

Dedicated to Professor Fred Wudl on the occasion of his 60th birthday

Abstract: Grafting of a ferrocene-containing liquid-crystalline malonate derivative to C60 led to the mixed fullerene–ferrocene material 1 which gave rise to a smectic A phase. Cholesterol was used as liquid-crystalline promoter. X-ray diffraction experiments and volumetric measurements indicated that 1 is organized in double layered structures. The corresponding supramolecular organization within the mesomorphic lamellar phase is characterized by a microsegregation of the different units (ferrocene, fullerene, and cholesterol) in distinct sublayers. In such a smectic A phase, C60 imposes the arrangement of the other molecular moieties. Photo-physical studies revealed that electron transfer occurs from the donor ferrocene to the electron accepting fullerene. The formation of a long-lived radical pair, with lifetimes of the order of several hundred nanoseconds, was confirmed by time-resolved spectrometry, especially in the near infrared region, in which the radical anion of the fullerene moiety displays its characteristic fingerprint absorption.

Keywords: electron transfer • ferrocene • fullerenes • liquid crystals • materials science

Introduction

Fullerene (C60) has attracted considerable attention in materials science.[1] The possibility to develop materials possessing the unique properties of C60 motivated these studies. In particular, C60 has been incorporated into polymers,[2] dendrimers,[3] sol–gel matrices[4] and nanospheres.[5] Much research has also been devoted to the synthesis and photophysical studies of systems in which C60 behaves as an energy/electron acceptor in the ground or excited state[6] either in covalently linked dyads[7] or as heterogeneous blends[8] for the fabrication of photovoltaic devices.[9] Recently, C60 was used to construct a single layer organic LED.[10]

The search for fullerene-based materials prompted us to investigate fullerene-containing thermotropic liquid crystals.[11–14] Our concept, the use of liquid-crystalline malonates in the Bingel reaction,[15] led to mesomorphic mono-[1[–13] and hexa-[14] adducts of C60. The mono-adducts were prepared from an organic-type malonate,[11] a ferrocene-containing malonate,[12] and a ferrocene-based dendritic malonate.[13] In these compounds, cholesterol was used as the liquid-crystalline promoter. The hexa-adduct[14] was prepared from a malonate containing cyanobiphenyl groups, the latter acting as mesogenic fragments. The C60 derivatives gave rise to smectic A phases, and showed good thermal stability and good solubility in common organic solvents. Besides our work, two reports described liquid-crystalline fullerenes exhibiting either calamitic[16] or cubic[17] phases.

The fullerene–ferrocene derivative 1 (Scheme 1) was designed to develop photoactive liquid crystal switches by combining two sets of data: firstly, electron transfer was used to generate liquid-crystalline ferrocenium derivatives from non-mesomorphic ferrocenes,[14] and, secondly, photoinduced electron transfer from ferrocene to C60 was shown to occur in fullerene–ferrocene dyads.[18] Therefore, photoinduced electron transfer in fullerene–ferrocene liquid crystals could be
used to control the liquid-crystalline properties because of the presence of either the ferrocene (light off) or ferrocenium (light on) species.

The development of switchable liquid crystals based on C60 and ferrocene is a difficult task since several parameters, ranging from structure and liquid-crystalline properties to photophysical behavior, are involved. The synthesis and study of various derivatives are required to understand their photophysical properties in connection with their liquid-crystalline behavior. Compound 1 represents the first member of this class of materials and can be considered as a prototype from which other derivatives will be constructed. A detailed investigation of its properties is expected to bring important insights for the design of further compounds.

We describe, herein, the synthesis, liquid-crystalline properties and supramolecular organization of 1 and of its intermediates, as well as the photoinduced electron transfer of 1 in organic solvents. The general synthetic strategy for 1 and its mesomorphic behavior have been reported elsewhere.[12]

**Results and Discussion**

**Synthesis:** The synthesis of 1 is shown in Scheme 1. O-Alkylation of phenol derivative 2 with 6-bromohexanol gave alcohol intermediate 3, which was esterified with malonyl chloride to furnish the malonate derivative 4. Addition of the latter to C60 gave the targeted compound 1. Compounds 5 (n = 8, 12, 14) were prepared as shown in Scheme 2 by O-alkylation of cholesteryl 4-hydroxybenzoate[20] (6) with the appropriate 1-bromoalkane; they were prepared to determine the molecular volume of the cholesterol moiety by volumetric methods.

