

## Liquid-crystalline fullerene–oligophenylenevinylene conjugates

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### Functionalization of C<sub>60</sub>–oligophenylenevinylene derivatives with a cyanobiphenyl-terminated dendromesogen leads to new donor–acceptor systems with liquid-crystalline properties.

The synthesis and study of fullerene derivatives bearing  $\pi$ -conjugated oligomers have attracted considerable attention in recent years.<sup>1–3</sup> In particular, exploitation of their electronic properties for solar energy conversion has become a field of intense investigations.<sup>2,3</sup> For example, photovoltaic devices using thin films of fullerene–oligophenylenevinylene (C<sub>60</sub>–OPV) conjugates have shown promise for large area photo-detectors and solar cells.<sup>2,3</sup> This molecular approach is attractive for two major reasons: (1) it allows a detailed structure–activity exploration which will improve our understanding of the photovoltaic systems,<sup>2</sup> and (2) it offers the possibility of controlling the morphology of the organic film in the devices.<sup>4</sup> With this in mind, the use of liquid-crystalline C<sub>60</sub>–OPV conjugates could be of particular interest since such materials would spontaneously form ordered assemblies that could then be oriented and lead to high-performance thin films.

Recently, we have prepared liquid-crystalline fulleropyrrolidines from a dendritic mesomorphic aldehyde derivative (compound **5** in Fig. 1), C<sub>60</sub> and sarcosine.<sup>5</sup> The versatility of the 1,3-dipolar cycloaddition reaction<sup>6</sup> is an ideal platform for the introduction of various functional groups onto mesomorphic

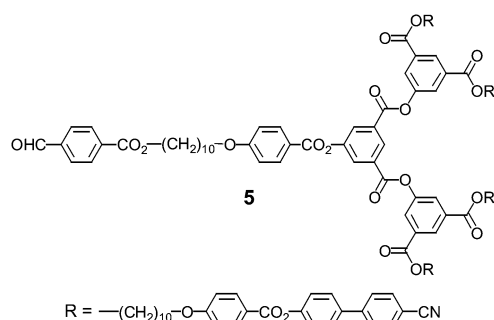
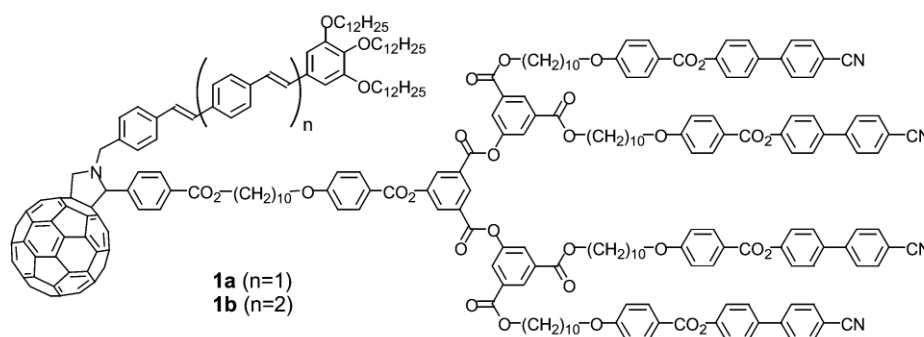


Fig. 1 Structure of the liquid-crystalline promoter **5**.



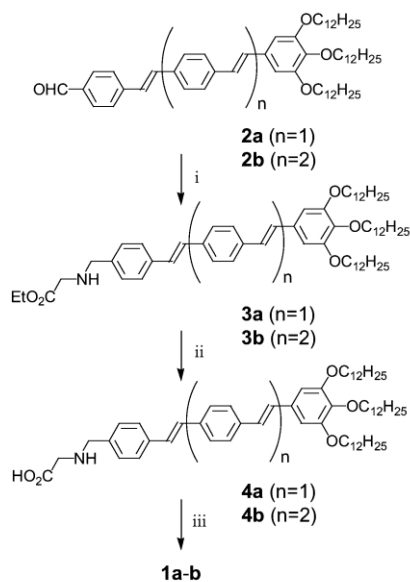
fullerenes. Therefore, we decided to apply this strategy for the design of new liquid-crystalline fullerenes bearing OPV frameworks. We describe, herein, the synthesis, mesomorphic behavior and optical properties of the C<sub>60</sub>–OPV derivatives **1a,b**.

