[F003]

Dendritic Liquid-Crystalline Fullerene-Ferrocene Dyads

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Abstract: *First- and second-generation ferrocene-based dendrimers, fullerene and a second-generation liquid-crystalline poly(arylester) dendrimer carrying four cyanobiphenyl units were assembled to elaborate polyfunctional materials displaying mesomorphic and electronic properties. The targeted compounds gave rise to enantiotropic smectic A phases and organized into bilayer structures within the smectic layers. Cyclic voltammetry investigations revealed oxidation and reduction processes in agreement with the presence of both ferrocene and fullerene units. Finally, strong quenching of the fluorescence was obtained for the fullerene-ferrocene dyads suggesting efficient elecron transfer from the ferrocene-based dendrimer to fullerene.*

1. INTRODUCTION

The design of photoactive [60]fullerene-based materials for applications in photovoltaic[1] and organic light emitting diode[2] technologies strongly motivated synthetic efforts. In the other hand, functionalized liquid-crystalline fullerenes are promising materials for applications in electronic and optical nanotechnologies as they combine the unique properties of C_{60} with the characteristics of liquid crystals.

ferrocene-based dendrimers display remarkable electrochemical properties and were used for the construction of batteries[3] and sensors.[4] The association of a ferrocene-containing dendrimer and C_{60} within a liquid-crystalline structure could lead to polyfunctional materials displaying interesting mesomorphic, photophysical and electrochemical properties.

We report, herein, the synthesis, liquid-crystalline properties, supramolecular organization, electrochemical and photophysical behavior of fullerene-ferrocene dyads **1** and **2** containing two and four ferrocene units, respectively. A second-generation poly(arylester) dendrimer functionalized with cyanobipenyl units was used as liquid-crystalline promoter (Chart 1).

Chart 1

1

2
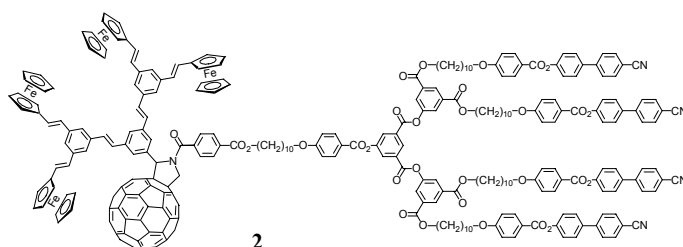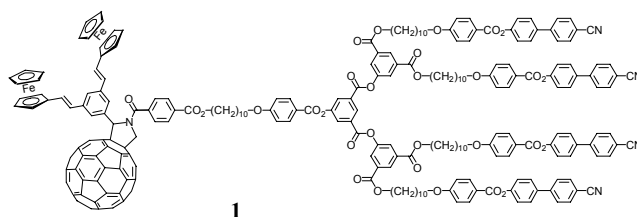
2. EXPERIMENTAL SECTION

2.1. Preparation of *N*-H-pyrrolidino[60]fullerenes

Fulleropyrrolidines **5** and **6** were prepared by 1,3-dipolar cycloaddition of C_{60} with the azomethine ylide[5] generated *in situ* from aldehyde functionalized dendrons **3** or **4** and glycine in refluxing chlorobenzene. A mixture of C_{60} (1.0 equiv.), the dendritc aldehyde, **3** or **4** (2.2 equiv.) and glycine (1.1 equiv.) was heated under reflux for 8 h in degassed anhydrous chlorobenzene (30 mL) under inert atmosphere. After removal of the solvents, the residue was purified over silica gel (toluene/hexane 7:3). The product was centrifuged with CH_3OH and n-pentane to give **5** and **6** (32-30%, respectively) as a dark brown solid.

