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Hydrogen Bond-Assembled Fullerene Molecular Shuttle

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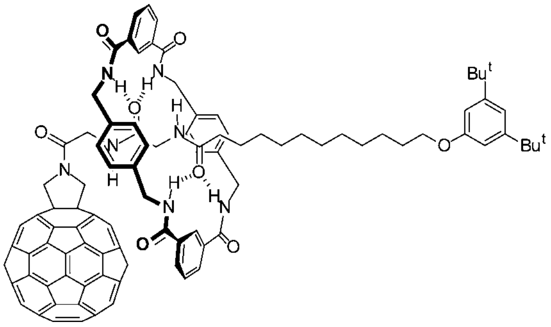
ABSTRACT



A novel [2]rotaxane has been prepared in which fullerene C_{60} behaves as both a stopper and a photoactive unit. The amphiphilic nature of the rotaxane thread can be used to shuttle the macrocycle from close to the fullerene spheroid (in nonpolar solvents) to far away (in polar solvents). The differing location of the macrocycle in dichloromethane and dimethyl sulfoxide gives rise to effects detectable by ^{1}H NMR and time-resolved spectroscopy.

Photoactive rotaxanes have attracted increasing interest in recent years due to their potential as components of molecular devices.[1] Fullerene C_{60} is particularly well suited as a rotaxane building block for several reasons. First of all, it is a bulky group, ideal for acting as a stopper. Second, C_{60} is highly electro- and photoactive.[2] Its incorporation into these potentially machine-like structures could give rise to a series of electrochemically induced or photoinduced events such as energy transfer or electron transfer for the construction of photoswitches, modulation of luminescence, etc.

Here we describe the synthesis of a novel hydrogen bond-assembled [2]rotaxane, **1**, which utilizes C_{60} as an active component.[3] The photophysical behavior of the rotaxane is also reported, probing the influence of the position of the macrocycle on the fullerene triplet excited state. The system is based on the hydrogen bond-directed assembly of a

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(3) Copper-complexed rotaxane with two fullerene stoppers has previously been reported (Diederich, F.; Dietrich-Buchecker, C.; Nierengarten, J.-F.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 781−782), and its properties have been studied (Armaroli, N.; Diederich, F.; Dietrich-Buchecker, C.; Flamigni, L.; Marconi, G.; Nierengarten, J.-F.; Sauvage, J.-P. *Chem. Eur. J.* **1998**, *4*, 406−416).

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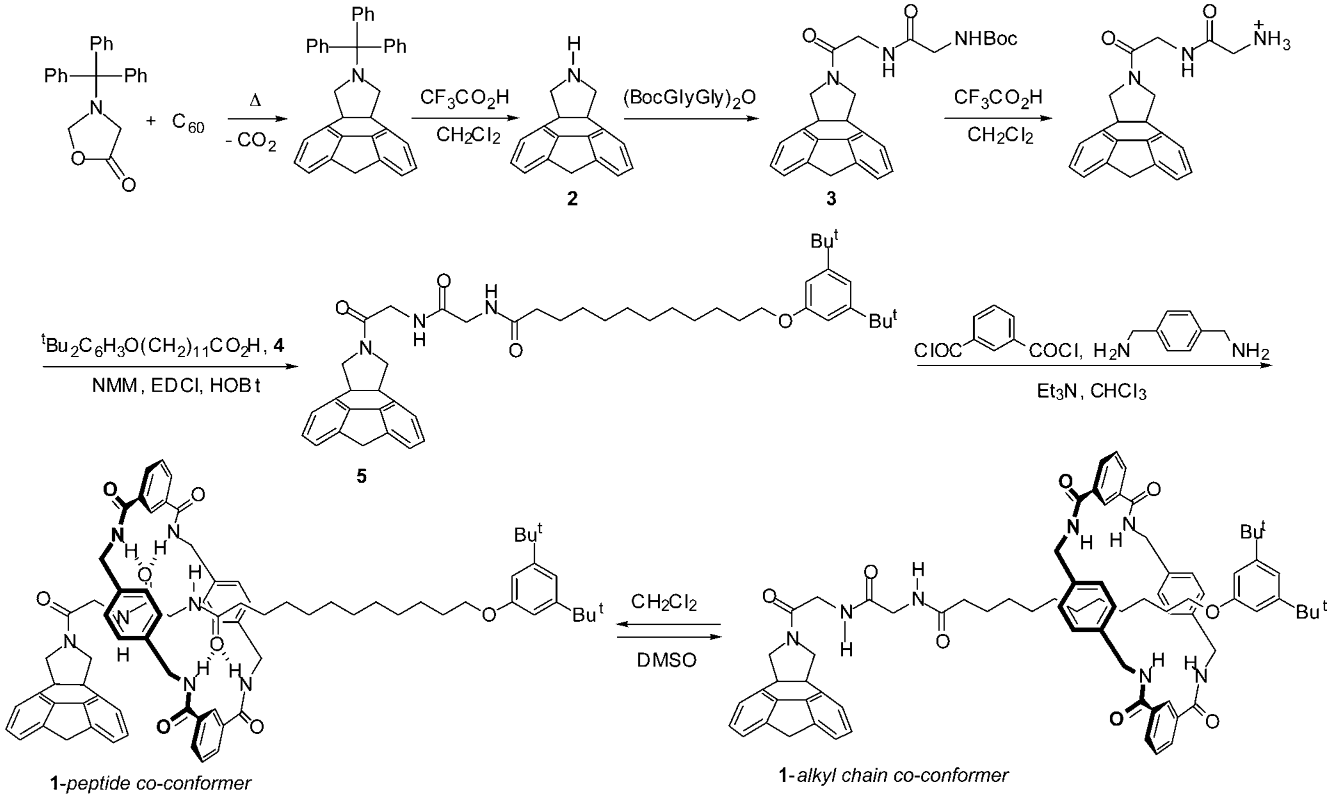
Scheme 1. Synthesis of Fullerene Molecular Shuttle **1**



