

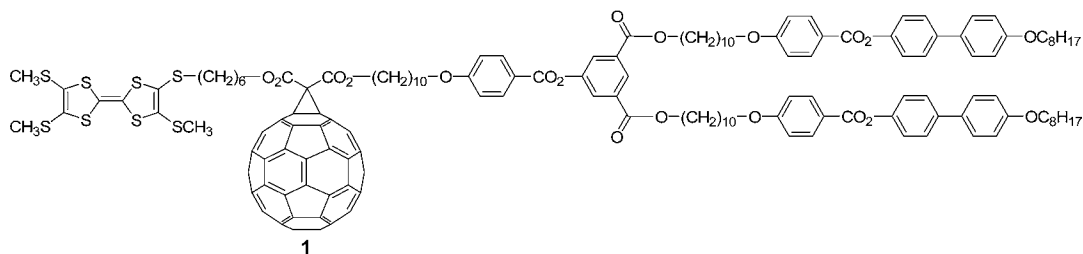
Liquid-Crystalline [60]Fullerene-TTF
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ABSTRACT



[60]Fullerene was functionalized with a TTF derivative and a bis-mesogenic fragment. The synthetic methodology was based on the addition of a malonate derivative to C₆₀ (Bingel-type reaction). Both the malonate and dyad showed smectic B and A phases. The supramolecular organization within the smectic layers was of the monolayer type for the malonate and of the bilayer type for the fullerene derivative. In the latter case, the supramolecular organization was governed by the C₆₀ unit.

[60]Fullerene (C₆₀) has attracted considerable attention in the field of supramolecular chemistry.¹ The development of materials that display the outstanding photophysical and electrochemical properties of C₆₀ motivated such studies. Thus, considerable efforts have been devoted to the development of donor-acceptor dyads,² for which photoinduced electron and/or energy transfer could be achieved. Such results open the doors for the elaboration of novel artificial photosynthetic systems, molecular electronic devices, and photovoltaic cells.

The design of fullerene-containing thermotropic liquid crystals, based on non-covalent or covalent concepts, has been reported. In the former approach, C₆₀ was complexed

by mesomorphic cyclotrimeratrylene (CTV) derivatives (nematic and cubic phases were obtained).³ In the covalent concept, two strategies have been developed. In the first one, attachment of five aromatic groups around one pentagon of C₆₀ yielded conical molecules, the stacking of which gave rise to columnar assemblies.⁴ In the second one, C₆₀ was functionalized with liquid-crystalline addends carrying various units such as cyanobiphenyl and cholesterol derivatives (nematic and smectic A phases were observed).⁵ The use of optically active mesomorphic groups led to the formation of the chiral nematic phase.⁶

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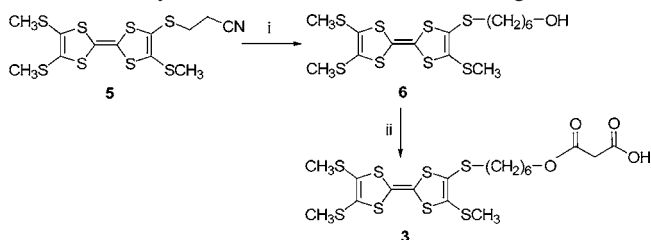
The second strategy was used for the preparation of liquid-crystalline fullerene-donor (OPV⁷ or ferrocene⁸) dyads. Such materials, which combine the physicochemical features of C₆₀-donor systems with the self-organizing properties of liquid crystals, could be used as supramolecular platforms in solar cell technology⁷ and for the development of photoactive liquid crystal switches.⁸ The major drawback of these chemicals is their short half-life (in solution) corresponding to the charge-separated state. However, improvement of this parameter is not straightforward because of the number of structural features related to it (i.e., distance between the donor and acceptor units, orientation of the donor and acceptor moieties with respect to each other, various conformations of the linkers, and redox potential of the donor and acceptor groups). To establish a structure-property relationship and identify the influence of each structural parameter on the photophysical characteristics of the dyads, further candidates need to be studied.

