Hydrogen-bonded rotaxanes: structure and dynamics of mechanically interlocked molecular shuttles
Gunbas, D.D.
Solvatochromic Rotaxane Molecular Shuttles*

Abstract

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. Hydrogen-bonding between the macrocycle and the imide alters the optical properties of the perylene imide chromophore: the absorption and the fluorescence spectra are red-shifted. The effects of various solvents are investigated by means of UV-Vis absorption, steady state and time-resolved fluorescence spectroscopies.

5.1 Introduction

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.\textsuperscript{1, 2} Manipulation of the intercomponent interactions can give rise to molecular switches and motors.\textsuperscript{3-7} 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.\textsuperscript{8} A number of rotaxanes containing fluorescent groups has been described in the literature,\textsuperscript{9-14} but with few exceptions\textsuperscript{15, 16} 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,\textsuperscript{15} in the present work we have incorporated a bright photostable and solvatochromic chromophore\textsuperscript{17} into a hydrogen-bonded rotaxane.

Molecular switch 1 was assembled using a protocol developed by Leigh and co-workers (Figure 1).\textsuperscript{18, 19} In order to place the macrocyclic ring directly in contact with an imide unit, a simple amide, linked to the imide by a CH\textsubscript{2} group, was introduced as a template. It is well known that an imide is not a particularly good binding site for the tetra-amide macrocycle.\textsuperscript{20-22} The macrocyclic ring can be formed using a simple amide as a template, albeit in low yield.\textsuperscript{23} The combination of amide and imide provides a template that resembles the ideal trans-1,4-dicarbonyl unit,\textsuperscript{18} but steric hindrance results from the second C=O group of the imide. As described in detail in Chapter 4, rotaxane 1 exists as a mixture of translational co-conformers in the ground state in which the macrocycle has a predominant affinity for the perylene unit. In order to get a more detailed picture of the influence of the macrocyclic ring on the spectroscopic properties of the perylene imide chromophoric unit, steady state and time-resolved fluorescence spectroscopies were employed. Hydrogen-bonding interactions between the benzylic amide macrocycle and the naphthalimide chromophore can be expected to result in absorption and emission spectra, which resemble those of the corresponding thread 2. On the other hand, localization of the macrocycle next to the perylene imide chromophore will give a response in the solvent sensitive absorption and emission spectra.
5.2 Results and Discussion

5.2.1 Absorption and Fluorescence Properties

In order to explore how encapsulation affects the fluorescence properties of the perylene chromophore absorption and steady state fluorescence emission spectra of the rotaxane 1 and the corresponding thread 2 were measured in several solvents. As an example, the absorption and emission spectra of rotaxane 1 in toluene and DMSO as compared with thread 2 are depicted in Figure 2. Optical spectra in other solvents are shown in Figure 3. The related spectroscopic data for all solvents are summarized in Table 1.

![Figure 2](image1.png)

**Figure 2.** A) Absorption spectra and B) Fluorescence spectra of rotaxane 1 (dashed) and thread 2 (solid) in toluene (blue) and in DMSO (red). All spectra are scaled to the same maximum.

![Figure 3](image2.png)

**Figure 3.** Absorption and emission spectra of A) Rotaxane 1 B) Thread 2 in various solvents. All spectra are scaled to the same maxima.
Comparison of the results shown in Table 1 reveals that the absorption maximum of rotaxane 1 appearing at 608 nm recorded in toluene occurs at lower energy by about 33 nm than that of thread 2. A similar effect was observed in the fluorescence spectra, in which the position of the emission spectrum of the rotaxane in toluene exhibited a red shift of 19 nm compared to that of the thread. This is ascribed to the hydrogen-bonding interactions between the carbonyls of the perylene imide and the amide hydrogens of the macrocycle. The extent of shifts in both absorption and emission spectra decreased with an increase in solvent polarity. In DMSO, which disrupts the hydrogen-bond between the macrocycle and the stations, the absorption and emission spectra of both compounds are identical regarding the peak shapes and peak positions (Figure 2). The observed shifts in absorption spectra are larger than those of the emission, which reveals that the hydrogen-bonding interactions are stronger in the ground state.

