of a dendrimer as a tool to control the characteristics and properties of modified [60]fullerenes was already successfully exploited: a carbohydrate-containing dendrimer was used to synthesize amphiphilic C_{60} derivatives in order to prepare organized molecular films by the Langmuir−Blodgett technique,[24] and a polycarboxylate-based dendrimer was employed to obtain a highly water-soluble C_{60} derivative.[25] Our studies open new opportunities in the design of [60]fullerene-based advanced materials: the elaboration of [60]fullerene-containing liquid-crystalline macromolecules.

Conclusions

The concept we developed to elaborate fullerene-containing thermotropic liquid crystals, i.e., addition

Scheme 4[a]



[a] Key: (a) triethylamine, room temperature, CH_2Cl_2, 55%; (b) [60]fullerene, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), I_2, room temperature, toluene, 12%. Chol: see Chart 2[18]

Table 1. Phase Transition Temperatures of the Investigated Compounds

compd	T_g[a] (°C)	transition[b]	T[c] (°C)	ΔH (J g^{-1})
6	*d*	Cr → S_A	77	13
		S_A → N*	119	0.1
		N* → I	130	0.6
2	26	Cr → S_A	112	6.4
		S_A → I	151	3.2
9	50	S_A → 1	130	3.2
12	54	S_A → I	160	4.8
16	*e*	S_A → I	169	5.2
1	*e*	S_A → I	157	3.5

[a] T_g = glass transition temperature. [b] Cr = crystal state, S_A = smectic A phase, N* = chiral nematic (cholesteric) phase, I = isotropic liquid. [c] The values correspond to the onset point determined during the second heating run except for the Cr → S_A transitions which were determined during the first heating run. [d] Not determined. [e] Not detected. A baseline change was noticed in the 50−60 °C temperature range; however, the baseline deflection was too small to certify that this even corresponded to the T_g.

reaction of a mesomorphic malonate derivative to C_{60},[4,8] was successfully extended to a dendritic architecture (this work). Of particular interest is the possibility to modify the structure of the dendrimer in order to engineer the liquid-crystalline properties of the fullerene-based dendrimer: ferroelectric behavior was recently reported for an optically active dendritic liquid-crystalline polymer.[26] The presence of the C_{60} and ferrocene units make such materials interesting for the development of switchable liquid-crystalline dendrimers.

Experimental Section

Materials. For the syntheses, CH_2Cl_2 (P_2O_5, under N_2), THF (sodium benzophenone, under N_2), and toluene (NaH, under N_2) were distilled prior to use. Dioxane (Fluka, puriss), pyridine (SDS, anhydrous analytical grade, ≥99.5%), triethylamine (Fluka, puriss p.a., ≥99.5%), and the other solvents were used as received. [60]Fullerene (99.5%) was purchased from Lancaster. Cholest-5-en-3β-yl 4-(10-hydroxydecyloxy)-benzoate[4] (see step c in Scheme 1), ferrocene-1,1′-dicarboxylic acid chloride (**3**),[19] 5-(benzyloxy)isophthalic acid (**8**),[20] and 4-[6-(hydroxyhexyl)oxy]benzoic acid (**14**)[21] were synthesized as described in the literature procedures.

Techniques. Column chromatography used silica gel 60 (0.060−0.200 mm, SDS). Transition temperatures (onset point, second heating run except for the Cr → S_A transitions which were determined during the first heating run) and enthalpies were determined with a differential scanning Mettler DSC 30 calorimeter connected to a Mettler TA 4000 processor, under N_2, at a rate of 10 °C min^{-1}. Mettler TA72.2/.5 Graphware was used for data treatment. Melting points (uncorrected) of intermediates **4** and **5** were determined on a Büchi 530 instrument. Optical studies were made using a Zeiss-Axioscop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N_2. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 200 spectrometer or a Bruker AMX 400 spectrometer, with the solvent as an internal standard. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrometer. Elemental analyses were done by Mikroelementaranalytisches Laboratorium ETH-Zurich.

Abbreviations. *N*,*N*′-dicyclohexylcarbodiimide = DCC; 4-pyrrolidinopyridine = 4-PPY; 1,8-diazabicyclo[5.4.0]undec-7-ene = DBU; triethylamine = Et_3N; column chromatography = CC.

