Tuning the self-assembly of a ditopic crown ether functionalized oligo(p-phenylenevinylene)

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A chiral ditopic crown ether functionalized oligo(p-phenylenevinylene), COPV, has been synthesized and fully characterized. The binding properties and the organization of COPV have been studied in solution and in the solid state. In chloroform, due to the benzo-15-crown-5 moieties, COPV is able to bind cations. In case of K+ a strong 2 : 2 complex is formed in which two COPVs are sandwiched between two potassium ions. Na+ is bound following a two-step negative cooperative process to form a 2 : 1 Na+/COPV complex. When COPV in the presence of potassium ions is drop-cast on a silicon substrate, fibers are formed. In water COPV forms stable helical aggregates as can be concluded from the Cotton effect, the UV-vis and fluorescence spectroscopy. AFM and light scattering studies show that ellipsoidal aggregates are present in water.

Introduction

Self-assembly of π-conjugated systems is an attractive approach to tune the morphology in plastic electronic devices and to construct functional nanosized objects suitable for supramolecular electronics.1 For these purposes, π-conjugated systems are required that contain units that are programmed to self-assemble with nanometric organizational precision.2 An interesting class of self-assembling units are crown ether moieties since they bind cations3 and show amphiphilic behaviour when connected to aliphatic tails4 enabling the tuning of self-assembly processes by solvent and additives. Crown ether functionalized π-conjugated polymers,5 oligomers6 and dyes7 have already been reported, however, in most cases with the aim to construct sensor materials8 rather than tuning self-assembly.9-11

Here, we report the synthesis of a chiral ditopic crown ether functionalized OPV (COPV, Scheme 1), and show that self-assembly can be tuned by solvent and additives yielding dimers, spheres and fibers. COPV consists of a hydrophobic OPV trimeric core with chiral aliphatic side chains and end-capped with hydrophilic benzo-15-crown-5 groups. COPV can be regarded as a ditopic (bola)amphiphile that may aggregate in water.12 More interestingly, benzo-15-crown-5 derivatives are able form a 1 : 1 complex with sodium and a sandwich structure with potassium cations13 and therefore the stacking of the OPV moieties can possibly be tuned.

Results and discussion

Synthesis

COPV (Scheme 1) was synthesized from 4-chloromethylbenzo-15-crown-5 1 which was converted into 2 by a Michaelis-Arbuzov reaction with triethyl phosphite. After Wittig-Horner coupling of 2 with 3, COPV was isolated and fully characterized by 1H NMR, 13C NMR, IR spectrometry, MALDI-TOF mass spectrometry (Fig. 1), and elemental analysis. COPV is highly soluble in organic solvents such as tetrahydrofuran (THF), chloroform, dichloromethane and methanol. The UV-vis spectrum of COPV in chloroform shows a broad absorption p-p* band at \( \lambda_{\text{max}} = 453 \) nm while the fluorescence maximum is positioned at \( \lambda_{\text{max}} = 518 \) nm (Fig. 1). CD spectra reveal no Cotton effect, supporting that COPV is molecularly dissolved in chloroform.

Binding of COPV to Na+ and K+ in chloroform

We have investigated the binding properties of COPV toward Na+ and K+ in chloroform by UV-vis, circular dichroism (CD), fluorescence spectroscopy and electrospray ionisation mass spectrometry (ESI-MS).

ESI-MS is a soft ionization technique ideally suited to the characterization of noncovalent complexes.6,7,9-14 The ESI mass spectrum of a 1 : 2 mixture of COPV and NaPF6 recorded under mild conditions (Fig. 2) displayed the most intense peak at \( m/z = 714.5 \).15 This double charged peak points to a 2 : 1 [2Na+–COPV] complex in which sodium ions are bound in the crown ether moieties of COPV. It should be noted that also minor peaks at \( m/z = 1406.84 \) are detected indicating 2 : 2 and 1 : 1 complexes of Na+ and COPV. In the case of KPF6, the most intense peak is found at \( m/z = 1421.8 \) (Fig. 2). This double charged peak can be assigned to a 2 : 2 complex.
Scheme 1  Reaction scheme for COPV. Reagents and conditions: a) P(OEt)$_3$, 12 h, 160 °C, yield 99%; b) DMF-THF, 3, KOC(CH$_3$)$_3$, 12 h, yield 12%.