### Table 1. Absorption and emission maxima (nm), Stokes shifts (cm$^{-1}$) of rotaxane 1 and thread 2 and the shifts induced by the presence of the macrocycle (cm$^{-1}$) in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{abs}}$</th>
<th>$\lambda_{\text{em}}$ $^b$</th>
<th>Stokes shift (×10$^3$)</th>
<th>$\lambda_{\text{abs}}$</th>
<th>$\lambda_{\text{em}}$ $^b$</th>
<th>Stokes shift (×10$^3$)</th>
<th>$\Delta\nu^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>608</td>
<td>717</td>
<td>2.74</td>
<td>557</td>
<td>698</td>
<td>3.21</td>
<td>785</td>
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<tr>
<td>Dibutylether</td>
<td>582</td>
<td>700</td>
<td>3.14</td>
<td>556</td>
<td>681</td>
<td>3.32</td>
<td>667</td>
</tr>
<tr>
<td>EtOAc</td>
<td>597</td>
<td>733</td>
<td>3.11</td>
<td>576</td>
<td>715</td>
<td>3.43</td>
<td>549</td>
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<tr>
<td>THF</td>
<td>597</td>
<td>758</td>
<td>3.18</td>
<td>580</td>
<td>716</td>
<td>3.39</td>
<td>510</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>621</td>
<td>748</td>
<td>2.67</td>
<td>610</td>
<td>737</td>
<td>2.86</td>
<td>353</td>
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<tr>
<td>Acetone</td>
<td>606</td>
<td>747</td>
<td>3.13</td>
<td>602</td>
<td>739</td>
<td>3.16</td>
<td>117</td>
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<tr>
<td>DMF</td>
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<td>756</td>
<td>3.05</td>
<td>613</td>
<td>751</td>
<td>3.05</td>
<td>100</td>
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<tr>
<td>MeOH</td>
<td>620</td>
<td>763</td>
<td>3.14</td>
<td>617</td>
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<td>3.10</td>
<td>78</td>
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<tr>
<td>Acetonitrile</td>
<td>618</td>
<td>755</td>
<td>2.90</td>
<td>620</td>
<td>754</td>
<td>2.85</td>
<td>78</td>
</tr>
<tr>
<td>DMSO</td>
<td>621</td>
<td>761</td>
<td>2.84</td>
<td>621</td>
<td>761</td>
<td>2.84</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$The spectra are shown in Figure 3. $^b\lambda_{\text{exc}} = \lambda_{\text{abs}}$ (max). $^c$Energy difference (in cm$^{-1}$) between the first absorption maximum of the thread and that of the rotaxane. $^d$Energy difference (in cm$^{-1}$) between the first fluorescence maximum of the thread and that of the rotaxane.

### 5.2.2 Solvatochromism

Solvatochromic compounds exhibit a pronounced change in the position and sometimes intensity of an electronic absorption, emission or both, accompanying a change in polarity of the medium. A bathochromic (or red) shift of the absorption or emission band with increasing solvent polarity is known as positive solvatochromism. The corresponding hypsochromic (or blue) shift is termed negative solvatochromism. Solvatochromic
compounds usually exhibit large differences in the dipole moments of their ground and excited states. 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. This can be found in electron donor-acceptor systems, which have a relatively small dipole moment in the ground state. When the more polar excited state is stabilized by the solvent relaxation (while the ground state is destabilized) positive solvatochromism is mainly expressed in the fluorescence. On the other hand, positive solvatochromism in absorption can occur when the dipole moments of the ground and the excited states are almost parallel since the excited state charge distribution interacts more favorably with the field induced by ground state dipole than the ground state itself. A variety of models can be employed to describe the effects of the solvent on the spectral properties. In the present case, we will start with the dielectric continuum models\textsuperscript{24-26} developed by Lippert\textsuperscript{27} and Mataga,\textsuperscript{28} which have been often used to estimate the ground state and excited state dipole moments. Solvent induced changes in the absorption and emission energies ($E_{\text{abs}}$ and $E_{\text{em}}$), relative to their vacuum values are described as follows:

\begin{align}
E_{\text{abs}} &= E_{\text{abs}}^0 - \frac{1}{\rho^3} \left[ \mu_e (\bar{\mu}_e - \bar{\mu}_g) (f(\varepsilon) - f(n^2)) + \frac{1}{2} (\mu_e^2 - \mu_g^2) f(n^2) \right] \\
E_{\text{em}} &= E_{\text{em}}^0 - \frac{1}{\rho^3} \left[ \mu_e (\bar{\mu}_e - \bar{\mu}_g) (f(\varepsilon) - f(n^2)) + \frac{1}{2} (\mu_e^2 - \mu_g^2) f(n^2) \right]
\end{align}

