[60] Fullerene-based liquid crystals acting as acid-sensitive fluorescent probes†‡

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Functionalization of [60]fullerene with liquid-crystalline dendrimers and a dibutylaniline-based phenylenevinylene moiety leads to supramolecular materials, the fluorescence of which responds to acid–base stimuli.

The design of organic materials which can be used for reversible optical data storage and for the construction of photochemical switches requires the synthesis and assembly of components, the physical properties of which can be modulated by light. Photonic processes display properties superior to those of electron processes for the following main reasons: (1) in the wavelength domain, multiple processing is achievable, (2) they present a high signal to noise ratio, and, more importantly, (3) since energy and electron transfer processes can occur on a subpicosecond timescale, it is possible to produce devices that respond with equal rapidity.

On the other hand, liquid crystals (LCs) are soft materials with great potential for sophisticated applications in advanced technologies. LCs exhibit unique properties such as self-organizing behavior within a precise temperature range or a change in refractive index by changing their alignment. Furthermore, LCs are of interest as supramolecular platforms in, e.g., solar cell technology (e.g., fullerene associated with oligophenylenevinylene derivatives) and for the development of photoactive switches (e.g., fullerene associated with ferrocene).

We report, herein, on the synthesis, liquid-crystalline properties, electrochemical and photophysical behavior of compounds 1a and 1b (Scheme 1) which contain three subunits, i.e. (1) a donor unit formed by two dibutylanilines located at the periphery of a phenylenevinylene-based dendron, (2) [60]fullerene (C_{60}) as an electron acceptor unit, and (3) a second- or third-generation poly(arylester) dendron carrying four or eight cyanobiphenyl mesogenic units, respectively, as a liquid-crystalline promoter. As we will see below, it is possible to control the fluorescence of both the donor and acceptor units by protonation.

The synthesis of 1a and 1b (Scheme 1) required the reaction of second- (4a) or third-generation (4b) dendron carrying a carboxylic acid function (Fig. 1) with thionyl chloride in CH_2Cl_2 to prepare the corresponding acid chlorides followed by their in situ condensation with fulleropyrrolidine 2 in CH_2Cl_2.

Fulleropyrrolidine 2 was prepared in 28% yield by [3 + 2] dipolar cycloaddition of C_{60} with the azomethine ylide generated in situ from aldehyde 3 and glycine in chlorobenzene. Aldehyde 3 was prepared in 91% yield using the

\[ 	ext{Scheme 1} \]

Reagents and conditions: (i) BuOK, THF, r.t., 2 h, then 1 M HCl, 91%; (ii) C_{60}, glycine, chlorobenzene, reflux, 6 h, 28%; (iii) 4a or 4b, thionyl chloride, CH_2Cl_2, reflux, 7 h, then 2, CH_2Cl_2, pyridine, r.t., 30 min, quantitative yields.

† Dedicated to the memory of our friend and colleague Professor Naomi Hoshino-Miyajima.
‡ Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/b808730j
The thermal and liquid-crystalline properties of 1a and 1b were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The phase transition temperatures and enthalpies are reported in Table 1. Compounds 4a and 4b display a smectic A phase.

Both 1a and 1b give rise to a smectic A phase, which was identified by POM from the observation of focal-conic and homeotropic textures when the sample was cooled from the isotropic fluid. As already observed for other fullerodendrimers bearing similar dendrons, the formation of the smectic A phase is due to the tendency of the cyanobiphenyl units to align parallel to one another to form lamellar phases. The clearing temperature increases with the dendrimer generation. This trend confirms that the stability of the mesophase increases with the number of mesogenic units.

The electrochemical features of 1a (Fig. S10) were probed by cyclic voltammetry at room temperature and compared with those of 2 (Fig. S11). As a general feature, both compounds give rise to three reversible one-electron reduction waves that reflect the first three one-electron reduction steps of the fullerene core. As expected, these reduction potential values are shifted to more negative values relative to pristine C60. Interestingly, the presence of the dendron (which is not electroactive in the observation window) in 1a, when compared with 2, gives C60 a higher electron affinity by ca. 70 mV (1a: $E_{\text{red}} = -1.02 \text{ V}$; 2: $E_{\text{red}} = -1.09 \text{ V}$), attributed to the $-I - K$ effects of the carbonyl group attached to the N-atom of the pyrroline ring. In the anodic scan, the N-butyl aniline groups show, in both 1a and 2, a non-reversible oxidation peak at 0.24 V. The results are summarized in Table 2.

Fig. 2 displays the UV–Vis spectra of 1a, 2 and 4a. As expected, the spectrum of 1a is the sum of the spectra of 2 and 4a.

![Fig. 1](image_url)  
**Fig. 1** Liquid-crystalline dendrimers of second (4a) and third (4b) generation.
Table 2  Redox potential data (CV) of 1a, 2, and C60

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{red}}^1 / V )</th>
<th>( E_{\text{ox}}^1 / V )</th>
<th>( E_{\text{red}}^2 / V )</th>
<th>( E_{\text{ox}}^2 / V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-1.02</td>
<td>1.42</td>
<td>-1.94</td>
<td>+0.24</td>
</tr>
<tr>
<td>2</td>
<td>-1.09</td>
<td>-1.48</td>
<td>-2.01</td>
<td>+0.24</td>
</tr>
<tr>
<td>C60</td>
<td>-0.98</td>
<td>-1.40</td>
<td>-1.89</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^{a}\) Solvent: o-dichlorobenzene–acetonitrile (4 : 1). V vs. Ag/AgNO3; glassy carbon electrode as the working electrode; 0.1 M TBAP; scan rate = 100 mV s\(^{-1}\); concentration: 1.4 \times 10^{-3} M.

**4a.** It should be noted that the mesogenic dendron 4a does not show absorption above 325 nm and is not excited in the fluorescence experiments described below.

The strong fluorescence at 498 nm shown by aldehyde 3,\(^{12}\) when excited at 380 nm in CH\(_2\)Cl\(_2\), is strongly quenched in 1a, 1b and 2. This result is consistent with an electron transfer process from the bis-(N,N-dibutylaminostyryl)benzene moiety to C\(_{60}\) as previously observed in related systems.\(^{12,13}\) No emission at 710 nm (ascribed to the fullerene cage) is observed under these conditions.

Upon addition of TFA to a solution of 1a, both the absorption (Fig. S12\(^{a}\)) and emission (Fig. 3) spectra are modified. Upon excitation at 336 nm (isosbestic point for the protonated and non-protonated species in the UV–Vis spectrum), the emission at 498 nm is quenched and a new emission appears at 710 nm due to an energy transfer process to C\(_{60}\); this process is reversible and addition of Et\(_3\)N allows an electron transfer process from the nitrogen electron pair to fullerene to be effective again (Fig. S13\(^{a}\)).

In conclusion, the acid-triggered “switch on” of emission intensity suggests that 1a and 1b might be useful acid-sensing fluorophore liquid crystals, the supramolecular organization of which can be controlled by the nature of the liquid-crystal-line dendrimers.

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**Notes and references**