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Tubular Conjugated Polymer for Chemosensory Applications

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Supporting Information

ABSTRACT: In this paper, we present the concept of a soluble tubular conjugated polymer (TCP). We report on a fluorescent 5,5′-Bicalixarene-based polymer where the calixarene units are seamlessly incorporated in the conjugated polymeric chain that can respond to a small molecule complexation inside the hydrophobic cavity. In particular, our system demonstrated a *reversible* rapid fluorescence quenching upon interaction of gaseous nitric oxide with the calixarene moiety.

Rigid cone-shaped calix[4]arene (calixarene) molecules have long been recognized as valuable receptors for various organic and inorganic analytes.[1−3] Their lower, phenolic rim can be functionalized to selectively coordinate main-group and transition metal ions, while the hydrophobic cavity of the calixarene scaffold can accommodate various organic molecules and gases.[4−7] This versatility of the calixarene molecules as receptors was studied extensively in the design of chemosensory materials.[8] A particularly powerful method to enhance the sensitivity of the calixarene-based chemosensors is to attach them to a conjugated polymeric network based on a "molecular wire" approach. In this method, higher sensitivity is obtained due to the collective response of the polymer bound receptors, involving both intra- and intermolecular charge delocalization.[9] There are only a few reports of the incorporation of calixarene-based receptors into "molecular wire" networks, mainly as pendant groups (Figure 1a).[10,11] The direct attachment of the calixarene unit (at the upper rim) to a conjugated polymer has also been reported by Swager and co-workers and has resulted in rigid zigzag structures (Figure 1b).[12] However, short conjugated fragments combined with the nonlinear geometry gave rather moderate sensory responses with selected analytes. To enhance the sensitivity, we decided to prepare conjugated materials where calixarene scaffolds would be the part of uninterrupted linear polymeric backbone. Herein, we present the first polymer of this family, utilizing the intrinsically tubular calixarene scaffolds as building blocks for new conjugated materials.

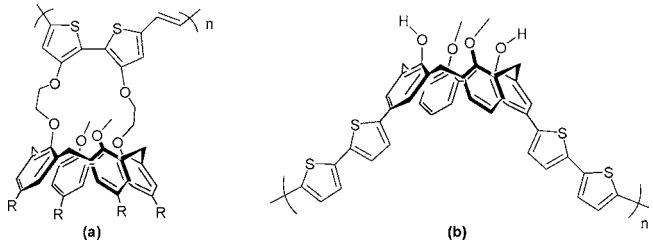

Figure 1. Representative conjugated polymers with attached calixarene scaffolds.[10,12]

As the building block, we chose the 5,5′-Bicalixarene scaffold that was first reported by Neri et al.[13] This and similar bicalixarene molecules are known to complex electron-deficient organic compounds as well as fullerenes.[14−16] Thus, 5,5′-Bicalixarene **2** was prepared via the oxidation with $FeCl_3$ (Scheme 1). The removal of the benzylic protecting groups and the selective replacement of one of the free OH groups with trifluoromethane sulfonate (triflate) at both calixarene moieties provided monomer **3**, which was tested in the direct Sonogashira-type cross-coupling polymerization with 1,4-diethynylbenzene. Unfortunately, no conjugated polymer incorporating the 5,5′-Bicalixarene scaffold was obtained under our improved conditions[17] of the original cross-coupling method,[18] as mainly the homocoupling of the diethynylbenzene spacer was observed. As the cross-coupling of the sterically encumbered electron-rich triflate proved inefficient in the condensation-polymerization, we chose to circumvent the problem by replacing the triflate with the $Et_3Si{-}C{\equiv}C{-}$ group.[19] Under our standard cross-coupling conditions,[20] the desired **4** was isolated in a 48% yield (Scheme 1). The replacement of the phenolic oxygens with alkyne did not adversely affect the complexation properties of new bicalixarenes. For example, upon the addition of 1 equiv of *N*-methylpyridinium triflate to **4**,[13,15] complete encapsulation of the cationic guest was observed in the ^{1}H NMR spectrum (Figure S1). The spectrum was in agreement with the organic cation complexed within *both* calixarene cavities (closed conformer). The removal of the Et_3Si groups in **4** gave the free acetylene **5** which, followed by the attachment of the solubilizing hexanoyl groups at the free phenolic positions, furnished diacetylene **6** in the overall 60% yield.

As **6** was prone to undergo oxidative coupling in the presence of Pd(II) and Cu(I) catalysts, we decided to use this Glaser-type reaction to prepare polymeric **7**, which was obtained in a 70% yield (Scheme 2). The extended conjugation had a profound effect on the UV/vis and fluorescence properties of the calixarene compounds. While compounds **4**−**6** showed only weak fluorescence, **7** was highly fluorescent with about 30 nm Stokes shift (Figure 2).