**Liquid-crystalline properties:** The mesomorphic and thermal properties of 1–5 were investigated by polarized optical

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**Scheme 1.** a) 6-Bromohexanol, K2CO3, THF, 24 h, 36%. b) Malonyl chloride, triethylamine, CH2Cl2, 2 h, 77%. c) [60]Fullerene, diazabicyclo[5.4.0]undec-7-ene (DBU), iodine, toluene, 3 h, 34%.

**Scheme 2.** Different n-bromoalkanes, K2CO3, DMF/THF, 120°C.
microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The phase transition temperatures and enthalpies are reported in Table 1.

Compounds 1–4 gave smectic A phases. An additional chiral nematic phase (cholesteric phase) was observed for 3.

Table 1. Phase transition temperatures and enthalpy changes of compounds 1–5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition[a]</th>
<th>Temperature [°C]</th>
<th>ΔH [kJ mol⁻¹]</th>
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<tr>
<td>2</td>
<td>Cr – S₅[b]</td>
<td>112</td>
<td>6.5</td>
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<td></td>
<td>S₅ – I</td>
<td>151</td>
<td>3.1</td>
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<tr>
<td>3</td>
<td>Cr – S₅[b]</td>
<td>63</td>
<td>15.1</td>
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<tr>
<td></td>
<td>S₅ – N⁺</td>
<td>125</td>
<td>– h]</td>
</tr>
<tr>
<td></td>
<td>N⁺ – I</td>
<td>127</td>
<td>2.9[6]</td>
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<tr>
<td>4</td>
<td>Cr – S₅[b]</td>
<td>73</td>
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<td>S₅ – I</td>
<td>134</td>
<td>6.4</td>
</tr>
<tr>
<td>1</td>
<td>Cr – S₅[b]</td>
<td>66</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>S₅ – I</td>
<td>118</td>
<td>11.7</td>
</tr>
<tr>
<td>5 (α = 8)[b]</td>
<td>Cr – S₅</td>
<td>136</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>S₅ – N⁺[c]</td>
<td>173</td>
<td>–</td>
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<td></td>
<td>N⁺ – I</td>
<td>218</td>
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<td>5 (α = 12)</td>
<td>Cr – S₅</td>
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<tr>
<td></td>
<td>S₅ – N⁺</td>
<td>176</td>
<td>0.7</td>
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<tr>
<td></td>
<td>N⁺ – I</td>
<td>198</td>
<td>0.7</td>
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<tr>
<td>5 (α = 14)</td>
<td>Cr – S₅</td>
<td>115</td>
<td>28.1</td>
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<tr>
<td></td>
<td>S₅ – N⁺</td>
<td>175</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>N⁺ – I</td>
<td>189</td>
<td>1.1</td>
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</table>

[a] Cr = crystal, S₅ = smectic A phase, N⁺ = chiral nematic (cholesteric) phase, I = isotropic fluid. [b] Observed during the first heating run. [c] Peak overlap. The enthalpy value corresponds to the sum of both enthalpies. [d] A monotropic phase might form below the smectic A phase. This behavior was not investigated. [e] Observed by polarized optical microscopy.

The liquid-crystalline phases were identified by POM: the smectic A phases gave focal-conic and homeotropic textures, and the cholesteric phase gave the plane texture. Identification of the liquid-crystalline phase displayed by 1 was more difficult; because of higher viscosity than the fullerene-free compounds 2–4, small focal conics appeared only when the sample was cooled very slowly from the isotropic fluid.

By DSC, the melting points of 1–4 were detected during the first heating only. From the first cooling run, a glass transition temperature was recorded revealing a low tendency of 1–4 to recrystallize under the experimental conditions applied. The low enthalpy value associated with the melting process observed for 1–3 was an indication of a semicrystalline nature of the samples. The DSC traces of 1 are shown in Figure 1.

The nature of the smectic A phase of 1–4 was confirmed by XRD. Diffraction patterns typical of disordered smectic phases were registered. In the low-angle region, they consisted of two sharp diffraction peaks, the corresponding spacings of which are in a 1:2 ratio, and in the wide-angle region, of a diffuse signal. A representative diffractogram of 1 is shown in Figure 2.

