Hydrogen-bonded rotaxanes: structure and dynamics of mechanically interlocked molecular shuttles
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CHAPTER 6

Ultrafast Shuttling of Mechanically Interlocked Molecules in the Excited State*

Abstract

A molecular shuttle consisting of perylene imide and napthalimide units as both stoppers and fluorescent units has been constructed. The system can be described as an equilibrium mixture of two translational co-conformers, populated in a particular ratio depending on the relative strengths of the noncovalent hydrogen-bonding interactions between the macrocyclic ring and the two stations that it can bind to. The relative position of the ring with respect to the highly fluorescent perylene imide unit gives a strong response in the spectral domain, which makes it possible to distinguish between the fluorescence emission and excitation spectra of two translational isomers. Evidence for the shuttling process taking place after selective excitation of the \( \textit{ni} \) co-conformer was obtained by means of time-resolved fluorescence spectroscopy. Detection at the blue side of the emission band reveals a faster component along with a long-lived component, whereas the detection at the red side of the emission band gives only the longer decay time component. The short lifetime can be ascribed to the ultrafast translocation of the macrocycle from the napthalimide to the perylene side in the excited state.

6.1 Introduction

Rotaxanes comprising two different recognition sites have received considerable interest in the design and construction of molecular switches\textsuperscript{1-3} and molecular machines\textsuperscript{4-6}, since the ring and dumbbell components of rotaxanes are capable of exchanging the position of one component relative to that of the other. These motions, in principle, can be induced by an application of an external impetus such as chemical,\textsuperscript{7, 8} electrochemical\textsuperscript{9, 10} and photoochemical\textsuperscript{11-13} stimuli. Controlling the co-conformational changes and shuttling dynamics together with discrimination of the states of the system with high sensitivity and high time resolution are among the main challenges for the desired applications. The possibility to detect dynamical processes down to picosecond time scales makes fluorescence spectroscopy\textsuperscript{14-20} potentially an ideal approach compared to other methods for monitoring fast molecular shuttles such as such as NMR,\textsuperscript{21} absorption\textsuperscript{3, 22} and circular dichroism\textsuperscript{5} spectroscopies. We have previously described the synthesis and photophysical properties of a perylene imide/naphthalimide rotaxane in which the localization of the macrocyclic ring next to the perylene imide chromophore gave a strong response in the spectral domain.\textsuperscript{23} The main question, however, remained unanswered: Is it possible to use fluorescence spectroscopy to detect the shuttling process in this kind of systems? Here we address this issue by reporting an efficient synthesis and fluorescence study of rotaxane 1 in which the macrocyclic ring is placed in a direct contact with a chromophore introducing the ability to monitor the shuttling behavior by fluorescence spectroscopy. The molecular shuttle 1 consists of a benzylic amide macrocycle mechanically interlocked onto a thread molecule featuring perylene imide and naphthalimide chromophores (which also acts as stoppers) separated by C\textsubscript{12} aliphatic spacer (Figure 1). Glycine hydrogen-bonding sites or “stations” are positioned on both sides of the thread allowing the fast translocation of the ring along the thread due to the weaker binding interactions between the two components compared to succinamide-based rotaxanes.\textsuperscript{12} Different from the rotaxane described in Chapter 4 and 5, the substituents on the bay area of the perylene imide chromophore are removed to increase its stability towards photodecomposition. The lack of solubility of the compound and possible dethreading of the ring from the axle was overcome by the introduction of a tritylphenol group. In addition, using a relatively longer alkyl chain as a spacer reduces the possibility of the presence of bridged co-conformers in which the ring can be hydrogen-bonded to both stations at the same time.
6.2 Results and Discussion

6.2.1 Design and Synthesis

The synthetic route for the fabrication of rotaxane 1 is shown in Scheme 1. The preparation of thread 2 was started with the reaction of hydroxypyrrolidine with di-tert-butyl-dicarbonate in the presence of Et$_3$N, affording compound 3 (79%), which was subsequently coupled with 4-tritylphenol to give 4 in 75% yield by employing a Mitsunobu reaction in the presence of diisopropylazodicarboxylate (DIAD) and Ph$_3$P. Removal of the Boc protecting group under acidic conditions resulted in the formation of compound 5, quantitatively. In accordance with the literature, bromination of perylene monoimide 6 in the presence of a catalytic amount of iodine resulted in the formation of 7 (96%). Following standard Buchwald-Hartwig conditions, the reaction of 7 with 5 led to the formation of 8 (75%). Saponification of compound 8 by an excess of KOH in tBuOH, and subsequent acid-mediated dehydration with acetic acid provided perylene anhydride 9 in 50% yield. A coupling reaction of compound 9 with glycine tert-butyl ester gave compound 10 (85%), and a subsequent removal of the tert-butyl protecting group resulted in the formation of 11, quantitatively. Reaction of naphthalimide stopper 12 with N-Boc-1,12-diaminododecane, both prepared according to literature, afforded intermediate 13 (90%), which on hydrolysis with TFA in CH$_2$Cl$_2$ provided amine 14, quantitatively. Finally, a coupling reaction between 10 and 13 in the presence of BOP and DIPEA in DMF at room temperature accomplished the synthesis of desired thread 2 (90%). The thread 2 underwent the five-component clipping reaction with the corresponding precursors p-xylylenediamine and isophthaloyl dichloride to give a mixture of the desired rotaxane 1 (12%) and unreacted thread 2 (82%). The reason for the lower yield (12%) in comparison with that found for a similar perylene imide/naphthalimide rotaxane (16%)$^{23}$ is the limited solubility of thread 2 which reduced the extent of the formation of rotaxane 1.
Scheme 1. Synthesis of molecular shuttle 1

\[ \text{Scheme} \]

* (i) Boc anhydride, Et, N, CH, Cl, 0 °C to RT, 16 h, 79%; (ii) 4-tritylphenol, DIAD, Ph, P, THF, 0 °C to RT, overnight, 75%; (iii) TFA, CH,Cl, 0 °C to RT, 3 h, 99%; (iv) Br, I, AcOH, 5 h, RT, 96%; (v) Compound 5, Pd,(dba), BINAP, NaOtBu, toluene, 100 °C, overnight, 75%; (vi) a) KOH, tBuOH, reflux, 3 h; b) AcOH,
overnight, 50%; (vii) Glycine tert-butyl ester hydrochloride, K₂CO₃, DMF, 100 °C, overnight, 85% (viii) TFA, CH₂Cl₂, 0 °C to RT, 3 h, 99%; (ix) N-Boc-1,12-diaminododecane, BOP, DIPEA, DMF, RT, overnight, 90%; (x) TFA, CH₂Cl₂, 0 °C to RT, 99%; (xi) Compound 11, BOP, DIPEA, DMF, RT, overnight, 80%; (xii) Isophthaloyl dichloride, p-xylylene diamine, Et₃N, CHCl₃, RT, 20 h, 12%.

