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Reverse Shuttling in a Fullerene-Stoppered Rotaxane

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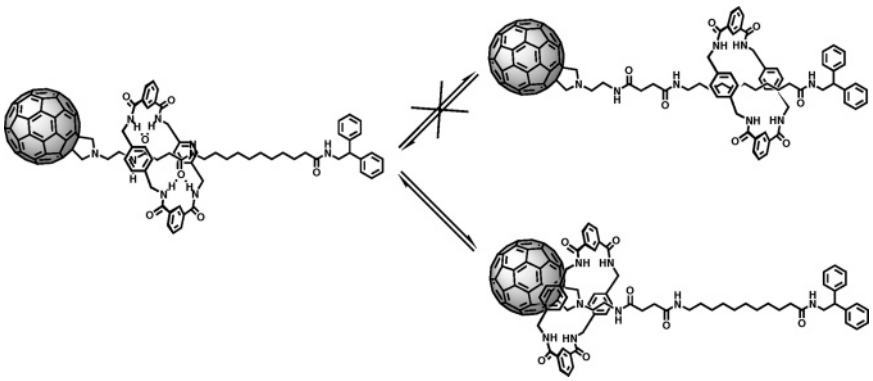
ABSTRACT



The preparation and characterization of a solvent-switchable rotaxane that shuttles in the opposite direction to that expected are reported. The reverse shuttling is confirmed by NMR spectroscopy and can be monitored by cyclic voltammetry. The electrochemically generated anions on the fullerene moiety are stabilized by the closer proximity of the macrocycle.

The usefulness of rotaxanes relies directly on their abacus-like structure. The search for new and efficient manners for shuttling the macrocycle along the thread, which can be employed to vary the chemical and physical properties of the molecule, is an important field of research. Several groups, active in this field, have developed a wide variety of switches to shuttle the macrocycle between two different and well-defined parts of the thread, which include solvent,[1−5] acid-base,[6−9] chemical,[10] electrochemical,[11,12] allosteric,[13] counterion,[14,15] and light-based switches.[16−21] Although electrochemical and light switches are among the best for triggering the translocation of the macrocycle for practical technological applications, solvent-switchable rotaxanes have been shown to be very useful when efficient switching without the need of further chemical transformation is required. In this light, solvent-switchable rotaxanes have been

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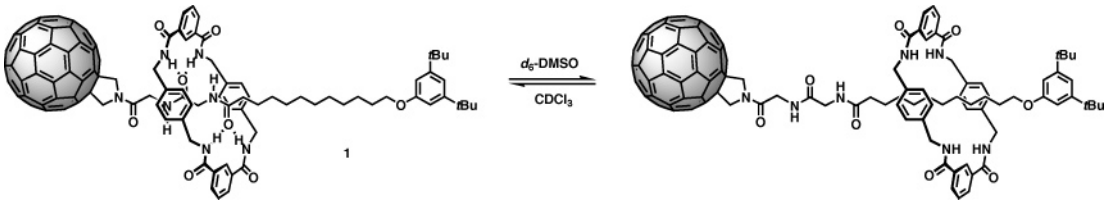
Scheme 1. Typical Behavior of Solvent-Switchable Molecular Shuttles