2.2. Preparation of LC triads

The synthesis of targeted compounds **1** and **2** involved reaction of acid **7a** with thionyl chloride in CH_2Cl_2 to prepare the corresponding acid chloride **7b** followed by condensation of the latter with **5** or **6** in refluxing CH_2Cl_2. A mixture of **7a** (2.25 equiv.) and thionyl chloride (72 equiv.) was heated under reflux for 7 h in anhydrous CH_2Cl_2. The solvent was evaporated under reduced pressure and added to a solution of **5** or **6** (1 equiv.) in 25 mL of CH_2Cl_2 and anhydrous pyridine (1.25 equiv.). The mixture was stirred at room temperature for 2 h. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (toluene/hexane 4:1). A further purification by centrifugation with CH_3OH afforded **1** or **2** in quantitative yield as a dark brown solid.
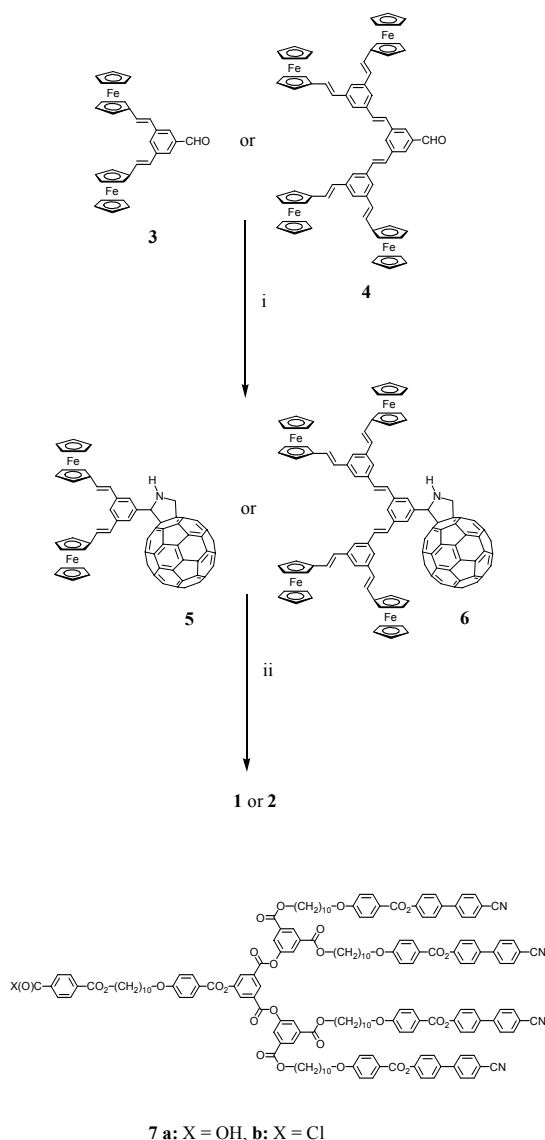
Scheme 1. *Reagents and conditions*. i) C_{60}, glycine, chlorobenzene, reflux, 8 h, yield: 32 % for **5**, 30 % for **6**. ii) **7a**, thionyl chloride, CH_2Cl_2, reflux, 7 h, then **5** or **6**, CH_2Cl_2, pyridine, room temperature, 2 h, quantitative yields.

2.3.   Characterization

All new compounds were characterized by ^1H and ^{13}C NMR, FT-IR and MALDI-TOF mass spectrometry. The analytical data were in agreement with the structures. High resolution ^1H NMR spectra showed the *E*-configuration of the vinyl hydrogens in the ferrocene-based dendrimer (J = 16–17 Hz). The typical pyrrolidine protons [two doublets (AB system) and one singlet] appeared in the 4-5 ppm range.

3. RESULTS AND DISCUSSION

3.1.   Liquid-crystalline properties

Compounds **1**, **2** and **7a** gave rise to smectic A phases which were identified by POM from the observation of typical focal-conic and homeotropic textures. Fullerene derivatives **1** and **2**

showed a lower clearing point than liquid-crystalline dendrimer **7a**. This behavior is in agreement with results obtained for other fullerene-containing liquid crystals,[13] and is attributed to the presence of bulky ferrocene and C_{60} units.

Table 1: Phase-transition temperatures[a] and enthalpy changes of **1**, **2** and **7a**.

Compound	$T_g{}^b$ [°C]	$S_A \rightarrow I$ [°C]	ΔH [kJ/mol]
1	47	171[c]	7.3
2	34	168[c]	13.3
7a	45	203[d]	18.6

[a]T_g = glass transition temperature, S_A = smectic A phase, I = isotropic liquid.

[b]Determined during the first cooling run.

[c]Determined as the maximum of the peak obtained during the second heating run.

[d]Determined as the onset of the peak obtained during the second heating run.

