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Liquid-crystalline fullerene–oligophenylenevinylene conjugates

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Received (in Cambridge, UK) 20th December 2001, Accepted 28th January 2002

First published as an Advance Article on the web 27th February 2002

Functionalization of C_{60}–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 π-conjugated oligomers have attracted considerable attention in recent years.[1–3] In particular, exploitation of their electronic properties for solar energy conversion has become a field of intense investigations.[2,3] For example, photovoltaic devices using thin films of fullerene–oligophenylenevinylene (C_{60}–OPV) conjugates have shown promise for large area photodetectors and solar cells.[2,3] 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,[2] and (2) it offers the possibility of controlling the morphology of the organic film in the devices.[4] With this in mind, the use of liquid-crystalline C_{60}–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_{60} and sarcosine.[5] The versatility of the 1,3-dipolar cycloaddition reaction[6] is an ideal platform for the introduction of various functional groups onto mesomorphic 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_{60}–OPV derivatives **1a**,**b**.

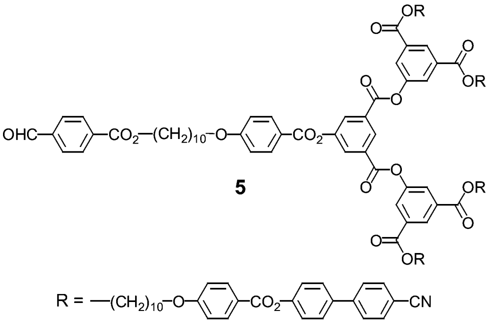


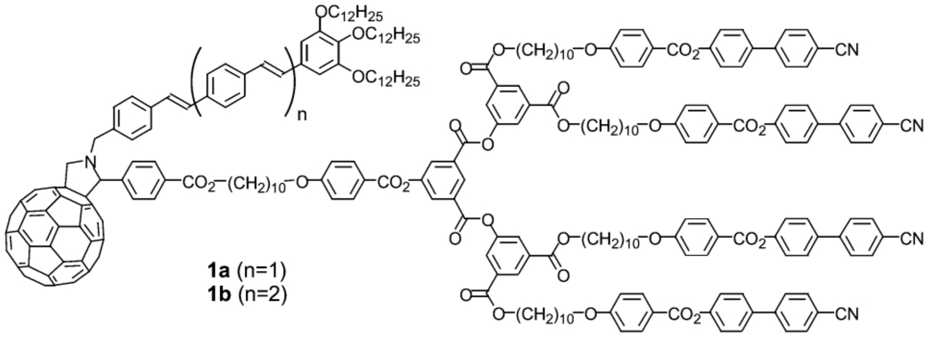
Fig. 1 Structure of the liquid-crystalline promoter **5**.

The synthesis of **1a**,**b** is depicted in Scheme 1. Reductive amination of **2a**,**b**[7] 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_{60} in refluxing toluene gave **1a**,**b**. The structure and purity of all new compounds were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry and elemental analysis.†

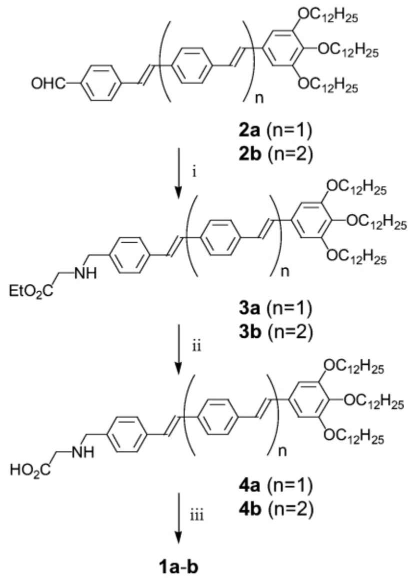
The UV-Vis spectra of **1a**,**b** correspond to the sum of the spectra of their component units indicating that there are no significant intramolecular ground state interactions between the chromophores. Interestingly, preliminary luminescence measurements in CH_2Cl_2 solutions show a dramatic quenching 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.[2,3]