The location of the macrocycle on the thread can be deduced from ¹H NMR experiments. ¹H NMR spectra of the rotaxane 1 and thread 2 recorded in CD₂Cl₂ are shown in Figure 2. The striking upfield shifts of H₄ (Δδ = -0.381 ppm) and H₁₁ (Δδ₁₁ = -0.834 ppm) are due to shielding by the aromatic ring current of p-xylylene rings.

The total shielding of the glycine protons in rotaxane 1 (Δδ = -1.215 ppm) is larger than those found for a structurally related rotaxane (Δδ = -0.740 ppm) with a C₉ aliphatic spacer as described in Chapter 4. In addition, the extent of shielding is also increased in magnitude in comparison with those observed in the degenerate rotaxane with a C₉ aliphatic spacer (Δδ = -0.821 ppm). Assuming that the intrinsic shielding of the two CH₂ groups by the p-xylylene rings is the same, the shielding of H₄ vs. that of H₁₁ indicates that rotaxane 1 is present as two translational isomers in a ratio of 2:1 with the macrocycle predominantly located over the pery-gly station (Figure 3). Moreover, the resonances associated with H₆ and H₉ protons are shifted to higher field (δ = 2.88, and δ = 2.79 ppm, respectively) relative to thread 2 (δ = 3.26, and δ = 3.21 ppm, respectively) as a consequence of being in close proximity to the macrocyclic ring. On the other hand, the signals corresponding to amide protons (H₅ and H₁₀) exhibit substantial downfield shifts.
of 0.639 and 0.759 ppm in rotaxane 1, with respect to those in thread 2, which implies that they are strongly involved in hydrogen-bonding interactions with the macrocycle. The greater deshielding of H10 protons is also consistent with the proposed major co-conformer of rotaxane 1 with the ring preferentially hydrogen-bonded to the perylene imide chromophore.

Localization of the macrocyclic ring next to the naphthalamide chromophore (ni co-conformer) is not expected to give rise to a significant effect on the electronic absorption and emission spectra of the perylene imide unit. If the macrocycle, however, hovers over the pery-gly station (pery co-conformer), both electronic absorption and emission spectra of the perylene will be red shifted compared to those of the thread. With this in mind, we decided to employ steady state absorption and emission spectra of rotaxane thread 2 to explore the influence of the macrocyclic ring on the optical spectroscopic properties of the perylene imide chromophoric unit.

6.2.2 Steady State Absorption and Fluorescence Spectroscopy

6.2.2.1 Absorption and Emission Spectra

The rotaxane 1 and thread 2 were initially characterized by means of UV-Vis absorption and steady state fluorescence spectroscopy in solvents of varying polarity. The selected data for a representative set of solvents (toluene (ε = 2.37), dichloromethane (ε = 8.93), acetone (ε = 20.5) and acetonitrile (ε = 35.7)) are listed in Table 1. UV-Vis absorption and

\*\* ε refers to the dielectric constant of the solvents.
steady state fluorescence emission spectra of both compounds in these solvents are depicted in Figure 4.

A)

Figure 4. Normalized UV-Vis absorption (line) and fluorescence emission spectra (dashed) of A) Rotaxane 1 B) Thread 2 in toluene (purple), CH₂Cl₂ (green), acetone (red) and acetonitrile (blue).

For rotaxane 1 nor thread 2 additional absorption or emission bands emerged, indicating no significant ground state interaction between the naphthalimide and perylene imide units. The absorption spectra of 1 and 2 show the expected bands of the naphthalimide (compound 13) and perylene imide chromophores (model compound 8) as illustrated in Figure 5.

B)

Figure 5. Absorption spectra (solid line), fluorescence emission spectra (dashed line) of rotaxane 1 (red), thread 2 (blue), compound 13 (green), compound 8 (purple) and calculated UV-Vis absorption (8+13) (black solid line) in toluene.
Chapter 6

The small difference between the spectra of thread 2 and the reference compound 8 can be attributed to the intramolecular hydrogen-bonding interactions between the amide hydrogen of the glycine unit and the carbonyls of the perylene imide chromophore forming a seven-membered ring as shown in Figure 6.

Figure 6. Representation of the intramolecular hydrogen-bonding interactions between the glycine unit and perylene imide.

Bathochromic shifts of the absorption maximum from 579 (toluene) to 602 nm (CH₂Cl₂) for rotaxane 1 and from 555 (toluene) to 590 nm (CH₂Cl₂) for thread 2 were observed, which are similar to solvent dependent shifts found for structurally related perylene imide-based rotaxanes. Both absorption and emission maxima of rotaxane 1 shifted to lower energy in each solvent in comparison with those of thread 2. As an example, the absorption and emission spectra of rotaxane 1 and thread 2 in toluene are depicted in Figure 7. The absorption and emission maxima of thread 2 in toluene are located at 555 and 685 nm, respectively, whereas for rotaxane 1 a red shift of 24 nm (from 555 to 579 nm) was found in absorption and 16 nm (from 685 to 701 nm) in emission spectra. The lower excitation energies of the perylene imide chromophore in the rotaxane are attributed to the hydrogen-bonding between the carbonyl group of the perylene imide unit and amide hydrogens of the macrocycle as previously described in Chapter 5. The shifts of the absorption maxima are larger compared to those of the fluorescence indicating the presence of stronger hydrogen-bonding interactions in the Franck-Condon ground state than in the relaxed excited state. Interestingly, the similarities of the band position for rotaxane 1 and thread 2 in acetonitrile implies that the macrocycle does not have much influence on the perylene imide chromophore in this solvent. This is attributed to the weakening of the hydrogen-bonding interactions between the macrocycle and the perylene imide by the highly polar acetonitrile.

Figure 7. Absorption and fluorescence spectra of 1 (red dash-dotted line) and 2 (blue solid line) in toluene. All spectra are scaled to the same maximum.
Table 1. Absorption and emission maxima (nm), Stokes shifts (cm⁻¹) of rotaxane 1 and thread 2, the shifts (cm⁻¹) induced by the presence of the macrocycle and quantum yields in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt;</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Stokes Shift</th>
<th>Φ&lt;sub&gt;Fl&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Φ&lt;sub&gt;Fl&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Δν&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Abs</th>
<th>Em</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>579</td>
<td>701</td>
<td>3050</td>
<td>0.38</td>
<td>555</td>
<td>685</td>
<td>3540</td>
<td>0.34</td>
<td>770</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>602</td>
<td>721</td>
<td>2810</td>
<td>0.40</td>
<td>590</td>
<td>711</td>
<td>2990</td>
<td>0.33</td>
<td>361</td>
</tr>
<tr>
<td>Acetone</td>
<td>590</td>
<td>722</td>
<td>3180</td>
<td>0.38</td>
<td>583</td>
<td>719</td>
<td>3240</td>
<td>0.38</td>
<td>175</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>595</td>
<td>727</td>
<td>3080</td>
<td>0.28</td>
<td>573</td>
<td>725</td>
<td>3590</td>
<td>nd&lt;sup&gt;e&lt;/sup&gt;</td>
<td>538</td>
</tr>
</tbody>
</table>

<sup>a</sup> Using perylene red as the standard (Φ<sub>Fl</sub> = 0.96 in CHCl₃).<sup>29</sup> <sup>b</sup> λ<sub>exc</sub> = 570 nm. <sup>c</sup> λ<sub>exc</sub> = 560 nm. <sup>d</sup> Energy difference (cm⁻¹) between the first maximum of the thread and that of the rotaxane. <sup>e</sup> Could not be determined due to poor solubility.

