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Alkali cation induced liquid crystalline properties of an oligophenylenevinylene-benzocrown ether conjugate

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Abstract—An oligophenylenevinylene-benzocrown ether conjugate has been prepared and its binding selectivity for alkali metal ions evaluated by electrospray mass spectrometry. Whereas this benzocrown-ether derivative does not exhibit any liquid crystalline properties, the self-assembly by coordination to potassium or cesium leads to supramolecular sandwich complexes with mesomorphic properties. © 2003 Elsevier Science Ltd. All rights reserved.

Organic semiconducting materials have been extensively investigated for their electronic properties,¹ and the mesoscopic organization of this class of compounds appears today as an important issue for their applications. In this respect, π -conjugated derivatives exhibiting liquid crystalline properties are of particular interest,² as they spontaneously form ordered assemblies that can be easily oriented. In recent years, the self-assembly of π -conjugated oligomers based on noncovalent interactions is an emerging area of investigations^{3,4} and the potential of the resulting discrete assemblies has not been fully explored yet for the preparation of new liquid crystalline materials. As a part of this research, we have developed the synthesis of versatile mesogenic oligophenylenevinylene (OPV) building blocks.⁴ In particular, we have shown that the self-assembly of OPV molecular units through Hbonds^{4a} or coordination to a transition metal^{4b} is an efficient strategy for the preparation of supramolecules with liquid crystalline properties. We now report the functionalization of our OPV building blocks with a benzocrown ether and show that the complexation of the resulting ligand with potassium and cesium affords a new class of alkalinomesogens. In addition, the binding properties of this new crown ether derivative have been investigated by electrospray mass spectrometry (ES-MS). The later technique is particularly interesting

to estimate the binding selectivities as it is very fast and requires small amounts of analyte.

The preparation of the crown ether derivative 1 is depicted in Scheme 1. Compound 2 was obtained in five steps from methyl 3.4.5-trihydroxybenzoate as previously reported.⁵ Reduction of aldehyde 2 with $LiAlH_4$ gave 3 in 80% yield. Treatment of 3 with trimethylsilyl bromide (TMSBr) in CHCl₃ yielded bromide 4. It is worth noting that the choice of the appropriate conditions for the preparation of bromide 4 was the key to this synthesis. The bromination step could also be achieved with CBr₄/PPh₃; however, the separation of the resulting bromide from the triphenylphosphine oxide by-product could not be achieved by crystallization, neither by column chromatography. Actually, benzylic bromide 4 was found to be unstable and quantitative hydrolysis was observed when chromatographic separation on SiO_2 or Al_2O_3 was attempted. In contrast, under bromination conditions using TMSBr, the volatile by-products can be eliminated by simple evaporation and no further purification step was required. Therefore, compound 4 could be used in the next step as received. Treatment of bromide 4 with P(OEt)₃ under Arbuzov conditions then gave phosphonate 5 in 76% yield. Finally, reaction of 5 with aldehyde 6^6 in the presence of *t*-BuOK in THF afforded the OPV-benzocrown ether conjugate 1 in 82% yield. All the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.

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Scheme 1. *Reagents and conditions*: (i) LiAlH₄, THF, 0°C (80%); (ii) TMSBr, CHCl₃, 0°C; (iii) P(OEt)₃, 150°C (76% from 3); (iv) 5, *t*-BuOK, THF, 0°C to rt (82%).

In particular, coupling constants of ca. 17 Hz for the two AB systems corresponding to the two sets of vinylic protons in the ¹H NMR spectrum confirmed the E stereochemistry of both double bonds in **1**.

The ability of crown ethers to form host–guest complexes with alkali cations has been largely documented.⁷ The stability of the complexes and the binding selectivity depend on the size of the crown-ether macrocycle, the best bound cation being that which fits best to the cavity. In the present study, the binding properties of crown ether **1** were investigated by electrospray mass spectrometry (ESMS). To determine the selective complexation of **1** with K⁺, Na⁺ and Cs⁺, a competitive experiment was carried out with an equimolar mixture (10^{-4} M) of CH₃CO₂Na, CH₃CO₂K, CH₃CO₂Cs, and **1** in CH₃OH:CH₂Cl₂ (1:1). The resulting ES mass spectrum recorded at an extraction cone voltage of 60 V is depicted in Figure 1. At this cone voltage no fragmentation was observed and reproducible spectra in terms



Figure 1. ES mass spectrum ($V_c = 60$ V) recorded from an equimolar mixture (10^{-4} M) of CH₃CO₂Na, CH₃CO₂K, CH₃CO₂Cs, and 1 in CH₃OH:CH₂Cl₂ (1:1).

of relative peak intensities were obtained. As expected, the ES mass spectrum reveals the presence of three peaks corresponding to the $[1 \cdot Na^+]$, $[1 \cdot K^+]$, and $[1 \cdot Cs^+]$ 1:1 host-guest complexes. The relative proportions, obtained by summing the relative intensities, including the isotope distribution, of each complex ion observed in the ES mass spectrum are 8.4% ($[1 \cdot Na^+]$), 84.0% ($[1 \cdot K^+]$), and 7.6% ($[1 \cdot Cs^+]$). As shown earlier,⁸ the proportion of the various host-guest complexes deduced from the ES-MS measurements can be directly related to the binding selectivity of compound 1 for Na⁺, K⁺, and Cs⁺. The preferred complexation of K⁺ with 1 is in good line with previous studies on related crown ethers^{8a} showing the high capability and reliability of the ES-MS method.