benzylic amide macrocycle around a dipeptide thread, a method that has previously been shown to provide a straightforward route to functionalized, solvent-switchable molecular shuttles.[4]

Fulleropyrrolidine **2**, prepared according to a previous work,[5] was condensed with Boc-gly-gly[6] to afford fullerodipeptide **3** (Scheme 1).[7] After deprotection in acidic conditions, the resulting free amino group was coupled with acid **4** to give the thread **5**. Macrocyclization around the glycylglycine residue of **5** gave the fullerene [2]rotaxane **1** in 25% yield using standard rotaxane-forming conditions (*p*-xylylenediamine, isophthaloyl dichloride, Et_3N, $CHCl_3$).

It has previously been shown that amphiphilic peptide [2]rotaxanes exist as different co-conformers depending on the polarity of the environment.[4] In nonpolar solvents such as dichloromethane or chloroform, the macrocycle hydrogen bonds to the peptide residue; in highly polar solvents such as DMSO, the hydrogen bonding between the macrocycle and the peptide is disrupted by the competing solvent and polarophobic interactions locate the macrocycle preferentially over the alkyl chain. Indeed in $CDCl_3$ or CD_2Cl_2, the glycyl methylene protons of rotaxane **1** are shielded by nearly 1 ppm compared to the analogous protons of the thread, **5**, indicating that the macrocycle resides on the peptide residue in these solvents (**1**-*peptide* co-conformer). In DMSO-d_6, however, the peptide methylene groups appear at similar chemical shifts in both thread **5** and rotaxane **1**, and it is the alkyl chain protons that are shielded by nearly 1 ppm by the aromatic rings on the macrocycle, indicating that the macrocycle has shuttled down the thread to produce the **1**-*alkyl chain* co-conformer (Scheme 1).

Computer modeling of the co-conformations in the different types of solvents was performed using the Spartan program on a Silicon Graphics workstation (Figure 1).

In dichloromethane, the hydrogen bonding between the dipeptide and the macrocycle brings the latter very close to the fullerene spheroid. In DMSO, on the other hand, the macrocycle is located on the aliphatic portion of the thread and there should be no significant interactions between the fullerene moiety and the aryl groups of the macrocycle. The differences in co-conformation encouraged us to investigate the proximity effects of the macrocycle on the fullerene moiety using time-resolved spectroscopy.

The fullerene fluorescence and the fullerene triplet excited-state features in rotaxane **1**, thread **5**, and a fullerene reference that bears a solubilizing triethylenglycol chain [N-$(CH_2CH_2O)_3CH_3$ fulleropyrrolidine **6**][8] were investigated in both CH_2Cl_2 and DMSO. In CH_2Cl_2, the fluorescence of

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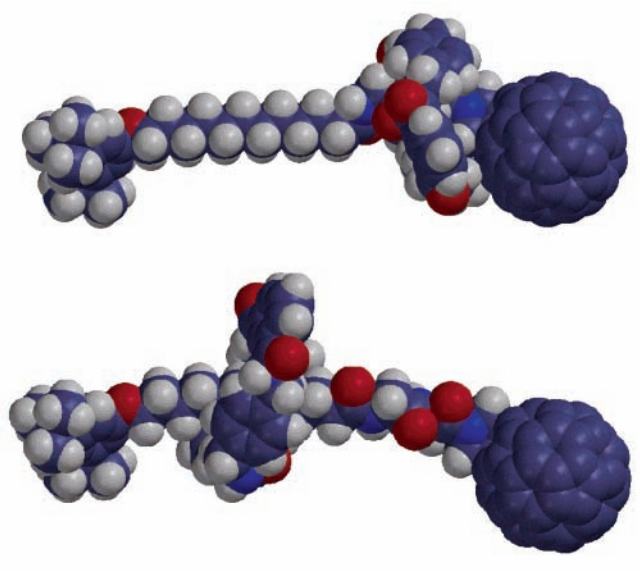

