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## COMMUNICATION

## Solvatochromic rotaxane molecular shuttles†

Duygu Deniz Günbaş, Leszek Zalewski‡ and Albert M. Brouwer\*

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A strongly fluorescent bistable rotaxane is described in which the relative position of the macrocyclic ring with respect to a solvatochromic fluorophore gives a strong response in the spectral domain.

Mechanically interlocked architectures, such as catenanes and rotaxanes, offer an attractive framework for the study of relatively weak intermolecular interactions, without the complications of dissociation of the assemblies in solution.<sup>1</sup> Manipulation of the intercomponent interactions can give rise to molecular switches and motors.<sup>2</sup> One of the challenges in this field is not only to control the co-conformational isomerism and the dynamics of the shuttling motion in which the macrocyclic ring moves back and forth between stations, but also to be able to detect the state of the system with high time resolution and high sensitivity. Fluorescence spectroscopy is potentially ideal for this, because it can be used to detect processes down to the picosecond time scale, and its sensitivity even allows the observation of the properties of individual molecules.3 A number of rotaxanes containing fluorescent groups have been described in the literature,<sup>4,5</sup> but with few exceptions<sup>6,7</sup> the fluorophores do not have sufficient brightness and photostability to be suitable for single molecule observation. In order to make the properties of the fluorophore sensitive to interaction with the moveable ring,<sup>6</sup> in the present work we have incorporated a bright and solvatochromic chromophore<sup>8</sup> into a hydrogen-bonded rotaxane.

Molecular switch 1 (Scheme 1) was assembled using a protocol developed by Leigh and co-workers.<sup>9,10</sup> In order to place the macrocyclic ring directly in contact with an imide unit, a new template was introduced in this work, consisting of a simple amide, linked to the imide by a  $CH_2$  group. It is well known that an imide is not a good binding site for the tetra-amide macrocycle.<sup>11</sup> The macrocyclic ring can be formed using a simple amide as a template, albeit in low yield.<sup>12</sup> The combination of amide and imide provides a template that resembles the ideal *trans*-1,4-dicarbonyl unit,<sup>9</sup> but steric

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‡ Present address: Reckitt Benckiser Produktions GmbH, Ludwig-Bertram-Str. 8–10, 67059 Ludwigshafen, Germany.



Scheme 1 Two translational co-conformers of rotaxane 1.

hindrance results from the second C=O group of the imide. The yield of the ring closure reaction forming the rotaxane is relatively low, 16% based on the amount of thread subjected to the reaction.

The <sup>1</sup>H NMR spectra of rotaxane **1** and thread **2** in CD<sub>2</sub>Cl<sub>2</sub> (Fig. 1) indicate that the CH<sub>2</sub> groups between the imide and the glycine carbonyl groups in the rotaxane ( $H_d$  and  $H_k$ ) are substantially shielded due to the aromatic ring current effect of



Fig. 1  $^{1}$ H NMR spectra of rotaxane 1 and thread 2 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K). Resonances are labelled as shown in Scheme 1.

Van't Hoff Institute for Molecular Sciences, University of Amsterdam, P.O. Box 94157, 1090 GD Amsterdam, The Netherlands. E-mail: a.m.brouwer@uva.nl; Fax: +31 205255680;

Tel: + 31 205255491

the *p*-xylylene units of the macrocyclic ring.<sup>9,13</sup> The two co-conformers **1**-*pery* and **1**-*ni* are both present, and in rapid equilibrium on the NMR time scale. Remarkably,  $H_k$  is much more shielded (-0.520 ppm) than  $H_d$  (-0.221 ppm), indicating a distinct preference for co-conformer **1**-*pery* over **1**-*ni*. If we make the reasonable assumption that the inherent shielding of the CH<sub>2</sub> hydrogen atoms in both co-conformers is the same, we arrive at a population ratio of **1**-*pery* to **1**-*ni* of about 7 : 3. This finding can be explained by the higher electron density on the carbonyl groups of the electron donor substituted perylene imide, which strengthens the hydrogen bonds to the *pery* station.<sup>6</sup>