In Equations 1 and 2, $\bar{\mu}_e$ and $\bar{\mu}_g$ represent the ground state and excited state dipole moments, respectively, $\rho$ is the radius of the cavity (assumed to be spherical). The Onsager polarity functions, $f(\varepsilon)$ and $f(n^2)$ are given in Equations 3 and 4. The function $f(\varepsilon)$ describes the full dielectric response of the solvent, including effects of electronic polarization and molecular orientation in the field of the solute dipole. The difference $\Delta f = f(\varepsilon) - f(n^2)$ is the measure of the latter contribution only.

\begin{align}
f(\varepsilon) &= \frac{2(\varepsilon - 1)}{2\varepsilon + 1} \\
f(n) &= \frac{2(n^2 - 1)}{2n^2 + 1}
\end{align}

The Stokes shift, which is the difference between the absorption and emission maxima, then is expressed by Equation 5.

\begin{align}
E_{\text{abs}} - E_{\text{em}} &= E_{\text{abs}}^0 - E_{\text{em}}^0 + \frac{1}{\rho^3} \left[ (\bar{\mu}_e - \bar{\mu}_g)^2 (f(\varepsilon) - f(n^2)) \right]
\end{align}

The plot of the Stokes shift versus $\Delta f$ gives the changes between the ground state and the excited state dipole moments. The slope of the curve is determined by the cavity radius of the molecule and $(\bar{\mu}_e - \bar{\mu}_g)^2$. The molecular volume is generally derived on the basis of
molecular densities or from molecular computation and $\rho$ is taken as the radius of the corresponding sphere ($V = 4\pi\rho^3/3$). The solvatochromic behaviors of rotaxane 1 and thread 2 were explored in solvents of differing polarities. As illustrated in Figure 3, for both compounds, marked bathochromic shifts are observed in the absorption and emission spectra upon increase in the polarity of the solvent. The spectroscopic data are summarized in Table 1. The positive solvatochromism in absorption from 575 nm in toluene to 621 nm in DMSO and the corresponding emission shifts from 698 to 761 nm for thread 2 are in accordance with the values observed for the closely related pyrrolidine substituted perylene monoimide 3, which lacks the bay substituents.17, 29 For rotaxane 1, however, the solvatochromic shifts are smaller. The absorption and the emission maximum shifts from 608 to 621 nm and from 717 to 761 nm, respectively, as the solvent is changed from nonpolar toluene to highly polar DMSO.

A plot of the Stokes shift of rotaxane 1 and thread 2 against the solvent polarity, which is described by the function $\Delta f = f(\varepsilon) - f(n^2)$, revealed that the solvatochromic behavior of both compounds did not follow the linear dependence predicted by Lippert-Mataga relationship (Figure 4). The Stokes shifts do not increase with increasing polarity function $\Delta f$, which suggests that the Lippert-Mataga approximation does not offer a good description for the system under study. A similar lack of solvent dependence of the Stokes shift was found for 3. This is attributed to the fact that the solvatochromic shift in this case is to a large extent due to a solvent induced change in the electronic structure, leading to a larger ground state dipole moment in more polar solvents.17 In this respect, 3 behaves much like merocyanine dyes.30-32 Model compound 4 which has the same chromophore as 1 and 2 behaves qualitatively similarly to 3.29

![Figure 4](image.png)

**Figure 4.** Variation of Stokes shift of rotaxane 1 and thread 2 with solvent polarity function ($\Delta f = f(\varepsilon) - f(n^2)$). The lines are fits to Equation 5; rotaxane 1 slope = $250 \pm 320$ and intercept = $2890 \pm 150$; thread 2 slope = $-100 \pm 300$ and intercept = $3830 \pm 150$. 

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The overall medium effect on the frequency of the solvatochromic band reflects both
general (non-specific) solvent polarity effects and the specific (hydrogen-bond) solute-
solvent interactions. A multiparameter solvent polarity scale can be used for investigation
of the multitude of solute/solvent interactions on the molecular microscopic level. 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 the hydrogen-bond accepting or
donating ability of the solvents on absorption and fluorescence spectra according to
Kamlet-Taft solvatochromic relationships:

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

In Equation 6, $\tilde{\nu}$ is the property correlated (absorption or fluorescence maxima for the
different solvent polarities in this case), $\nu_0$ is a constant, and $\alpha$, $\beta$, $\pi^*$ are measures of the
solvent’s hydrogen-bond donating, hydrogen-bond accepting ability and “dipolarity-
polarizability”, respectively. The $a$, $b$ and $s$ values give a measure of sensitivity of $\tilde{\nu}$ to
these parameters. The observed absorption and fluorescence maxima in wavenumbers
together with the parameters for the solvents used ($\alpha$, $\beta$, $\pi^*$) are given in Table 2. Fitting
the data and the parameters with Equation 6 gives the coefficients listed in Table 3.

