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Calix[4]oligophenylenevinylene: a new rigid core for the design of π-conjugated liquid crystalline derivatives

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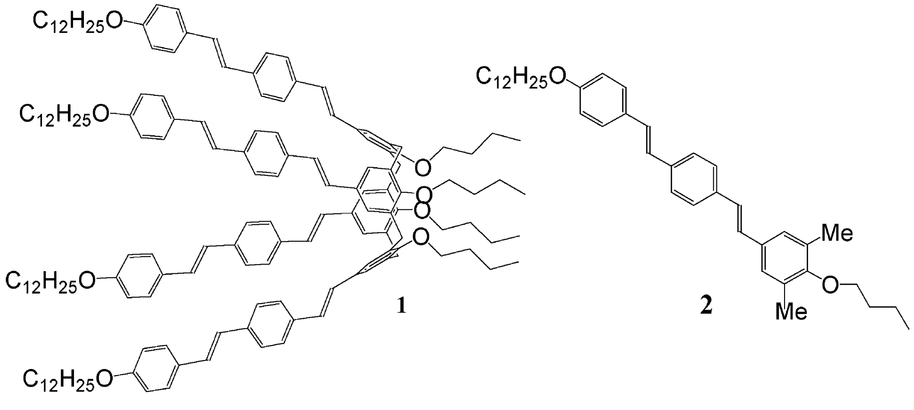
Abstract—The synthesis and the liquid crystalline properties of a new class of conjugated derivatives that assembled four oligophenylenevinylene (OPV) moieties arising from a calix[4]arene core are described. Photophysical investigations also revealed strong electronic coupling between the four OPV fragments of the calix[4]OPV derivative. © 2001 Elsevier Science Ltd. All rights reserved.

Organic semiconducting materials have been extensively investigated in the past few years for their electronic properties,[1] and structural studies of these kind of compounds appear today as an important issue in their applications. Actually, in light-emitting diodes (LEDs)[2] or photovoltaic devices,[3] the functional characteristics are affected by the morphology of the organic films.[4] For the purpose of gaining insight into the relationship between the morphology of the thin films and the electroluminescence or the charge-transport properties, π-conjugated derivatives exhibiting liquid crystalline properties are of particular interest[5] because they spontaneously form ordered assemblies that can be easily oriented. As part of this research, we now report the synthesis and the liquid crystalline properties of a new strongly luminescent conjugated derivative that assembles four oligophenylenevinylene (OPV) moieties arising from a calix[4]arene core. We also show that the electronic properties of the calix[4]oligophenylenevinylene derivative **1** are not directly related to the corresponding OPV model compound **2**, suggesting strong electronic coupling between the four OPV fragments of the calix[4]OPV derivative.

The synthesis of the calix[4]OPV derivative **1** is depicted in Scheme 1. Reaction of 4-hydroxybenzyl alcohol (**3**) with 1-bromododecane in DMF at 70°C in the presence of K_2CO_3, followed by oxidation of the resulting 4-



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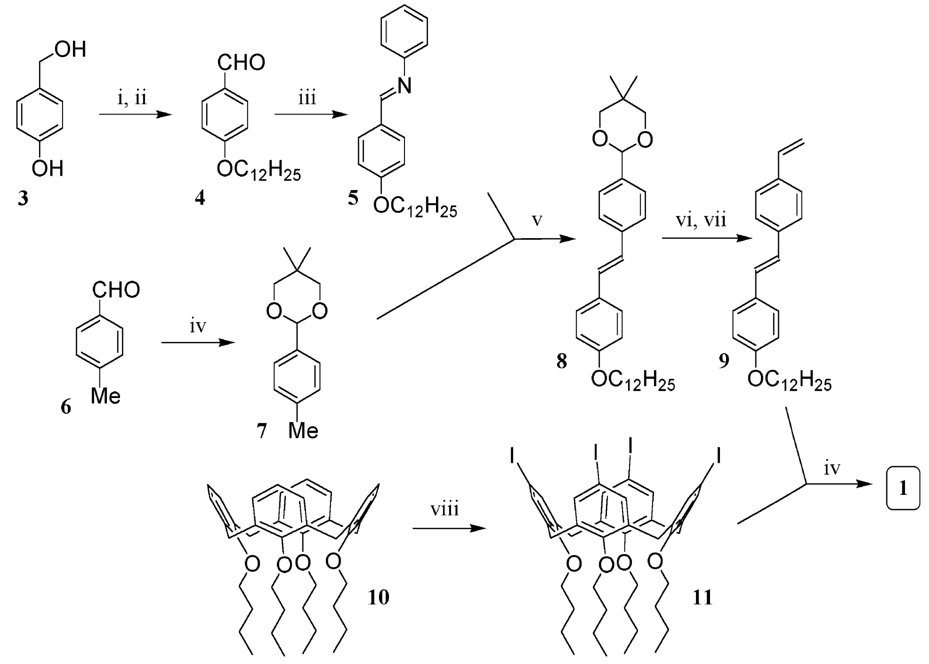