The dependence of the d-layer spacing as a function of temperature was determined for 1–4 (Figure 3). Interestingly, d = f(T) did not follow the typical variation observed for the smectic A phase for which a decrease of the d-layer spacing is observed with increasing temperature. Here (Figure 3), the d-layer spacing either increased for compounds 2–4 or remained nearly constant as for 1 when the temperature was raised. For each compound, the d-layer spacing was determined at 80 °C and compared with the molecular length estimated by Corey–Pauling–Kolton (CPK) space-filling molecular models in the fully extended conformation (Table 2).

The d-layer spacing values found for 2 and 3 were close to their molecular lengths which led to d/L ratios of 1.00 and 0.97 for 2 and 3, respectively. The d-layer spacing values found for 4 and 1 were smaller than their molecular lengths and gave d/L ratios of 0.49 and 0.62 for 4 and 1, respectively.

The increase of d observed on going from 4 to 1, that is upon addition of C₆H₆ to 4, should reflect a different supramolecular
organization of 4 and 1 within the liquid-crystalline phase. Indeed, the molecular length of 1 and 4 are almost identical (Table 2).

**Supramolecular organization:** To describe the molecular organization within the smectic A layers, it is necessary to take into account the fact that the different molecular moieties, which form such a large molecule as 1, have quite different cross-sectional areas. For example, the molecular areas of C60 and classical mesogenic groups are about 100 \( \text{Å}^2 \) and 25-30 \( \text{Å}^2 \), respectively, whereas that of ferrocene is close to 44 \( \text{Å}^2 \). As for the cholesterol moiety, it was decided to perform XRD and dilatometry experiments on the cholesterol derivatives 5 (n = 8, 12, 14) to determine its cross-sectional area. Indeed, compounds 5 (n = 8, 12, 14) show smectic A and cholesteric phases (Table 1), and therefore can be regarded as ideal candidates for such a purpose: in the smectic A phase, the cross-sectional area corresponds to the molecular area determined experimentally, since the molecules are normal to the layers.

The variation of the d-layer spacing as a function of temperature in the smectic A phase for compounds 5 (n = 8, 12, 14) is shown in Figure 4. There is a slight decrease of d with increasing temperature. Such a behavior is usual in the case of smectic A phases and corresponds to an increase of the lateral distances between the molecules together with a spreading of the aliphatic chains at the interface between the layers. This spreading induces a decrease of the aliphatic sublayer thickness and, therefore, of the d value itself. Interestingly, the d values are close to those of the molecular lengths L calculated for stretched conformation of the molecules (Table 2). Moreover, the variation of d is linear with n, with an increase of 1.15 ± 0.05 \( \text{Å} \) per methylene group. This value is close to that expected for a completely stretched conformation of the chains (1.27 \( \text{Å} \)) and indicates that the chains are, on average, almost normal to the smectic layers.

Dilatometry measurements have been performed on compounds 5 (n = 8, 12); as for 5 (n = 14), the molecular volume \( V_m \) has been calculated by additivity of the values of \( V_m \) obtained for 5 (n = 12) with those of the known values of methylene groups in the smectic A phase. When combining the data thus obtained with those of the layer spacing obtained by XRD, it is possible to deduce the molecular area \( S \) occupied by one molecule in the plane of the layers with \( S = V_m/d \). This parameter is quite important to describe the molecular arrangement within the layers.

![Figure 5](image_url) Figure 5. Dependence of the molecular area \( S \) of 5 as a function of temperature in the smectic A phase.
cholesterol moieties per molecule ($S/N_{\text{chol}}$) as a function of temperature. The values thus determined are close to those obtained for 5 at low temperature (if we consider the extrapolated values of 5 towards the lower temperatures), but become quite different at higher temperatures. This is in agreement with the increase of $d$ as a function of temperature in the smectic A phase (Figure 3) reported above, and, most likely, due to a small rearrangement of the cholesterol moieties. In the low temperature range, the cholesterol moieties form a single-layered arrangement similar to that found for compounds 5. When the temperature increases, the cholesterol moieties tend to form a slightly partial bilayered arrangement, resulting in an increase of $d$ and a decrease of the molecular area $S$. It is important to point out that the intrinsic values of $S$, in the range between 25.5 and 28.5 Å$^2$, are significantly smaller than the cross-sectional area of the ferrocene moieties. This implies the models proposed in Figures 8 to 11.