Tetrathiafulvalene (TTF) and π -extended TTF derivatives, that transform into aromatic structures upon oxidation, have been used in the preparation of C₆₀-based dyads⁹ and triads.¹⁰ Upon photoexcitation, long-lived charge-separated states were detected.¹¹ On this basis, liquid-crystalline C₆₀-TTF dyads appear as candidates of choice. Furthermore, TTF derivatives have been shown to give rise to liquid crystals (nematic, smectic A, and columnar phases were observed).¹²

We report, herein, the synthesis, liquid-crystalline properties, supramolecular organization, and electrochemical behavior of mesomorphic C₆₀-TTF derivative **1**, which represents the first member of this new family of liquid crystals.

The synthesis of **1** required the preparation of non-symmetrical malonate derivative **2**. The latter was obtained from **3**, carrying the TTF unit, and **4**, bearing the liquid-crystalline promoter. The syntheses of **1–4** are described in Schemes 1–3.

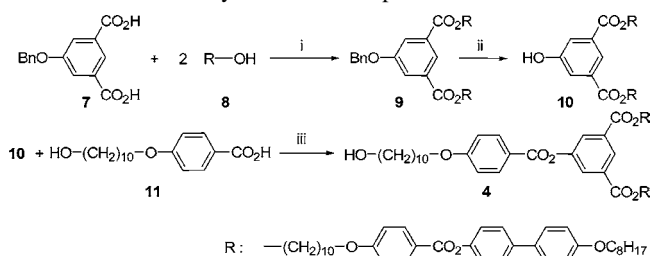
Scheme 1. Synthesis of Tetrathiafulvalene Analogues **3** and **6**^a



^a Reagents and conditions: (i) CsOH·H₂O, DMF, 25 °C, N₂, then 6-bromo-1-hexanol, 80%; (ii) Meldrum acid, toluene, 70 °C, N₂, 95%.

The TTF intermediates **5** and **6** were prepared by applying the Becher's strategy (Scheme 1).¹³ Reaction of alcohol **6** with Meldrum acid led to TTF derivative **3**.

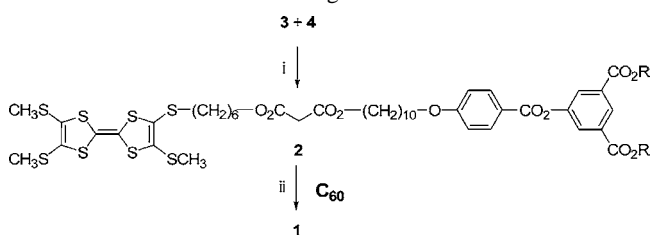
Scheme 2. Synthesis of Compounds **9–10** and **4**^a



^a Reagents and conditions: (i) *N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino) pyridinium toluene-*p*-sulfonate (DPTS), CH₂Cl₂, 25 °C, 93%; (ii) H₂, Pd/C (10%), CH₂Cl₂/EtOH, 25 °C, 90%; (iii) DCC, DPTS, 4-pyrrolidinopyridine (4-PPy), CH₂Cl₂, 25 °C, 95%.

Scheme 2 shows the synthesis of liquid-crystalline promoter **4**. Esterification of diacid **7** with alcohol **8**, which was obtained analogously to the synthesis of cyanobiphenyl derivatives already published,^{5c} gave protected **9**. Removal of the benzyl protecting group under hydrogenation conditions led to phenol intermediate **10**, the condensation of which with **11**^{5c} gave alcohol **4**.

Scheme 3. Synthesis of Fullerene–TTF Dyad **1** and TTF Analogue **2**^a



^a Reagents and conditions: (i) DCC, DPTS, 4-PPy, CH₂Cl₂, 25 °C, N₂, 95%; (ii) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), tetrabromomethane, toluene, 25 °C, N₂, 42%. For R, see Scheme 2.

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Scheme 3 illustrates the synthesis of **1**. Condensation of **3** and **4** led to malonate **2**. Finally, addition of **2** with C₆₀ via the *Bingel* reaction¹⁴ gave methanofullerene **1**.