X-ray diffraction patterns recorded at room temperature from as-obtained samples of **1** and **2** were consistent with the formation of smectic A phases. By applying Bragg's law to these maxima, layer spacings of 93 and 105 Å were obtained for **1** and **2**, respectively.

The room-temperature phase was a frozen smectic A phase with the same structure of the high-temperature liquid crystal phase but lacking fluidity. Temperature had no significant effect on the molecular conformations or on the extent of interdigitation.

3.2.   Supramolecular organization

1 and **2** organized into a bilayer smectic structure with alternate sublayers of cyano-biphenyl units, fullerene units and ferrocene units (Figure 1). Interdigitation the cyanobiphenyl units from one layer to the adjacent one should contribute to the stabilization of the layers.
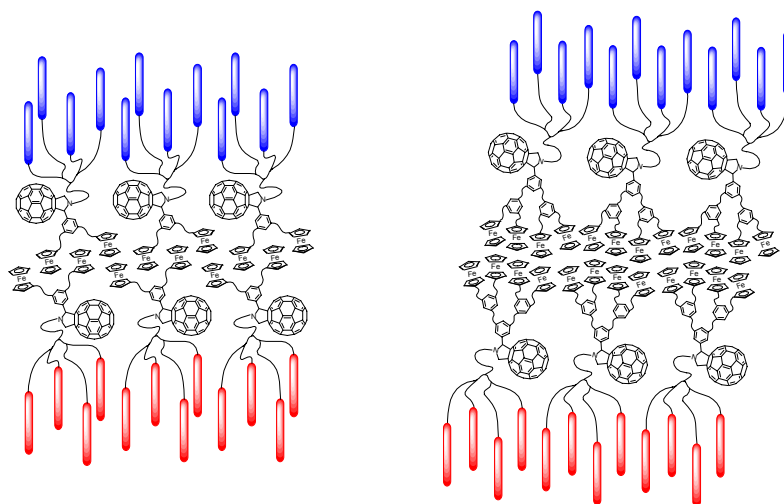

Figure 1. Postulated supramolecular organization of **1** (left) and **2** (right) within the smectic A phase.

3.3. Electrochemistry

In the cathodic scan, three reversible reduction waves were observed and presumably, fullerene centred, but shifted to more negative values than those observed for C_{60} because of the saturation of one double bond of the C_{60} cage.[4] An additional non-reversible reduction wave was observed for **1** and **2** at around -2.10 V, which was assigned to the reduction of the mesogenic dendrimer by comparison with the reduction wave observed for **7a**. In the anodic scan, the observed oxidation process is ferrocene-based because no oxidation can be observed for **7a** in this region.

Table 2. Osteryoung Square Wave Voltammetry (OSWV) data in o-dichlorobenzene/acetonitrile (4/1)[a]

	E_{red}^{1} (V)	E_{red}^{2} (V)	E_{red}^{3} (V)	E_{red}^{4} (V)	E_{ox}^{1} (V)
1	-1.02	-1.41	-1.96	-2.11	0.01
2	-1.01	-1.40	-1.96	-2.08	-0.03
5	-1.10	-1.49	-2.00		0.03
6	-1.04	-1.44	-1.98		
7a				-2.08	
C_{60}	-0.99	-1.38	-1.85		
Ferrocene					0.04

[a] V vs. Ag / AgNO$_3$; glassy carbon electrode as the working electrode; 0.1 M TBAP; scan rate = 100 mV s^{-1}; concentration: 1.4 x 10^{-3} M.
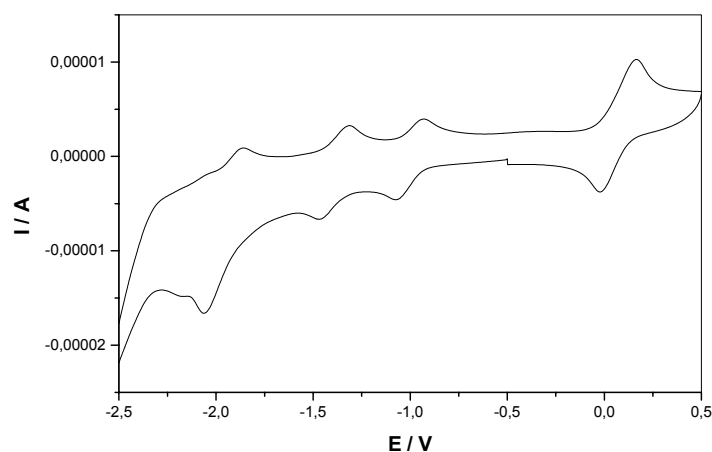

Figure 2. Cyclic voltamogram of **1**.