Synthesis. 1-Carboxy-1′-[4-(benzyloxy)phenoxycarbonyl]ferrocene (4). A solution of hydroquinone monobenzyl ether (12.6 g, 62.9 mmol) in CH_2Cl_2 (500 mL) was added dropwise to a refluxing solution of ferrocene-1,1′-dicarboxylic acid chloride (**3**) (21.6 g, 69.5 mmol) and Et_3N (12.0 g, 119 mmol) in CH_2Cl_2 (350 mL). The mixture was stirred overnight under reflux, cooled to room temperature, and evaporated to dryness. Purification of the solid residue by CC (first CH_2Cl_2, then CH_2Cl_2/AcOEt 10:1, and finally CH_2Cl_2/AcOEt/CH_3OH 10:1:0.1) gave pure **4** (19.1 g, 67%). Mp = 156 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44−7.35 (m, 5 H, aromatic protons, benzyl), 7.15 (d, 2 H, aromatic protons), 7.01 (d, 2 H, aromatic protons), 5.07 (s, 2 H, CH_2Ph), 4.99 (t, 2 H, HCp), 4.94 (t, 2 H, HCp), 4.55 (t, 2 H, HCp), 4.53 (t, 2 H, HCp). ^{13}C NMR (50 MHz, $CDCl_3$): δ 176.39, 169.35, 156.49, 144.53, 136.92, 128.68, 128.08, 127.55, 122.64, 115.52, 73.63, 73.56, 72.45, 72.32, 72.25, 71.78, 70.49. Anal. Calcd for $C_{25}H_{20}O_5Fe$ (456.28): C, 65.81; H, 4.42. Found: C, 65.71; H, 4.33.

1-Chlorocarbonyl-1′-[4-(benzyloxy)phenoxycarbonyl]-ferrocene (5). A mixture of **4** (7.1 g, 15.6 mmol), oxalyl chloride (17.7 g, 139 mmol), and pyridine (0.49 g, 6.19 mmol)

in CH_2Cl_2 (250 mL) was stirred under reflux for 4 h, cooled to room temperature, and evaporated to dryness. The solid residue was extracted (Soxhlet) with hot ligroin (60−95 °C). Evaporation of the solvent gave **5** (6.0 g, 81%), which was used in the next step without further purification. Mp = 78−79 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44−7.33 (m, 5 H, aromatic protons, benzyl), 7.15 (d, 2 H, aromatic protons), 7.01 (d, 2 H, aromatic protons), 5.08 (s, 2 H, C*H*$_2$Ph, and t, 2 H, HCp), 5.02 (t, 2 H, HCp), 4.72 (t, 2 H, HCp), 4.64 (t, 2 H, HCp).

1-[10-{4-[(Cholest-5-en-3*β*-yloxy)carbonyl]phenoxy}-decyloxycarbonyl]-1′-[4-(benzyloxy)phenoxycarbonyl]-ferrocene (6). A solution of cholest-5-en-3*β*-yl 4-(10-hydroxydecyloxy)benzoate (5.7 g, 8.6 mmol) and Et_3N (1.27 g, 12.6 mmol) in CH_2Cl_2 (100 mL) was added to a solution of **5** (6.0 g, 12.6 mmol) in CH_2Cl_2 (200 mL). The mixture was heated under reflux for 48 h, cooled to room temperature, washed (water), dried ($MgSO_4$), and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2 then CH_2Cl_2/AcOEt 20:1) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **6** (8.49 g, 90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.98 (d, 2 H, aromatic protons), 7.43−7.33 (m, 5 H, aromatic protons, benzyl), 7.15 (d, 2 H, aromatic protons), 7.01 (d, 2 H, aromatic protons), 6.89 (d, 2 H, aromatic protons), 5.43 (d, 1 H, CH═C, cholesteryl), 5.08 (s, 2 H, C*H*$_2$Ph), 4.96 (t, 2 H, HCp), 4.91 (t, 2 H, HCp), 4.9−4.7 (broad m, 1 H, CHO, cholesteryl), 4.50 (t, 2 H, HCp), 4.49 (t, 2 H, HCp), 4.20 (t, 2 H, $CpCO_2CH_2$), 3.99 (t, 2 H, CH_2O), 2.45 (d, 2 H, cholesteryl), 2.05−0.69 (57 H, cholesteryl and $(CH_2)_8$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.34, 169.36, 165.77, 162.77, 156.39, 144.50, 139.76, 136.83, 131.47, 128.58, 127.99, 127.43, 122.98, 122.62, 122.54, 115.43, 113.93, 74.14, 73.44, 73.19, 72.76, 72.00, 71.87, 71.70, 70.41, 68.12, 64.69, 56.67, 56.12, 50.03, 42.30, 39.72, 39.49, 38.27, 37.04, 36.63, 36.16, 35.77, 31.91, 31.86, 29.45, 29.44, 29.30, 29.22, 29.08, 28.76, 28.21, 27.99, 27.92, 25.95, 24.27, 23.81, 22.80, 22.55, 21.03, 19.36, 18.70, 11.84. Anal. Calcd for $C_{69}H_{88}O_8Fe$ (1101.30): C, 75.25; H, 8.05. Found: C, 75.38; H, 7.92.