All compounds were purified by column chromatography (silica gel). The ¹H NMR spectra of **1** and **2** in CD₂Cl₂ are similar and display the expected features of the liquid-crystalline core and TTF unit. For **1**, we note the disappearance of the malonate methylene protons and the downfield shift of the *O*-decyl methylene protons (CO₂CH₂). The UV–visible spectrum of **1** displays the characteristic features of [6,6]-closed methanofullerene structures (426 and 687 nm). High-resolution Maldi-TOF spectra of **1** and **2** show molecular ion peaks that are in agreement with the theoretical isotopic distributions.

The thermal and liquid-crystalline properties of **1** and **2** were investigated by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction. The phase transition temperatures and enthalpies are reported in Table 1.

Table 1. Phase Transition Temperatures and Enthalpy Changes of Compounds **1** and **2**

compd	<i>T</i> _g ^a (°C)	transition ^b	<i>T</i> ^c (°C)	Δ <i>H</i> (kJ mol ^{−1})
1	64	S _B → S _A	129	8.0
		S _A → I	156	29.0
2	53	S _B → S _A	120	8.6
		S _A → I	133	22.1

^a *T*_g = glass transition temperature determined during the second heating.
^b S_B = smectic B phase, S_A = smectic A phase, I = isotropic liquid.
^c Temperatures are given as the onset of the peaks obtained during the second heating.

Similar mesomorphic behavior was obtained for **1** and **2**. They both gave rise to a glass transition temperature followed by two liquid-crystalline phases. When the samples were cooled from the isotropic fluid, small focal conic and homeotropic textures were observed for the high-temperature liquid-crystalline phase. No apparent modifications of the texture were observed for the low-temperature liquid-crystalline phase. This result indicated that both mesophases are smectic and that the molecules are oriented normal to the smectic layers. From POM investigations, the mesophases were identified as smectic A and smectic B. No decomposition of **1** and **2** was detected either by POM or DSC.

The liquid-crystalline phases were unambiguously identified by small-angle X-ray diffraction on powder samples. Similar X-ray patterns were obtained for both samples, and the smectic nature of both mesophases, suggested by POM, was confirmed. The X-ray patterns recorded at 120 and 140 °C for **1** and at 110 and 125 °C for **2** exhibited two sharp

small-angle reflections in a 1:2 ratio, corresponding to the smectic layering of the molecules, and a diffuse scattering halo in the wide-angle region, centered around 4.6 Å, associated with the liquid-like order of the molten chains. In the case of the low-temperature liquid-crystalline phases, an additional sharp peak was observed in the wide-angle region at ca. 4.4 Å, pointing to a long-range, hexatic order within the smectic layers, as expected for smectic B phases.

The *d*-layer spacings of **1** and **2** (Table 2), determined by

Table 2. Layer Spacings, Approximate Molecular Length, Molecular Volumes, and Cross-Sectional Areas of **1** and **2**

compd	phase	<i>d</i> (Å) ^a	<i>L</i> (Å) ^b	<i>d</i> / <i>L</i>	<i>V</i> (Å ³) ^c	<i>A</i> (Å ²) ^d
1	S _B	88.3 ^e	87.6	1.0	4470	100 ⁱ
	S _A	87.4 ^f		1.0	4522	100 ^j
2	S _B	76.8 ^g	87.5	0.87	3744	48.8 ^j
	S _A	78.4 ^h		0.89	3783	48.3 ^j

^a *d*-layer spacings determined by X-ray diffraction. ^b Molecular length estimated by Hyperchem software. ^c Molecular volume: *V* = (*M*/0.6022)(*V*_{CH₂}(*T*)/*V*_{CH₂}(*T*⁰)), where *M* is the molecular weight; *V*_{CH₂}(*T*) = 26.5616 + 0.02023*T* (*T* in °C, *T*⁰ = 22 °C), volume C₆₀ ≈ 700 Å³. ^d Molecular area. ^e At 120 °C. ^f At 140 °C. ^g At 110 °C. ^h At 125 °C. ⁱ See ref 5c. ^j *A* = *V*/*d*.

XRD, were compared to the molecular length in the extended conformation. The *d*-layer spacings found for **1** were close to the molecular length, giving rise to *d*/*L* ratios close to unity. For **2**, the *d*-layer spacings were smaller than the molecular length and led to *d*/*L* ratios of 0.87 and 0.89 in the smectic B and smectic A phases, respectively.