In the case of compounds 2–4, the molecular organization of one layer is characterized by three sublayers of different chemical nature and bulkiness segregating from one another and piling up one over the other to form the lamellar stacking of the smectic A phase. In the cholesteric sublayer, two adjacent cholesterol moieties occupy an average area of about 55 Å$^2$, resulting from their partial bilayer arrangement, as explained above. In the ferrocene sublayer, the molecular area available for each group is thus 55 Å$^2$ and is larger than its natural bulkiness ($\approx 45$ Å$^2$ at 100 °C). Therefore, the ferrocene moieties are constrained to tilt with respect to the normal to the layers. However, there is no long range correlation of the tilt angle in order to keep the uniaxial property of the phase. In the aliphatic sublayers, the chains are spread over an area of 55 Å$^2$, which is more than twice the area occupied by a melted chain ($\approx 23$ Å$^2$ at 100 °C). This indicates that they are strongly disorganized and folded. For compounds 2 and 3, possible hydrogen bonding between the hydroxy groups probably contribute to the stabilization of the layering.

In the case of 1, there is a fourth sublayer constituted by the fullerene moieties. The cross-sectional area of $C_{60}$ ($\approx 100$ Å$^2$) is about twice the area occupied by two adjacent cholesterol moieties. This implies that in order to describe the supramolecular organization, two molecules have to be taken into account in the elementary cell. The cholesterol, ferrocene, and aliphatic sublayers can be described as for compounds 2–4. The fullerene moieties form a double sublayer inserted between aliphatic sublayers. In fact, the molecules organize themselves in double layers, where $C_{60}$ plays the predominant role. Due to its large molecular area, $C_{60}$ imposes the arrangement of the other molecular moieties. The space filling is thus obtained through a micro-segregation of the different molecular species together with a good adequacy between the interfaces of the different sublayers.
Photophysical properties: Photoinduced phenomena including electron transfer (ET) in 1 were studied in solution by steady-state fluorescence and complemented by time-resolved transient absorption spectroscopy. The fluorescence of 1 and of the model diethyldioxyllatate methanofullerene derivative 7 was taken in solvents of different polarity. The scope of these experiments was to measure the extent of fluorescence quenching in 1 relative to 7, where the electron donating ferrocene moiety is absent. In addition, the increase in solvent polarity was meant to lower the energy of the charge-separated state and, in turn, to increase the free energy changes associated with the intramolecular ET event. This change in driving force is only made possible on the basis that the energy of the electron accepting state, namely the fullerene singlet state, remains independent of the solvent environment.

Emission spectra of the methanofullerene reference 7 in toluene and in benzonitrile at room temperature show the same maxima around 700 nm, with the same moderate yield of about $6.0 \times 10^{-4}$. This implies that the energy of the fullerene singlet excited state is not affected by the solvent polarity. In agreement with the hypothesis of an intramolecular ET between the electron donating ferrocene and the photoexcited fullerene, the fullerene fluorescence of 1 is indeed noticeably quenched in toluene relative to 7 (Table 3). Moreover, the fluorescence quantum yields are subject to a systematic decrease with the following order: toluene > THF > CH$_2$Cl$_2$ > benzonitrile (Figure 12).

Complementary fluorescence lifetime measurements (i.e., recording the fullerene emission at 700 nm) also reveal faster decay of the fullerene emission of 1 in all solvents investigated relative to reference 7 (Figure 13). Again, the lifetime decreased in the same order as derived from the steady-state emission experiments, namely toluene > THF > CH$_2$Cl$_2$ > benzonitrile (Table 3).

Considering the fluorescence measurements summarized above, an intramolecular ET can be inferred. To obtain direct spectroscopic evidence in support of this assumption, transient absorption spectra were acquired following either a 18 ps or a 6 ns laser pulse at 355 and 337 nm, respectively. In conjunction with the short laser pulses (i.e., 18 ps) the decay
dynamics of the fullerene singlet excited state are probed in light of the forward ET. On the other hand, the longer laser pulses (i.e., 6 ns) are employed to shed light on the lifetime of the charge-separated state.