The absorption and fluorescence spectra of rotaxane 1 and thread 2 show solvatochromic shifts, both absorption and emission appearing at longer wavelengths in more polar solvents. Fig. 2 depicts the absorption and fluorescence spectra of rotaxane 1 in toluene and DMSO as compared with thread 2. Optical spectra in other solvents are given in the ESI<sup>†</sup> (Fig. S7), and the data for all solvents used are summarized in Table 1. In DMSO, the absorption and emission spectra of thread and rotaxane are identical. This is not unexpected, because this solvent is known to disrupt hydrogen bonds.<sup>4</sup> In toluene, on the other hand, the absorption and emission maxima of the rotaxane are substantially red-shifted relative to those of the thread.

In solvents of intermediate polarity, the bands gradually shift to longer wavelengths with increasing solvent polarity.



**Fig. 2** Absorption and fluorescence spectra of **1** (red) and **2** (blue) in toluene (line) and DMSO (dotted). All spectra are scaled to the same maximum.

**Table 1** Absorption and emission maxima (nm) and Stokes shifts  $(cm^{-1})$  of thread 1 and rotaxane 2 in different solvents<sup>*a*</sup>

	1			2			
Solvent	$\lambda_{abs}$	$\lambda_{\rm em}{}^b$	Stokes shift $(\times 10^{-3})$	$\lambda_{abs}$	$\lambda_{\rm em}{}^b$	Stokes shift $(\times 10^{-3})$	
Toluene	608	717	2.74	575	698	3.21	
Dibutylether	582	700	3.14	556	681	3.32	
EtOAc	597	733	3.11	576	715	3.43	
THF	597	758	3.18	580	716	3.39	
CH <sub>2</sub> Cl <sub>2</sub>	621	748	2.67	610	737	2.86	
Acetone	606	747	3.13	602	739	3.16	
DMF	620	756	3.05	613	751	3.05	
MeOH	620	763	3.14	617	764	3.10	
Acetonitrile	618	755	2.90	620	754	2.85	
DMSO	621	761	2.84	621	761	2.84	
<sup><i>a</i></sup> The spectra are shown in Fig. S1 in the ESI.† <sup><i>b</i></sup> $\lambda_{\text{exc}} = \lambda_{\text{abs (max)}}$ .							

The solvatochromic shifts of 1 are similar to those of a closely related pyrrolidine substituted perylene monoimide which lacks the bay substituents.<sup>8,14</sup> The Stokes shifts for thread 2 do not show a systematic dependence on solvent polarity. It is smallest in the most polar solvents used. For rotaxane 1, however. Stokes shifts are more similar in all the solvents and the values are slightly smaller than those found for thread 2. Positive solvatochromic shifts in absorption and emission as observed here are normally interpreted in terms of an increase in the molecular dipole moment upon excitation. The remarkable lack of solvent dependence of the Stokes shift can be attributed to a solvent induced change in the electronic structure, leading to a larger ground state dipole moment in more polar solvents.<sup>8,14</sup> Upon excitation of the naphthalimide chromophore at 345 nm the red fluorescence of the pervlene unit was observed, indicating an efficient excited state energy transfer from the naphthalimide to the pervlene chromophore (90-97%) (Fig. S11 and Table S3, ESI<sup>+</sup>). No systematic difference between thread 2 and rotaxane 1 was observed.

A linear regression of the frequency of the solvatochromic bands of **1** and **2** with solvent properties was carried out to evaluate the influence of hydrogen-bond accepting or donating ability of the solvents on absorption and fluorescence spectra according to Kamlet–Taft solvatochromic relationships:<sup>15</sup>

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$$\dot{\nu} = \nu_0 + a\alpha + b\beta + s\pi^* \tag{1}$$

where  $\tilde{\nu}$  is the property correlated (absorption or emission maxima of **1** or **2** in the different solvents),  $\nu_0$  is a constant, and  $\alpha$ ,  $\beta$ ,  $\pi^*$  are measures of the solvent's hydrogen-bond donating ability, hydrogen-bond accepting ability and "dipolarity–polarizability", respectively. The *a*, *b* and *s* values give a measure of the sensitivity of  $\tilde{\nu}$  to these factors. The observed absorption and emission maxima in wavenumbers together with the parameters for the solvents used ( $\alpha$ ,  $\beta$ ,  $\pi^*$ ) are given in Table S2 in the ESI.† Fitting the data and the parameters with eqn (1) gives the coefficients listed in Table 2.