The fluorescence quantum yields were measured in various solvents within 10% experimental error and the values are collected in Table 1. As the data in Table 1 reveal, the quantum yields of 1 and 2 are slightly dependent on solvent polarity and they are similar to the values observed for previously studied pyrrolidine substituted perylene derivatives.<sup>30</sup>

6.2.2.2 Wavelength dependent Fluorescence Emission and Excitation Behavior

In order to understand in more detail the dynamics of the co-conformational equilibria and to investigate whether the two possible translational isomers of rotaxane 1 (pery and ni) can be detected separately by their own characteristic spectra, wavelength dependencies of the fluorescence emission and fluorescence excitation spectra were studied. When the rotaxane exists as the ni co-conformer, in which the macrocycle is bound to the naphthalimide unit, both fluorescence excitation and fluorescence emission spectra of rotaxane 1 should resemble those of thread 2, whilst localization of the macrocyclic ring in contact with the perylene imide chromophore can be expected to give rise to a significant red shift in both spectra. As shown in Figure 8A, the fluorescence emission spectra of rotaxane 1 were recorded for excitation wavelengths ranging from 510 to 640 nm. At first glance, the emission spectra of rotaxane 1 recorded at different excitation wavelengths look almost identical. Nevertheless, close inspection of the emission spectra obtained from the excitation in short and long-wavelength regions gives essential information regarding the co-conformational equilibria of rotaxane 1. When rotaxane 1 is excited at the blue side of the absorption band (at 510 nm), the fluorescence maximum (λ<sub>em max</sub>) is observed at 698 nm. Interestingly, as can be seen from Figure 8B, as the excitation wavelength is progressively shifted toward the red side of the absorption maximum, a small but a steady shift of the fluorescence maximum is clearly visible.
Excitation at 640 nm results in a fluorescence spectrum whose maximum is located at 706 nm. On the basis of the assumption made above, the emission spectra obtained for the excitation at shorter wavelengths can be ascribed to the *ni* co-conformer, in which the macrocyclic ring has no or little influence on the perylene imide chromophore. However, the emission spectra recorded at longer wavelengths point to an interaction between the macrocycle and the perylene imide chromophore leading to the observed red shifts of the emission maxima. Therefore, the emission spectra for the excitation at the red side of the absorption band can be attributed to the *pery* co-conformer in which the macrocycle is located next to the perylene imide chromophoric unit. In comparison, thread 2 exhibited a smaller excitation wavelength dependent shift of the fluorescence maximum (Figure 8C and 8D). In this case the red-shifted component may be due to the intramolecular hydrogen-bond formation (Figure 6).

Next, the effect of the detection wavelength on the fluorescence excitation spectra of rotaxane 1 was investigated. Figure 9A illustrates the fluorescence excitation spectra of rotaxane 1 in toluene recorded at different emission wavelengths. Changing the detection wavelength from 740 to 640 nm results in a hypsochromic shift in the excitation maximum. The similarity between the excitation spectrum of rotaxane 1 recorded at 640 nm and the excitation spectrum of thread 2 at 685 nm (or any other wavelength) indicates
that the 640-nm fluorescence predominantly originates from the *ni* co-conformer. On the other hand, examination of the fluorescence excitation spectra detected at longer wavelengths reveals a bathochromic shift, which is ascribed to the *pery* co-conformer. By comparison, excitation spectra of the emission for thread 2 were only slightly dependent on the selected emission wavelength (Figure 9B). The small difference between the fluorescence excitation spectra of the thread recorded for the emission at the shorter and longer wavelength region could be due to the intramolecular hydrogen-bonding interactions between the glycine unit and the perylene imide as illustrated in Figure 6. These findings are in accordance with the results obtained from the fluorescence emission spectra.

Figure 9. Fluorescence excitation spectra of A) Rotaxane 1; B) Thread 2 in toluene. For comparison, the excitation spectrum of thread 2 recorded at an emission wavelength of 685 nm is shown in the excitation spectra of rotaxane 1. Arrow indicates the spectral changes upon increasing emission wavelength.

The wavelength dependencies of the fluorescence excitation and fluorescence emission spectra were further investigated in solvents of different polarity. Emission spectra of rotaxane 1 and thread 2 were collected by using excitation wavelengths from 510 to 640 nm in CH$_2$Cl$_2$, acetone and acetonitrile. Due to the solubility problems encountered, the measurements could not be performed in acetonitrile for thread 2. The corresponding emission curves for both compounds in each solvent with respect to changing excitation wavelength are depicted in the Appendix of this chapter (Figure 32 and Figure 33). Figure 10 summarizes the shifts of the fluorescence emission maxima of rotaxane 1 as the excitation wavelength was increased from 510 to 640 nm in solvents of differing polarities. The shifts are 8, 5, 1, and 5 nm in toluene, dichloromethane, acetonitrile and acetone, respectively. By comparison, thread 2 exhibited normal fluorescence behavior with negligible excitation wavelength dependence in different media.
Figure 10. Fluorescence emission maxima (nm) observed for rotaxane 1 for two different excitation wavelengths (510 and 640 nm) in different media.

Fluorescence excitation spectra of rotaxane 1 were collected by using emission wavelengths from 640 to 760 nm in dichloromethane, acetonitrile and acetone. Figure 11 summarizes the shift values observed for rotaxane 1 in various solvents for emission wavelengths on the blue and red side of the emission band. In toluene and dichloromethane, a blue shift of 15 nm was detected in the excitation maxima for the emissions monitored at 640 and 740 nm. This effect is less pronounced in acetone and acetonitrile in which only shifts of 6 and 9 nm were observed. The trend is comparable to the shifts observed in fluorescence emission spectra recorded for excitations at shorter and longer wavelength region of the absorption spectrum. This is obviously different from thread 2, which shows no detection wavelength dependence in dichloromethane, acetone or in toluene. As mentioned before, the measurements for thread 2 could not be performed in acetonitrile due to the limited solubility of the compound in this solvent.

Figure 11. Fluorescence excitation maxima (nm) observed for rotaxane 1 for two different emission wavelengths (640 and 740 nm) in different media.