In particular, picosecond excitation of the reference 7 reveals the following absorption characteristic: immediately after the laser pulse, a strong absorption was observed. A maximum around 920 nm is a clear fingerprint of the fullerene singlet–singlet absorption, which formation lies within the resolution of the applied laser pulses. The singlet excited state absorption decays with clean first order kinetics and a time constant of 6.5 × 10⁸ s⁻¹. Simultaneously with the decay of the 920 nm absorption, a new transient grows in at around 720 nm. The decay and grow-in kinetics are in reasonably good agreement, which leads to the conclusion that a spin-forbidden intersystem crossing (ISC) governs the fate of the singlet excited state. This allows the assignment of the 720 nm absorption maximum to the triplet–triplet absorption. Further evidence for the transformation of the singlet excited state (1.77 eV) to the energetically lower lying triplet excited state (1.50 eV) stems from the presence of an isosbestic point at around 735 nm. It should be noted that the triplet excited state exhibits another maximum around 360 nm, which is, however, outside the detectable wavelength range of our picosecond apparatus. The singlet ground state recovered through a clean first-order process affording a triplet lifetime of nearly 100 μs. While this is due at low fullerene concentration and low laser power, the kinetics become, however, more complicated at higher fullerene concentration and

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<tr>
<td>toluene</td>
<td>2.39</td>
<td>4.4 × 10⁻⁴</td>
<td>1.11</td>
<td>1.02</td>
<td></td>
<td>6.0 × 10⁻⁴</td>
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<td>3.8 × 10⁻⁴</td>
<td>1.07</td>
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<tr>
<td>CH₂Cl₂</td>
<td>9.08</td>
<td>3.0 × 10⁻⁴</td>
<td>0.81</td>
<td>0.72</td>
<td>27</td>
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<td>0.62</td>
<td>0.5</td>
<td>115</td>
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<td>benzonitrile/DMF</td>
<td>30.8</td>
<td>2.2 × 10⁻⁴</td>
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higher laser power. In particular, they are affected by efficient i) triplet–triplet and ii) triplet–ground state annihilation processes. This is in agreement with previous studies.[31, 26]

The liquid-crystalline material 1 shows, upon a 18 ps laser pulse, formation of the same 920 nm absorption seen for 7 (see above). In contrast to the slow ISC kinetics (6.5 × 10⁶ s⁻¹), the singlet excited state absorption decays rather rapidly with rate constants typically ranging between 9.8 × 10⁶ s⁻¹ (toluene) and 2.0 × 10⁷ s⁻¹ (benzonitrile). Importantly, no spectral evidence is found on the picosecond time-scale (i.e., up to 6000 ps) that resembles the triplet absorption around 720 nm, namely the product of the ordinary ISC. Instead, in the monitored wavelength region (500 and 960 nm), a very broadly absorbing transient was found.

With the scope to monitor the full spectral range (UV, visible and NIR), especially the range characteristic for the fullerene π-radical anion absorption around 400 nm and 1040 nm, complementary nanosecond experiments seemed necessary.[27] However, differential absorption changes recorded immediately after a 6 ns laser pulse of 1 in deoxygenated toluene showed no characteristic absorption at all. This suggests that the low solvent polarity is an insufficient means to stabilize the initially formed charge-separated radical pair and that rapid charge recombination prevails on a faster time scale.

Solvents with a higher dielectric constant, such as benzonitrile or DMF, should be potent enough to prevent the fast charge recombination. Indeed, differential absorption changes following the 337 nm laser excitation of 1 in benzonitrile show maxima at 400 and 1040 nm in the visible and NIR regions, respectively. Especially, the NIR maximum is a clear fingerprint absorption of the one-electron reduced fullerene, which suggests the formation of the charge-separated radical pair (Figure 14). On the other hand, no spectral identification can be made for the one-electron oxidized form of ferrocene, since it shows only a very weak absorption maximum at 625 nm (ε = 500 L·mol⁻¹·cm⁻¹).[28]

In addition, the fullerene π-radical anion absorption is a meaningful probe for determining the lifetime of the charge-separated state. From the corresponding decay kinetics, we derived lifetimes of 115, 420 and 27 ns in oxygen-free benzonitrile (ε = 24.8), in an oxygen-free mixture of benzonitrile/DMF (1: 1 v/v) (ε = 30.8) and in oxygen-free CH₂Cl₂ (ε = 9.08), respectively.

