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

Laura Pérez, Julie Lenoble, Joaquín Barberá, Pilar de la Cruz, Robert Deschenaux and Fernando Langa

Functionalization of [60]fullerene with liquid-crystalline dendrimers and a dibutylamidine-based phenylevinylene 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.¹ Photonic processes display properties superior to those of electron processes² 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.³ 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 oligophenylevinylene derivatives)⁴ and for the development of photoactive switches (e.g., fullerene associated with ferrocene).⁵

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 dibutylamines located at the periphery of a phenylevinylene-based dendron, (2) [60]fullerene (C₆₀) as an electron acceptor unit, and (3) a second- or third-generation poly(aryl ester) 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)⁶ or third-generation (4b)⁷ dendron carrying a carboxylic acid function (Fig. 1) with thionyl chloride in CH₂Cl₂ to prepare the corresponding acid chlorides followed by their in situ condensation with fulleropyrrolidine 2 in CH₂Cl₂.

Fulleropyrrolidine 2 was prepared in 28% yield by [3 + 2] dipolar cycloaddition of C₆₀ with the azomethine ylide⁸ generated in situ from aldehyde 3 and glycine in chlorobenzene. Aldehyde 3 was prepared in 91% yield using the

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* Dedicated to the memory of our friend and colleague Professor Naomi Hoshino-Miyajima.

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Scheme 1  Reagents and conditions: (i) 'BuOK, THF, r.t., 2 h, then 1 M HCl, 91%; (ii) C₆₀ glycine, chlorobenzene, reflux, 6 h, 28%; (iii) 4a or 4b, thionyl chloride, CH₂Cl₂, reflux, 7 h, then 2, CH₂Cl₂, pyridine, r.t., 30 min, quantitative yields.
Table 1 Phase transition temperatures and enthalpies of fullerodendrimers 1a and 1b*  

<table>
<thead>
<tr>
<th>Compd</th>
<th>$T_g$/°C</th>
<th>Transition</th>
<th>Temperature/°C</th>
<th>$\Delta H$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>53</td>
<td>SmA $\rightarrow$ I</td>
<td>137</td>
<td>11.4</td>
</tr>
<tr>
<td>1b</td>
<td>40</td>
<td>SmA $\rightarrow$ I</td>
<td>197</td>
<td>30.7</td>
</tr>
</tbody>
</table>

* $T_g$ = glass transition temperature, SmA = smectic A phase, I = isotropic liquid. Temperatures (onset of the peaks) and $T_g$s were obtained during the second heating run (rate: 10 °C min$^{-1}$).
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 CH₂Cl₂, 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 C₆₀ as previously observed in related systems.12 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) 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 from the conjugated system to C₆₀.14 This process is reversible and addition of Et₃N allows an electron transfer process from the nitrogen electron pair to fullerene to be effective again (Fig. S13).

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-crystalline dendermers.

Financial support from Ministerio de Educación y Ciencia of Spain, FEDER funds (Projects CTQ2007-63363/PPQ, CTQ2006-15611-C02-01/BQU and Consolider project HOPE CSD2007-00007) and the Junta de Comunidades de Castilla-La Mancha (Project PC108-038) is gratefully acknowledged.

### Table 2 Redox potential data (CV) of 1a, 2, and C₆₀

<table>
<thead>
<tr>
<th></th>
<th>E⁺⁺ vs. C₀/C₀</th>
<th>E⁺⁺ vs. C₀/C₀</th>
<th>E⁺⁺ vs. C₀/C₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>–1.02</td>
<td>1.42</td>
<td>–1.94</td>
</tr>
<tr>
<td>2</td>
<td>–1.09</td>
<td>–1.48</td>
<td>–2.01</td>
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<tr>
<td>C₆₀</td>
<td>–0.98</td>
<td>–1.40</td>
<td>–1.89</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 × 10⁻³ M.

### Notes and references