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Construction of a Multiwired Molecular Cable of Micrometer Length by a Self-Assembly Process

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The engineering of molecules and molecular systems that can form nanometer-sized structures is currently receiving a great deal of attention. An interesting challenge is the construction of molecular wires and molecular channels capable of transporting electrons and ions. For example, phthalocyanines substituted with long hydrocarbon side chains have been reported to form conducting mesophases in which the molecules are stacked in columns. Electron conduction within the columns is fast, whereas it is slow between the columns. In previous papers we have shown that crown ether molecules can be stacked to create ion conducting channels. Here we describe a novel liquid-crystalline molecule (1) that self-assembles in chloroform solution to form a molecular cable. This cable contains a central wire of stacked phthalocyanines, four molecular

channels built up from stacked crown ether rings and a surrounding hydrocarbon mantle. Isolated cables with molecular thickness and a length of several micrometers can be recognized in electron microscopy images.

Phthalocyanine 1 was prepared from crown ether 12 by a cyclization reaction (see Scheme 1). The crown ether was synthesized from 11, which in turn was assembled from the building blocks 6 and 10. The starting compound for 6 was 3,4-dihydroxybenzaldehyde (2). This compound was alkylated with decyl

chloroform solution to form a molecular cable. This cable contains a central wire of stacked phthalocyanines, four molecular
bromide (– 3) and subsequently converted into 3,4-bis(decoxy)phenol (4) by a Baeyer–Villiger type of oxidation.\(^{10}\) Treatment of the phenol with Fremy’s radical\(^{10}\) under phase transfer conditions yielded 4,5-bis(decoxy)-1,2-benzoquinone (5), which was converted into 1,2-bis(acetoxy)-4,5-bis(decoxy)benzene (6; for characterization see Table 1) by reduction with zinc/acetic acid/acetic anhydride. The overall yield of 6 from 2 was 38%. The synthesis of the second building block 10 was performed using more standard reactions. Catechol (7) was brominated and subsequently alkylated with tetrahydropyranyl-ether (THP)-protected diethyleneglycol monochloride to give, after in situ deprotection, compound 9. Reaction of 9 with p-toluenesulfonyl chloride gave compound 10 as a highly viscous oil in 42% overall yield (Table 1). The coupling of the two fragments was carried out by first hydrolyzing 6 and subsequently treating the resulting catechololate in situ with 10. The two bromine atoms of 11 were substituted by nitrile groups with copper cyanide in N,N-dimethylformamide (DMF). Finally, the resulting crown ether 12 was converted into phthalocyanine 1 by refluxing in N,N-dimethylaminethanol (overall yield from 6 and 10 13%). Compound 1 was purified by repeated recrystallization from chloroform. Spectroscopic and elemental analysis were consistent with the proposed structure (Table 1).

Crown ether phthalocyanine 1 showed thermotropic liquid crystalline behavior as was evident from differential scanning calorimetry (DSC), polarizing microscopy, and small angle X-ray scattering (SAXS) measurements. A transition to a highly viscous, birefringent mesophase was observed at 148 °C on heating (ΔH = 130 kJ mol\(^{-1}\)). Large hysteresis was observed on cooling: the transition to the crystalline phase occurred at 105 °C. No transition to the isotropic phase was observed below the decomposition temperature of the compound (320 °C). The large number of peaks in the SAXS measurements at room temperature indicated a crystalline mesophase. In the mesophase at 170 °C an intense peak, corresponding to a spacing of 35.10 Å, and a very broad peak, corresponding to 4.5 Å, were visible. The former peak probably is the (100) reflection of a hexagonal columnar phase with an intercolumnar distance of 40.5 Å.

Generally, alkoxy- and crown-ether-substituted phthalocyanines are highly soluble in organic solvents. Surprisingly, it was only soluble in boiling chloroform and in boiling toluene. A solution of 1 (at a concentration of 7 mg mL\(^{-1}\)) in chloroform formed a gel on cooling. A UV/Vis spectrum of a dilute solution (1 μL) of 1 in chloroform at 50 °C showed a split Q-band at 650 and 700 nm that is typical for nonaggregated metal-free phthalocyanines. However, when this solution was cooled to room temperature a blue shift of the bands and a broadening of the signals was observed, which is characteristic of aggregated phthalocyanine species (Fig. 1).