6.2.3 Time-Resolved Emission Spectroscopy

The results of the preceding section agree with the hypothesis that the 560- and 600-nm fluorescence excitation bands are due to the ni and pery translational isomers of rotaxane 1, respectively, responsible for the 640- and 740-nm fluorescence emission bands. Therefore, excitation on the blue side of the absorption band and time-resolved detection
on the blue side of the emission band will reveal the dynamics of the \textit{ni} co-conformer. Fluorescence lifetimes were determined in toluene, dichloromethane, acetone and acetonitrile by a single photon counting apparatus with excitation at 510 nm, where the effect of the \textit{ni} co-conformer of 1 is most pronounced. The fluorescence decays of rotaxane 1 obtained at two emission wavelengths: 640 and 720 nm in toluene are shown in Figure 12. When the emission was monitored at the blue side of the emission band (640 nm), the fluorescence decay curve consisted of a rapidly decaying component and a slower one, whereas the fluorescence decay collected at the red side of the emission spectrum (720 nm) showed only the long-lived component. The decays were globally analyzed to obtain lifetimes that are common to all the decays and amplitudes varying with the wavelength. Global analysis for the simultaneous fitting of multiple fluorescence decays is a very useful technique for the accurate estimate of parameters that are common to all the data. The main advantage of this method is the reduction in the number of free parameters to be optimized and hence increased confidence limits on the obtained parameters. The quality of the fit was evaluated by the $\chi^2$ values and residual plots. For rotaxane 1, a double-exponential global analysis of multiple fluorescence decays collected as a function of emission wavelength from 640 to 720 nm gave two lifetimes of 2.8 and 0.81 ns in toluene with the amplitudes varying with the emission wavelength. The time constant of the short- and long-lived components increased from 0.81 (in toluene) to 1.6 (in acetone) and from 2.8 (in toluene) to 3.6 ns (in acetonitrile), respectively. The values are compiled in Table 2 and the short-lived ($\tau_1$) and long-lived ($\tau_2$) distributions recovered by global fitting are displayed in Figure 13. A decrease of the magnitude of the amplitude associated with the short-lived component is observed with increasing emission wavelength. The contribution of $\tau_1$ and $\tau_2$ components to the total intensity is roughly 70\% and 30\%, respectively, for detection in the shorter wavelength region in toluene. However, the amplitudes of the short-lifetime component decreased with an increase in solvent polarity.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig12.png}
\caption{Normalized fluorescence intensity decays of rotaxane 1 (3.7×10^{-6} M) in toluene at emission wavelengths of 640 and 720 nm. $\lambda_{ex} = 510$ nm.}
\end{figure}
On the other hand, the fluorescence kinetics of thread 2 was well described by a single-exponential curve at all wavelengths. No general trend for the effect of solvent polarity on the fluorescence lifetime of 2 was observed.

Table 2. An overview of the fluorescence lifetimes ($\tau$) of rotaxane 1 and thread 2 in various solvents obtained from global fitting:\(^a\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.81</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>1.1</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.6</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.4</td>
<td>3.7</td>
<td>4.2</td>
</tr>
</tbody>
</table>

$^a\lambda_{exc} = 510$ nm. $^\lambda_{det} = 640, 650, 660, 670, 685, 700$ and 720 nm.

Figure 13. Relative amplitudes ($\alpha_1$ and $\alpha_2$) of two lifetimes ($\tau_1$ and $\tau_2$) obtained by the global analysis of multiple fluorescence decays collected at different emission wavelengths with the excitation at 510 nm of rotaxane 1 A) in toluene; B) in CH$_2$Cl$_2$; C) in acetone and D) in acetonitrile. Square and open circle represent the amplitudes of short and long decay time components, respectively.
6.2.4 Temperature Effects

6.2.4.1 Temperature and Wavelength Dependent Fluorescence Emission and Fluorescence Excitation Spectra

If the observed wavelength dependence of the fluorescence excitation and emission spectra is indeed due to the selective excitation of the pery and nico co-conformers, it can be expected to depend on temperature: at lower temperature, the more stable pery co-conformer will be more predominant, but the conversion of the excited nico co-conformer to the pery co-conformer will be slowed down. Since the greatest shifts are observed in toluene, the temperature dependent steady state measurements were performed in toluene. The limited solubility of thread 2 at lower temperature obstructed the investigation of temperature dependence of fluorescence emission and fluorescence excitation spectra below 253 K. For both 1 and 2, the spectral changes observed on changing the temperature are fully reversible. The emission of rotaxane 1 was recorded at temperatures in the range of 343-193 K with cooling steps of 10 K. In Figure 14, the spectra obtained at 343 K and 193 K are depicted for excitation wavelengths in the range 510 to 640 nm.

The emission spectra are rather broad and structureless and their shape changes slightly with temperature; a shoulder appears at about 768 nm and it becomes more and more distinct with decreasing temperature. At 298 K, the emission maximum is at 698 nm and 706 nm for excitation at 510 and 640 nm, respectively. At 343 K, the emission maximum for the excitation at 640 nm is shifted from 706 to 703 nm, whereas the maximum for the excitation at 510 nm remained constant. At 193 K, the fluorescence emission maxima are located at 709 and 714 nm when the compound is excited at 510 and 640 nm, respectively. Figure 15 summarizes the results for the dependence of the fluorescence emission band maximum on temperature for excitation at 510 and 640 nm. A decrease in the extent of shifts of the fluorescence maximum for the excitation at the shorter and longer

![Figure 14.](image-url)
wavelength region as well as the observed red shifts in the position of the fluorescence maxima along with a decrease in temperature might be ascribed to the increasing population of pery co-conformer with decreasing temperature. This results in a red shift of 11 nm in the fluorescence emission maxima of rotaxane 1 for the excitation wavelength at 640 nm.

![Figure 15. Fluorescence emission maxima (nm) observed for rotaxane 1 for excitation at 510 (blue triangle) and 640 nm (red circle) with respect to lowering temperatures.](image)

In contrast with rotaxane 1, thread 2 did not display an appreciable temperature dependent shift of the fluorescence maximum as the excitation wavelength was increased from 510 to 640 nm within the temperature range 298-253 K studied (For spectra see Figure 34 in the Appendix of this Chapter). The influence of the temperature on the fluorescence emission maximum of thread 2 recorded upon excitation at 510 and 640 nm is illustrated in Figure 16.

![Figure 16. Fluorescence emission maxima (nm) observed for thread 2 for excitation at 510 (blue triangle) and 640 nm (red circle) at 298, 273 and 253 K.](image)

A small shift of 2 nm for the emission recorded at 298 and 253 K for the excitation wavelengths at the short and long wavelength region was attributed to the changes in the dielectric constant and the refractive index of the solvent with a decrease in temperature. The density of liquids increases upon cooling, leading to an increase in its refractive index. Due to decreasing thermal motion of solvent molecules the dielectric constant will increase, which leads to a more efficient solvation. These two effects result in a stabilization of a dipolar state with decreasing temperature. For molecules which have a
higher dipole moment in the excited state than in the ground state the energy gap between the ground and excited state will decrease, leading a red shift in the emission spectra.

To further understand the role of temperature on the steady state spectral properties of translational co-conformers of rotaxane 1, the temperature dependence of fluorescence excitation spectra collected using detection wavelengths from 650 to 740 nm was studied over the temperature range from 363 to 233 K with cooling steps of 10 K. The spectra obtained at 343 and 233 K for different emission wavelengths in the range from 640 and 740 nm are depicted in Figure 17. At lower temperatures equilibration of the populations of the emitting species may be reached slowly, and the population of excited ni co-conformer, which is at higher energy than pery co-conformer is expected to be smaller. Lowering the temperature leads to a blue shift in the excitation maximum of the species emitting on the blue side of emission band. In contrast, the excitation spectra of the species emitting on the red side of the emission band shifts to longer wavelengths as the temperature decreases. Conversely, increasing the temperature results in a decrease in the extent of wavelength dependency of the excitation spectrum.

