Enhanced Hydrogen Bonding Induced by Optical Excitation: Unexpected Subnanosecond Photoinduced Dynamics in a Peptide-Based [2]Rotaxane

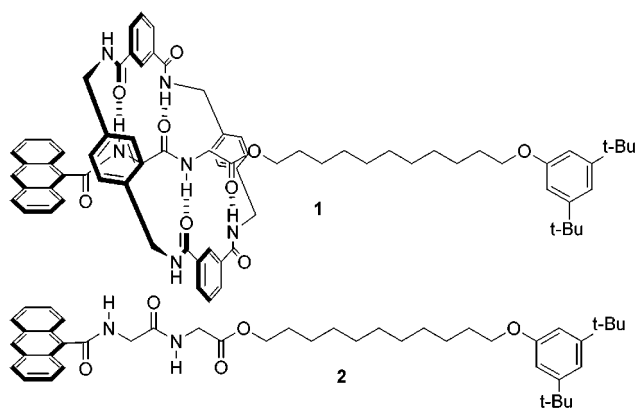George W. H. Wurpel,[†] Albert M. Brouwer,*,[†]
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Control of the shuttling process in rotaxanes using external sources has been the subject of considerable recent research.[1] Photoinduced motions are particularly interesting because of the convenient use of this stimulus in possible future device applications. Up to now, however, translational shuttling in photoactive rotaxanes has required external reagents or catalysts to occur (sacrificial reductants, sensitizers etc.), and generally takes place over relatively long time scales.[2] Here we report on the excited-state dynamics of rotaxane **1**, and show that in nonpolar solvents at room temperature an unexpected photoinduced co-conformational[3] change takes place that requires no external assistance and occurs on a *subnanosecond* time scale. It involves a rearrangement in the pattern of hydrogen bonds between thread and macrocycle leading to a shift of the latter from the peptide site toward the anthracene-9-carboxamide stopper which has a greatly enhanced hydrogen bonding affinity in the excited state.

Rotaxane **1** (Figure 1) consists of a thread containing a glycylglycine recognition motif used to promote rotaxane formation[4,5] and a bulky anthracene stopper. ^{1}H NMR studies, supported by X-ray crystallography of a close analogue of **1** (both included as Supporting Information), show that in relatively nonpolar solvents (e.g. CDCl_3, 1,4-dioxane, etc.) **1** principally adopts co-conformations with the macrocycle surrounding the peptide part of the thread (Figure 1). It appears that the nonplanarity of the anthracene-9-carboxamide unit prevents the macrocycle from

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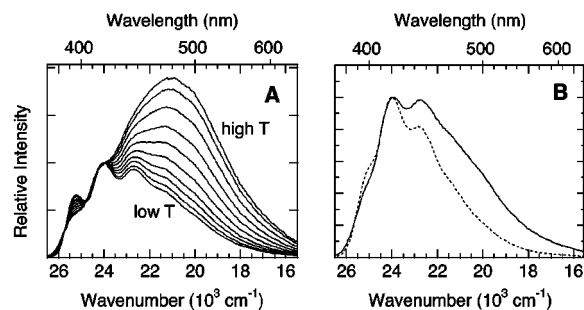
(1) For comprehensive reviews see: (a) Benniston, A. C. *Chem. Soc. Rev.* **1996**, *25*, 427. (b) Sauvage, J. P. *Acc. Chem. Res.* **1998**, *31*, 611−619. (c) Balzani, V.; Gomez-Lopez, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405−414. (d) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391.

(2) (a) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N. *J. Am. Chem. Soc.* **1997**, *119*, 7605−7606. (b) Armaroli, N.; Balzani, V.; Collin, J. P.; Gaviña, P.; Sauvage, J. P.; Ventura, B. *J. Am. Chem. Soc.* **1999**, *121*, 4397−4408. (c) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Dress, K. R.; Ishow, E.; Kleverlaan, C. J.; Kocian, O.; Preece, J. A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558−3574. (d) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. H. *Science* **2001**, *291*, 2124−2128.

(3) "Co-conformation" refers to the relative positions of the mechanically interlocked components with respect to each other, see: Fyfe, M. C. T.; Glink, P. T.; Menzer, S.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2068−2070.

(4) Lane, A. S.; Leigh, D. A.; Murphy, A. *J. Am. Chem. Soc.* **1997**, *119*, 11092−11093.

(5) Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 728−732.