3.4.   Photophysical studies

The absorption spectra of **5** and **6** were measured in CHCl$_3$ (Figure 3a). **5** and **6** behave as an assembly of two and four vinylferrocene moieties sharing a phenyl ring, because conjugation is not extended by meta substitution. Both fullerene-ferrocene dendrimers show the typical small band for [6,6]-bridged fullerene derivatives at 431 nm.
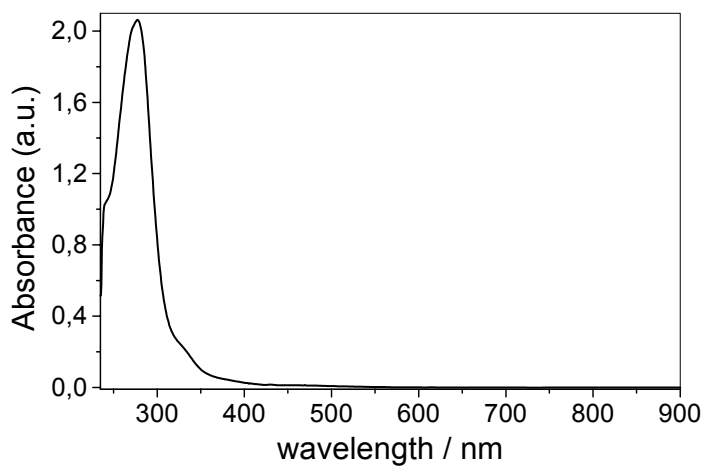
a)
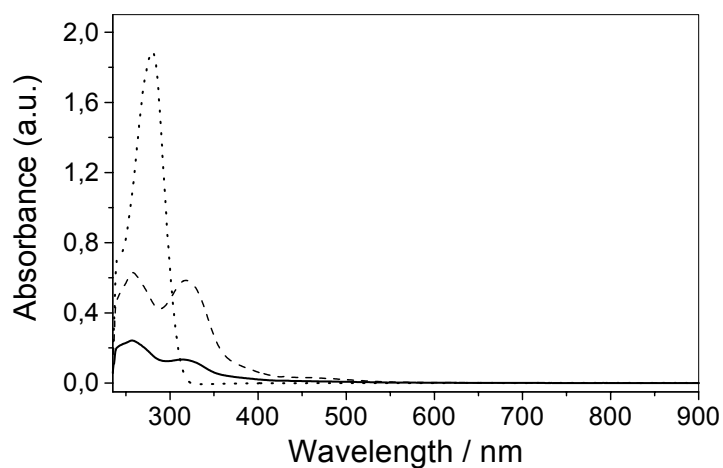
b)

Figure 3. a) Absorption spectra in chloroform (10^{-5} M) of **5** (solid line), **6** (dashed line) and **7a** (dotted line). b) Absorption spectra in chloroform (10^{-5} M) of **1**.

In toluene, the fluorescence observed at 714 nm for *N*-methylfulleropyrrolidine was almost totally quenched in **5** and **6** (only a weak emission at 704 nm is observed) independently of the generation of the dendrimer (Figure 4a). When the most polar benzonitrile solvent was used, the fluorescence was totally quenched. These findings suggested the occurrence of an efficient electron transfer process from the ferrocene-based dendrimer to C_{60}. Newly incorporated mesogenic dendrimer did not influence the photophysical behavior of the studied materials.

a)
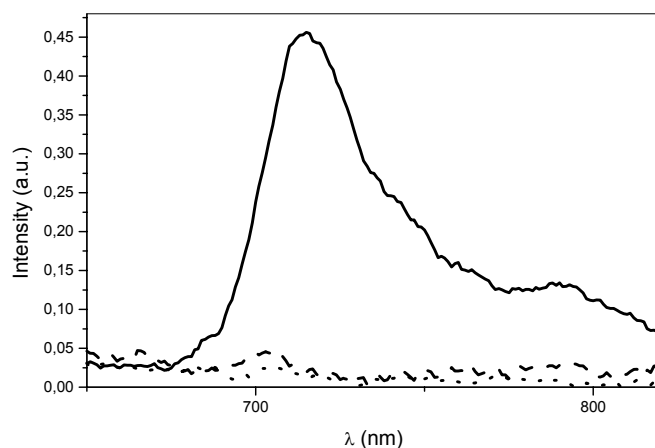
b)

