

[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.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.

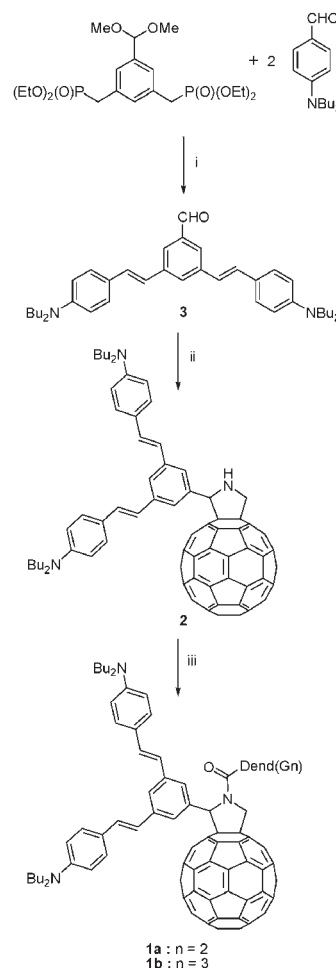
On the other hand, liquid crystals (LCs) are soft materials with great potential for sophisticated applications in advanced technologies.³ LCs exhibit unique properties such as self-organizing behavior within a precise temperature range or a change in refractive index by changing their alignment. Furthermore, LCs are of interest as supramolecular platforms in, *e.g.*, solar cell technology (*e.g.* fullerene associated with oligophenylenevinylene 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 dibutylanilines located at the periphery of a phenylenevinylene-based dendron, (2) [60]fullerene (C₆₀) 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**)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



Scheme 1 Reagents and conditions: (i) ^tBuOK, 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.

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

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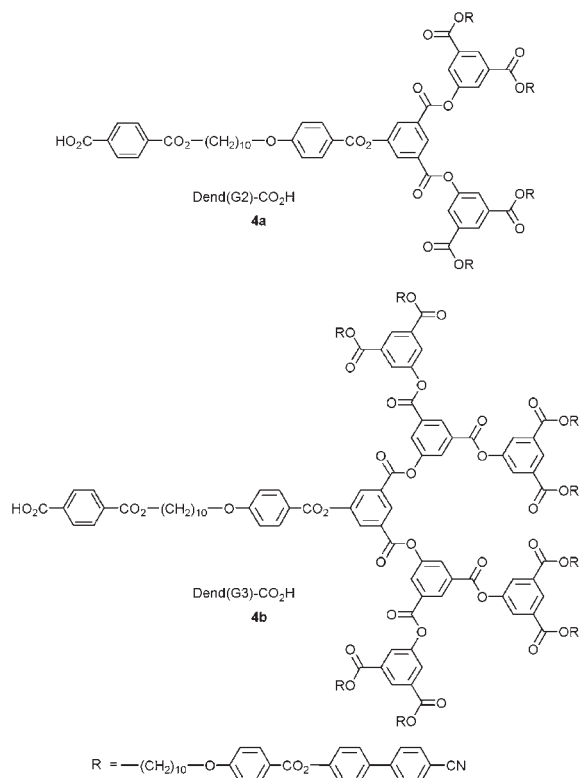


Fig. 1 Liquid-crystalline dendrimers of second (**4a**) and third (**4b**) generation.

Horner–Wadsworth–Emmons reaction between 3,5-bis-(diethoxyphosphorylmethyl)benzaldehyde dimethyl acetal and 4-(dibutylamino)benzaldehyde.⁹

All new compounds were characterized by ¹H, ¹³C NMR and FTIR spectroscopy, and MALDI-TOF mass spectrometry (see ESI†).

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**⁶ and **4b**⁷ 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.¹⁰ The clearing temperature increases with the dendrimer generation. This trend confirms that the stability of the mesophase increases with the number of mesogenic units.¹¹

Table 1 Phase transition temperatures and enthalpies of fullerodendrimers **1a** and **1b**^a

Compd	$T_g/^\circ\text{C}$	Transition	Temperature/ $^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
1a	53	SmA → I	137	11.4
1b	40	SmA → I	197	30.7

^a 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: $10^\circ\text{C min}^{-1}$).