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 ~ 50 °C; $S_A \rightarrow I$: 171 °C, ΔH = 22 kJ mol^{-1}) and **1b** (T_g ~ 50 °C; $S_A \rightarrow I$: 169 °C, ΔH = 19 kJ mol^{-1}) 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.[5,8,9]

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-



DOI: 10.1039/b111595b



Scheme 1 *Reagents and conditions:* i, glycine ethyl ester hydrochloride, Et_3N, EtOH–THF, overnight, room temp.; then $NaBH_4$, 1 h, 0 °C, **3** (n = 1): 60%, **3** (n = 2): 56%; ii, aq. NaOH, EtOH–THF, room temp., 1 h, **4** (n = 1): 63%, **4** (n = 2): 92%; iii, aldehyde **5** (see Fig. 1), 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 Å, 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.[10]

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

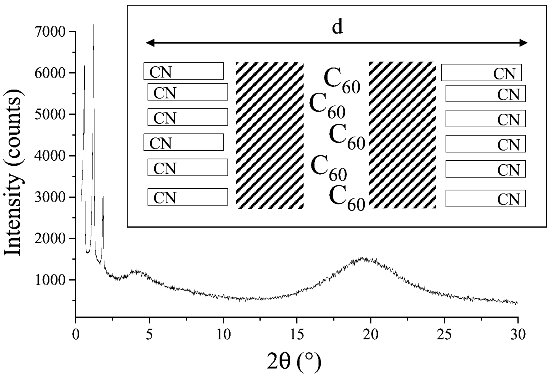


Fig. 2 X-Ray diffraction pattern of **1b** recorded at 140 °C. Insert: schematic representation of a smectic layer (the rectangles are for the cyano mesogenic groups, and the oblique lines for the aromatic and aliphatic spacers).

In conclusion, we have shown that the functionalisation of 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.

We thank B. Heinrich for his help with the X-ray measurements and L. Oswald for technical assistance. RD acknowledges the Swiss National Science Foundation for financial support (grant No 20-58956.99). The French–Swiss international program of scientific collaboration PICS No. 742 is also gratefully acknowledged.

Notes and references

† † *Selected analytical data*. For **1a**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 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°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. -CO_2CH_2), 4.32 (t, J = 7.0, 2H, benz-CO_2CH_2), 4.26 (d, J = 9.5, 1H, pyrrolidine), 4.03 (t, J = 6.5, 14H, 7 CH_2O), 3.98 (t, J = 6.5, 2H, OCH_2), 3.82 (d, J = 14.0, 1 benzyl. H), 1.85–1.72 (m, 26H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.47–1.27 (m, 114 aliph. H), 0.88 (t, J = 6.5, 9H, CH_3).UV-Vis (λ_{max} in nm (ε in dm^3 mol^{-1} cm^{-1}), CH_2Cl_2): 271 (288000), 367 (78600), 430 (4150), 701 (330). FAB-MS: 4315.7 (MH^+). Anal. calcd. for $C_{289}H_{259}N_5O_{32}$ (4314.24): C, 80.46; H, 6.05; N, 1.62%. Found: C, 80.67; H, 6.15; N 1.63%.

For **1b**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 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 °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. -CO_2CH_2), 4.31 (t, J = 6.5, 2H, benz-CO_2CH_2), 4.20 (d, J = 9.5, 1H, pyrrolidine), 4.03 (t, J = 6.5, 14H, 7 CH_2O), 3.98 (t, J = 6.5, 2H, OCH_2), 3.71 (d, J = 13.0, 1 benzyl. H), 1.87–1.76 (m, 26H, $CO_2CH_2CH_2$ and CH_2CH_2O), 1.46–1.27 (m, 114 aliph. H), 0.89 (t, J = 6.5, 9H, CH_3). UV-Vis (λ_{max} in nm (ε in dm^3 mol^{-1} cm^{-1}), CH_2Cl_2): 272 (322100), 389 (108400), 701 (380). MALDI-TOF-MS: 4418.4 (MH^+). Anal. Calcd. for $C_{297}H_{265}N_5O_{32}$ (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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