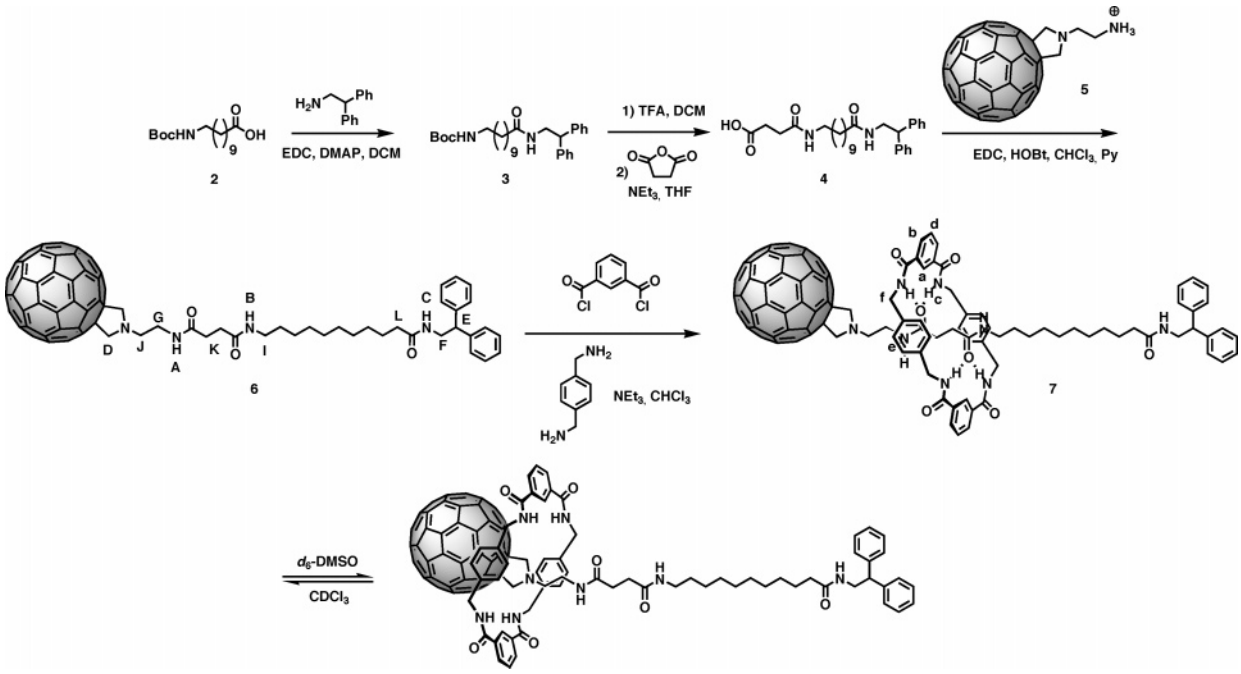


used for the preparation of solvent and pH sensors.[3] Rotaxane **1** is a good example of a solvent-switchable rotaxane equipped with a C_{60} stopper (Scheme 1).[1] In solvents that do not disturb hydrogen bonds, the macrocycle resides over the glycylglycine (GlyGly) template by complementary hydrogen bond recognition. Instead, in solvents that interfere with hydrogen bonds strongly such as DMSO, the macrocycle is positioned over the alkyl chain. This behavior is typical of this type of rotaxanes and is independent of the stopper used.[3,5] Fullerenes possess well-defined chemical, photophysical, and electrochemical properties.[22,23] Such properties can be affected by the presence or the position of the macrocycle,[1,24] providing a useful way to monitor shuttling. To further investigate the applicability of rotaxanes in research fields where fullerenes play an active role (i.e., photovoltaics, nonlinear optics, self-organization[25]), we decided to prepare an equivalent and more accessible rotaxane based on building block **5**[26−29] (Scheme 2) as the starting point, which is easier to process than N-H fulleropyrrolidine, used in the synthesis of rotaxane **1**. Surprisingly, in the analogous rotaxane **7**, the macrocycle switched in the opposite direction to that expected and positioned next to the fullerene stopper. The opportunity to have a third station opens new possibilities in fullerene-containing rotaxanes. Here, we describe the unexpected reverse shuttling of the new fullerene rotaxane.

Thread **6** displays a chemical structure equivalent to that of rotaxane **1**. It is comprised of a fullerene stopper attached to a succinamide template, functionalized with an alkyl chain that is equipped with a non-fullerenic stopper at the other end. Succinamide and GlyGly templates can be considered equivalent because they have the same internal degrees of freedom and bind weakly the macrocycle compared to other templates such as fumaramides,[30] which allows easier translocation of the macrocycle. 2,2′-Diphenylethylamine was coupled with 11-Boc-aminoundecanoic acid, previously activated using EDC/HOBt (Scheme 2). This was followed by deprotection of the amine and nucleophilic ring opening of succinic anhydride to give **4**. Then, fulleropyrrolidine **5** was coupled with **4** in pyridine, leading to the corresponding fullerene thread **6**.