1-[10-{4-[(Cholest-5-en-3*β*-yloxy)carbonyl]phenoxy}-decyloxycarbonyl]-1′-[4-(hydroxyphenoxy)carbonyl]ferrocene (2). A mixture of **6** (3.50 g, 3.18 mmol), Pd (10%)/C (0.35 g), CH_2Cl_2 (150 mL), and EtOH (40 mL) was stirred at room temperature under 4 bar of H_2 for 6 h. The mixture was filtered (silica gel, CH_2Cl_2) and evaporated to dryness. Purification of the solid residue by precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **2** (2.80 g, 87%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2 H, aromatic protons), 7.04 (d, 2 H, aromatic protons), 6.87 (d, 2 H, aromatic protons), 6.81 (d, 2 H, aromatic protons), 5.67 (s, 1 H, OH), 5.39 (d, 1 H, CH═C, cholesteryl), 4.92 (t, 2 H, HCp), 4.88 (t, 2 H, HCp), 4.83−4.75 (broad m, 1 H, CHO, cholesteryl), 4.49 (t, 2 H, HCp), 4.48 (t, 2 H, HCp), 4.18 (t, 2 H, $CpCO_2CH_2$), 3.97 (t, 2 H, CH_2O), 2.43 (d, 2 H, cholesteryl), 2.03−0.67 (57 H, cholesteryl and $(CH_2)_8$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.68, 169.81, 166.02, 162.86, 153.65, 144.15, 139.80, 131.57, 123.00, 122.69, 116.07, 114.05, 74.33, 73.47, 73.29, 72.87, 72.12, 71.91, 71.83, 68.23, 64.88, 56.75, 56.18, 50.09, 42.37, 39.79, 39.57, 38.33, 37.09, 36.71, 36.24, 35.86, 31.95, 29.76, 29.49, 29.34, 29.29, 29.12, 28.82, 28.29, 28.07, 26.01, 24.36, 23.88, 22.88, 22.63, 21.10, 19.44, 18.77, 11.93. Anal. Calcd for $C_{62}H_{82}O_8Fe$ (1011.18): C, 73.65; H, 8.17. Found: C, 73.53; H, 8.18.

Compound 9. A mixture of **2** (2.76 g, 2.73 mmol), 5-(benzyloxy)isophthalic acid (**8**) (0.37 g, 1.36 mmol), DCC (0.64 g, 3.10 mmol), 4-PPY (50 mg, 0.34 mmol), THF (10 mL), and CH_2Cl_2 (80 mL) was stirred at 0 °C for 30 min and at room temperature for 2 h. The mixture was filtered and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/AcOEt 40:1 and then 20:1) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **9** (2.03 g, 66%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.64 (t, 1 H, aromatic proton), 8.07 (d, 2 H, aromatic protons), 7.97 (d, 4 H, aromatic protons), 7.47−7.37 (m, 5 H, aromatic protons, benzyl), 7.32 (s, 8 H, aromatic protons), 6.88 (d, 4 H, aromatic protons), 5.41 (d, 2 H, CH═C, cholesteryl), 5.23 (s, 2 H, C*H*$_2$Ph), 4.98 (t, 4 H, HCp), 4.92 (t, 4 H, HCp), 4.90−4.75 (broad m, 2 H, CHO, cholesteryl), 4.53 (t, 4 H, HCp), 4.51 (t, 4 H, HCp), 4.21 (t, 4 H, $CpCO_2CH_2$), 3.98 (t, 4 H, CH_2O), 2.44 (d, 4 H, cholesteryl), 2.03−0.69 (114 H, cholesteryl and $(CH_2)_8$). Anal. Calcd for $C_{139}H_{172}O_{19}Fe_2$ (2258.58): C, 73.92; H, 7.68. Found: C, 74.02; H, 7.72.

