Communication

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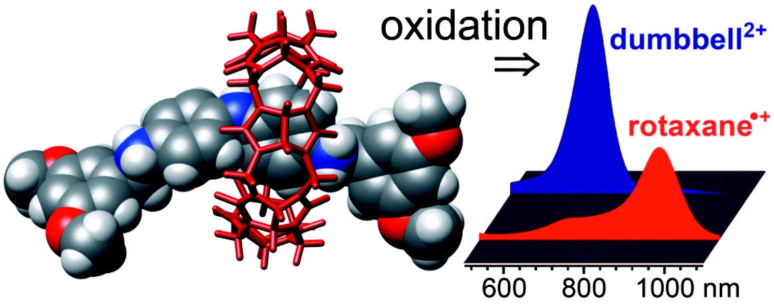
J. Am. Chem. Soc., **2007**, 129 (41), 12384-12385• DOI: 10.1021/ja074997i • Publication Date (Web): 21 September 2007



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Radical Cation Stabilization in a Cucurbituril Oligoaniline Rotaxane

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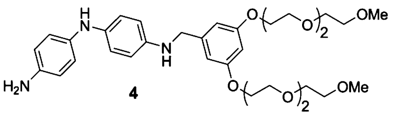
Polyaniline (PANI) is a remarkable conjugated polymer with application in electrochromic devices, sensors, electromechanical actuators, and rechargeable batteries and as a hole-transporting material in organic LEDs.[1] It can be doped to its conducting emeraldine state through a unique combination of oxidation and protonation, leading to conductivities as high as 1000 S cm^{-1}.[1,2] Recently, we and others have shown that the stability and optoelectronic properties of conjugated π-systems can be enhanced by molecular-scale encapsulation.[3] With the ultimate goal of developing materials and devices based on insulated PANI molecular wires, we are investigating the synthesis and properties of encapsulated monodisperse oligoanilines. Here, we report the synthesis of a cucurbit[7]uril-insulated oligoaniline [2]rotaxane **1**$\subset$CB[7]. The radical cation of this rotaxane, which resembles the conducting emeraldine state of PANI, is stabilized by the presence of the threaded cucurbituril macrocycle. This implies that the encapsulation of conjugated polymers in cucurbiturils can have more than just a passive insulating effect and can dramatically change the oxidation potential of the threaded π-system.

Previously, polyaniline chains have been threaded through β-cyclodextrins[4] and α-cyclodextrin-based nanotubes[5] to form pseudopolyrotaxanes, and wrapped in helical polysaccharides.[6] However, the formation of these supramolecular inclusion complexes is reversible and solvent-dependent, which limits the extent to which they can be purified or processed into devices. The polydisperse, and frequently paramagnetic, nature of these PANI inclusion complexes also makes it difficult to determine their structures and stoichiometries, and characterization has relied heavily on scanning probe techniques.[5] We therefore chose to synthesize monodisperse oligoaniline rotaxanes that would be kinetically stable in various solvents and would allow thorough structural characterization, to elucidate the effects of insulation on the properties of PANI and related oligoanilines.



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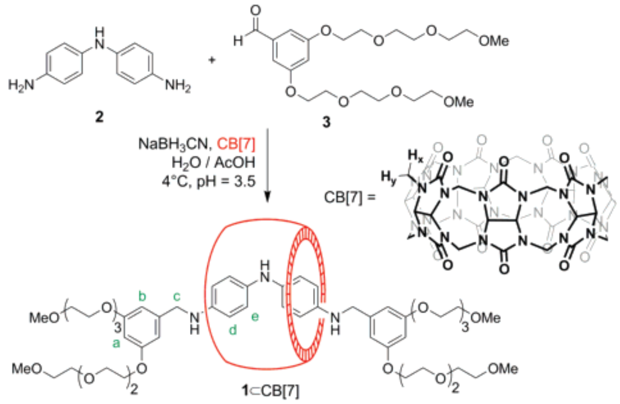
Cucurbit[*n*]urils (CB[*n*]'s) bind strongly to cationic guests in aqueous solutions,[7] so rotaxane **1**$\subset$CB[7] was synthesized via protonated oligoaniline **2** in dilute aqueous acetic acid (5.9 mM HOAc, pH 3.5), by reductive amination with aldehyde stopper **3** (Scheme 1). UV/vis titration showed that, under these conditions, both oligoaniline **2** and half-dumbbell **4** have high affinities for CB[7] ($K > 2.2 \times 10^6$ M^{-1} and $(2.8 \pm 0.6) \times 10^5$ M^{-1}, respectively); in contrast, **2** binds weakly to β-cyclodextrin under the same conditions ($K = (4.1 \pm 0.1) \times 10^2$ M^{-1}). Reaction of **2** with 1.9 equiv of stopper **3** in the presence of 2 equiv of CB[7] afforded a mixture of rotaxane **1**$\subset$CB[7] and half-dumbbell **4**. Rotaxane **1**$\subset$CB[7] was isolated as a white solid in 52% yield. The yield of rotaxane **1**$\subset$CB[7] can be increased (up to 85%) by increasing the amount of stopper aldehyde **3** present during the reaction, but this also leads to the formation of a second [2]rotaxane, from 3-fold reductive amination, which is difficult to separate from the desired rotaxane.