To elucidate a possible energy transfer mechanism, the excited state energies of the ferrocene unit should be considered and compared to those of the C₆₀ unit (Figure 15).

![Figure 15. Energy diagram illustrating the different deactivation channels following the photoexcitation of 1.](image)

The ferrocene singlet excited state (≈ 2.46 eV)[29] is sufficiently separated from the fullerene singlet excited state (1.77 eV) to render a singlet–singlet excited state transfer from the photoexcited C₆₀ endothermic and, therefore, unlikely to occur. In contrast, the low-lying ferrocene triplet excited state (1.64 eV)[31] opens, in principle, the opportunity for an energy transfer but only in the form of a singlet–triplet transfer. The C₆₀ triplet excited state (1.50 eV), on the other hand, could only interact with the ferrocene unit via a possible equilibrium, which would lead, nonetheless, to a minor population of the ferrocene triplet excited state (≈ 0.5 %).

The optical characterization of the charge-separated radical pair (λₘₐₓ ≈ 400 and ≈ 1040 nm) speaks definitively against an energy transfer mechanism. Furthermore, the solvent dependence (Table 3) cannot be explained by a simple energy transfer. In particular, it should be taken into account that the excited state energies remain nearly constant in solvents of different polarities. This, in turn, leads to no significant variations in the free energy changes, for example, between a reaction in non-polar toluene and polar benzonitrile. Thus, intramolecular energy changes should proceed with the same dynamics. Conversely, the energy of the charge-separated radical pair is strongly solvent dependent, with its highest and lowest energies in non-polar and polar solvents, respectively. From the data collected in Table 3, we conclude that the noted solvent dependence is a crucial argument in favor of an electron transfer mechanism rather than an energy transfer mechanism.

Decisive support for an electron transfer mechanism, as the major deactivation pathway of the C₆₀ singlet excited state, comes from the energy of the charge-separated radical pair. The latter is, for instance, 1.53 eV in CH₂Cl₂ considering the
reduction potential of the fullerene unit (−0.57 V vs SCE)[33] and the oxidation potential of the ferrocene unit (−0.96 V vs SCE).[33] In other words, a significantly larger driving force exists for the electron transfer (−ΔG_{red,trans} = 0.24 eV) relative to the energy transfer (−ΔG_{energy,trans} = 0.13 eV), and note that −ΔG_{electron,trans} further increases in polar benzenetrile.

Conclusion

Photoinduced intramolecular electron transfer was observed in organic solvents for a fullerene–ferrocene liquid-crystal-line material. This observation is of interest for the development of photo-active molecular switches based on the photophysical properties of C_{60}. The role of each subunit (i.e., cholesterol, ferrocene, and fullerene) for governing the supramolecular organization within the liquid-crystalline phases could be understood. This will allow the design of new structures with tailor-made liquid-crystalline and photophysical properties. In the smectic A phase, a relative order with microsegregation of the different units (ferrocene, fullerene and cholesterol) was observed. This order might be important to control the electron transfer processes upon light irradiation. Studies in solution reveal that the ferrocene–fullerene system does indeed give rise to intramolecular electron transfer with relatively long-lived charge-separated species. It is then expected that in the pure liquid-crystalline phase or in liquid-crystalline phases obtained by dissolution of the dyad in liquid crystal solvents (such as E7) control of electron-transfer rates should be achieved. Experiments addressing these issues are currently underway.

Experimental Section

Materials: Toluene (NaH), CH_{2}Cl_{2}, (MgSO_{4}, then P_{2}O_{5}) and THF (KOH, then Na/benzophenone) were dried and distilled under nitrogen prior to use. [60] Fullerene (99.5 %) was purchased from Southern Chemical Group (Georgia, USA). 1-[10-[4-(Cholest-5-en-3-yl)oxy)]carbonyl[phenolyl]-de-cyloxy carbonyl]-1-[4-(hydroxyphenoxy)carbonyl][ferrocene][23] (2) and chole-steryl 4-hydroxybenzoate[23] (6) were synthesized as described in the literature.