Figure 1. Rotaxane **1** and thread **2**. The hydrogen bond pattern shown in **1** corresponds to that found in the X-ray structure of a similar exo-pyridyl macrocycle containing rotaxane (Supporting Information).
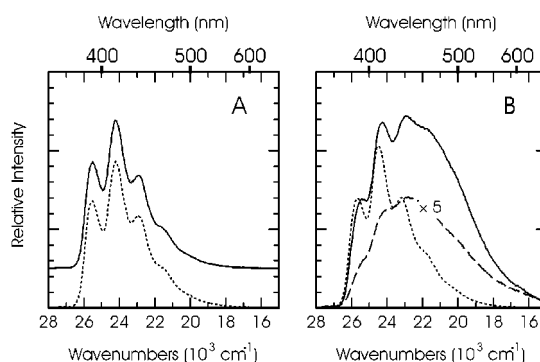
Figure 2. (A) Fluorescence spectra of rotaxane **1** (continuous) and thread **2** (dotted) in DMSO (note the vertical offset). (B) Fluorescence spectra of **1** (continuous) and **2** (dotted) in 1,4-dioxane and **2** in 2,2,2-trifluoroethanol (dashed). All spectra have been scaled to the same absorbance at the excitation wavelength (330 nm).

simultaneously binding to both amide carbonyl groups in the normally preferred manner for peptide rotaxanes.[4,5]

Rotaxane **1** was originally intended as an "inactive" model compound for studies aimed at investigating energy transfer or electron transfer between the mechanically interlocked components of rotaxanes. Since energy transfer or electron transfer from the excited anthracene to this macrocycle is impossible on thermodynamic grounds[6] one would expect the fluorescence of **1** to be virtually identical with that of the thread **2**. As shown in Figure 2A, this is in fact the case in dimethyl sulfoxide (DMSO), a solvent in which the hydrogen bonding between the peptide station and the macrocycle is disrupted and the macrocycle resides on the alkyl chain of the thread, far from the anthracene unit.[4] In non-hydrogen bond disrupting solvents such as 1,4-dioxane (Figure 2B), however, the fluorescence of the rotaxane is considerably broader and more intense than that of the thread. Since some of the vibrational fine structure of the anthracene emission is retained, it seems likely that the broad emission band is composed of two contributions, viz. one that resembles the thread spectrum and an additional broad red-shifted band.

The fluorescence of anthracene-9-carboxamide has been studied by Werner and Rogers,[7] who observed that the spectrum is broadened and red-shifted in the strongly hydrogen bond donating solvent 2,2,2-trifluoroethanol. The thread **2** shows the same effect

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(6) The lowest excited singlet state is located on the anthracene−carboxamide moiety and has an $E_{00} = 3.22$ eV. Its oxidation potential (1.6 V vs SCE) is not sufficient to allow reduction of any group in the ring.

(7) Werner, T. C.; Rodgers, J. *J. Photochem.* **1986**, *32*, 59−68.

Figure 3. Fluorescence spectra of rotaxane **1** excited at 330 nm: (A) CH_2Cl_2 at 307.7, 285.7, 266.7, 250.0, 235.3, 222.2, 210.5, 200.0, 190.5, 181.8 K and (B) glassy sucrose octaacetate at 30 °C (dashed) and molten at 140 °C (continuous). All spectra were scaled to the same intensity at 24000 cm^{-1}.

(Figure 2). Werner and Rogers explained their observation by assuming that in the excited singlet state the conformation changes from one in which the planes of the amide group and the anthracene ring are essentially perpendicular to a planar configuration, in which a considerable transfer of charge onto the carbonyl oxygen atom occurs, leading to enhanced hydrogen bonding.[8]
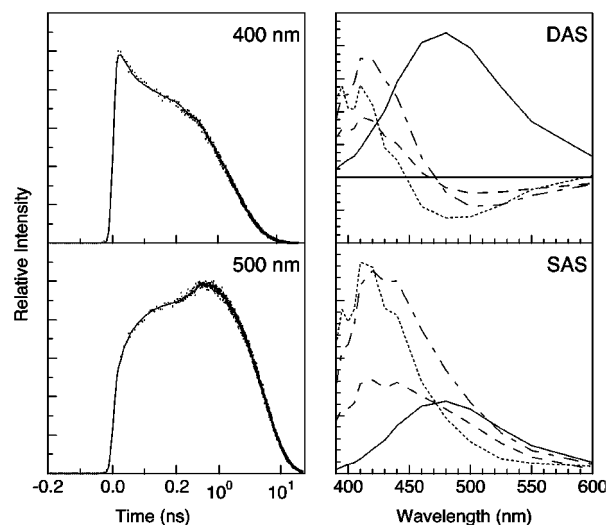
Considering that the broad red-shifted contribution to the spectrum of **1** is not observed in DMSO, where the macrocycle is displaced from the peptide station to the hydrocarbon tail, we attribute the occurrence of the long-wavelength shoulder to emission from a relaxed co-conformation in which the macrocycle is bound to the anthracene amide. The question remains whether this is a static or a dynamic effect.

