

Photoactive [2]Rotaxanes Formed by Multiple π -Stacking

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Abstract: A [2]rotaxane has been synthesized having an anthracenyl "stopper" at each end of a flexible polyether "thread" which folds to facilitate π -stacking between the centralized cyclophane and the anthracene moieties, forming a five-membered π -stack.

Interaction between an electron donor and a complementary electron acceptor can form a charge-transfer (CT) complex possessing a distinct absorption transition in the visible spectral range. Illumination into this absorption band results in spontaneous generation of an intimate radical ion pair due to electron transfer from donor to acceptor within the complex.¹ In most cases, ultrafast charge recombination² restores the ground state complex, although solvent penetration and diffusive separation may compete with reverse electron transfer.³ The ability to selectively excite into the CT absorption band and the highly efficient forward electron-transfer step make such CT complexes attractive modules for construction of photoactive supramolecular systems.⁴ However, concerns about the poorly defined geometry of the CT complex and the rapid rates of charge recombination have to be addressed. The structure of the complex can be better defined by incorporating it into a rotaxane of the type shown in Figure 1 while the energy wasting charge-recombination step can be curtailed by covalent attachment of a secondary electron donor to the rotaxane such that sequential electron transfer might occur.⁵

In the latter case, it is essential that electron transfer from the oxidized form of the primary donor to the secondary donor competes effectively with charge recombination within the radical ion pair. For a useful device, it is also necessary that electron transfer between the oxidized secondary donor and the primary acceptor is relatively slow.⁶ This daunting requisite might be achieved if the secondary donor can be closely associated with the CT complex via π -stacking in such a way that secondary electron transfer is followed by unwinding of the thread (Figure 2). We now show that rotaxane 1 (Figure 1) appears to undergo multiple [intramolecular] π -stacking between the central and terminal subunits. The importance of this effect cannot be overstated. Such close-packing of the subunits is essential if secondary electron transfer is to compete effectively with the inherently rapid charge-recombination process and it is only by using a flexible thread that the subsequent restoration of the ground state system will be kept sufficiently slow. In principle, the rate of this final electron-transfer step could be modulated by varying the length of the thread.

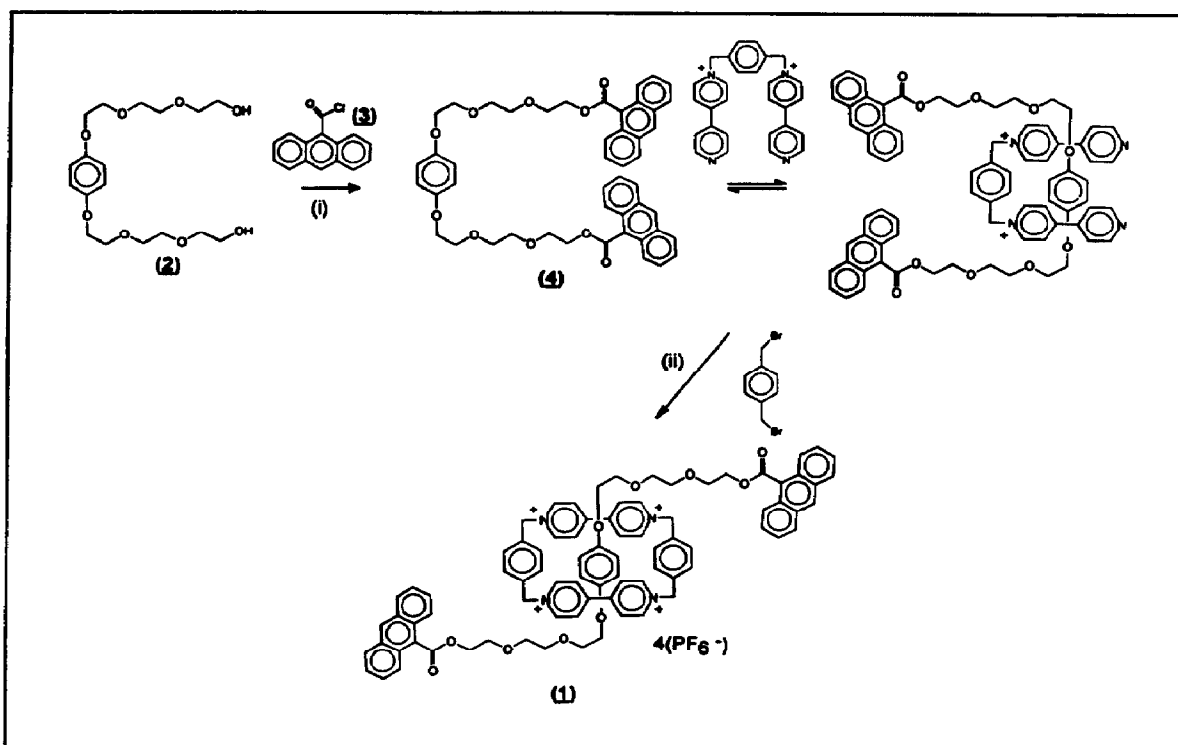


Figure 1. Synthetic route used for preparation of the [2]rotaxane 1: (i) reflux in dry acetonitrile, silica chromatography, yield 45%. (ii) AgPF_6 , acetonitrile at 25 °C for 7 days, silica chromatography, ion exchange, yield 25%.