In Figure 5, plots of observed absorption and fluorescence maxima versus the maxima
predicted by Equation 6 are illustrated, which show the correlation between the
experimental data and the model. The correlations between the fluorescence maxima and
the solvent properties for 1 and 2 ($R^2 = 0.969$ and $R^2 = 0.976$, respectively) are slightly
higher than those observed for the absorption maxima ($R^2 = 0.970$ and $R^2 = 0.918$,
respectively).

In general, for both rotaxane 1 and thread 2, $a$ values are bigger in magnitude than those
obtained for $b$, which indicates that the hydrogen-bond donating solvents interact more
strongly with the molecules. The coefficient $a$ is negative, implying that the hydrogen-
bond donating solvents stabilize the excited state. This effect is stronger for thread 2 than
for rotaxane 1 due to the competing interaction between the chromophore and the
macrocycle with the chromophore and the solvent in the latter. For rotaxane 1, a small
positive $b$ value is observed for the absorption spectra, whereas the fluorescence spectra
gives rise to a negative $b$ value. The negligible magnitude of $b$ indicates that the frequency
of the solvatochromic band is insensitive to the solvent’s hydrogen-bond accepting ability.
This can be ascribed to the stabilization of the ground state by the electron donating
solvents. By 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. On the other hand, for thread 2 both absorption and emission spectra afforded
negative $b$ values which are larger in absolute magnitude compared to those observed for
rotaxane 1. The effect is larger for absorption than for the fluorescence maxima indicating
the presence of stronger interactions in the ground state. Considering the effects seen in
the absorption spectra of the rotaxane 1 and the thread 2 we can conclude that the
macroyclic ring suppresses the interaction between the amide units in the thread and the
solvent. The $s$ values are negative for both compounds and relatively larger 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.

However, the stabilizing effect of the polarity is larger than the destabilizing effect on the
hydrogen bonds, which gives a net stabilizing effect with the negative sign for the $s$
values. Furthermore, comparison of the results with those reported previously by
Baggerman et al. for a perylene diimide rotaxane\textsuperscript{15} reveals that the $s$ values are
significantly larger in the present case due to the highly solvatochromic nature of 1 and 2
which stems from the pyrrolidine ring attached to the perylene imide chromophore.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1</th>
<th>2</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_{abs}$ ($\times 10^4$)</td>
<td>$v_{em}$ ($\times 10^4$)</td>
<td>$v_{abs}$ ($\times 10^4$)</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.66</td>
<td>1.38</td>
<td>1.74</td>
</tr>
<tr>
<td>Dibutylether</td>
<td>1.73</td>
<td>1.41</td>
<td>1.80</td>
</tr>
<tr>
<td>EtOAc</td>
<td>1.67</td>
<td>1.36</td>
<td>1.73</td>
</tr>
<tr>
<td>THF</td>
<td>1.67</td>
<td>1.35</td>
<td>1.73</td>
</tr>
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<td>Acetonitrile</td>
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<tr>
<td>DMSO</td>
<td>1.59</td>
<td>1.31</td>
<td>1.62</td>
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</tbody>
</table>

$^a$Hydrogen-bond donating ability. $^b$Hydrogen-bond accepting ability. $^c$Dipolarity-polarizability values.
**Table 3.** Coefficients and standard deviations for the Kamlet-Taft expression obtained by fitting the data in Table 2 to Equation 6.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Absorption</th>
<th>Fluorescence</th>
<th>Absorbance</th>
<th>Fluorescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_o$</td>
<td>17700 ± 150</td>
<td>14600 ± 130</td>
<td>18700 ± 360</td>
<td>15300 ± 160</td>
</tr>
<tr>
<td>$a$</td>
<td>-550 ± 120</td>
<td>-520 ± 100</td>
<td>-970 ± 290</td>
<td>-760 ± 130</td>
</tr>
<tr>
<td>$b$</td>
<td>90 ± 180</td>
<td>-450 ± 150</td>
<td>-880 ± 420</td>
<td>-550 ± 190</td>
</tr>
<tr>
<td>$s$</td>
<td>-1730 ± 200</td>
<td>-1250 ± 170</td>
<td>-1820 ± 480</td>
<td>-1810 ± 210</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.970</td>
<td>0.969</td>
<td>0.918</td>
<td>0.976</td>
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</table>

**Figure 5.** Plots of the maxima obtained from fitting the absorption and fluorescence maxima of rotaxane 1 (A and B, respectively) and thread 2 (C and D, respectively) to the Kamlet-Taft Equation versus observed maxima.