Fig. 1 (a) Normalized absorption (---) and fluorescence (- - -) spectra ($\lambda_{ex} = 453$ nm) of COPV at 20 °C in chloroform. (b) MALDI-TOF spectrum of COPV (inset: expansion of the most intense peak).

Fig. 2 ESI-mass spectra of COPV in the presence of NaPF$_6$ (a) and KPF$_6$ (b). Insets: expansion of the most intense peaks.
complex \([\text{COPV--K}^+]_2\) and indicates a sandwich structure. Low intensity peaks are found at \(m/z = 959.3\) and 730.4 which can be attributed to \(2:3\) and \(1:2\) complexes, respectively. The sandwich structure is extremely stable since the double charged species is still visible with a collision voltage of \(V_c = 50\) V.\(^6\) Our mass data nicely show that COPV is able to bind \(K^+\) and \(Na^+\) in which the stoichiometry is determined by the size of the cation.

The cation--COPV complexes in chloroform were further investigated by fluorescence spectroscopy (Fig. 3). Upon addition of \(NaPF_6\), the fluorescence of COPV slightly reduces while the emission maximum shifts from \(\lambda_{\text{max}} = 518\) nm to \(\lambda_{\text{max}} = 525\) nm. After addition of one equivalent of \(Na^+\), the emission maximum remains at \(\lambda_{\text{max}} = 525\) nm while the intensity increases only slightly. Adding a large excess of \(Na^+\) did not alter the emission spectra. During the titration the UV-vis spectrum did not change and no CD effect was observed. These data reveal that binding of sodium cations has a marginal effect on the optical properties, a result that has been observed earlier for crown ether-appended dyes.\(^1\) When the fluorescence intensity at \(\lambda = 518\) nm is plotted versus the \(Na^+/\text{COPV}\) ratio one can observe that the binding occurs in two steps (Fig. 3). The binding could be analyzed with a \(1:2\) binding model resulting in two association constants, \(K_1 = 1.5 \times 10^7\) M\(^{-1}\) and \(K_2 = 2.5 \times 10^5\) M\(^{-1}\) and an overall association constant \(K_a = 3.8 \times 10^{12}\) M\(^{-2}\).\(^6\) The binding energies are: \(\Delta G_1 = -39.2\) kJ mol\(^{-1}\), \(\Delta G_2 = -32.5\) kJ mol\(^{-1}\). The binding constants are high in comparison with binding constants previously reported for sodium bound by benzo-15-crown-5 derivatives.\(^1\) The difference between binding of the first and the second sodium cations is \(\Delta G = 6.7\) kJ mol\(^{-1}\).\(^6\) The interaction parameter \(\alpha = 4K_2/K_1 = 0.07\) is lower than 1, which is the expected value for two identical binding sites,\(^6\)\(^,\)\(^1\) revealing a strong negative cooperative binding process. This effect is possibly due to electrostatic repulsion thereby weakening the binding of the second sodium cation.\(^1\) Similar negative cooperativity behaviour has been reported earlier for rigid bis-benzo-15-crown-5 ditopic host binding to sodium (\(\alpha = 0.01-0.4\) depending on substituent).\(^1\)\(^,\)\(^2\)

The addition of \(KPF_6\) to COPV (\(7.1 \times 10^{-7}\) M\(^{-1}\)) shows different behavior. The fluorescence intensity (Fig. 3) is more significantly quenched and the emission maximum is red-shifted by 16 nm to \(\lambda_{\text{max}} = 534\) nm with a shoulder at \(\lambda_{\text{max}} = 573\) nm. Furthermore an isobestic point is visible at \(\lambda = 568\) nm (Fig. 3). Fluorescence quenching and the shift to longer wavelength are typical for stacked OPVs (vide infra,