The appeal of ES-MS stems also from its ability to produce intact molecular ions (or pseudomolecular ions) from the solution to the gas phase.⁹ Due to the numerous successful characterizations by ES-MS of large noncovalently bound complexes in solution,9 the technique may be advantageously applied to the characterization of the highly labile 1:2 sandwich complexes that compound **1** is able to form with alkali metal ions. For this study, a mixture of CH₃CO₂Na, CH₃CO₂K, CH₃CO₂Cs and 1 in a 1:1:1:9 molar ratio was prepared in $CH_3OH:CH_2Cl_2$ (1:1) and analyzed by ES-MS. The resulting ES mass spectrum recorded in the positive mode at an extraction cone voltage of 40 V is depicted in Figure 2. It gives rise to three peaks dominated by the peak at m/z = 2272.2 corresponding to the $[Cs^+ \cdot (1)_2]$ sandwich complex (calculated m/z = 2272.1). The two other peaks are identified as the $[K^+(1)_2]$ (calculated m/z = 2178.3, and the $[Rb^{+}(1)_2]$ (calculated m/z =2224.6) sandwich complexes, respectively. The observation of the Rb⁺ complex is due to the presence of traces of rubidium salt into the commercially available alkali metal salts. In good agreement with previous studies on 18-C-6 crown ethers, no peak corresponding to the $[Na^{+}(1)_2]$ sandwich complex could be observed.⁹



Figure 2. ES mass spectrum ($V_c = 40$ V) recorded from a mixture of CH₃CO₂Na, CH₃CO₂K, CH₃CO₂Cs and 1 in a 1:1:1:9 molar ratio in CH₃OH:CH₂Cl₂ (1:1) (\bigstar = non-identified impurity, $\blacksquare = Rb^{+} \cdot (1)_2$ sandwich complex resulting from the presence of traces of rubidium salt into the commercially available alkali metal salts).

The alkali metal ion complexes of crown ether 1 were prepared by slow evaporation of CH₂Cl₂/MeOH (1:1) solutions of 1 and $CH_3CO_2^-M^+$ (M⁺ = Na⁺, K⁺ or Cs⁺) in various proportions. Homogeneous samples were only obtained when the stoichiometry of the initial mixture of 1 and CH₃CO₂⁻M⁺ was appropriate. In other words, the complexes were obtained in a pure form when the molar ratio of 1 and CH₃CO₂⁻M⁺ corresponded to the stoichiometry of the host-guest complex. In the case of sodium, only equimolar mixtures afforded homogeneous samples suggesting the formation of the 1:1 host-guest complex $[Na^+ \cdot 1]$. In contrast, the potassium and cesium host-guest species were obtained as 2:1 sandwich complexes. These observations are in good agreement with the ESMS studies. Effectively, 2:1 complexes have been observed for potassium and cesium, but not for sodium.

The thermal properties of 1, $[Na^+ \cdot 1]$, $[K^+ \cdot (1)_2]$ and $[Cs^{+}(1)_2]$ were investigated by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction studies. Whereas uncomplexed 1 and $[1 \cdot Na^+]$ do not exhibit any liquid crystalline behavior, the sandwich complexes $[K^+$. $(1)_2$ and $[Cs^+ \cdot (1)_2]$ show mesomorphic properties. POM investigations revealed a fluid birefregent phase from 84 to 106°C for $[K^+(1)_2]$ and from 82 to 108°C for $[Cs^+$ $(1)_{2}$]. However, the liquid-crystalline phases could not be identified by POM. Effectively, in both cases, the birefregent optical textures observed on cooling the samples from the isotropic phase were non-characteristic. The phase transitions observed by POM were confirmed by the DSC studies. During the heating, DSC analysis of $[K^+ \cdot (1)_2]$ gave three endotherms at 70°C (crystal-crystal phase transition, associated enthalpy value: $\Delta H = 24.7$ J/g), 84°C (melting point, $\Delta H = 16.5$ J/g) and 106°C (clearing point, $\Delta H = 1.3$ J/g). On cooling, three exotherms were observed and reversibility of the cooling transitions was observed during the following heating run. DSC analysis of $[Cs^+ \cdot (1)_2]$ gave similar results. Finally, the X-ray diffraction patterns of both sandwich complexes were typical of a mesomorphic phase with a sharp diffraction peak in the small angle region and a diffuse band in the wide angle region. The exact structure determination of these mesophases is still under progress.

In conclusion, a new OPV-benzocrown ether conjugate was prepared and its binding selectivity for alkali metal ions evaluated by ESMS. Interestingly, treatment of **1** with a potassium or a cesium salt afforded sandwich complexes with new properties. Effectively, **1** itself does not exhibit any liquid crystalline properties, but the association of two ligands **1** by coordination leads to supramolecular assemblies with mesomorphic properties. In addition, it can be added that the OPV-benzocrown conjugate **1** is a strongly luminescent compound and further studies aiming to determine its potential as a sensor for the detection of cations are under progress.

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