**5.2.3 Fluorescence Quantum Yields and Fluorescence Lifetimes**

In order to get further insights into the origin of the interaction between the macrocyclic ring and the perylene imide chromophore, fluorescence lifetimes of 1 and 2 were determined in various solvents using a single photon counting apparatus with excitation at 405 nm. The obtained values are compiled in Table 4. Detection at different wavelengths ranging from 680 to 720 nm gave identical traces.
Table 4. Fluorescence quantum yields ($\Phi_{FL}$)\(^a\) and fluorescence decay times ($\tau$)\(^b\) with respective amplitudes in brackets of rotaxane 1 and thread 2 in several solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Phi_{FL}$</th>
<th>$\tau$ (ns)$^c$</th>
<th>$\Phi_{FL}$</th>
<th>$\tau$ (ns)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.45</td>
<td>2.9</td>
<td>0.47</td>
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</tr>
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<td>Dibutyl ether</td>
<td>3.2</td>
<td>3.2</td>
<td>3.8</td>
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</tr>
<tr>
<td>EtOAc</td>
<td>2.9</td>
<td>2.9</td>
<td>3.5</td>
<td></td>
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<td>THF</td>
<td>2.9</td>
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<td>3.3</td>
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<tr>
<td>CH$_2$Cl$_2$</td>
<td>0.36</td>
<td>2.9</td>
<td>0.36</td>
<td>3.1</td>
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<td>Acetone</td>
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<td>3.0</td>
<td>0.33</td>
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<td>Acetonitrile</td>
<td>0.30</td>
<td>2.9</td>
<td>0.27</td>
<td>3.1</td>
</tr>
<tr>
<td>DMSO</td>
<td>2.7 (0.80)</td>
<td></td>
<td>2.8 (0.74)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.2 (0.20)</td>
<td></td>
<td>0.2 (0.26)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The standard used is perylene red in CHCl$_3$ with a quantum yield of 0.96.\(^34\) \(^b\) Excitation wavelength for lifetimes is 405 nm. \(^c\) $\lambda_{exc}$ = 560 nm. \(^d\) $\Phi_{FL}$ ± 0.02. Absorbance of the solution ~ 0.1. \(^e\) Detection at 720 nm. \(^f\) Detection at 700 nm.

For thread 2, fluorescence decay times between 3.4 and 2.1 ns were determined and they are similar to the values reported by Zoon et al. for compound 3.\(^17\) The obtained fluorescence decay in each solvent was well described by a mono-exponential curve except in the case of DMSO. In DMSO, a small contribution (26%) from an additional fast decay time component (0.2 ns) has been detected, which might be ascribed to some conformational relaxation in the excited state. For rotaxane 1, fluorescence lifetimes are between 3.2 and 2.1 ns and show no clear dependence on solvent polarity. Notably, the decay times are shorter than those of thread 2. These trends are rationalized - in line with previous work - on the basis of hydrogen-bond induced non-radiative decay pathways.\(^15\) The decay curves for 1 exhibit a bi-exponential nature for each detection wavelength in DMSO but a mono-exponential behavior in all the other solvents studied. Furthermore, as the data in Table 4 reveal, quantum yields of 1 and 2 show a slight decrease with increasing solvent polarity and they are in accordance with the values described for structurally related perylene derivatives.\(^17\)

5.2.4 Fluorescence Resonance Energy Transfer (FRET)

Fluorescence Resonance Energy Transfer (or Förster Resonance Energy Transfer), FRET, is the energy transfer mechanism between two fluorescent dyes through long range dipole-dipole interactions.\(^35\) The donor is excited (at its specific absorption wavelength) and the
excited state energy is transferred non-radiatively to the acceptor, which becomes excited, while the donor returns to the ground state. The acceptor chromophore in solution rapidly loses some energy through vibrational and rotational relaxation. Thus, the energy match with the donor is lost, meaning that energy cannot be returned to the donor. The acceptor eventually returns to the ground state by its intrinsic radiative and non-radiative pathways. FRET can only take place when two fluorescent chromophores are in close proximity, usually less than 10 nm, and the probability of the energy transfer is strongly dependent on the inter-dye distance.