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**Fig. 3** Emission spectra of COPV (\(\lambda_{\text{ex}} = 453\) nm) in chloroform (\(4.4 \times 10^{-6}\) mol l\(^{-1}\)) upon adding \(NaPF_6\) (a) and \(KPF_6\) (c), and the change in emission intensity at \(\lambda = 518\) nm as a function of the ratio \(Na^+/\text{COPV}\) (b) and \(K^+/\text{COPV}\) (d).
assembly of COPV in water) although the changes are small.\textsuperscript{12} Remarkably, during the titration the UV-vis spectrum hardly changes and no CD effect is observed. When the intensity change of the fluorescence spectra at $\lambda = 518$ nm is plotted versus the K$^+$/COPV ratio, an inflection point is observed after addition of one equivalent of potassium (Fig. 3). The binding isotherm could be analyzed with a 2 : 2 binding model\textsuperscript{21} resulting in $K_F = 3 \times 10^{18}$ M$^{-3}$ for the formation of a 2 : 2 complex and $K_R = 4 \times 10^2$ M$^{-1}$ for breaking up the 2 : 2 complex to form a 1 : 2 complex. The binding constant is comparable to that found for 2 : 2 complexation between K$^+$ and a ditopic crown ether-appended metalloporphyrin.\textsuperscript{11} Assuming that COPV has two independent binding sites, this gives for the association between one potassium ion and one binding site $K_a = 10^5$ M$^{-1}$. In the absence of reliable data for the non-cooperative 1 : 1 complexation of benzo-15-crown-5 ethers to KPF$_6$ (due to their strong tendency to form sandwich complexes), it is not possible for us to estimate the reference constant for intermolecular process ($K_{\text{inter}}$) for this system, and hence the intramolecular binding constant ($K_{\text{intra}}$) cannot be independently determined either.\textsuperscript{22} The effective molarity (EM), which is a measure for the chelate effect and is usually defined as $EM = K_{\text{intra}}/K_{\text{inter}}$,\textsuperscript{22,23} however, can be estimated from the measured $K_B$ value, using the relation $K_B = 16/(EM \cdot z_L^2)$.\textsuperscript{24} Assuming that the cooperativity factor of the ligand ($z_L$) equals 1 for K$^+$, we obtain $EM = 0.04$ M. We can therefore safely conclude that the dominating species in solution under the conditions used here ($<10^{-6}$ M), is the cyclic 2 : 2 complex, as the acyclic 2 : 2 complex (and related oligomers) will not appear until the concentration of binding sites equals or exceeds the EM (0.04 M).\textsuperscript{22} Additionally, the concentration necessary to break up 50% of the 2 : 2 complex by dilution, \textit{i.e.} the $c_{50}$ value, is around $3 \times 10^{-7}$ M.\textsuperscript{21}

We have also studied the morphology of drop-cast solutions on silicon oxide surfaces of COPV in chloroform (7.1 $\times$ 10$^{-7}$ M$^{-1}$) in the absence and presence of sodium and potassium by tapping mode atomic force microscopy (TM-AFM). In the case of chloroform solutions of COPV ill-defined objects were formed and the addition of sodium ions did not have any effect. However, in the presence of excess potassium, elongated structures are observed (Fig. 4). The smallest fiber structures are about 2 nm in height, 15 nm wide and are micrometers long. The height corresponds to the height of COPV, suggesting that the fibers are composed of COPVs held together by potassium cations.