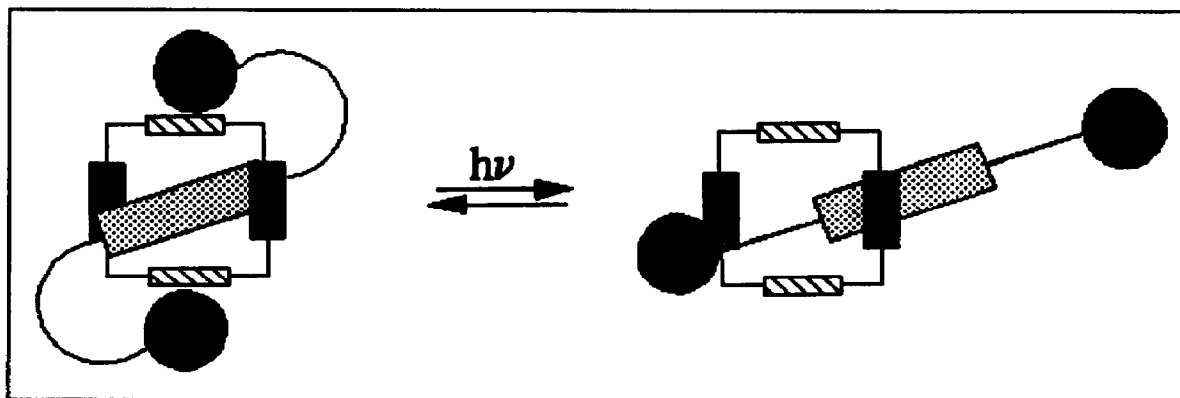


Figure 2. Cartoon showing the light-induced and subsequent thermal conformational changes expected for the [2]rotaxane.

The synthetic route employed to prepare the [2]rotaxane **1** is depicted in Figure 1; the final material was purified by ion-exchange and extensive column chromatography on silica. 9-Anthroyl chloride (**3**),⁷ 1,4-bis[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]benzene (**2**)⁸ and 1,1'-[1,4-phenylenebis(methylene)]-bis-4,4'-bipyridinium bis(hexafluorophosphate) (**5**)⁸ were prepared by literature methods. The terminally disubstituted thread **4**⁹ was prepared in average yield of 45% by refluxing **2** with a slight molar excess of **3** in dry acetonitrile, followed by column chromatography on silica. Cyclization of **5**⁸ with α,α' -dibromo-*p*-xylene in the presence of the corresponding thread **4** was carried out using the template method pioneered by Stoddart *et al.*⁸, and gave the corresponding rotaxane **1**¹⁰ in an unexpectedly high [unoptimized] yield of 25%. We attribute this apparently facile cyclization step, which occurs in much higher yield than found for most other comparable [2]rotaxanes,¹¹ to the additional templating effect produced by the appended anthracene groups, which can π -stack with the 4,4'-bipyridinium subunits prior to cyclization. In this manner, the 4,4'-bipyridinium groups are locked into position by both internal and external templating effects such that clipping of the second xylene subunit is expected to proceed smoothly.

Preliminary X-ray crystallographic data collected for **1** confirm a folded conformation in which both anthracene moieties are in van der Waals contact with the N,N'-bipyridinium groups of the cyclophane. Thus, the centralized dialkoxybenzene donor and each of the terminal anthracene moieties are spatially separated by one of the N,N'-bipyridinium subunits. Significant upfield shifts observed for the anthracene protons in the ¹H NMR spectra indicate that similar folding and π -stacking also occurs in CD₃CN solution at 25 °C; for example, the easily identified singlet H₁₀ proton on the anthracene residues is shifted upfield by *ca.* 0.4 ppm relative to the thread **4**. This intramolecular self-assembly process has the effect of aligning five aromatic nuclei into a single π -stack and ensures close electronic contact between the terminal stoppers and the central CT complex in both solution and solid phases. This means that secondary electron transfer can take place via π -orbitals on the aromatic spacer rather than along the σ -bonding framework of the aliphatic chain and, in turn, this should represent a considerable enhancement in rate.