The smectic nature of the mesophases was confirmed by X-ray diffraction both at room temperature and 80°C . The X-ray patterns recorded for compound **1a** contain two sharp maxima in the small-angle region with a reciprocal spacing ratio of 1 : 2. This ratio is characteristic of lamellar systems and the two maxima correspond to the first and second order reflections, respectively. By applying Bragg's law to these reflections, d -layer spacings of 96 and 97 \AA were obtained at room temperature and 80°C , respectively. The X-ray patterns recorded for compound **1b** contain two small-angle sharp maxima in a reciprocal spacing ratio of 1 : 4. In spite of being different from those described for **1a**, this pattern is also consistent with a layered mesophase. The two maxima correspond to the first and fourth order reflections, respectively, and give d -layer spacings of 104 and 105 \AA at room temperature and 80°C , respectively. Apart from these features, the X-ray patterns of both compounds do not exhibit any other reflections, except for a diffuse scattering halo in the wide-angle region which is characteristic of the liquid-like arrangement of the mesomorphic groups. The diffraction patterns did not change significantly after thermal treatment of the samples, which were heated up to the isotropic liquid and then cooled down to room temperature, or at different temperatures above the glass transition.

The molecular lengths (L) of **1a** and **1b** were estimated in their extended conformation using HyperChem software, and were found to be about 75 and 79 \AA for **1a** and **1b**, respectively. Thus, the calculated d/L ratio is about 1.29 for **1a** and 1.33 for **1b** at 80°C . Those values suggest that the molecules adopt a bilayer organization similar to that reported for other fullerene-containing liquid crystals based on similar dendrons.¹¹ The molecules are located face to face in the layers and, for each molecule, the cyanobiphenyl units point in the same direction and are interdigitated with the cyanobiphenyl units of the neighboring layer. The C_{60} and donor groups are located in the central slab of the layer. Thus, the resulting organization consists of alternating sublayers containing the C_{60} moieties, the donor units and the mesogenic units. The fact that the layer thickness practically does not change with temperature is in agreement with the smectic A nature of the mesophase and suggests that the temperature has no significant effect on the molecular conformation or supramolecular organization.

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 C_{60} . Interestingly, the presence of the dendron (which is not electroactive in the observation window) in **1a**, when compared with **2**, gives C_{60} a higher electron affinity by *ca.* 70 mV (**1a**: $E_{\text{red}}^1 = -1.02\text{ V}$; **2**: $E_{\text{red}}^1 = -1.09\text{ V}$), attributed to the $-I$, $-K$ effects of the carbonyl group attached to the N-atom of the pyrrolidine 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

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

	$E_{\text{red}}^1/\text{V}$	$E_{\text{red}}^2/\text{V}$	$E_{\text{red}}^3/\text{V}$	E_{ox}^1/V
1a	-1.02	1.42	-1.94	+0.24
2	-1.09	-1.48	-2.01	+0.24
C ₆₀	-0.98	-1.40	-1.89	—

^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.

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.^{12,13} 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[†]) 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 dendrimers.

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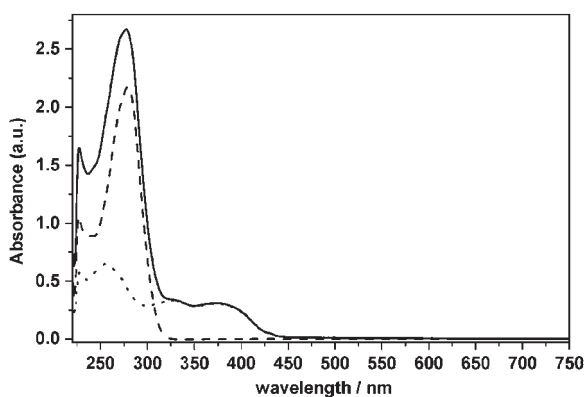


Fig. 2 Absorption spectra of fulleropyrrolidines **1a** (—), **2** (---) and **4a** (···).

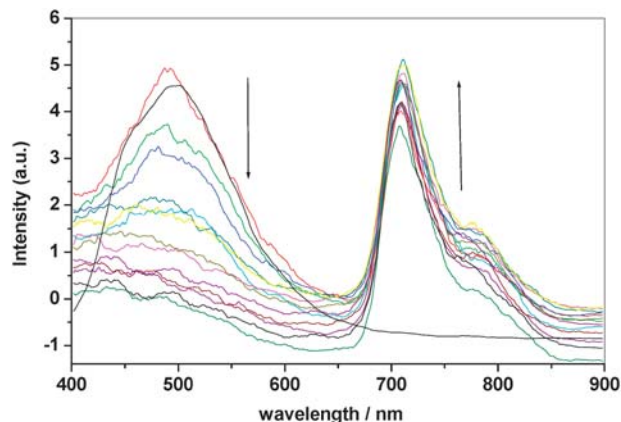


Fig. 3 Emission spectra of fulleropyrrolidine **1a** in dichloromethane upon addition of TFA ($\lambda_{\text{exc}} = 336$ nm).

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