### Self-assembly in water

Previously we have found that OPVs equipped with ethylene oxides\textsuperscript{12} are able to form vesicles in water. Because of the great similarity between COPV and those previously reported OPVs, we have investigated the self-assembly of COPV in water. In comparison with chloroform solutions, the UV-vis absorption maximum in water is blue shifted to $\lambda_{\text{max}} = 435$ nm with the appearance of a vibronic shoulder at 480 nm (Fig. 5). The fluorescence intensity (Fig. 5) is strongly quenched in water and red-shifted to $\lambda_{\text{max}} = 543$ and 583 nm. The absorption and fluorescence data show that the OPV oligomers are aggregated. A bisignate Cotton effect\textsuperscript{25} (Fig. 5) was observed for COPV in water at the $\pi-\pi^*$ band with a negative Cotton effect at $\lambda_{\text{max}} = 406$ nm (g$_{\text{abs}} = 1.1 \times 10^{-2}$) and a positive Cotton effect at $\lambda_{\text{max}} = 467$ nm (g$_{\text{abs}} = 1.4 \times 10^{-2}$). Compared to the OPVs end capped with ethylene oxide tails\textsuperscript{12} these values are one order of magnitude higher, indicating the formation of stronger exciton coupled aggregates. The zero-crossing of the CD signal ($\lambda = 429$ nm) lies close to the absorption maximum of the chromophore ($\lambda_{\text{max}} = 435$ nm). The observations in CD originate from the exciton coupling of neighbouring COPV molecules. Temperature dependent measurements did not affect the UV-vis, fluorescence and CD spectra. Remarkably adding potassium and sodium ions hardly had an effect on the supramolecular assembly, indicating that the ions are presumably not bound to COPV in water.

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**Fig. 4** TM-AFM images. Height (a) and amplitude (b) image (1.5 μm by 1.5 μm, z-scale 5 nm) of COPV (0.7 $\times$ 10$^{-6}$ M in chloroform) with 40 equivalents of KPF$_6$ on a silicon wafer.

**Fig. 5** Optical properties of COPV (1.6 $\times$ 10$^{-5}$ M) in water at room temperature as studied with UV-vis, fluorescence ($\lambda_{\text{ex}} = 453$ nm) and CD spectroscopy.
To elucidate the shape of the assemblies light scattering and AFM studies were performed. The data obtained by static light scattering could be fitted by assuming ellipsoidal aggregates26 (Fig. 6), having average radii of \( r_1 \approx 85 \) and \( r_2 = r_3 \approx 350 \) nm. These dimensions were confirmed by angle dependent dynamic light scattering. TM-AFM reveals that flat objects are formed on the surface having diameters varying between 100 and 300 nm and a height of 8 nm. The height corresponds to twice the length of COPV and could indicate that single walled ellipsoids are formed that collapse on a silicon wafer yielding a bilayer structure.12

Conclusions

A chiral ditopic crown ether functionalised oligo(p-phenylenevinylene), COPV, has been synthesized and fully characterized and we have shown that its self-assembly can be tuned by choice of the solvent and additives yielding dimers, spheres or fibers. COPV is able to bind cations forming a 2:1 complex in the case of \( \text{Na}^+ \) in a negative cooperative process and a strong sandwich 2:2 complex in the case of \( \text{K}^+ \). When COPV in the presence of \( \text{K}^+ \) is drop-cast on a silicon substrate, fibers are formed. In water COPV acts as a bola-amphiphile and forms stable ellipsoidal aggregates.

Our studies show that crown ethers are an interesting class of units for self-assembly. Therefore, a wide variety of self-assembled \( \pi \)-conjugated objects can be created that are potentially interesting for supramolecular electronics.