Compound 10. A mixture of **9** (2.03 g, 0.899 mmol), Pd (10%)/C (0.21 g), CH_2Cl_2 (90 mL), and EtOH (10 mL) was stirred at room temperature under 4 bar of H_2 for 4 h. The mixture was filtered (silica gel, CH_2Cl_2) and evaporated to dryness. Purification of the solid residue by precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **10** (1.51 g, 77%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.58 (t, 1 H, aromatic proton), 7.98 (d, 4 H, aromatic protons), 7.96 (d, 2 H, aromatic protons), 7.31 (s, 4 H, aromatic protons), 7.30 (s, 4 H, aromatic protons), 6.95 (s, 1 H, OH), 6.87 (d, 4 H, aromatic protons), 5.42 (d, 2 H, CH═C, cholesteryl), 4.97 (t, 4 H, HCp), 4.92 (t, 4 H, HCp), 4.90−4.75 (broad m, 2 H, CHO, cholesteryl), 4.54 (t, 4 H, HCp), 4.51 (t, 4 H, HCp), 4.22 (t, 4 H, $CpCO_2CH_2$), 3.98 (t, 4 H, CH_2O), 2.45 (d, 4 H, cholesteryl), 2.05−0.69 (114 H, cholesteryl and $(CH_2)_8$). Anal. Calcd for $C_{132}H_{166}O_{19}Fe_2$ (2168.45): C, 73.11; H, 7.72. Found: C, 73.00; H, 7.79.

5-(Benzyloxy)isophthaloyl Dichloride (11). A mixture of 5-(benzyloxy)isophthalic acid (**8**) (71 mg, 0.26 mmol), thionyl chloride (0.46 g, 3.9 mmol), and CH_2Cl_2 (40 mL) was stirred under reflux for 6 h and cooled to room temperature. Evaporation of the mixture to dryness gave **11** (78 mg, 97%), which was used in the next step without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.45 (t, 1 H, aromatic proton), 7.98 (d, 2 H, aromatic protons), 7.49−7.35 (m, 5 H, aromatic protons, benzyl), 5.20 (s, 2H, C*H*$_2$Ph). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.19, 159.34, 135.41, 135.07, 128.95, 128.77, 127.77, 126.24, 123.24, 71.14.

Compound 12. A solution of **10** (0.20 g, 0.092 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of **11** (14 mg, 0.045 mmol) and Et_3N (73 mg, 0.72 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred under reflux for 12 h, cooled to room temperature, and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/heptane/acetone 10:2.5:0.5) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **12** (0.18 g, 87%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.98 (t, 2 H, aromatic protons), 8.71 (t, 1 H, aromatic proton), 8.38 (d, 4 H, aromatic protons), 8.14 (d, 2 H, aromatic protons), 7.96 (d, 8 H, aromatic protons), 7.53−7.40 (m, 5 H, aromatic protons, benzyl), 7.34 (s, 16 H, aromatic protons), 6.88 (d, 8 H, aromatic protons), 5.41 (d, 4 H, CH═C, cholesteryl), 5.27 (s, 2 H, C*H*$_2$Ph), 4.98 (t, 8 H, HCp), 4.92 (t, 8 H, HCp), 4.90−4.75 (broad m, 4 H, CHO, cholesteryl), 4.53 (t, 8 H, HCp), 4.51 (t, 8 H, HCp), 4.21 (t, 8 H, $CpCO_2CH_2$), 3.98 (t, 8 H, CH_2O), 2.44 (d, 8 H, cholesteryl), 2.05−0.69 (228 H, cholesteryl and $(CH_2)_8$). Anal. Calcd for $C_{279}H_{340}O_{41}Fe_4$ (4573.13): C, 73.28; H, 7.49. Found: C, 73.32; H, 7.71.