For both rotaxane 1 and thread 2, absolute values of a are larger than those of b, which indicates that the hydrogen-bond donating solvents interact more strongly with the chromophore. The coefficient a is negative, implying that the hydrogen-bond donating solvents stabilize the excited state more than the ground state. This effect is stronger for thread 2 than for rotaxane 1 because in the latter the interaction between the chromophore and the macrocycle competes with the interaction between the chromophore and the solvent. For rotaxane 1, a small positive b value is observed for the absorption spectra,

**Table 2** Coefficients (cm<sup>-1</sup>) and standard deviations for the Kamlet– Taft expression obtained by fitting the absorption and emission energies (Table S1, ESI<sup>†</sup>) to eqn (1)<sup>a</sup>

	1		2		
Coefficient	Abs (×10 <sup>-3</sup> )	Em (×10 <sup>-3</sup> )	Abs (×10 <sup>-3</sup> )	Em (×10 <sup>-3</sup> )	
$\nu_{0}$	$17.7 \pm 0.2$	$14.6 \pm 0.1$	$18.7 \pm 0.4$	$15.3 \pm 0.2$	
a	$-0.6 \pm 0.1$	$-0.5 \pm 0.1$	$-1.0 \pm 0.3$	$-0.8 \pm 0.1$	
b	$0.1 \pm 0.2$	$-0.5 \pm 0.2$	$-0.9\pm0.4$	$-0.6\pm0.2$	
S	$-1.7\pm0.2$	$-1.3\pm0.2$	$-1.8\pm0.5$	$-1.8\pm0.2$	
<i>a</i> The sheets	- f - h				

"The plots of observed absorption and fluorescence maxima *versus* the maxima predicted by eqn (1) are illustrated in Fig. S9 in the ESI.†

whereas the fluorescence spectra give a negative b value. The negligible magnitude of b implies that the frequency of the solvatochromic band is insensitive to the solvent's hydrogenbond accepting ability. In contrast, negative b values obtained for the fluorescence spectra mean that as basicity of the solvents increased, the frequency of the fluorescence band of rotaxane 1 decreased. For thread 2 both absorption and emission spectra afforded negative b values and these are larger in absolute magnitude than those observed for rotaxane 1.

Considering the effects seen in the absorption spectra of the rotaxane 1 and the thread 2 it can be concluded that the macrocylic ring reduces solvent effects on the spectroscopic properties of 1.

The *s* values are negative for both compounds and relatively larger in absolute magnitude for thread **2**. The negative values imply the stabilization effect of highly polar solvents on the excited state. In the case of rotaxane **1** this effect is smaller because chromophore–solvent interactions are weakened by the presence of the macrocycle. Comparison of the results with those reported previously by Baggerman *et al.* for a perylene diimide rotaxane<sup>6</sup> reveals that the *s* values are significantly larger in the present case due to the highly solvatochromic nature of **1** and **2**.

Rotaxane 1 containing a fluorescent perylene imide chromophore provides a key element for detection of the co-conformers by their different fluorescence emission and excitation spectra, particularly in solvents of low polarity. Because perylene imide chromophores are bright and photostable it should be possible to distinguish the co-conformers at the level of individual molecules.<sup>16</sup> The dynamics of interconversion of the co-conformers can then be investigated using fluorescence fluctuation spectroscopy.<sup>17</sup>

Perturbation of the co-conformational equilibrium in rotaxane 1 can be achieved by electrochemical reduction or oxidation, or by protonation of the amino group. In these ways the translational motion of the ring can be studied. Work along these lines is in progress.

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