The absorption spectrum recorded for **1** in acetonitrile shows both the characteristic Gaussian-shaped CT band, centered at 486 nm, and the well-resolved absorption peaks located at 330, 346, 362, and 382 nm due to (π,π^*) transitions localized on the anthracene moieties. The position of the CT absorption maximum is *ca.* 16 nm red-shifted relative to that found with nonaromatic stopper groups; a finding consistent with the alleged π -stacking. Complete quenching of the anthracene fluorescence is observed in dilute acetonitrile solution ($\Phi_f < 0.001$; $\tau_f < 30$ ps)¹² due to rapid electron donation from the excited singlet state to the electron-affinic cyclophane. Direct excitation into the CT band with a short laser pulse results in immediate generation of the radical ion pair⁴ which decays rapidly back to the ground state *via* charge recombination. Secondary electron transfer from the oxidized dialkoxybenzene π -radical cation to one of the appended anthracene moieties does not occur in this system, despite their close proximity, because of the unfavorable thermodynamic driving force ($\Delta^0 \approx 0.25$ eV). However, having established the concept of effective π -stacking between stopper and central CT complex it should now be possible to design and synthesize second generation prototypes possessing more readily oxidizable stoppers that also undergo π -stacking.

ACKNOWLEDGMENTS

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7. Goeckner, N. A.; Synder, H. R. *J. Org. Chem.* **1973**, *38*, 481-483. **Analytical data** ^1H NMR (250 MHz; CDCl_3): 7.51-7.69 (m, 4H); 8.03-8.07 (d, 2H, $J = 8.5$ Hz); 8.10-8.15 (d, 2H, $J = 8.5$ Hz); 8.58 (s, 1H). FT-IR (Nujol mull): 1800 cm^{-1} (C=O). Melting point $96-97^\circ\text{C}$: Lit. $103-104^\circ\text{C}$.
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9. **Analytical data** ^1H NMR (250 MHz; CDCl_3): 3.76-3.81 (m, 12H); 3.93-3.98 (m, 8H); 4.77-4.81 (t, 4H, $J = 4.6$ Hz); 6.74 (s, 4H); 7.43-7.56 (m, 8H); 7.98-8.01 (d, 4H, $J = 7.9$ Hz); 8.12-8.15 (d, 4H, $J = 7.9$ Hz); 8.51 (s, 2H). ^{13}C NMR (62.9 MHz; CDCl_3): 64.54; 67.93; 69.11; 69.93; 70.70; 70.82; 115.45; 125.15; 126.92; 128.50; 129.41; 130.93; 152.97; 169.45. FAB-MS (NBA matrix): 782 (M) $^+$; 577 (M-C₁₅H₉O) $^+$.
10. **Analytical data** ^1H NMR (250 MHz; CD_3CN): 2.99 (s, 4H); 3.28-3.30 (m, 4H); 3.60-3.69 (m, 4H); 3.88-3.92 (m, 8H); 4.09-4.11 (m, 4H); 4.77-4.79 (m, 4H); 5.30 (s, 8H); 6.98-7.01 (d, 8H, $J = 6.9$ Hz); 7.37-7.46 (m, 8H); 7.48 (s, 8H); 7.69-7.73 (d, 4H, $J = 8.8$ Hz); 7.75-7.78 (d, 4H, $J = 8.2$ Hz); 8.22 (s, 2H); 8.83-8.85 (d, 8H, $J = 6.9$ Hz). ^{13}C NMR (62.9 MHz; CD_3CN): 65.33; 67.42; 70.29; 70.59; 71.25; 71.52; 113.32; 125.29; 125.47; 127.18; 128.27; 128.70; 129.53; 130.68; 131.31; 137.11; 144.50; 145.32; 150.44; 169.07. FAB-MS (NBA matrix): 1737 (M-PF₆) $^+$; 1592 (M-2PF₆) $^+$; 1447 (M-3PF₆) $^+$.
11. A relatively high yield of a [2]rotaxane (i.e., 32%) has been reported previously and attributed to an internal templating effect similar to that described here. See: Anelli, P. L.; Spencer, N.; Stoddart, J. F. *J. Am. Chem. Soc.* **1991**, *113*, 5131-5133.
12. For ethyl anthracen-9-oate in acetonitrile solution the fluorescence quantum yield (Φ_f) is 0.21 [Shao-Lin Shon, R.; Cowan, D. O.; Schmiegel, W. W. *J. Phys. Chem.* **1975**, *79*, 2087-2092] and the fluorescence lifetime (τ_f) is 7.0 ns.

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