Figure 17. Temperature dependence of fluorescence excitation spectra of rotaxane 1 at A) 233 K; B) 343 K. All spectra are scaled to the same intensity. Arrow denotes the spectral changes upon increasing emission wavelength.

Figure 18 illustrates the dependence of the 640 and 740 nm fluorescence band position on temperature. In order to make a better comparison between the low temperature results, the position of fluorescence excitation maxima were determined by fitting the experimental data with a profile composed of a sum of Gaussians. At 298 K, the excitation maxima are centered at 558 and 579 nm for detection at 640 and 740 nm, respectively. On the other hand, at 233 K the excitation maximum for detection at 740 nm exhibited a substantial red shift of 21 nm, whereas the position of the fluorescence band corresponding to detection at 640 nm shifted to 547 nm. These data suggest that the translocation of the macrocycle between ni-gly and pery-gly stations was slowed down with decreasing temperature, which facilitates the detection of two co-conformers with their own characteristic excitation spectra. In contrast, increasing the temperature speeds
up the shuttling process, which reduces the extent of shifts from 21 (at 298 K) to 13 nm (at 343 K).

![Figure 18](image)

**Figure 18.** Fluorescence excitation maxima observed for rotaxane 1 for detection at 640 (blue triangle) and 740 nm (red circle) at 363, 343, 298, 288, 278, 273, 263, and 253 K.

For comparison, the temperature dependent fluorescence excitation spectra of thread 2 were also obtained under similar conditions but in the temperature range from 298 to 253 K. Fluorescence excitation spectra of thread 2 illustrated a smaller dependence on temperature than those of rotaxane 1. The fluorescence band maximum for emission detected at 740 nm shifted from 556 to 564 nm with a decrease in temperature, whereas no substantial change in the band position upon decreasing the temperature was observed for detection at 640 nm (Figure 20). The bathochromic shifts observed for thread 2 are assigned to an increase of the dielectric constant and refractive index of toluene with decreasing temperature. The slight dependence of the excitation spectrum on detection wavelength at low temperatures could arise from the presence of different conformers of thread 2 (intramolecular hydrogen-bonding interactions with glycine, see Figure 6) in the excited state with their own emission spectrum, and that on the fluorescence time-scale these conformers now become more clearly distinguishable.

![Figure 19](image)

**Figure 19.** Temperature dependence of fluorescence excitation spectra of thread 2 at A) 253 K; B) 298 K. All spectra are normalized to the same intensity. Arrow indicates the spectral changes upon increasing emission wavelength.
6.2.4.2 Temperature Dependence of Fluorescence Lifetimes

On the basis of the observations discussed above, we thought that the temperature dependent time-resolved fluorescence decay investigations would be helpful in understanding the nature of the short lifetime observed for rotaxane 1. If the fastest component corresponds to the shuttling of the macrocycle in the excited state, lowering the temperature must slow this process down. Investigation of the effect of the temperature on the time dependent fluorescence parameters were carried out by time-correlated single photon counting in the temperature range from 213 to 298 K. The multiple fluorescence decays collected at various wavelengths ranging from 640 to 720 nm for an excitation wavelength of 510 nm was globally fitted to a double-exponential function with where linked long- and short-lifetime components, and the amplitudes of the two components are wavelength dependent. The temperature variation of the short and long decay times ($\tau_1 \sim 1$ ns and $\tau_2 \sim 3$ ns, respectively) for a detection wavelength of 640 nm is depicted in Figure 21 and the data for other emission wavelengths are given in Figure 35 (in the Appendix of this Chapter). An inspection of Figure 21 reveals that the lifetime of the long-lived component increases only slightly as the temperature decreases, whereas the value of the shorter decay time increases with a decrease in the temperature range 298-213 K. At 213 K, the fluorescence lifetime of the faster component is more than twice than at 298 K. These findings are in accordance with the results obtained from steady state spectroscopic measurements and might be attributed to slowing of the dynamical process.
Figure 21. Fluorescence decay times ($\tau_1$ and $\tau_2$) and relative amplitudes ($\alpha_1$ and $\alpha_2$) of rotaxane 1 as a function of temperature. Subscripts 1 and 2 represent the short- and long-lived components, respectively. The amplitudes correspond to the data obtained for detection at 640 nm.

To facilitate discussion of our experimental results, we have used the simple scheme shown in Scheme 2. Here $A$ and $B$ represent the two different co-conformers of rotaxane 1 (ni and pery, respectively) in the ground electronic state and similarly for the excited state species $A^*$ and $B^*$. In the excited state, $B^*$ is lower in energy than $A^*$, and therefore after its formation, $A^*$ rapidly (approximately 1 ns) converts to $B^*$. The decay rates of these two species are given by $k_A = k_{fA} + k_{rA}$ and $k_B = k_{fB} + k_{rB}$, where $k_{fA}$ and $k_{fB}$ are the radiative decay rates and $k_{rA}$ and $k_{rB}$ are the rates of radiationless decays. $k_{AB}^*$ and $k_{BA}^*$ are the rate constants of the interconversion from $A^*$ to $B^*$ and from $B^*$ to $A^*$, respectively. The observed lifetimes in this two-state reaction model are related to the four rate constants mentioned above in the following way:

$$
\tau_1^{-1}, \tau_2^{-1} = \frac{1}{2} \left\{ (\gamma_A + \gamma_B) \pm \sqrt{(\gamma_A - \gamma_B)^2 + 4k_{AB}k_{BA}} \right\}^{1/2}
$$

where $\gamma_A = k_A + k_{AB}$ and $\gamma_B = k_B + k_{BA}$. In the specific case of irreversible reaction where $k_{AB}^* \ll k_B$ the two lifetimes of $\tau_1$ and $\tau_2$ become:

$$
1/\tau_1 = k_A + k_{AB}^* \quad (2)
$$

$$
1/\tau_2 = k_B \quad (3)
$$

Scheme 2. Photophysical scheme for rotaxane 1 excited state shuttling.
If we assume that $k_A = k_B$, then an Arrhenius plot of $\ln k_{AB}$ (shuttling rate, $k_s$) versus $1/T$ can be constructed (Figure 22). From this the activation energy and pre-exponential factor of the dynamic process was obtained to be $E_a = 1.8$ kcal mol$^{-1}$ and $A = 2.0 \times 10^{10}$ s$^{-1}$, respectively.