The synthesis of **1a,b** is depicted in Scheme 1. Reductive amination of **2a,b** with glycine ethyl ester hydrochloride followed by saponification of the resulting **3a,b** furnished the carboxylic acid intermediates **4a,b**, which after treatment with aldehyde **5** (Fig. 1) and C<sub>60</sub> in refluxing toluene gave **1a,b**. The structure and purity of all new compounds were confirmed by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy, mass spectrometry and elemental analysis.<sup>†</sup>

The UV-Vis spectra of **1a,b** correspond to the sum of the spectra of their component units indicating that there are no significant intramolecular ground state interactions between the chromophores. Interestingly, preliminary luminescence measurements in CH<sub>2</sub>Cl<sub>2</sub> solutions show a dramatic quenching of the OPV fluorescence by the fullerene unit in both derivatives upon selective excitation at the OPV band maximum (**1a**: 367 nm; **1b**: 389 nm). The latter observation indicates the occurrence of intramolecular photoinduced processes, thus showing that **1a,b** are suitable candidates for photovoltaic applications.<sup>2,3</sup>

The liquid-crystalline and thermal properties of **1a,b** have been examined by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). Fullerene derivatives **1a** ( $T_g \sim 50$  °C; S<sub>A</sub> → I: 171 °C,  $\Delta H = 22$  kJ mol<sup>-1</sup>) and **1b** ( $T_g \sim 50$  °C; S<sub>A</sub> → I: 169 °C,  $\Delta H = 19$  kJ mol<sup>-1</sup>) gave rise to liquid-crystalline properties. The mesophases have been identified by POM: slow cooling of the samples from the isotropic melt revealed the formation of small focal conics and large homeotropic areas, typical of smectic A phases. Compounds **1a,b** exhibit similar results indicating that the overall behavior is mainly governed by the dendritic framework in good agreement with results obtained for other fullerene-containing liquid-crystalline dendrimers.<sup>5,8,9</sup>

The mesomorphism of **1a,b** was confirmed by XRD. For **1b**, a typical signature of a disordered smectic type organization has been obtained. As depicted in Fig. 2, the X-ray diffraction pattern recorded at 140 °C shows a diffuse reflection in the wide angle region at *ca.* 4.5 Å and three sharp peaks in the small angle region corresponding to lateral distances between the meso-

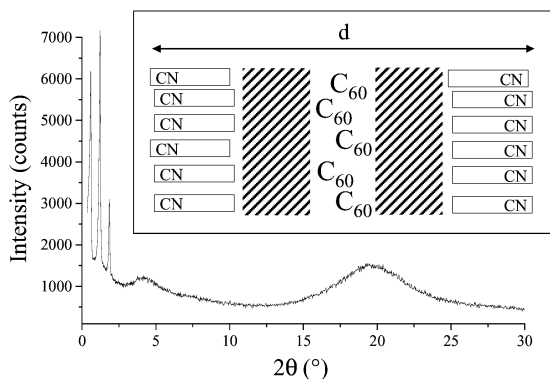


**Scheme 1** Reagents and conditions: i, glycine ethyl ester hydrochloride,  $\text{Et}_3\text{N}$ ,  $\text{EtOH}$ - $\text{THF}$ , overnight, room temp.; then  $\text{NaBH}_4$ , 1 h,  $0\text{ }^\circ\text{C}$ , **3** ( $n = 1$ ): 60%, **3** ( $n = 2$ ): 56%; ii, aq.  $\text{NaOH}$ ,  $\text{EtOH}$ - $\text{THF}$ , room temp., 1 h, **4** ( $n = 1$ ): 63%, **4** ( $n = 2$ ): 92%; iii, aldehyde **5** (see Fig. 1),  $\text{C}_{60}$ , toluene, overnight, reflux, **1** ( $n = 1$ ): 46%, **1** ( $n = 2$ ): 31%.