Polymer **7** has an intrinsically hollow tubular structure containing only carbon and hydrogen atoms at its core. With the pinched cone opening at the upper rim of ca. 1 nm, it can be viewed as a conjugated "hydrocarbon nanotube" that can be filled by small molecule guests. Both, open (shown in the

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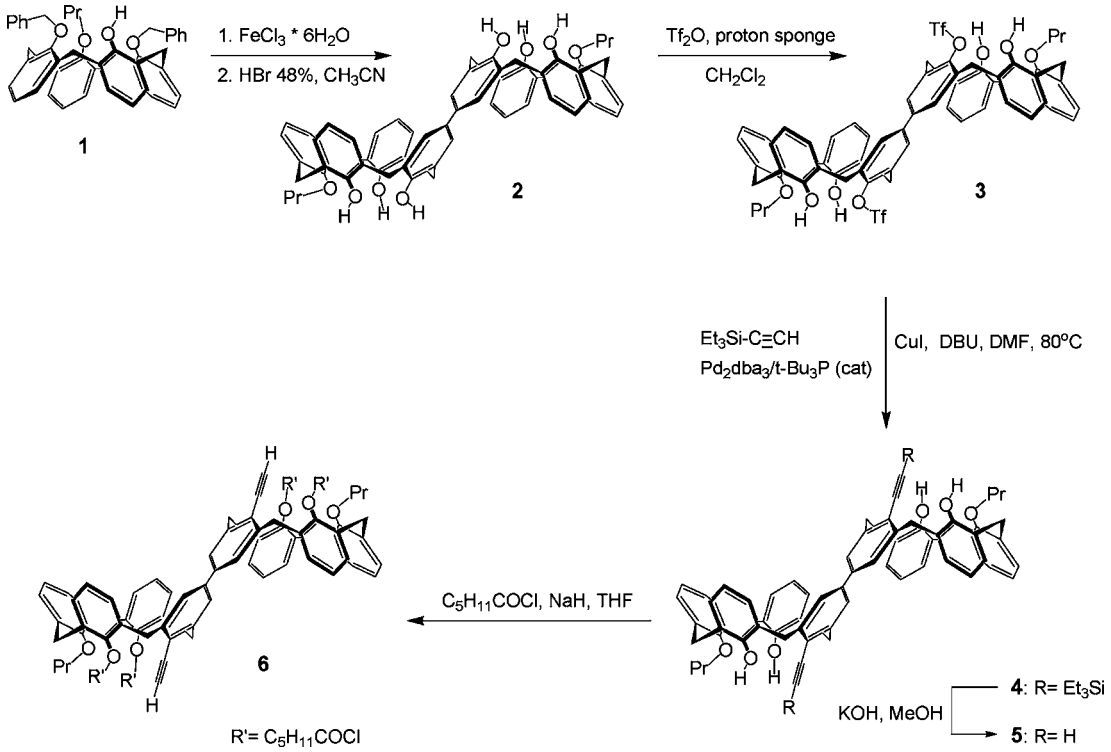
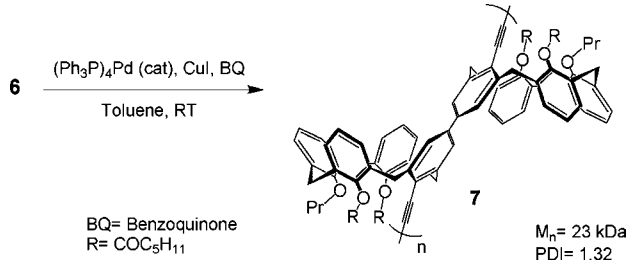
Scheme 1



Scheme 2



Schemes) and closed (capsule-type) conformations have been established for 5,5′-Bicalixarene molecules,[13,16] with the latter being proposed to significantly enhance the complexation properties of the calixarene scaffold. Thus, we were eager to explore the fluorescence response of **7** to the presence of important analytes. One such analyte is nitric oxide (NO), a small gaseous molecule with an enormous importance in human physiology.[21,22] Many fluorescent probes for NO sensing have been reported, most of them relying either on the formation of an "NO^+" equivalent in the presence of an oxidant or on the complexation to a transition metal center.[23−25] NO entrapment within the nonfluorescent calixarene systems has also been documented, the reaction being based on the oxidation of the calixarene moiety.[26] The removal of the guest molecule could only be achieved by adding a reducing reagent allowing for the release of free NO.[27] We were delighted to find that the fluorescence of **7** rapidly decreases in the presence of NO. Although no color change or effect on the NMR signals set was observed upon brief exposure of a chloroform solution of **7** to NO vapor, the fluorescence was quenched. Importantly, the NO could easily be removed in a vacuum, with a few seconds of low vacuum restoring the fluorescence of **7** (Figure 3). The signal could not