To describe the supramolecular organization of **1** and **2** within the smectic layers, it is necessary to take into account the cross-sectional areas of C₆₀ and of the mesogenic and TTF units (for efficient space filling).

The molecular area, *A*, calculated from the molecular volume and the layer periodicity, was compared to the area per mesogenic unit, *a*_m (i.e., area occupied by one terminal unit, ca. 20–24 Å²). It was found that for **2**, *A* does not change between the two mesophases and is equal to ca. 48–49 Å² (i.e., twice the expected cross section of one molten alkyl chain in orthogonal smectic phases). This result supports the assignment of the mesophases and confirms the elongated conformation of the molecules in both smectic phases with the peripheral anisotropic groups being almost perpendicular to the layers. Thus, the supramolecular organization of **2** can be explained as follows: the molecules adopt the extended conformation (as for dimer-type liquid crystals¹⁵) and are distributed in a head-to-tail disposition within the monolayers. Due to geometric constraints, the branched mesogenic groups should be tilted to match the molecular area of the two peripheral mesogens, the tilt order being short-range.¹⁶

By applying the same reasoning to **1**, one obtains a molecular area of 50–52 Å². Obviously, this value is not

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compatible with the molecular area of C₆₀ (ca. 100 Å²).^{5c} Therefore, to explain the supramolecular organization of **1**, we should consider two molecules in their extended conformation ($A' = 2V/d$) arranged in a head-to-tail fashion, with the C₆₀ units slightly shifted. Peripheral mesogenic groups of neighboring molecules from adjacent layers can fill empty gaps in an efficient way. With such a disposition, donor-acceptor interactions between C₆₀ and TTF units can take place, stabilizing the packing (TTF/C₆₀ interactions have been observed in the solid state¹⁷). This leads to an overall smectic layer structure in which the active moieties (C₆₀ and TTF) are confined in sublayers, separated from each other by organic outer layers. This strategy is a perfect illustration of the use of liquid crystals to confine active layers. Similar organizations were already proposed for other liquid-crystalline fullerenes.^{5c} Therefore, grafting of C₆₀ onto **2** induces a marked modification of the arrangement of the molecular units within the mesophases (monolayers for **2** and bilayers for **1**).

The electrochemical properties of **1**, **2**, and C₆₀ were studied by cyclic voltammetry (Table 3). Dyad **1** gave rise

Table 3. Cyclic Voltammetry Data at Room Temperature for Dyad **1**, Parent TTF **2**, and C₆₀^a

compd	E^1_{ox}	E^2_{ox}	E^1_{red}	E^2_{red}
C ₆₀			−0.54	−0.92
1	0.52	0.78	−0.60	−0.99
2	0.52	0.79		

^a Experimental conditions: dichloromethane, glassy carbon electrode as the working electrode, $E_{1/2}$ (V), Ag/AgCl as a reference, Bu₄NClO₄ (0.1 M), scan rate = 100 mV s^{−1}, room temperature.

to two quasi-reversible, one-electron reduction waves, which corresponded to the reduction of C₆₀.¹⁸ As expected, those reduction potentials are shifted to more negative values relative to C₆₀.¹⁹ This shift is due to the saturation of a double

bond in C₆₀, which raises the LUMO energy.^{19,20} Two reversible oxidation waves were observed, which corresponded to the formation of the radical cation and dication species of the TTF fragment. Those oxidation potentials are similar to those of **2** and of various tetraalkylthio-TTFs.²¹ Therefore, in **1**, both the donor and acceptor units preserve their individual electroactive identity.

In conclusion, the design of a liquid-crystalline dyad based on C₆₀ and TTF was successfully achieved. Photoinduced electron transfer studies are currently under investigation. The ultimate goal is the elaboration of photoactive molecular switches for which different supramolecular organizations could be obtained depending on the oxidation state of the TTF unit (light off, neutral species; light on, cationic species).

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Supporting Information Available: Synthetic procedures and analytical data of all new compounds and supramolecular organization of **1** and **2** within the smectic layers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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