genic cyanobiphenyl units and to the smectic layering, respectively. The layer spacing thus determined,  $d = 142\text{ \AA}$ , indicates a bilayered arrangement of the molecules within the smectic layer, on the basis of the molecular dimensions deduced from molecular modeling studies. Such a bilayered organization is driven by the strong dipole-dipole interactions between cyano groups, as found in the smectic  $A_2$  phase of low molecular weight cyano liquid-crystalline compounds.<sup>10</sup>

It should be emphasized that the intensity of the second order reflection is stronger than that of the first order one. This indicates the presence of a sublayer with a high electronic density located in the middle of the smectic layer, this sublayer obviously contains the fullerene units. The smectic layer is thus formed by three alternating sublayers: the fullerene and the cyanobiphenyl ones being separated by an intermediate layer formed by the aromatic and aliphatic spacers, as schematically shown in Fig. 2. Finally, the X-ray diffraction pattern of **1b** shows the presence of an additional diffuse reflection corresponding to a distance of about  $22\text{ \AA}$ . This corresponds presumably to a periodicity parallel to the smectic planes and should be analyzed in more detail, specifically with the help of oriented samples.

Concerning **1a**, its mesomorphic behaviour is also confirmed by the presence of a diffuse band at  $4.5\text{ \AA}$  in the wide-angle region of the X-ray diffraction pattern. However, the small angle region is characterised by a series of sharp reflections which indicate a more complex supramolecular organisation



**Fig. 2** X-Ray diffraction pattern of **1b** recorded at  $140\text{ }^\circ\text{C}$ . Insert: schematic representation of a smectic layer (the rectangles are for the cyano mesogenic groups, and the oblique lines for the aromatic and aliphatic spacers).

than the lamellar arrangement of **1b**, and requires additional experiments for a complete description.

In conclusion, we have shown that the functionalisation of  $\text{C}_{60}$ -OPV conjugates with a dendritic mesogenic group allows the liquid-crystalline ordering of such donor-acceptor systems which present all the characteristic features required for photovoltaic applications. Incorporation of compounds **1a,b** in solar cells is now under investigation.

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## Notes and references

†† Selected analytical data. For **1a**:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (t,  $J = 1.5$ , 1 arom. H), 8.64 (t,  $J = 1.5$ , 2 arom. H), 8.35 (d,  $J = 1.5$ , 2 arom. H), 8.16 (d,  $J = 8.5$ , 2 arom. H), 8.14 (d,  $J = 9.0$ , 10 arom. H), 8.11 (d,  $J = 1.5$ , 4 arom. H), 8.05–7.95 (br, 2 arom. H, in  $d_8$ -toluene,  $60\text{ }^\circ\text{C}$ ), 7.75–7.60 (series of d, 28 arom. H), 7.55–7.45 (m, 4 arom. H), 7.32 (d,  $J = 8.5$ , 8 arom. H), 7.19 (s, 2 vinyl. H), 7.06–6.96 (d,  $J = 9.0$ , 10 arom. H + m, 2 vinyl. H), 6.73 (s, 2 arom. H), 5.31 (s, 1H, pyrrolidine), 4.96 (d,  $J = 9.5$ , 1H, pyrrolidine), 4.58 (d,  $J = 13.0$ , 1 benzyl. H), 4.36 (t,  $J = 6.5$ , 8H, isoph.  $-\text{CO}_2\text{CH}_2$ ), 4.32 (t,  $J = 7.0$ , 2H, benz- $\text{CO}_2\text{CH}_2$ ), 4.26 (d,  $J = 9.5$ , 1H, pyrrolidine), 4.03 (t,  $J = 6.5$ , 14H, 7  $\text{CH}_2\text{O}$ ), 3.98 (t,  $J = 6.5$ , 2H,  $\text{OCH}_2$ ), 3.82 (d,  $J = 14.0$ , 1 benzyl. H), 1.85–1.72 (m, 26H,  $\text{CO}_2\text{CH}_2\text{CH}_2$  and  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.47–1.27 (m, 114 aliph. H), 0.88 (t,  $J = 6.5$ , 9H,  $\text{CH}_3$ ). UV-Vis ( $\lambda_{\text{max}}$  in nm ( $\epsilon$  in  $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ),  $\text{CH}_2\text{Cl}_2$ ): 271 (288000), 367 (78600), 430 (4150), 701 (330). FAB-MS: 4315.7 ( $\text{MH}^+$ ). Anal. calcd. for  $\text{C}_{289}\text{H}_{259}\text{N}_5\text{O}_{32}$  (4314.24): C, 80.46; H, 6.05; N, 1.62%. Found: C, 80.67; H, 6.15; N 1.63%.