On the basis of the efficient overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor chromophoric units in rotaxane 1 and thread 2 we can expect the possibility of an efficient FRET process (Figure 6). Indeed, upon excitation of 1 and 2 at 345 nm, fluorescence emission of the perylene unit at about 700-800 nm was observed in all the solvents studied indicating an energy transfer from the naphthalimide to the perylene imide chromophore (Figure 7). The emission arising from naphthalimide unit at ~ 380 nm, however, is still detectable. FRET occurs mainly via higher excited state of the perylene unit absorbing at 400 nm, which is not solvatochromic.

![Figure 6](image-url)

**Figure 6.** A) Fluorescence emission spectra of compound 13 (donor, green line, right axis) and absorption spectrum of rotaxane 1 (red line, left axis) in toluene with shaded area representing the spectral overlap. B) Fluorescence emission spectra of compound 13 (donor, green line, right axis) and absorption spectrum of thread 2 (blue line, left axis) in toluene with shaded area representing the spectral overlap.

![Figure 7](image-url)

**Figure 7.** Fluorescence emission spectra (λ<sub>exc</sub> = 345 nm, 298 K) of A) Rotaxane 1, B) Thread 2 in various solvents.
For a better qualification of the FRET, time-resolved fluorescence spectroscopy was employed. The observed fluorescence lifetimes are collected in Table 5. For comparison, model compound 5 was used to obtain the donor-only decay times. On excitation of the naphthalimide unit in 2 at 324 nm in toluene, strong quenching of its fluorescence was observed as the fluorescence lifetime was drastically reduced to 0.2 and 0.09 ns for non-polar toluene and highly polar acetonitrile, respectively, compared to the reference compound 5 (τ = 2.6 and τ = 2.2 ns for toluene and acetonitrile, respectively). Likewise, for rotaxane 1, significantly shortened fluorescence lifetimes were found for the naphthalimide unit upon detection at 390 nm compared with those of reference compound 5. The observed lifetimes are reduced to values of 0.1 ns (in toluene) and 0.08 ns (in acetonitrile). Fluorescence quenching of the naphthalimide unit in 1 is more pronounced than in thread 2. In both 1 and 2, the acceptor is always excited to some extent because the acceptor absorbs (ε324 = 6130 M⁻¹cm⁻¹) at the excitation wavelength used to excite the donor. Since the acceptor is fluorescent, the light absorbed by the donor and transferred to the acceptor appears as enhanced acceptor emission. In the time domain, the characteristics of an excited state reaction are a rise time in the time dependent intensities and a negative pre-exponential factor in the multi-exponential analysis. In the present case, however, a sensitization of the emission of the perylene imide unit with a rise time could not be detected because most of the perylene emission is due to the intrinsic decay of the directly excited perylene imide chromophore rather than by FRET. The decays at 720 nm were fitted mono-exponentially for both rotaxane 1 and thread 2 in all solvents. Fluorescence lifetimes range from 3.1 (in Toluene) to 1.9 ns (in MeOH) for rotaxane 1 and they are similar to those found for thread 2. As expected, the decay times at 720 nm are very similar to those obtained with direct excitation at 405 nm (Table 4).

![Structure of the reference compound 5.](image)
Table 5. Fluorescence lifetimes ($\tau$) with respective amplitudes in brackets of rotaxane 1, thread 2 and the reference compound 5 in various solvents.$^b$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1 $\tau$ (ns)$^c$</th>
<th>1 $\tau$ (ns)$^d$</th>
<th>2 $\tau$ (ns)$^c$</th>
<th>2 $\tau$ (ns)$^d$</th>
<th>5 $\tau$ (ns)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.10 (0.97)</td>
<td>3.0</td>
<td>0.2 (0.95)</td>
<td>3.4</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>1.3 (0.03)</td>
<td></td>
<td>1.4 (0.05)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>0.09 (0.98)</td>
<td>3.0</td>
<td>0.10 (0.97)</td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>0.60 (0.02)</td>
<td></td>
<td>0.70 (0.03)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>0.10</td>
<td>2.9</td>
<td>0.10 (0.98)</td>
<td>3.2</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.3 (0.20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>0.09 (0.85)</td>
<td>3.1</td>
<td>0.10 (0.80)</td>
<td>3.3</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1.8 (0.15)</td>
<td></td>
<td>1.8 (0.20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>0.11 (0.96)</td>
<td>2.8</td>
<td>0.11 (0.98)</td>
<td>2.9</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.30 (0.04)</td>
<td></td>
<td>0.50 (0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeOH</td>
<td>0.08</td>
<td>1.9</td>
<td>0.09 (0.93)</td>
<td>1.8</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.7 (0.07)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.08</td>
<td>2.9</td>
<td>0.09 (0.95)</td>
<td>3.0</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.1 (0.05)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>nd$^e$</td>
<td>2.7 (0.80)</td>
<td>nd$^e$</td>
<td>2.8 (0.80)</td>
<td>nd$^e$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 (0.20)</td>
<td></td>
<td>0.2 (0.20)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $\lambda_{exc} = 324$ nm. $^b$ All spectra were recorded at room temperature. $^c$ $\lambda_{det} = 390$ nm. $^d$ $\lambda_{det} = 720$ nm. $^e$ Values could not be determined as the signal falls within the time response of the instrument (~ 20 ps).