Compound 7. A mixture of **12** (0.35 g, 0.077 mmol), Pd (10%)/C (72 mg), CH_2Cl_2 (40 mL), and EtOH (5 mL) was stirred at room temperature under 4 bar of H_2 for 4 h. The mixture was filtered (silica gel, CH_2Cl_2) and evaporated to dryness. Purification of the solid residue by precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **7** (0.27 g, 78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.96 (t, 2 H, aromatic protons), 8.62 (t, 1 H, aromatic proton), 8.34 (d, 4 H, aromatic protons), 8.05 (d, 2 H, aromatic protons), 7.97 (d, 8 H, aromatic protons), 7.34 (s, 16 H, aromatic protons), 6.86 (d, 8 H, aromatic protons), 5.42 (d, 4 H, CH═C, cholesteryl), 4.97 (t, 8 H, HCp), 4.92 (t, 8 H, HCp), 4.90−4.75 (broad m, 4 H, CHO, cholesteryl), 4.53 (t, 8 H, HCp), 4.51 (t, 8 H, HCp), 4.21 (t, 8 H, $CpCO_2CH_2$), 3.95 (t, 8 H, CH_2O), 2.45 (d, 8 H, cholesteryl), 2.03−0.68 (228 H, cholesteryl and $(CH_2)_8$). Anal. Calcd for $C_{272}H_{334}O_{41}Fe_4$ (4483.01): C, 72.88; H, 7.51. Found: C, 73.04; H, 7.24.

4,4′-[Malonyl bis(1,6-hexyldioxy)]dibenzoic Acid (15). A solution of Et_3N (1.70 g, 16.8 mmol) in THF (200 mL) was added dropwise to a solution of **14** (4.00 g, 16.8 mmol) and malonyl chloride (1.18 g, 8.37 mmol) in THF (200 mL). The mixture was stirred under reflux for 12 h, cooled to room temperature, poured onto a water/ice mixture, and filtered.

Purification of the precipitate by crystallization (EtOH) gave **15** (2.30 g, 50%). ^{1}H NMR (200 MHz, $CDCl_3$ + 1 drop of acetone-d_6): δ 7.98 (d, 4 H, aromatic protons), 6.86 (d, 4 H, aromatic protons), 4.15 (t, 4 H, CO_2CH_2), 3.97 (t, 4 H, CH_2-OPh), 3.36 (s, 2 H, $O_2CCH_2CO_2$), 1.79 (m, 4 H, CH_2CH_2OPh), 1.68 (m, 4 H, $CO_2CH_2CH_2$), 1.46 (2 m, 8 H, C$H_2CH_2CH_2CH_2$-OPh). Anal. Calcd for $C_{29}H_{36}O_{10}$ (544.60): C, 63.96; H, 6.66. Found: C, 63.82; H, 6.76.

Bis{6-[(4-chlorocarbonyl)phenoxy]hexyl} Malonate (13). A mixture of **15** (60.7 mg, 0.111 mmol), thionyl chloride (0.49 g, 4.12 mmol), DMF (50 nL, 6.5×10^{-4} mmol), and CH_2Cl_2 (10 mL) was stirred under reflux for 4 h. Evaporation of the solvent gave **13** (63.5 mg, 98%, oil), which was used in the next step without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.07 (d, 4 H, aromatic protons), 6.95 (d, 4 H, aromatic protons), 4.17 (t, 4 H, CO_2CH_2), 4.05 (t, 4 H, CH_2-OPh), 3.38 (s, 2 H, $O_2CCH_2CO_2$), 1.83 (m, 4 H, CH_2CH_2OPh), 1.70 (m, 4 H, $CO_2CH_2CH_2$), 1.48 (2 m, 8 H, C$H_2CH_2CH_2CH_2$-OPh).