Scheme 1. Synthesis of [2]Rotaxane **1**$\subset$CB[7]



^{1}H NMR NOE experiments on the protonated rotaxane (in d_6-DMSO/TFA(2%)) revealed correlations from the axial H_x protons of the CB[7] to protons H_b, H_d, and H_e of the threaded oligoaniline dumbbell component **1** (Scheme 1). These NOEs are consistent with the calculated structure (Figure 1; minimum distances from H_x to protons H_b, H_c, H_d, and H_e = 3.8, 4.4, 3.9, and 3.7 Å, respectively). In this structure, the CB[7] forms two hydrogen bonds to one terminal ammonium center; however, these hydrogen bonds must be dynamic because the two ends of the rotaxane are equivalent on the NMR time scale.

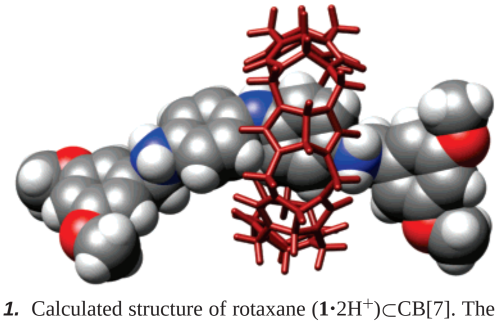


Figure 1. Calculated structure of rotaxane ($\mathbf{1}\cdot 2H^+$)$\subset$CB[7]. The CB[7] is shown in red; oligoethyleneglycol side chains are omitted for clarity.

No unthreading was detected, even after prolonged heating of the neutral **1**$\subset$CB[7] rotaxane (MeCN, 80 °C, 48 h), demonstrating that the stoppers are large enough to form a kinetically robust CB[7] rotaxane. To the best of our knowledge, only one CB[7] rotaxane has been reported previously.[8] In contrast to native CB[7], rotaxane **1**$\subset$CB[7] is soluble in most polar organic solvents, including MeOH, NMP, DMF, DMSO, and MeCN.

To investigate the influence of CB[7] encapsulation on the redox chemistry of this oligoaniline, rotaxane **1**$\subset$CB[7] and dumbbell **1** were oxidized in buffered aqueous solution (phosphate buffer, pH

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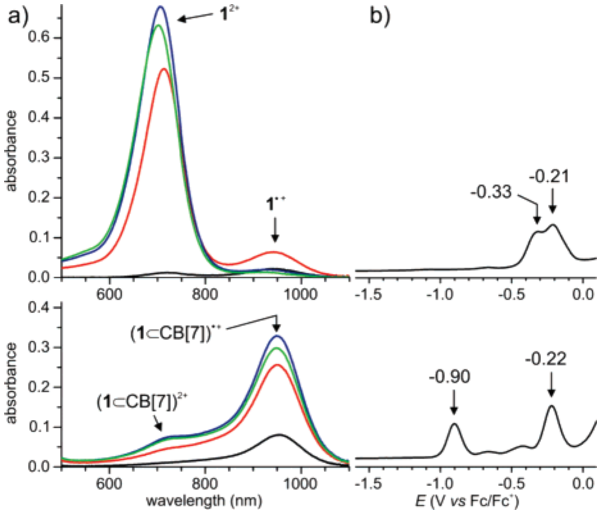

Figure 2. Oxidation of dumbbell **1** (top) and rotaxane **1**$\subset$CB[7] (bottom). (a) Absorption spectra showing chemical oxidation by $(NH_4)_2S_2O_8$ in water (phosphate buffer, pH 7.0), after 0 (black), 6 (red), 20 (blue), and 30 min (green), at an equal initial concentration of **1** and **1**$\subset$CB[7] of 42 μM. (b) Square wave voltammograms of **1** (top) and **1**$\subset$CB[7] (bottom), in DMSO with 0.1 M Bu_4NBF_4.