Based on the above-mentioned photophysical data, the influence of the solvent polarity on the energy transfer rates and efficiencies was studied. The rate of energy transfer was calculated using the following equation:

$$k_T = \frac{1}{\tau_{DA}} - \frac{1}{\tau_D}$$

(7)

where $\tau_{DA}$ and $\tau_D$ represent the decay of the donor in the presence and in the absence of acceptor, respectively. Furthermore, the efficiency of the energy transfer can be calculated according to Equation 8.

$$E = 1 - \frac{\tau_{DA}}{\tau_D}$$

(8)

The results for both rotaxane 1 and thread 2 are summarized in Table 6. The respective rate constants for 1 are $k_T = 1.0 \times 10^{10}$ s$^{-1}$ for all solvents, whereas they range from $k_T = 4.6 \times 10^8$ s$^{-1}$ (in toluene) to $k_T = 1.1 \times 10^9$ s$^{-1}$ (in acetonitrile) for the corresponding thread 2. The efficiency of the transfer process from naphthalimide to perylene imide chromophore is
close to 1.0 for both compounds in all solvents. No general trend for the effect of solvent polarity on the transfer rates was observed which is in good agreement with the solvent independency usually observed for Förster-type resonance energy transfer.

Table 6. Evaluation of time-resolved fluorescence photophysical properties of rotaxane 1 and thread 2 according to the Förster theory.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_T \times 10^{10} \text{ s}^{-1}$</th>
<th>$E$</th>
<th>$k_T \times 10^{10} \text{ s}^{-1}$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.96</td>
<td>0.96</td>
<td>0.46</td>
<td>0.92</td>
</tr>
<tr>
<td>THF</td>
<td>1.0</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>1.0</td>
<td>0.94</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.0</td>
<td>0.95</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>DMF</td>
<td>1.1</td>
<td>0.92</td>
<td>0.81</td>
<td>0.90</td>
</tr>
<tr>
<td>MeOH</td>
<td>1.2</td>
<td>0.97</td>
<td>1.1</td>
<td>0.96</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.2</td>
<td>0.96</td>
<td>1.1</td>
<td>0.96</td>
</tr>
</tbody>
</table>

5.3 Conclusions

We have presented a novel rotaxane 1 which can exist as a mixture of translational co-conformers in the ground state with the macrocycle preferentially located near the perylene imide chromophore. Whereas the donor-substituted perylene imide has a large dipole moment, the naphthalimide is much less dipolar. This explains the preference for the pery co-conformer over the ni co-conformer. There is a higher electron density on the carbonyl groups of the perylene imide, which strengthens the hydrogen bonds to the perylene side. The absorption and emission maxima exhibited a red shift due to the hydrogen-bonding interactions between the amide groups of the macrocycle and the carbonyl groups of the perylene imide chromophore. The larger spectral shifts were observed in nonpolar solvents such as toluene in which the strengths of hydrogen-bonding interactions are the largest. In contrast, in solvents of high polarity and high hydrogen-bond accepting ability no spectral differences between the rotaxane 1 and the thread 2 were observed as a result of disruption of the hydrogen-bonding between the perylene imide unit and the macrocycle by competing interactions with the solvent. Both compounds displayed significant positive solvatochromic shifts in their absorption and emission. As in previously studied 3, no general trend for the effect of solvent polarity on Stokes shifts of 1 and 2 was observed. The influence of the different types of solvent/solute interactions on the absorption and fluorescence spectra is analyzed with the Kamlet-Taft expression.
Existence of an efficient energy transfer between two chromophoric units has been detected, which is one of the few examples of FRET among mechanically interlocked molecules.16