![Figure 22. ln$k_s$ against 1/T (Arrhenius plot) of the shuttling process in the excited state.](image)

**6.2.5 Matrix Effects**

**6.2.5.1 Steady State Fluorescence Spectroscopy**

For common solvents, molecules are surrounded by a homogeneous environment in which maximum solvation can be accomplished by the interaction with the solvent molecules averaged over many molecular encounters. For a solid solution, however, the solute and solvents molecules may “freeze” at certain geometries and remain at approximately the same orientation and molecular separation.$^{32}$ Similar behavior could, in principle, be observed for the fluid phase with the application of pressure or with increasing viscosity. Additionally, medium polarity or effective solvation may alter during a cooling process or a phase transition. Unimolecular processes in rigid media tend to be restricted to relatively low-energy conformers, a situation that is quite different from that present in isotropic liquid phases since conformational equilibria are severely restricted in the solid phase.

The peculiar wavelength dependent fluorescence emission and excitation behavior observed for rotaxane 1 were further studied as a way of confirming whether it was due to a static or dynamic effect. If the effect is dynamic, it must be retarded in a solid matrix because of restrictions placed by the solid medium on the reorganization of solvent dipoles and molecular shuttle.

In the same way, the excitation wavelength dependency of the fluorescence emission of rotaxane 1 in sucrose octaacetate (SOA) matrix was investigated by employing the excitation wavelengths from 510 to 640 nm. When the rotaxane was excited at the red side (at 640 nm) of the absorption maximum, fluorescence emission centered at 696 nm closely resembled the emission spectrum obtained in toluene. However, excitation at the blue
side (at 510 nm) results in a significantly blue-shifted emission spectrum in SOA matrix. In SOA organic glass, the absence of solvent reorganization attenuates the stabilization of the highly polar excited state and restricts the rotational and translational freedom of the conformations of the translational isomers of rotaxane 1. The reduced ability to adopt the lowest-energy conformation where the macrocyclic ring is located next to the perylene imide unit resulted in a blue shift of the fluorescence of 11 nm in the solid media compared to that in the solution (Figure 23A). This is in a good agreement with the previous results obtained from temperature dependent fluorescence emission experiments. For comparison, the influence of excitation wavelength on fluorescence emission spectra of thread 2 was explored under the same conditions. The emission spectra of thread 2 were not dependent upon the excitation wavelength in fluid medium, but, for SOA glass the peak wavelengths of fluorescence for thread 2 were moderately dependent on excitation wavelength. As the excitation wavelength was increased from 510 to 640 nm in SOA, the emission spectrum of thread 2 exhibited a blue shift of 6 nm relative to those obtained in toluene (Figure 23B).

For a fluid solution, solute molecules are solvated through dipole, hydrogen-bond, and other interactions. If the electronic structure of a solute is changed upon a transition to another state (e.g., upon photoexcitation), a new solvation equilibrium will be accomplished by reorganization of the surrounding solvent molecules. In a solid matrix, however, most of the excited state molecules will not experience the completion of such solvent reorganization within the lifetimes of their fluorescent states. For the solid state, solute molecules may occupy different microscopic solvation sites in an otherwise macrohomogeneous environment. Therefore, solute molecules at distinct solvation sites lead to subtly different emission spectra, which can explain the observed excitation wavelength dependent fluorescence behavior of thread 2. Another possible reason of the observed differences in the emission spectra of the thread could be the intramolecular hydrogen-bonding interactions as shown in Figure 6.

A) B)

Figure 23. Fluorescence emission spectra in toluene (red) and glassy SOA (blue) of A) Rotaxane 1 (3.7 µM); B) Thread 2 (3.7 µM) for two different excitation wavelengths ($\lambda_{\text{exc}} = 510$ and $\lambda_{\text{exc}} = 640$ nm).
In order to further investigate the nature of the emitting species and how they depend on the solid medium, fluorescence excitation studies of rotaxane 1 and thread 2 were performed in SOA glass. Figure 24 depicts the excitation spectra recorded in SOA glass as a function of detection wavelength in the range from 640 to 740 nm. The excitation maximum experienced a significant blue shift of 44 nm upon reducing the emission wavelength from 740 to 640 nm. The location of the maximum at 550 nm of rotaxane 1 fluorescence excitation band obtained for emission monitored at 640 nm coincide with the fluorescence band of thread 2 detected at 640 nm. These findings are in good accordance with the hypsochromic shifts observed in emission spectra and further supports the conclusion given above, with the excitation spectra collected at 640 nm belonging to the \( ni \) co-conformer of rotaxane 1. By comparison, a hypsochromic shift of 23 nm was observed for thread 2 with decreasing wavelength from 740 to 640 nm for the same reason as explained for the emission spectra.

![Figure 24. Fluorescence excitation spectra of A) Rotaxane 1; B) Thread 2 in SOA. For comparison, the excitation spectrum of thread 2 recorded at an emission wavelength of 640 nm is shown in the excitation spectra of rotaxane 1. Arrow denotes the spectral changes upon increasing excitation wavelength.](image)

### 6.2.5.2 Time-Resolved Fluorescence Measurements in Solid SOA

In order to evaluate excited state dynamics, we have performed fluorescence lifetime measurements of rotaxane 1 and the corresponding thread 2 in SOA glass with the use of time-correlated single photon counting upon excitation at 510 nm. As illustrated in Figure 25, for rotaxane 1 the short-lived component vanished in the solid matrix and identical fluorescence decays were obtained for the emission monitored over the whole emission wavelength from 640 to 720 nm, with a lifetime of 3.2 ns. Similarly, for thread 2 a mono-exponential function was sufficient to describe the decays leading to a lifetime of 3.3 ns irrespective of the emission wavelength.
6.2.6 Fluorescence Resonance Energy Transfer (FRET)

Fluorescence energy transfer (often also called “Förster”, dipole-dipole or “coulombic” energy transfer) is driven by the through-space-dipole-dipole interaction of donor and acceptor.\textsuperscript{34,35} For this transfer mechanism, donor-acceptor orbital overlap is not necessary but instead spectral overlap is required, allowing the chromophores to be spatially separated by relatively large distances (10 to 80 Å).\textsuperscript{36}

On the basis of the overlap of the absorption band of the perylene imide and the emission band of the naphthalimide in rotaxane 1 and thread 2 we can include the possibility of FRET process (See Figure 5). The existence of efficient energy transfer in both compounds could be observed in steady state fluorescence emission measurements. Upon photoexcitation of naphthalimide chromophore at 324 nm fluorescence emission of the perylene imide chromophore at 699 nm (in toluene) with a quenched fluorescence intensity of the naphthalimide unit is observed, indicating efficient energy transfer between the two chromophores (Figure 26). The impact of solvent polarity on energy transfer process was investigated by varying the polarity of the solvent from toluene to acetonitrile.

Further insights into the FRET process were gained by employing time-resolved fluorescence spectroscopy. The natural decay time of the donor was measured using a control molecule 13 (Scheme 1) that is comparable to the donor-acceptor pair except that it lacks the acceptor (donor-alone molecule). The observed fluorescence lifetimes are compiled in Table 3 and the respective emission traces obtained in toluene are depicted in Figure 27 as an example.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fluorescence_decay_traces.png}
\caption{Fluorescence decay traces of rotaxane 1 at two detection wavelengths (640 and 720 nm) in glassy SOA. The decay curves are scaled to the same intensity for a better comparison.}
\end{figure}
Ultrafast Shuttling of Mechanically Interlocked Molecules in the Excited State

Figure 26. Fluorescence emission spectra (normalized at perylene emission maximum) excited at 324 nm of A) Rotaxane 1; B) Thread 2 in different solvents. For thread 2, emission spectrum in acetonitrile could not be performed due to the low solubility of the compound.