Techniques: Column chromatography: silica gel 60 (0.060–0.200 mm, SD5). Transition temperatures (onset point) 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; data treatment used Mettler TA722.5 GRAPHWAVE. Optical studies were conducted using a Zeiss-Axiscop, and a Linkam-THMS-600 variable-temperature stage, under N_{2}. 'H NMR spectra were taken on a Varian GEMINI 200 spectrometer or a Bruker AMX 400 spectrometer, with the solvent as an internal standard. Elemental analyses were done by the Mikroelementaranalytisches Laboratorium ETH-Zürich.

X-ray diffraction studies: X-ray patterns were recorded on samples filled in Lindemann glass capillaries with two setups based on focalized linear CuKα beams produced with sealed tubes and bent quartz monochromators. The patterns were systematically recorded as a function of temperature by using a home-made oven which is controlled by an INSTECH unit (residual temperature fluctuations ≤±0.02°C) and an INEL CPS 120 counter. For a better signal-background ratio, long-time patterns were registered at several temperatures on KODAK scientific imaging films with a second setup equipped with a home-made vacuum stand alone oven (residual temperature fluctuations of ±1°C). The films were scanned using an EPSON GT-7000 scanner and the images background corrected and integrated in order to get the diffraction intensity as a function of the diffracted angle.

Dilatometry experiments: The technique used to measure the molar volume as a function of temperature was developed by Kovacs[29] for the study of polymers, and afterwards applied to liquid crystals[80]. The measurements were performed with a high precision home-built apparatus, automatically computer controlled, including data acquisition and temperature control (±0.03°C).

Photophysical studies: Picoscopic laser flash photolysis were carried out with 355 nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP (Continuum) Nd:YAG laser system (pulse width ca. 18 ps, 2–3 mJ per pulse). Passing the fundamental output through a D_{2}O/H_{2}O solution generated the white continous picoscope probe pulse. Nanosecond laser flash photolysis experiments were performed with laser pulses from a Moleclectron UV-400 (Laser Photonics; PRA Model UV-24) nitrogen laser system (337.1 nm, 8 ns pulse width, 1 mJ per pulse) in a front face excitation geometry. The photomultiplier output was digitized with a Tektronix 7912 AD programmable digitizer. Absorption spectra were recorded with a Milton Roy Spectronic 3000 Array spectrophotometer.

Fluorescence spectra were measured at room temperature with a SLM/ Amicon® 8100 Spectrophuorometer (Spectronic Instruments). A 570 nm long-pass filter in the emission pass was used in order to eliminate the interference from the solvent and stray light. Long integration times (20 s) and low increments (0.1 nm) were applied. The slits were 2 and 8 nm. Each spectrum was an average of at least five individual scans.

Synthesis

Compound 3: A mixture of 6-bromohexanol (0.40 mL, 3.06 mmol), 2 (2.45 g, 2.42 mmol), K_{2}CO_{3} (2.00 g, 14.47 mmol), acetonitrile (180 mL), and THF (20 mL) was stirred at 60 °C for 24 h. The mixture was cooled to room temperature and filtered. The solid residue was washed with acetonitrile. The organic solvents were combined and evaporated to dryness. Purification of the solid residue by CC (CH_{2}Cl_{2}/AcOEt 20:1) and precipitation (dissolution in CH_{2}Cl_{2} and precipitation by pouring the solution into CH_{2}OH) gave pure 3 (0.98 g, 36.5%). 'H NMR (200 MHz, CDCl_{3}), δ = 7.98 (2, d, 2H, ArH), 7.13 (2, d, ArH), 6.92 (2, d, ArH), 6.89 (2, d, ArH), 5.41 (1, d, CH–C, chol), 4.95 (t, 2H, HC(O)), 4.90 (t, 2H, HC(O)), 4.85–4.80 (br, 1H, CHO, chol), 4.51–4.48 (m, 4H, HC(O)), 4.20 (t, 2H, CH_{2}OCH_{2}), 3.98 (t, 2H, CH_{2}OPH), 3.71–3.62 (m, 2H, CH_{2}OH), 2.45 (2d, chol), 1.95–0.66 (65H, chol, (CH_{3}), (CH_{2})), elemental analysis calc (%) for C_{67}H_{56}FeO_{10} (11133): C 73.49, H 8.53; found: C 73.50, H 8.39.