7.0) using 10 equiv of ammonium persulfate as the oxidant, and the process was monitored by UV−vis spectroscopy (Figure 2a). During oxidation of the free dumbbell **1**, initial formation of a broad band at 950 nm is observed. This wavelength is typical for a radical cation such as $\mathbf{1}^{\bullet+}$.[9] Further reaction rapidly results in the growth of a strong band at 700 nm and disappearance of the 950 nm band, indicative of oxidation of $\mathbf{1}^{\bullet+}$ to the benzoquinoid dication $\mathbf{1}^{2+}$. In the case of rotaxane **1**$\subset$CB[7], a similar but much stronger band at 950 nm is observed upon oxidation. In stark contrast to dumbbell **1**, only a weak shoulder around 700 nm is observed, even after prolonged reaction times and addition of a large excess of oxidant. EPR spectroscopy in DMSO supports the relative persistence of $(\mathbf{1}\subset\mathrm{CB[7]})^{\bullet+}$ versus $\mathbf{1}^{\bullet+}$. We also observed that solutions of the colorless rotaxane **1**$\subset$CB[7] rapidly oxidize to the blue radical cation in the presence of molecular oxygen, whereas aerobic oxidation does not occur with the free dumbbell under these conditions.

To explore the origin of this remarkable difference in oxidation behavior, the electrochemistry of **1** and **1**$\subset$CB[7] was investigated. Square wave voltammetry gave well-defined peaks for the first and second oxidations of both compounds (Figure 2b). The first and second oxidation are observed at −0.33 and −0.21 V for **1** and −0.90 and −0.22 V for **1**$\subset$CB[7], all relative to Fc/Fc$^+$. The first oxidation potential of rotaxane **1**$\subset$CB[7] is 570 mV lower than that of dumbbell **1**, which explains the sensitivity of the rotaxane to oxygen. However, the second oxidation potentials of **1** and **1**$\subset$CB[7] are nearly the same. The thermodynamic stabilization of the rotaxane radical cation $(\mathbf{1}\subset\mathrm{CB[7]})^{\bullet+}$ is a consequence of the strong affinity of the CB[7] macrocycle for cationic guests.[7c,10] The lack of a similar stabilization in the $(\mathbf{1}\subset\mathrm{CB[7]})^{2+}$ dication may be due to the geometrical inability of the cucurbituril to hydrogen bond simultaneously with both terminal N−H groups (Figure 1) and also to the low polarizability of the environment inside the CB[7] cavity.[3c] The persistence of the $(\mathbf{1}\subset\mathrm{CB[7]})^{\bullet+}$ radical toward further chemical oxidation appears to be a kinetic stabilization effect.

In conclusion, we have synthesized a CB[7]-encapsulated oligoaniline rotaxane using aqueous reductive amination. The CB[7] macrocycle binds strongly to the oligoaniline intermediates, resulting in a high yield of the desired rotaxane. UV−vis absorption, EPR and electrochemical measurements show that encapsulation by CB[7] increases the thermodynamic and kinetic stability of the radical cation of the threaded oligoaniline; the first oxidation potential of the π-system is reduced by 570 mV, corresponding to an increase of the comproportionation constant by a factor of 10^9. This radical cation has a stoichiometry similar to that of the conducting emeraldine salt form of PANI (i.e., 1 spin per 2 aniline monomers), so we anticipate that threading with CB[7] will have a dramatic effect on the electronic behavior of this conjugated polymer. Investigations along these lines are currently underway.

Acknowledgment. We thank Dr. T. D. W. Claridge for advice with the NMR experiments, A. Brown and Dr. M. T. Stone for preliminary experiments leading to this project, Dr. L. Isaacs for valuable discussion, and the Oxford Centre for Advanced ESR for their support. Financial support was provided by The Netherlands Organization for Scientific Research (NWO, Rubicon Fellowship, R.E.), the European Commission (Marie Curie Fellowship, R.E., and MRTN-CT-2006-036040), and the EPSRC.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA074997I