For compound 13, the obtained fluorescence decay in each solvent was well described by a single-exponential curve. The fluorescence lifetime of the donor varied from 2.6 ns (in toluene) to 1.4 ns (in CH$_2$Cl$_2$). The presence of the acceptor results in a decrease in the donor decay time and its decay is no longer a single-exponential. A significant decrease in the fluorescence lifetime of the donor for the rotaxane 1 and the thread 2 was observed compared to reference compound 13 along with a rise in the perylene excited state profile, which indicates an efficient energy transfer. In rotaxane 1, the longest (0.18 ns) and shortest value (0.07 ns) for the lifetime of the donor decaying by FRET is observed in acetone and toluene, respectively. In the case of thread 2, the lifetimes of the donor decaying by energy transfer changes from 0.11 ns (in CH$_2$Cl$_2$) to 0.41 ns (in toluene).

Figure 27. Time-resolved emission traces in toluene with $\lambda_{exc} = 324$ nm of A) Rotaxane 1 ($\lambda_{det} = 390$ nm (blue) and $\lambda_{det} = 700$ nm (red); B) Thread 2 ($\lambda_{det} = 390$ nm (blue) and $\lambda_{det} = 685$ nm (red). In both diagrams the emission of reference compound 13 is shown in black for comparison.
Table 3. Fluorescence lifetimes ($\tau$) with respective amplitudes in brackets of rotaxane 1, thread 2 and the reference compound 13 in various solvents.$^a$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tau$ (ns)$^b$</th>
<th>$\tau$ (ns)$^c$</th>
<th>$\tau$ (ns)$^b$</th>
<th>$\tau$ (ns)$^d$</th>
<th>$\tau$ (ns)$^e$</th>
<th>$\tau$ (ns)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.07 (0.99)</td>
<td>0.07 (-0.48)</td>
<td>0.40 (0.98)</td>
<td>0.41 (-0.28)</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>2.6 (0.01)</td>
<td>2.7 (0.52)</td>
<td>1.9 (0.02)</td>
<td>2.7 (0.72)</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.20 (0.97)</td>
<td>0.18 (-0.51)</td>
<td>0.18 (0.97)</td>
<td>0.11 (-0.46)</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.3 (0.03)</td>
<td>3.5 (0.49)</td>
<td>1.4 (0.03)</td>
<td>3.5 (0.54)</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.17 (0.74)</td>
<td>0.18 (-0.16)</td>
<td>0.17 (0.75)</td>
<td>0.19 (-0.17)</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.8 (0.26)</td>
<td>3.2 (0.84)</td>
<td>1.8 (0.25)</td>
<td>3.2 (0.83)</td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.8 (0.02)</td>
<td>3.5 (0.74)</td>
<td>1.9 (0.34)</td>
<td></td>
<td></td>
<td>2.1</td>
</tr>
</tbody>
</table>

$^a$ $\lambda_{\text{exc}} = 324$ nm. $^b$ All spectra were recorded at room temperature. $^c$ $\lambda_{\text{det}} = 390$ nm. $^d$ $\lambda_{\text{det}} = 700$ nm. $^e$ $\lambda_{\text{det}} = 685$ nm. $^f$ Could not be determined due to low solubility, and low sensitivity for detection at 700 nm. The solutions were saturated with argon for 20-30 minutes prior to measurements to get oxygen free samples.

In both 1 and 2 the perylene imide unit absorbs light ($\epsilon_{324(\text{tol}n)} = 3240$ L mol$^{-1}$ cm$^{-1}$) at 324 nm used to excite the naphthalimide chromophore. Therefore, the acceptor was excited by two routes: by direct excitation and by FRET from the donor. In the time domain the characteristics of an acceptor being excited by the donor are rise time in the time dependent intensities, and a negative pre-exponential factor in the multi-exponential analysis. A component due to the energy transfer from naphthalimide to perylene imide unit with values ranging from $\tau = 0.07$ ns (toluene) to $\tau = 0.18$ ns (in acetone) and from $\tau = 0.41$ ns (in toluene) to $\tau = 0.19$ ns (in acetone) for rotaxane 1 and thread 2, respectively. These values are in a reasonable agreement with the main quenched naphthalimide excited state lifetimes observed for 1 (0.07 and 0.17 ns in toluene and acetone, respectively) and 2 (0.40 and 0.17 ns in toluene and acetone, respectively). According to these time-resolved emission results, the observed energy transfer rates were calculated from the main decay of the naphthalimide unit by employing Equation 4.

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

(4)

In Equation 4, $\tau_{DA}$ 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 5. All transfer rate and transfer efficiency values are summarized in Table 4 and Table 5.

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

(5)
The experimentally obtained energy transfer rates can be compared to the calculated rate constants employing the Förster theory. Accordingly, the transfer rate depends on the following factors: the extent of spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, the quantum yield of the donor, the relative orientation of the donor and acceptor transition dipoles, and the distance between the donor and acceptor molecules. The Förster distance \( R_0 \) (the distance at which the energy transfer efficiency is 50%) can thus be calculated according to the simplified Equation 6:

\[
R_0 = 0.211\left[\kappa^2 n^{-4} \Phi_D J(\lambda)\right]^{1/6} \tag{6}
\]

In Equation 6, \( \kappa^2 \) is the orientation factor, \( n \) the refractive index of the medium, \( \Phi_D \) the fluorescence quantum yield of the donor in the absence of acceptor, and \( J(\lambda) \) the overlap integral of the donor emission and the acceptor absorption spectra. The orientation factor \( \kappa^2 \) between the donor and acceptor dipole moments is given by:

\[
\kappa^2 = (\cos \Theta_T - 3 \cos \Theta_D \cos \Theta_A)^2 \tag{7}
\]

\[
\kappa^2 = (\sin \Theta_D \sin \Theta_A \cos \phi - 2 \cos \Theta_D \Theta_A)^2
\]