The structure of the aggregates was elucidated with the help of transmission electron microscopy (TEM). Compound 1 (7 mg) was boiled in chloroform (1 mL), and after the solution had cooled, a drop of the resulting gel was placed on a carbon-coated copper grid. After one minute the grid was blotted dry and shadowed with platinum at an angle of approximately 45°. Two representative TEM pictures are shown in Figure 2. At low magnifications fibers with a length in the order of micrometers, which form a network structure, are observed. At higher magnifications these fibers are seen to consist of bundles of single parallel strands. The thickness of these strands equals the diameter of a molecule of 1 as estimated from CPK space-filling molecular models, that is, 50–60 Å. Several isolated strands can be observed with the same diameter. At lower concentrations of 1 in chloroform, that is, below the gel-forming point, fibers are still present, but they are smaller, and no network is formed.

The conclusion from these experiments is that crown ether phthalocyanine 1 self-assembles into extremely long stacks of molecular thickness, which consist of more than 10⁴ molecules. To the best of our knowledge, evidence for the formation of such large phthalocyanine aggregates has not been reported before. Apparently, the attractive forces between the molecules are so strong that complete solvation is prevented at room temperature.
Complexes of Partially Fluorinated Macrocycles with a Metal-Fluorine σ-Donor Bond and Their Suitability as Metal Ion Indicators**

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Even though a rather large number of macrocyclic polyethers is known,14 only few fluorine-containing crown ethers12 have been reported, and in most of these all of the hydrogen atoms are substituted by fluorine. As a result of the electron-withdrawing nature of the CF2 units, the oxygen or nitrogen atoms in these polyethers no longer exhibit Lewis basicity and therefore cannot form stable metal complexes. The goal of our research work is the synthesis of macrocycles that have only a few fluorine atoms incorporated into the cyclic structure. Upon complexation of metal ions, the fluorine should act as a “detector,” since the 19F NMR signals shift upon complexation.65 The high sensitivity, combined with a large signal dispersion and the absence of a natural background make 19F NMR spectroscopy an ideal tool for investigation.64

Recently we reported the synthesis of a partially fluorinated [2.2.2]cryptand.65 This compound forms complexes with metal ions; however, the 19F NMR signals shift only slightly upon complexation, since no direct metal–fluorine contacts are formed. Such an interaction becomes more likely if a carbon–fluorine bond is directed towards the center of the crown ether. The relatively small steric demand of the fluorine atom is not expected to interfere with the binding of metal ions; on the contrary it is hoped that formation of a σ-donor bond between fluorine and the metal ion will increase the stability of the metal complexes.

The building block used for the synthesis of the fluorine-containing macrocycles was 1,3-bis(bromomethyl)-2-fluorobenzene (1), which was treated with tetraethylene glycol, ethyleneglycol, or azacrown ethers to yield fluorocrown ethers (Scheme 1).66

The macrocyclic ligands 2–6 were obtained in yields of 30 to 80%. In these compounds the carbon–fluorine bond is directed towards the region that is expected to be the binding site for metal ions.

The reaction of compounds 2, 4, 5, and 6 with metal salts leads to the complexation of a metal ion, while at the same time the 1H, 13C, and 19F NMR resonances of the ligands are shifted; in contrast, no such effects were observed for 3. The 19F NMR resonances (300 K) reported for the various metal complexes represent the averaged 19F NMR signals for the metal-free and metal-containing ligands (fast exchange). The absolute values of these signal shifts are, however, only large in the 19F NMR spectra, in which values up to Δδ = 8.8 have been observed.

Figure 1 shows the differences in chemical shift (Δδ) obtained by adding an approximately tenfold molar excess of metal salt to the fluoroxylene bis(crown ethers) 4–6; however, in most cases addition of metal salt beyond a twofold excess does not markedly change the position of the signals. It was


Scheme 1. a) KO/Bu, tetraethylene glycol, b) KO/Bu, ethyleneglycol, c) Na2CO3, 

Add water (1) to the fluorocrown ethers (Scheme 1).