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

Cornelus F. van Nostrum, Stephen J. Picken, and Roeland J. M. Nolte

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

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bromide (→ 3) and subsequently converted into 3,4-bis(decoxy)phenol (4) by a Baeyer–Villiger type of oxidation. Treatment of the phenol with Frey's radical60 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 tetrahydroprpyranyl- (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 catecholate in situ with the proposed structure (Table 1).

Table 1. Characteristic physical data of 1, 6, and 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ [nm]</th>
<th>[ε]</th>
<th>MS (CI):  m/z [M + Na]+</th>
<th>MS (FAB): m/z [M + H]+</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>338-349 (11), 430 (ArH), 770 (CO)</td>
<td>800</td>
<td>506</td>
<td>752</td>
</tr>
<tr>
<td>6</td>
<td>380-390 (11), 400 (ArH), 770 (CO)</td>
<td>700</td>
<td>515</td>
<td>752</td>
</tr>
<tr>
<td>10</td>
<td>360-390 (11), 400 (ArH), 770 (CO)</td>
<td>650</td>
<td>515</td>
<td>752</td>
</tr>
</tbody>
</table>

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 fibers with a length in the order of micrometers, which form a network structure, are observed. At higher magnifications fibers with a length in the order of micrometers, which form a network structure, are observed. At higher magnifications fibers with a length in the order of micrometers, which form a network structure, are observed. At higher magnifications fibers with a length in the order of micrometers, which form a network structure, are observed.
Complexes of Partially Fluorinated Macro cyclics with a Metal–Fluorine σ-Donor Bond and Their Suitability as Metal Ion Indicators**

Herbert Plenio* and Ralph Diodone

Even though a rather large number of macrocyclic polyethers is known, only few fluorine-containing crown ethers 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. 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.

Recently we reported the synthesis of a partially fluorinated compound that 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 (I), which was treated with tetraethylenglycol, ethyleneglycol, or azacrown ethers to yield fluorocrown ethers (Scheme 1).