Compound 16. A solution of **13** (5.81 mg, 0.010 mmol) in CH_2Cl_2 (0.9 mL) was added dropwise to a solution of **7** (91.0 mg, 0.020 mmol) and Et_3N (2 mg, 0.02 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 12 h and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2/heptane/acetone 10:2:0.5) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into CH_3OH) gave pure **16** (51.8 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (t, 2 H, aromatic protons), 8.97 (t, 4 H, aromatic protons), 8.41 (d, 4 H, aromatic protons), 8.39 (d, 8 H, aromatic protons), 8.19 (d, 4 H, aromatic protons), 7.96 (d, 16 H, aromatic protons), 7.33 (s, 32 H, aromatic protons), 7.00 (d, 4 H, aromatic protons), 6.87 (d, 16 H, aromatic protons), 5.40 (d, 8 H, CH=C, cholesteryl), 4.97 (t, 16 H, HCp), 4.92 (t, 16 H, HCp), 4.82−4.78 (broad m, 8 H, CHO, cholesteryl), 4.52 (t, 16 H, HCp), 4.50 (t, 16 H, HCp), 4.21 (t, 16 H, $CpCO_2CH_2$), 4.18 (t, 4 H, $H_2CO_2CCH_2CO_2CH_2$), 4.06 (t, 4 H, CH_2OPh), 3.97 (t, 16 H, CH_2OPh), 3.39 (s, 2 H, $O_2CCH_2CO_2$), 2.43 (d, 16 H, cholesteryl), 2.03−0.68 (472 H, cholesteryl, $(CH_2)_8$ and $(CH_2)_4$). Anal. Calcd for $C_{573}H_{700}O_{90}Fe_8$ (9 474.58): C, 72.64; H, 7.45. Found: C, 72.78; H, 7.43.

Compound 1. A solution of DBU (3.8 mg, 25×10^{-3} mmol) in toluene (0.1 mL) was added dropwise to a solution of [60]-fullerene (12 mg, 17×10^{-3} mmol), **16** (0.12 g, 13×10^{-3} mmol), and I_2 (3.3 mg, 13×10^{-3} mmol) in toluene (7 mL). The mixture was stirred at room temperature for 6 h and evaporated to dryness. Purification of the solid residue by CC (toluene/AcOEt 10:1 and then toluene/AcOEt/heptane 10:1.2:2) and then by precipitation (dissolution in toluene and precipitation by pouring the solution into CH_3OH) gave pure **1** (16 mg, 12%) as a brownish solid. Several purifications by CC were required to remove **16** from **1**. Under the applied conditions, C_{60} eluted first, followed by **1**, and then by **16**. UV−vis (λ_{max} in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 426 (4270), 458 (4140), 686 (212). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (t, 2 H, aromatic protons), 8.97 (t, 4 H, aromatic protons), 8.40 (d, 4 H, aromatic protons), 8.38 (d, 8 H, aromatic protons), 8.17 (d, 4 H, aromatic protons), 7.96 (d, 16 H, aromatic protons), 7.33 (s, 32 H, aromatic protons), 6.99 (d, 4 H, aromatic protons), 6.87 (d, 16 H, aromatic protons), 5.40 (d, 8 H, CH=C, cholesteryl), 4.97 (t, 16 H, HCp), 4.91 (t, 16 H, HCp), 4.82−4.77 (broad m, 8 H, CHO, cholesteryl), 4.54 (t, 4 H, $C_{60}CO_2CH_2$), 4.52 (t, 16 H, HCp), 4.50 (t, 16 H, HCp), 4.20 (t, 16 H, $CpCO_2CH_2$), 4.07 (t, 4 H, CH_2OPh), 3.97 (t, 16 H, CH_2OPh), 2.43 (d, 16 H, cholesteryl), 2.03−0.68 (472 H, cholesteryl, $(CH_2)_8$ and $(CH_2)_4$). Anal. Calcd for $C_{633}H_{698}O_{90}Fe_8$ (10 193.23): C, 74.59; H, 6.90. Found: C, 74.66; H, 7.08.

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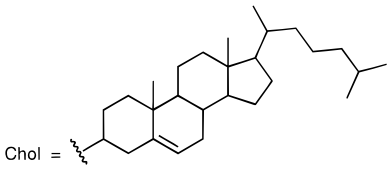
(18) **Chart 2**



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