Rotaxane **7** was assembled by simultaneous addition of isophthaloyl chloride and *p*-xylylenediamine to a solution of thread **6** in the presence of triethylamine. The structure of the rotaxane **7** was confirmed by NMR (^{1}H and COSY) MS, IR, and UV-vis-NIR. The low solubility of thread **6**

Scheme 2. Synthesis of the Reverse Solvent-Switchable Rotaxane **7**



and rotaxane **7** in organic solvents did not allow the acquisition of ^{13}C spectra. The position of the macrocycle along the thread can be monitored by NMR spectroscopy due to the anisotropy effect of the aromatic macrocycle over the thread. In $CDCl_3$ and THF-d_8, protons K (the assignments correspond to the lettering shown in Scheme 2) were shielded by nearly 1.4 ppm relative to the thread, showing that the macrocycle was located over the succinamide template[11] (Figure 1). In DMSO-d_6, the typical shielding of some protons in the aliphatic region was expected due to the location of the macrocycle over the alkyl chain. Surprisingly, the protons associated with the aliphatic chain underwent negligible shielding. Instead, the fulleropyrrolidine (D) and adjacent protons (G and J) were shifted upfield by as much as 0.8 ppm, which evidenced that the macrocycle was preferentially located in that region. A progressive deshielding of protons D, G, and J was observed together with the increase of the temperature in ^1H NMR spectra recorded in DMSO-d_6 up to 110 °C. Nevertheless, the rest of the signals remained mainly unaltered, indicative of faster pirouetting due to the higher temperatures.

The photophysical properties of thread **6** and rotaxane **7** were investigated by measurements centered on the fullerene stopper, which showed the typical characteristics of fulleropyrrolidines (see Supporting Information). However, almost identical features were observed for thread **6** and rotaxane **7** in the ground- and excited-state spectra recorded in DCM, PhCN, and DMSO. Such observations suggest that the macrocycle does not have a strong interaction with the fulleropyrrolidine stopper.

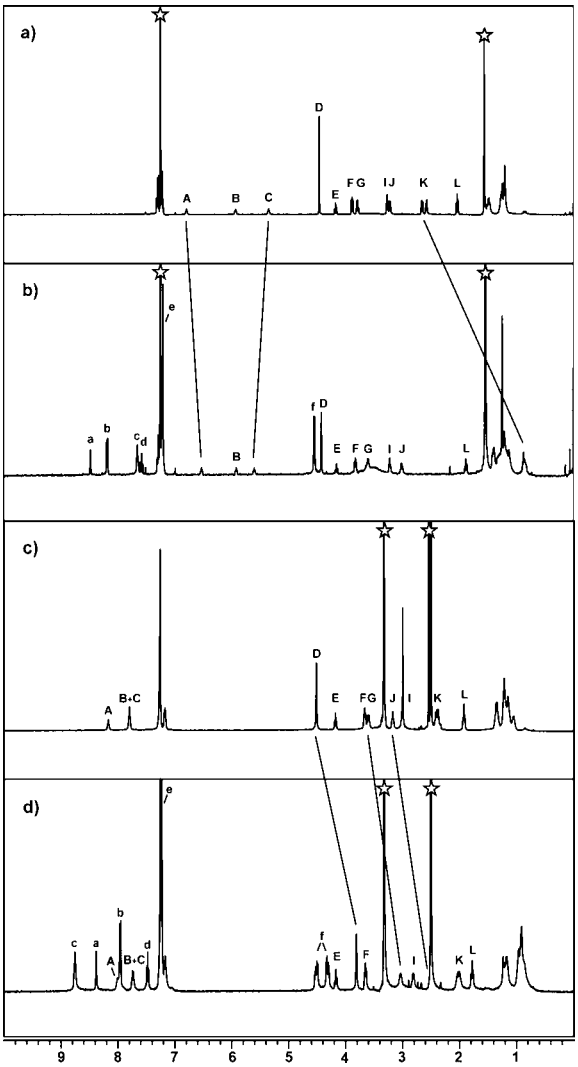


Figure 1. 400 MHz ^1H NMR spectra of (a) thread **6** in $CDCl_3$, (b) rotaxane **7** in $CDCl_3$, (c) thread **6** in DMSO-d_6, and (d) rotaxane **7** in DMSO-d_6. The peaks highlighted with stars correspond to residual solvent peaks.