Experimental

General methods

\(^1\)H NMR and \(^{13}\)C NMR spectra were recorded at room temperature on a Varian 300 or Varian Mercury 400. Chemical shifts are given in ppm (\( \delta \)) relative to tetramethylsilane. Abbreviations used are s = singlet, d = doublet, dd = double doublet, t = triplet and m = multiplet. Infrared spectra were run on a Perkin Elmer 1600 FT-IR spectrometer. ESI mass spectra were recorded on a Q-Tof Ultima Global mass spectrometer (Micromass, Manchester UK) equipped with a Z-spray source. The samples (3 µL of a 0.5 mM solution) were injected in the Flow Injection Analysis (FIA) mode. The HPLC-grade acetonitrile was pumped with a Shimadzu LC-10ADvp pump at a flow rate of 30 µL min\(^{-1}\). Electrospray ionization was achieved in the positive mode by applying 5 kV on the needle. The source block and the desolvation gas were heated to 60 °C. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilising an \( \alpha \)-cyano-4-hydroxycinnamic acid matrix. Elemental analyses were carried out on a Perkin Elmer 2400. UV-vis and fluorescence spectra were performed on a Perkin Elmer Lambda 40 spectrophotometer and Perkin Elmer LS-50 B. CD spectra were recorded on a JASCO J-600 spectropolarimeter. Static light scattering measurements were performed with a computerized homemade goniometer, in the angular range of 36 to 100 degrees. The scattering intensity was measured using a single mode optical fiber with a collimating lens in combination with an ALV/ISO-SIPD single photon detector. For dynamic light scattering the intensity signal was sent to an ALV5000/E digital correlator, using an acquisition time of 300 s for each angle. AFM images were recorded on silicon wafers with a Multimode IIIa, operating under ambient conditions in tapping mode. Microfabricated silicon cantilevers (FESP) were used with a spring constant of 1–5 N m\(^{-1}\).

Materials

4-Chloromethylbenzo-15-crown-527 1 and (E,E)-1,4-bis{4-formyl-2,5-bis[(S)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]benzene 328 were synthesised according to literature procedures. All solvents were of AR quality and chemicals were used as received. BioBeads SX-3 was obtained from Bio-Rad.

4-Diethylphosphonatebenzo-15-crown-5 (2)

A mixture of triethyl phosphite (4.15 g, 25 mmol) and 4-chloromethylbenzo-15-crown-5 (1, 1.2 g, 3.79 mmol) was stirred at 160 °C for 12 h. During this time, ethyl chloride was distilled off from the reaction mixture. Subsequently, the mixture was cooled to 70 °C and the excess of triethyl phosphite was distilled off under reduced pressure. The product was used without further purification (1.42 g, 99%).

\(^1\)H NMR \( \delta_H \) (300 MHz, CDCl\(_3\)): 1.29 (t, 6H, \( \text{CH}_3 \)), 3.13 (d, 2H, \( \text{PCH}_2 \)), 3.81 (s, 8H, \( \text{OCH}_2 \)), 3.96 (m, 4H, \( \text{OCH}_2 \)), 4.06 (m, 4H, \( \text{OCH}_2 \)), 4.19 (m, 4H, \( \text{OCH}_2 \)), 6.86 (s, 2H, Ar\( \text{H} \)), 6.92 (s, 1H, Ar\( \text{H} \)).
Under argon atmosphere, phosphonate 2 (0.83 g, 2.1 mmol) was added to a solution of dialdehyde 3 (0.59 g, 0.69 mmol) in 15 mL THF. Under argon atmosphere, phosphonate 2 (0.83 g, 2.1 mmol) was added to a solution of dialdehyde 3 (0.59 g, 0.69 mmol) in 15 mL THF. The reaction mixture was stirred overnight at room temperature. HCl (6 M; 250 mL) was added and the aqueous layer was extracted three times with dichloromethane. The collected organic layers were washed with HCl (3 M) and subsequently with demineralised water. THF was removed by heating to 80 °C in 50 ml THF and this solution was injected into 5 ml of 0 °C yielded pure COPV (0.11 g, 12%). Mp = 221 °C; C, 72.67; H, 8.46%; C84H 118Oi6 requires C, 72.91; H, 8.59%.

Sample preparation in water
The aqueous solutions for optical measurements were prepared via a THF injection method. COPV was dissolved in 50 μl THF and this solution was injected into 5 ml demineralised water. THF was removed by heating to 80 °C for 5 minutes.

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References