Compound 4: A solution of malonoyl chloride (44.0 mg, 0.31 mmol) in CH_{2}Cl_{2} (10 mL) was added dropwise to a solution of 3 (0.77 g, 0.69 mmol) and triethylamine (71.0 mg, 0.70 mmol) in CH_{2}Cl_{2} (80 mL). The mixture was stirred at room temperature for 2 h and evaporated to dryness. Purification of the solid residue by CC (CH_{2}Cl_{2}/AcOEt 20:1) and precipitation (dissolution in CH_{2}Cl_{2} and precipitation by pouring the solution into ligroin) gave pure 4 (0.55 g, 77%). 'H NMR (200 MHz, CDCl_{3}), δ = 7.97 (d, 4H, ArH), 7.12 (d, 4H, ArH), 6.92 (d, 4H, ArH), 6.89 (d, 4H, ArH), 5.42 (d, 2H, CH–C, chol), 4.85 (t, 1H, HC(O)), 4.90 (t, 1H, HC(O)), 4.85–4.80 (brm, 2H, CHO, chol), 4.51–4.48 (m, 8H, HC(O)), 3.98 (t, 4H, CH_{2}OPh), 3.98 (t, 4H, CH_{2}OPh), 3.71–3.62 (m, 2H, CH_{2}OH), 2.45 (2d, chol), 1.95–0.66 (65H, chol, (CH_{3}), (CH_{2})), elemental analysis calc (%) for C_{82}H_{84}FeO_{19} (229070): C 77.28, H 8.27; found: C 77.29, H 8.24.

Compound 1: A solution of DBU (1.4, 0.27 mL, 0.27 mmol) was added dropwise to a solution of C_{60} (98 mg, 0.136 mmol), 4 (310 mg, 0.135 mmol) and iodine (35 mg, 0.138 mmol) in toluene (100 mL). The mixture was stirred at room temperature for 3 h and evaporated to dryness. Purification of the solid residue by CC (toluene, then toluene/AcOEt 20:1) and precipitation (dissolution in toluene and precipitation by pouring the solution into CH_{2}OH) gave pure 1 (140 mg, 34%). 'H NMR (400 MHz, CDCl_{3}), δ = 7.97 (d, 4H, ArH), 7.11 (d, 4H, ArH), 6.93 (d, 4H, ArH), 6.88 (d, 4H, ArH), 5.41 (d, 2H, CH–C, chol), 4.94 (t, 4H, HC(O)), 4.89 (t, 4H, HC(O)), 4.88–4.80 (brm, 2H, CHO, chol), 4.52 (t, 4H, CH_{2}OCH_{2}), 4.50–
Compound 5 (n = 8): A mixture of 1-bromooctane (1.14 g, 5.90 mmol), cholesteryl 4-hydroxybenzoate (2.00 g, 3.95 mmol), K₂CO₃ (2.72 g, 16.68 mmol), DMF (40 mL), and THF (20 mL) was stirred under reflux for 20 h, cooled to room temperature and filtered. The solid residue was washed with THF. The organic solvents were combined and evaporated to dryness. Purification of the solid residue by CC (CH₂Cl₂) and crystallization (CH₂Cl₂/EtOH) gave pure 5 (n = 8) (1.9 g, 78%). ‘H NMR (200 MHz, CDCl₃): δ = 7.98 (2H, ArH), 6.90 (2H, ArH), 5.45 (1H, CH=C(chol)), 4.86 – 4.80 (brm, 1H, CH(OH)cho), 4.01 (t, 2H, CHO), 2.44 (2H, chol), 2.06 – 0.69 (56H, chol, CH(CH₃)₂); elemental analysis calcd (%) for C₆₅H₉₀O₈: C 81.50, H 10.75; found: C 81.26, H 10.63.

Compounds 5 (n = 12, 14) were prepared by analogy to the above procedure from 1-bromododecane [→ 5 (n = 12)] or 1-bromotetradecane [→ 5 (n = 14)]. The analytical data are in agreement with their structure.

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