The electrochemical properties of thread **6** and rotaxane **7** were investigated by cyclic voltammetry in THF as the hydrogen-bonding phase and in DMSO as the hydrogen-bond disrupting phase (see also Supporting Information). The voltammograms displayed five waves that correspond to the reduction of the fulleropyrrolidine stopper. The CV behavior of rotaxane **7** differs from that of thread **6** for anodic shifts of the half-wave potential values ($E_{1/2}$) for the first three cathodic processes (Table 1). In THF, $E_{1/2}$ values of rotaxane **7** were slightly affected by the presence of the macrocycle, by comparison with those of thread **6**, revealing weak interactions between the macrocycle and C_{60} that stabilizes the electrogenerated fullerene anions. When the electrochemical measurements were carried out in DMSO, more distinct shifts were observed, being especially substantial in

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Table 1. Half-Wave Potential Values ($E_{1/2}$, V) for the First Three Cathodic Processes in Different Solvents

wave	**6**[a]	**7**[a]	$\Delta E_{1/2}$[a]	**6**[b]	**7**[b]	$\Delta E_{1/2}$[b]
A	−0.603	−0.599	0.004	−0.395	−0.387	0.008
B	−1.132	−1.127	0.005	−0.828	−0.805	0.023
C	−1.757	−1.748	0.009	−1.432	−1.421	0.011

[a] THF (0.1 M $TBAPF_6$). [b] DMSO (0.1 M $TBAPF_6$).

the second reduction wave (23 mV), which is in agreement with the proximity of the macrocycle to the fulleropyrrolidine stopper (Figure 2). The $\Delta E_{1/2}$ values suggest that $\pi-\pi$ interactions might take place between the negatively charged fullerene and the macrocycle.

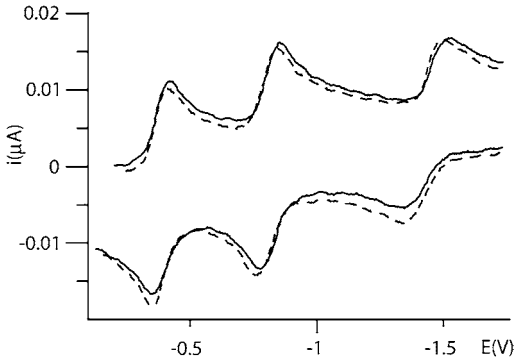

Figure 2. Cyclic voltammograms of thread **6** (—) and rotaxane **7** (- -) in DMSO (0.1 M $TBAPF_6$) at 1 V/s.

The ^{1}H NMR, photophysical, and electrochemical characterization of rotaxane **7** does not support the existence of strong interactions in the neutral state between the macrocycle and the fullerene stopper, and thus, reverse switching is explained as a result of solvation and solvophobic interactions.[2,3] Solvation of the peptide and the macrocycle by DMSO molecules results in decomplexation of the two components. In rotaxane **7**, the peptidic template is connected to the fulleropyrrolidine by two methylene groups (J and G), which allows shuttling in both directions. Weak interactions between the macrocycle and the spheroid might be responsible for the co-conformation where the macrocycle is positioned over the fulleropyrrolidine ring. Such interactions cannot be confirmed by changes in the UV-Vis absorption spectra. However, the presence of the macrocycle next to the fullerene spheroid does stabilize the electrochemically generated anions.

This effect and its applicability are currently under investigation because it provides a new way to induce shuttling that might be useful for the preparation of novel multistation rotaxanes.

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Supporting Information Available: Full experimental details and characterization, NMR and COSY spectra, and photophysical and electrochemical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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