Scheme 1. *Reagents and conditions*: (i) 1-bromododecane, K_2CO_3, DMF, 70°C, 24 h (80%); (ii) MnO_2, CH_2Cl_2, rt, 3 h (83%); (iii) aniline, C_6H_6, Δ, 24 h (80%); (iv) 2,2-dimethylpropane-1,3-diol, *p*-TsOH, C_6H_6, Δ, 24 h (96%); (v) *t*-BuOK, DMF, 80°C, 2 h (50%); (vi) CF_3CO_2H, H_2O, CH_2Cl_2, rt, 5 h (99%); (vii) methyl triphenylphosphonium bromide, *t*-BuOK, THF, rt (80%); (viii) CF_3CO_2Ag, I_2, $CHCl_3$, Δ, 3 h (91%); (iv) $Pd(OAc)_2$, tri-*o*-tolylphosphine, Et_3N, xylene, Δ, 48 h (68%).

dodecyloxybenzyl alcohol with MnO_2 in CH_2Cl_2, yielded **4** in an overall 66% yield. Subsequent condensation of benzaldehyde **4** with aniline in refluxing benzene afforded benzaldimine **5** in 80% yield. Reaction of *p*-tolualdehyde (**6**) with 2,2-dimethylpropane-1,3-diol in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) gave the protected aldehyde **7** in 96% yield. Benzaldimine **5** was subjected to the Siegrist reaction with compound **7** to give protected stilbene **8** in 50% yield. Subsequent treatment with CF_3CO_2H in CH_2Cl_2/H_2O and reaction of the resulting aldehyde with methyl triphenylphosphonium bromide under Wittig conditions afforded **9** in an overall 80% yield. Treatment of the tetra-*O*-alkylated cone calix[4]arene **10**[6] with iodine in the presence of CF_3CO_2Ag in refluxing $CHCl_3$ yielded **11** in 91% yield. For both **10** and **11**, the cone conformation was deduced from the ^1H and ^{13}C NMR spectra. In particular, the ^{13}C NMR chemical shifts (around δ 31 ppm) of the methylene groups connecting the aromatic rings were in good agreement with a cone conformation, as previously shown in the literature.[7] Calix[4]OPV **1** was then obtained in 68% yield from **9** and **11** under Heck type cross-coupling conditions. In the ^1H NMR spectrum of **1**, all the anticipated signals were present but some of them were large. The broadening observed in the spectrum of **1** suggests the existence of several conformers. Indeed, due to conjugation, the OPV moieties of **1** are not perpendicular to the calixarene core and restricted rotation can easily be explained by the tendency of the OPV moieties to stay in an extended planar conjugated conformation.[8] Therefore, two diametrically opposite OPV units can either be in an eclipsed or a staggered relative orientation. Free rotation of the four substituents on the upper rim of the calix[4]arene core is necessary to produce an NMR spectrum with sharp symmetric signals. A study of the temperature-dependent NMR spectrum shows a narrowing of some signals at 120°C, but a sharp symmetric spectrum could not be obtained below the maximum measurement temperature.

The absorption spectrum of **1** in CH_2Cl_2 solution is significantly different (both in shape and intensity) from that obtained by summing four model units **2** (Fig. 1). Compounds **1** and **2** display the typical intense fluores-