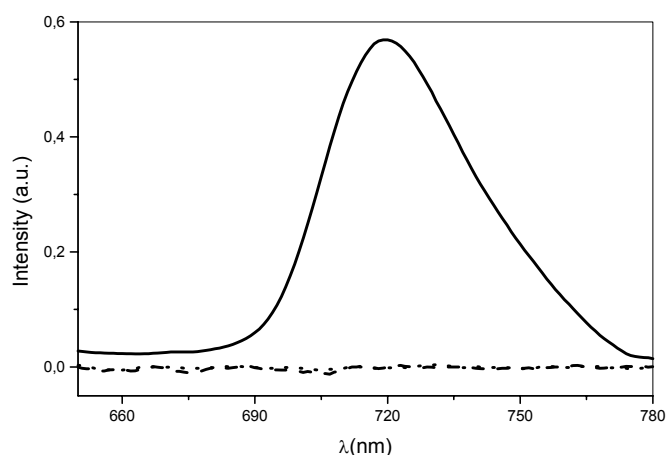**Figure 4.** a) Steady-state fluorescence (λ_{exc} = 430 nm) of **5** (dashed line), **6** (dotted line) and *N*-methylpyrrolidino[60]fullerene (solid line) measured in toluene. b) Steady-state fluorescence (λ_{exc} = 430 nm) of **1** (dashed line), **2** (dotted line) and *N*-methylpyrrolidino[60]fullerene (solid line) measured in benzonitrile.

4. Conclusion

We have designed a novel family of liquid-crystalline fullerene-ferrocene dyads by assembling a first or second ferrocene-based dendrimer, a second-generation mesomorphic poly(arylester) dendrimer carrying cyanobiphenyl units and fullerene. The materials dispayed smectic A phases, and the supramolecular organization was governed by steric constraints. The electrochemical behavior was in agreement with the redox-activity of the building-blocks. Steady-state emission spectra showed that the fluorescence was totally quenched, suggesting the existence of an efficient electron transfer process from the ferrocene dendrimer to C_{60}. Therefore, the use of

ferrocene-based dendrimers as electron donor moieties could be appealing to elaborate supramolecular switches based on fullerene and ferrocene.

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[1] a) Nierengarten, J.-F.; Eckert, J.-F; Nicoud, J.-F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617. b) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467. c) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J., *Science* **1995**, *270*, 1789. d) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15. e) Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841.

[2] Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *J. Am. Chem. Soc.* **1999**, *121*, 5611.

[3] Ruiz, J.; Pradet, C., Varret, F.; Astruc, D. *Chem. Commun.* **2002**, 1108.

[4] a) Valério, C.; Fillaut, J.-L.; Ruiz, J., Guittard, J.; Blais, J.-C.; Astruc D. *J. Am. Chem. Soc*. **1997**, *119*, 2588. b) Casado, C. M.; González, B.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *Angew. Chem. Int. Ed*. **2000**, *39*, 2135. c) Alonso, B.; Casado, C. M. Cuadrado, I.; Morán, M.; Kaifer, A. E. *Chem. Commun*. **2002**, 1778. d) Daniel, M.-C.; Ba, F.; Ruiz Aranzaes, J.; Astruc, D. *Inorg. Chem*. **2004**, *43*, 8649.

[5] a) Valério, C.; Fillaut, J.-L.; Ruiz, J., Guittard, J.; Blais, J.-C.; Astruc D. *J. Am. Chem. Soc*. **1997**, *119*, 2588. b) Casado, C. M.; González, B.; Cuadrado, I.; Alonso, B.; Morán, M.; Losada, J. *Angew. Chem. Int. Ed*. **2000**, *39*, 2135. c) Alonso, B.; Casado, C. M. Cuadrado, I.; Morán, M.; Kaifer, A. E. *Chem. Commun*. **2002**, 1778. d) Daniel, M.-C.; Ba, F.; Ruiz Aranzaes, J.; Astruc, D. *Inorg. Chem*. **2004**, *43*, 8649.