Figure 1. Space-filling model of rotaxane **1** in CH_2Cl_2 (top, peptide co-conformer) and DMSO (bottom, alkyl chain co-conformer).

the C_{60}-rotaxane **1** and the C_{60}-thread **5** is noticeably quenched (25% fluorescence quenching) relative to the fulleropyrrolidine reference.[2b] This is indicative of a weak electronic interaction between the fullerene in its singlet excited state and the adjacent amide linkages. Overall, this leads to a decrease in the fullerene fluorescence quantum yield. The proximity of the macrocycle to the fullerene actually contributes negligibly to the fluorescence quenching.

In contrast, in DMSO the strong interaction of the weakly redox active amide linkages with the solvents prevails over the possible engagement of the amide groups with the photoexcited fullerene. As a consequence, the fluorescence quantum yields of the C_{60}-rotaxane complex and the C_{60}-thread become comparable with that of the fulleropyrrolidine reference.

The triplet−triplet spectra of thread **5**, rotaxane **1**, and fullerene reference **6** all show identical spectral features in DMSO. In particular, the two maxima at 700 and 380 nm have nearly superimposeable extinction coefficients ($\epsilon_{700\ \mathrm{nm}} \approx 16\,100$ M^{-1} cm^{-1} and $\epsilon_{380\ \mathrm{nm}} \approx 10\,300$ M^{-1} cm^{-1}, respectively) (Figure 2a).[2b] Again, we rationalize this observation with insignificant perturbations of the fullerene core by both the macrocycle (distance effect) and the amide groups of the thread (neutralized by the hydrogen bonding solvent).

However, the situation is notably different in dichloromethane (Figure 2b). The most obvious difference is seen between the triplet spectra of the C_{60}-rotaxane **1** and the C_{60}-thread **5**. These deviate substantially from each other, suggesting that the triplet spectra are sensitive to effects stemming from the close proximity of the macrocycle and/or the inductive effects of the intercomponent hydrogen bonding. To underpin this argument, it is interesting to note that the triplet spectra of C_{60}-thread **5** and fulleropyrrolidine reference **6** resemble both each other and those recorded in DMSO quite well.

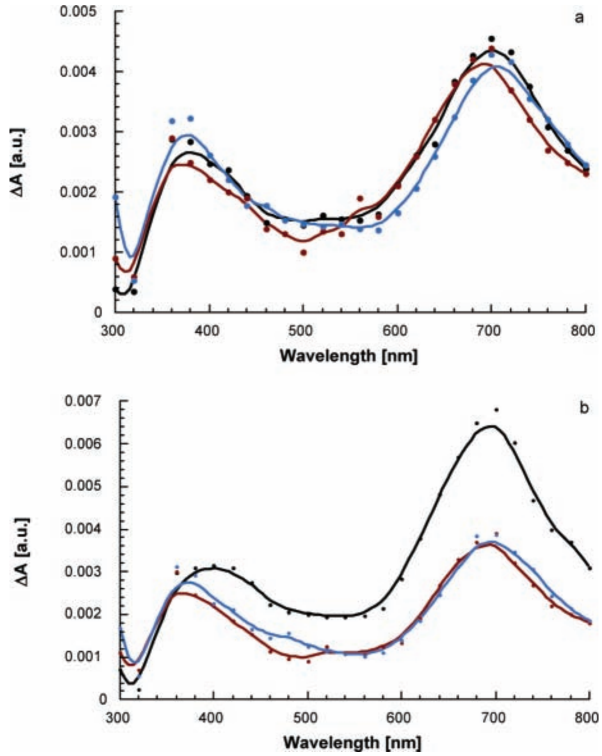

Figure 2. Triplet−triplet spectra of rotaxane **1** (black spectrum), *N*-TEG-fulleropyrrolidine **6** (red spectrum), and thread **5** (blue spectrum) in DMSO (a) and CH_2Cl_2 (b) following 337 nm laser excitation with a Nitrogen Laser of a solution that exhibited an absorption of 0.5 at the 337 nm excitation wavelength.

Finally, the triplet lifetimes follow exactly the trend seen in the fluorescence quantum yields. While in DMSO, the triplet lifetime is ~17 μs and nearly identical for all three compounds; only those of the C_{60}-rotaxane **1** and the C_{60}-thread **5** in dichloromethane are shorter by a factor of 1.7 (~10 μs).

In conclusion, we have synthesized a novel fullerene-containing [2]rotaxane in which the macrocycle can be shuttled between co-conformations that position it either close to or far away from the fullerene moiety. The proximity of the macrocycle does not affect fluorescence but has a significant effect on the triplet−triplet spectra of the fullerene fragment.

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Supporting Information Available: Full experimental details pertaining to the preparation of **1** and **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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