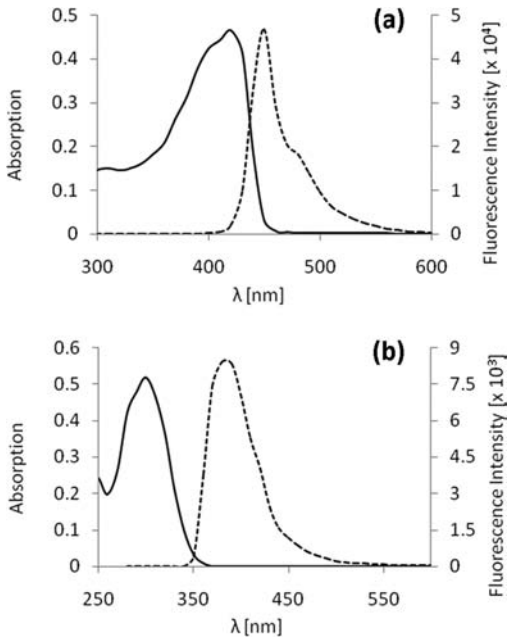


Figure 2. Absorption and emission (dashed line) spectra of polymer **7** (a, $CHCl_3$, excitation at 400 nm) and Bicalixarene **4** (b, $CHCl_3$, excitation at 280 nm).

be recovered in full, likely as the result of the *irreversible* reaction with small amounts of higher oxides of nitrogen. The exposure of **7** to NO_2 or NO^+ results in the irreversible fluorescence loss. Importantly, the fluorescence was not affected by the presence of the atmospheric oxygen or by the addition of carbon monoxide.

To verify that the calixarene moiety is indeed responsible for the interactions with NO, we prepared **8** and its linear analogue **9** which bears the same chromophore (Figure 4). The

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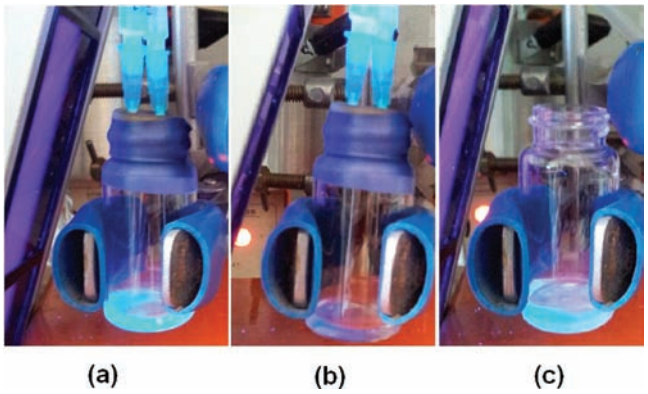

Figure 3. Fluorescence change of polymer **7** before the addition of NO (a), after the addition of NO (b) and after 30 s at ca. 200 mmHg (c).

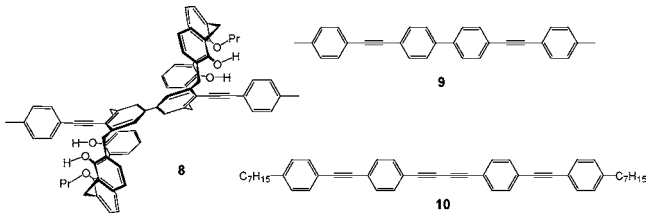

Figure 4. Fluorescent 5,5′-Bicalixarene **8** and linear chromophores, **9** and **10**. Only **8** undergoes fluorescence quenching in the presence of NO.

compounds show similar UV spectra and are fluorescent in their $CHCl_3$ solutions. While the fluorescence of **8** was fully quenched upon the exposure to NO, no effect on the fluorescence of **9** was observed, indicating the importance of the calixarene fragment for NO complexation. Fluorescent **10** (Figure 4) that has the diacetylene motif in its structure (in analogy to **7**) also showed no response in the presence of NO gas. Thus, the observed effect is unique as it shows a reversible supramolecular entrapment of gaseous NO by a soluble well-defined conjugated polymer.

In conclusion, we prepared the first tubular conjugated fluorescent polymer with fused calixarene cavities. The presence of the calixarenes allows for the detection of small molecules, such as NO, based on the reversible complexation. The detailed analysis of the NO fluorescence quenching in **7** and other applications of these new materials are currently under investigation in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete experimental details for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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