For **1b**:  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (t,  $J = 1.5$ , 1 arom. H), 8.64 (t,  $J = 1.5$ , 2 arom. H), 8.35 (d,  $J = 1.5$ , 2 arom. H), 8.16 (d,  $J = 8.5$ , 2 arom. H), 8.14 (d,  $J = 9.0$ , 10 arom. H), 8.11 (d,  $J = 1.5$ , 4 arom. H), 7.95–7.85 (br, 2 arom. H, in  $d_8$ -toluene,  $60\text{ }^\circ\text{C}$ ), 7.74–7.60 (series of d, 30 arom. H), 7.56–7.47 (m, 6 arom. H), 7.32 (d,  $J = 8.5$ , 8 arom. H), 7.19 (s, 2 vinyl. H), 7.13 (s, 2 vinyl. H), 7.06–6.96 (d,  $J = 9.0$ , 10 arom. H + m, 2 vinyl. H), 6.73 (s, 2 arom. H), 5.26 (s, 1H, pyrrolidine), 4.89 (d,  $J = 9.5$ , 1H, pyrrolidine), 4.53 (d,  $J = 13.5$ , 1 benzyl. H), 4.36 (t,  $J = 6.5$ , 8H, isoph.  $-\text{CO}_2\text{CH}_2$ ), 4.31 (t,  $J = 6.5$ , 2H, benz- $\text{CO}_2\text{CH}_2$ ), 4.20 (d,  $J = 9.5$ , 1H, pyrrolidine), 4.03 (t,  $J = 6.5$ , 14H, 7  $\text{CH}_2\text{O}$ ), 3.98 (t,  $J = 6.5$ , 2H,  $\text{OCH}_2$ ), 3.71 (d,  $J = 13.0$ , 1 benzyl. H), 1.87–1.76 (m, 26H,  $\text{CO}_2\text{CH}_2\text{CH}_2$  and  $\text{CH}_2\text{CH}_2\text{O}$ ), 1.46–1.27 (m, 114 aliph. H), 0.89 (t,  $J = 6.5$ , 9H,  $\text{CH}_3$ ). UV-Vis ( $\lambda_{\text{max}}$  in nm ( $\epsilon$  in  $\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ),  $\text{CH}_2\text{Cl}_2$ ): 272 (322100), 389 (108400), 701 (380). MALDI-TOF-MS: 4418.4 ( $\text{MH}^+$ ). Anal. Calcd. for  $\text{C}_{297}\text{H}_{265}\text{N}_5\text{O}_{32}$  (4416.37): C, 80.77; H, 6.05; N, 1.59%. Found: C, 80.69; H, 6.00; N, 1.56%.

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