If the effect is dynamic, it should be possible to prevent it by lowering the temperature and by placing the rotaxane in a solid matrix (Figure 3). Indeed, upon lowering the temperature the long-wavelength shoulder disappears. In solid sucrose octaacetate at room temperature, a structured anthracene-like emission is observed, and only upon melting of the matrix does the long-wavelength band appear again.

Finally, time-resolved fluorescence spectroscopy was performed by using picosecond Single Photon Counting. Decay traces were recorded at a number of wavelengths and globally analyzed.[9] Some of the results obtained in CH_2Cl_2 are shown in Figure 4.

In accordance with the proposed excited-state relaxation of anthracene-9-carboxamide, the thread **2** shows a biexponential decay. The initial perpendicular conformation relaxes in 78 ps to a more planar conformation, which has a decay time of 3.43 ns and is slightly red-shifted. For rotaxane **1** such a simple kinetic scheme is not applicable; for a good fit at least four exponentials are required. The Decay Associated Spectra (DAS, Figure 4) of 36 ps, 0.26 ns, and 1.82 ns possess negative amplitudes above 450 nm. This shows that the species emitting at long wavelength ($\tau = 4.33$ ns) is formed from a number of precursors on time scales of 36 ps, 0.26 ns, and 1.82 ns. The precursor species have anthracene-like structured emission at short wavelengths, consistent with the fact that they do not "distort" the chromophore by hydrogen bonding.

If we assume a model with two groups of co-conformations these fluorescence decays can be understood. The fastest component corresponds with the short-lived state in the thread. In this state, which is formed upon excitation, the various conformations of **1** are indistinguishable. After 36 ps two spectrally similar

(8) Preliminary ab initio calculations (HF/6-31G* for the ground state and CIS/6-31G* for the S_1 state) support this view.
(9) van Stokkum, I. H. M.; Scherer, T.; Brouwer, A. M.; Verhoeven, J. W. *J. Phys. Chem.* **1994**, *98*, 852−866.

Figure 4. (Left) Fluorescence decay traces of **1** in CH_2Cl_2 at two wavelengths, together with their fit. The time axis is linear up to 0.2 ns, and logarithmic thereafter. (Right) Results from the global and target analysis, showing the Decay Associated Spectra (DAS) and Species Associated Spectra (SAS). Key: 36 ps (dotted), 0.26 ns (dashed), 1.82 ns (dot−dashed), 4.33 ns (continuous).
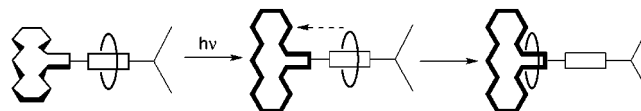
Figure 5. Proposed mechanism for the excited-state dynamics of **1**.

states have been formed which evolve with different decay times (0.26 and 1.82 ns) to the long-lived, broad, and red-shifted state. The Species Associated Spectra (SAS) for this model are shown in Figure 4.

Our results have led to the hypothesis that the emissive states with anthracene-like character correspond to co-conformations where the macrocycle is bound to the dipeptide motif. The broad, strongly red-shifted emission then arises from a co-conformation where the macrocycle forms hydrogen bonds with the carbonyl directly attached to the anthracene in a mechanism as shown in Figure 5.

In conclusion, we have shown that significant macrocycle motion can be induced in a rotaxane on a short time scale without the need for any additional external assistance besides photons. Although in the present system the displacement caused is not particularly large (approximately 3 Å), the concept of enhanced hydrogen bonding induced by optical excitation may lead toward more spectacular translational phenomena in molecular shuttles designed on this principle.

Supporting Information Available: Synthesis and characterization of **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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