Time-resolved fluorescence spectroscopy showed that the fluorescence lifetimes of rotaxane 1 are notably shorter than those of the thread 2 as a result of hydrogen-bonding interactions between the macrocycle and the perylene imide. In view of these results, rotaxane 1 containing a highly fluorescent perylene imide chromophore provides a starting point for the utilization of time-resolved fluorescence spectroscopy for monitoring shuttling processes. The co-conformers might be detectable by their different fluorescence emission and excitation spectra particularly in solvents of low polarity due to the fact that the interaction between the ring and the perylene imide has a large effect on the electronic absorption and emission spectra. Moreover, it will be possible to distinguish the co-conformers at the level of individual molecules37-39 since perylene imide chromophores are bright and photostable. The dynamics of interconversion of the co-conformers can then be investigated using fluorescence fluctuation spectroscopy.40

5.4 Experimental Section

Materials: Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich or Fluka and used without further purification. THF was dried and deoxygenated by distillation over sodium benzophenone under an atmosphere of argon. MeOH was distilled from Mg prior to use. For UV-Vis absorption and fluorescence emission experiments spectroscopy grade solvents were used. Oxygen-free solutions were obtained by bubbling for 20-30 min with argon.

5.4.1 Steady State Absorption

Electronic absorption spectra of solutions were recorded in quartz cuvettes (1 cm, Hellma) on a Hewlett-Packard 8543 diode array (range 190-1000 nm) or a Varian Cary 3E (range 190-900 nm) spectrophotometer.

5.4.2 Steady State Fluorescence

Emission spectra were measured on a Spex Fluorolog 3 spectrometer, equipped with a Xe arc light source, a Hamamatsu R928 photomultiplier tube detector and double excitation and emission monochromators. The fluorescence spectra were corrected for the wavelength response of the detection system. The fluorescence of compounds in solution was detected in right angle geometry. Fluorescence quantum yields41 were estimated by comparison of a standard solution of N,N’-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide (Φf = 0.96 in CHCl₃) and calculated according to the following:
\[
\Phi_{fi} = \Phi_r \frac{(A_r, I, n^2_s)}{(A_r, I, n^2_r)}
\]  
(9)

where \( \Phi \) is the quantum yield, \( A \) is the absorption factor (absorbance \( \sim 0.1 \)) at the excitation wavelength, \( I \) is the integrated emission intensity and \( n \) is the refractive index of the solvents. Subscripts \( s \) and \( r \) refer to the sample and the reference solutions, respectively.

5.4.3 Time-Resolved Fluorescence

Time-resolved emission measurements were performed using a picosecond time-correlated single photon counting (TCSPC) set-up.\(^{42}\) A mode-locked Ar\(^+\) laser (Coherent 486 AS Mode Locker and Coherent Innova 200 laser) was operated at \( \lambda = 514.5 \) nm (laser pulses of ca. 60 ps with a repetition rate of 76 MHz) and used to pump a DCM dye laser (Coherent model 700) coupled with a cavity dumper (Coherent 7200). The output at 3.8 MHz was doubled with a BBO crystal resulting in an excitation wavelength of 323 nm. Fluorescence was detected at a right angle to the incident beam direction after passing through a polarizer set to the magic angle (54.7\(^\circ\)), and a monochromator (Carl Zeiss M20 67583) before reaching the microchannel plate photomultiplier tube (Hamamatsu R3809).

![Figure 9. Schematic representation of picosecond single photon counting (SPC) set-up: 1 laser, 2 pulse picker, 3 photodiode, 4 sample, 5 monochromator, 6 photomultiplier, 7 photon counting system, 8 computer.](image)

The instrument response (~18 ps) was recorded using the Raman scattering of a doubly ionized water sample. Time windows (4000 channels) of 5 ns (1.25 ps/channel) – 50 ns (12.5 ps/channel) could be used facilitating a window for measurements going from 5 ns to 50 ns. The recorded traces were fitted to model decay functions convoluted with the system response using the computer program Fluofit (PicoQuant) or using similar procedures implemented in Igor Pro (Wavemetrics).

For fluorescence decay measurements at \( \lambda_{ex} = 405 \) nm a continuously tunable (690-1040 nm) Coherent Chameleon laser was used as the excitation source (fwhm=140 fs with a
pulse repetition rate of 80 MHz). The modified TC-SPC set-up is illustrated in Figure 9. A pulse picker (Angewandte Physics and Electronics (APE)) was employed to decrease the repetition rate to 4 MHz and to increase the observation time between the excitation pulses. The laser beam was passed through a BBO crystal to double the frequency yielding an excitation wavelength of 405 nm. A dichroic mirror separated the excitation beam from the fundamental beam. The rest of the set-up is the same as described above.

5.5 References


30. Bondarev, S.; Knyukshto, V.; Turban, A.; Ishchenko, A.; Kulinich, A., Effect of the polymethine chain length, the polarity and temperature of the medium on the