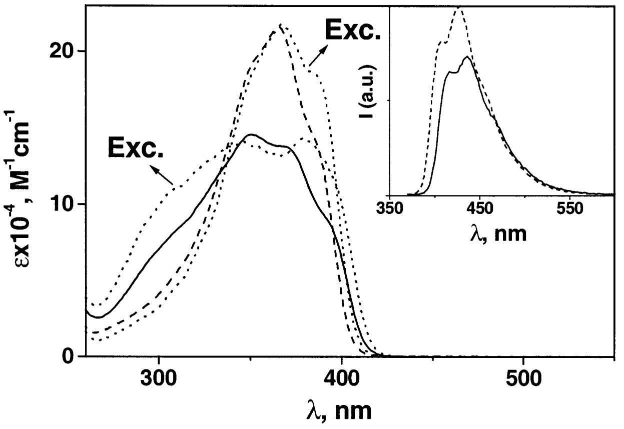

Figure 1. Absorption spectra of **2** (dashed line, multiplied by a factor of four) and **1** (full line). Inset: fluorescence spectra of optically matched solutions of **2** (dashed line) and **1** (full line); $\lambda_{exc}=365$ nm, O.D. = 0.17. The dotted lines represent the excitation spectra. All the experiments were carried out in CH_2Cl_2 solutions at 298 K.

Table 1. Luminescence data in CH_2Cl_2[a]

	298 K			77 K	
	λ_{max} (nm)	τ^b (ns)	Φ_{em}	λ_{max} (nm)	τ^b (ns)
1	436	1.0	0.61	425	1.0 (90%), 4.2 (10%)
2	428	1.0	0.81	412	1.2 (85%), 5.6 (15%)

[a] The fluorescence spectra and quantum yields were obtained upon excitation on the absorption maxima.

[b] $\lambda_{exc}=337$ nm, single photon counting apparatus.[3b]

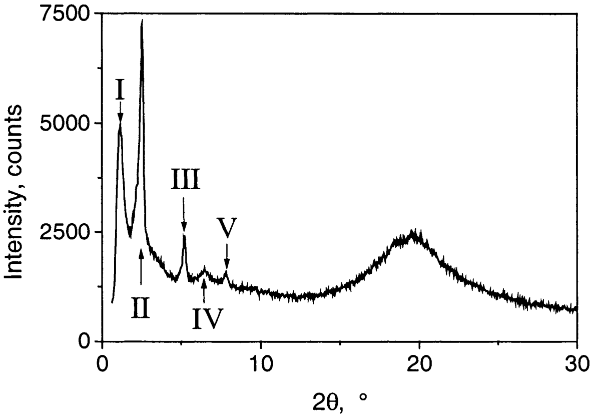

Figure 2. X-ray diffraction pattern of **1** recorded at 160°C.

cence of OPV's in CH_2Cl_2 both at 298 K and in a rigid 77 K matrix (Table 1). The luminescence lifetimes at room temperature are monoexponential (1.0 ns), whereas at 77 K biexponential decays are recorded (Table 1), probably as a consequence of the presence of different 'frozen' rotameric forms in the solid matrix.[3b] The luminescence spectra of **1** and **2** are qualitatively similar; however, it is worth pointing out that the fluorescence maxima of the calix[4]OPV is slightly red-shifted and the emission quantum yield lower (Table 1). The differences in the absorption and luminescence properties of **1** and **2** seem to suggest that interchromophoric interactions in the calix[4]OPVs take place.[9]

The liquid crystalline properties of compound **1** have been studied by differential scanning calorimetry (DSC), X-ray diffraction and optical investigations. Polarized optical microscopy observations revealed the slow apparition of a fluid birefringent phase at 140°C corresponding to the transition from an amorphous solid into a liquid crystalline phase. The clearing point was determined to be 180°C. Whereas the birefringent optical texture was non-characteristic on cooling the sample from the liquid isotropic phase, the X-ray diffraction patterns recorded for **1** were typical of a smectic type organization. As depicted in Fig. 2, the X-ray diffraction pattern shows a diffuse band in the wide angle region at ca. 4.5 Å and five sharp diffraction peaks (I–V) in the small angle region corresponding to the spacing ratios 1:2:4:5:6. It is noteworthy that the relative intensity of the even reflections when compared with the odd ones was temperature dependent, indicating an evolution of the organization within adjacent layers. From these data, we can deduce a thickness of 66 Å corresponding to approximately twice the length of compound **1**, and therefore to a bilayered arrangement.

A conjugated derivative that assembles four OPV moieties arising from a calix[4]arene core has been prepared and we have shown that it can act as a rigid core for the design of new π-conjugated liquid crystalline derivatives. As well as the potential use of such a compound in optoelectronic devices, the calix[4]OPV presented here is a strongly luminescent receptor and, therefore, is also potentially useful in the field of host–guest chemistry.[9,10]

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