In Equation 7, \( \Theta_T \) is the angle between the emission transition dipole of the donor and the absorption transition dipole of the acceptor, and \( \Theta_D \) and \( \Theta_A \) are the angles of these dipoles with the vector joining the donor and the acceptor and \( \phi \) being the angle between the planes (Figure 28). Depending on the relative orientation of donor and acceptor transition dipoles the values for \( \kappa^2 \) range from zero to four. For collinear and parallel orientation of the transition dipoles \( \kappa^2 \) equals 4, and for parallel orientation \( \kappa^2 \) equals 1, whereas for a perpendicular arrangement of the transition dipoles \( \kappa^2 \) vanishes to zero. Since the sixth root is taken to calculate the Förster distance (Equation 6), variation of \( \kappa^2 \) from 1 to 4 results in only 26% change in \( R_0 \). However, if the dipoles are oriented perpendicular to one another, \( \kappa^2 = 0 \), which would result in serious errors in calculated distances. By measurements of the fluorescence anisotropy of the donor and acceptor, one can set limits on \( \kappa^2 \) and thereby minimize uncertainties in the calculated distance. For a randomized arrangement of donors and acceptors due to rotational diffusion prior to energy transfer, \( \kappa^2 \) is generally assumed to be 2/3. Alternatively, one may assume that ranges of static donor-acceptor orientations are present, and that orientations do not change during the lifetime of the excited state. In this case \( \kappa^2 = 0.476 \).
By employing Equation 6, $R_0$ was calculated for rotaxane 1 as 30 Å, with $\kappa_2 = 1$ (assuming parallel orientation of chromophores), $n_{(\text{toluene})} = 1.4969$, $\Phi_D = 22\%$, $J(\lambda) = 1.92 \times 10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^4$. A Value of $R_0 = 28$ Å was obtained for thread 2 by using $J(\lambda) = 1.19 \times 10^{14}$ M$^{-1}$ cm$^{-1}$ nm$^4$. The corresponding $R_0$ values were calculated in different solvents for the rotaxane and the thread and the results are listed in Table 4 and Table 5, respectively. The representative overlaps integrals for energy transfer from naphthalimide to perylene imide unit in toluene for rotaxane 1 and thread 2 are shown in Figure 29. Due to the solubility problems encountered during the measurements, we could not calculate the values in acetonitrile for thread 2.

Typical values for the Förster distance reported in the literature range from 10 to 80 Å, which is in agreement with the obtained data. Moreover, the rate of energy transfer from a donor to an acceptor can be calculated using the following equation:

$$k_T = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6$$

where $r$ denotes the center-to-center distance of the donor and acceptor transition dipole, $\tau_D$ the fluorescence lifetime of the donor in the absence of the acceptor and $R_0$ the Förster distance. To get insights into the 3D structure and the most likely arrangement of the

Figure 28. Dependence of the orientation factor $\kappa'$ on the directions of the emission dipole of the donor and the absorption dipole of the acceptor.

Figure 29. 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.
chromophores, force field calculations of rotaxane 1 and thread 2 were performed (Macromodel 9.7 with the MM3* force field). The energetically most favorable structure for rotaxane 1 is represented in Figure 30 and that for thread 2 is shown in Figure 31.

The molecular structure reveals a center-to-center distance between the naphthalimide and perylene imide chromophoric units of $r = 23$ and $r = 24$ Å for rotaxane 1 and thread 2, respectively. This leads to calculated values for the energy transfer rate of $k_T$ in different solvents, which are illustrated in Table 4 and Table 5 for 1 and for 2, respectively. The afforded values and experimentally obtained constants differ somewhat. The difference could arise from the $\kappa^2$ values, which are based on an assumption. Another assumption in calculating the distance between the two chromophores was that a single conformation exist, and that there is a single donor-acceptor distance. However, for both compounds a variety of conformations can exist, which results in a range of donor-acceptor distances. Moreover, according to Equation 8 the rate of energy transfer is inversely proportional to $r^6$ and thus depends strongly on the center-to-center distance $r$ of the donor and acceptor transition dipoles. Hence, any phenomenon affecting the distance $r$ will also influence the transfer rate to a large extent and accordingly, minor changes in the center-to-center distance would lead to large differences in the calculated rate constants.

**Table 4.** Evaluation of selected time-resolved photophysical properties of rotaxane 1 according to the Förster theory.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_T$ (obs)</th>
<th>$E_T$</th>
<th>$J(\lambda)$</th>
<th>$R_0$</th>
<th>$k_T$ (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(×10$^{11}$ s$^{-1}$)</td>
<td></td>
<td>(M$^{-1}$ cm$^{-1}$ nm$^4$)</td>
<td>(Å)</td>
<td>(×10$^{11}$ s$^{-1}$)</td>
</tr>
<tr>
<td>Toluene</td>
<td>14</td>
<td>0.97</td>
<td>1.92×10$^{14}$</td>
<td>30</td>
<td>4.3</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>4.3</td>
<td>0.86</td>
<td>2.80×10$^{14}$</td>
<td>36</td>
<td>2.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.3</td>
<td>0.92</td>
<td>7.21×10$^{13}$</td>
<td>33</td>
<td>3.9</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>5.1</td>
<td>0.92</td>
<td>1.86×10$^{14}$</td>
<td>29</td>
<td>9.9</td>
</tr>
</tbody>
</table>

**Table 5.** Evaluation of selected time-resolved photophysical properties of thread 2 according to the Förster theory.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$k_T$ (obs)</th>
<th>$E_T$</th>
<th>$J(\lambda)$</th>
<th>$R_0$</th>
<th>$k_T$ (calcd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(×10$^{11}$ s$^{-1}$)</td>
<td></td>
<td>(M$^{-1}$ cm$^{-1}$ nm$^4$)</td>
<td>(Å)</td>
<td>(×10$^{11}$ s$^{-1}$)</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.0</td>
<td>0.84</td>
<td>1.19×10$^{14}$</td>
<td>28</td>
<td>1.0</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>4.6</td>
<td>0.87</td>
<td>1.16×10$^{14}$</td>
<td>30</td>
<td>2.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.3</td>
<td>0.92</td>
<td>2.42×10$^{14}$</td>
<td>34</td>
<td>5.0</td>
</tr>
</tbody>
</table>
6.3 Conclusions

We have presented a rotaxane 1 in which the macrocycle shuttles between *ni-gly* and *pery-gly* stations resulting in a population ratio of 2:1 in CD$_2$Cl$_2$ with the macrocycle principally residing nearby the perylene imide chromophore. The absorption and fluorescence spectra of rotaxane 1 exhibited substantial red shifts compared to those of the corresponding thread 2, which was attributed to the hydrogen-bonding interactions between the macrocycle and the perylene imide unit. The largest spectral shift in going from thread to rotaxane is observed in toluene, a nonpolar solvent, due to the more favorable hydrogen-bonding between the macrocycle and the thread. In polar solvents such as acetone and acetonitrile, the observed shift values were significantly decreased which implies that the interactions between the two components are weaker due to the competing interactions with the solvent molecules. Furthermore, rotaxane 1 exhibited an appreciable excitation wavelength dependent shift in the emission spectra. This
observation is less pronounced in acetonitrile. Similar effects were observed in the fluorescence excitation spectra where rotaxane 1 displayed a strong dependence on the emission wavelength. The observed red shift values of the fluorescence maxima are bigger in toluene and dichloromethane as compared to those in acetone and acetonitrile. The excitation wavelength dependence can take place when there exist a distribution of the molecules in the ground state that differ in their solvation and, hence, their energies. This inhomogeneity can originate from the difference in the interaction energies between the solvent and the molecule. However, the presence of an ensemble of energetically different molecules in the ground state alone does not guarantee an excitation wavelength dependent fluorescence behavior since rapid relaxation of the excited state, such as the solvation of the fluorescent state or energy transfer between the energetically different excited states of the molecules, is expected to give rise to emission from the lowest-energy state irrespective of the excitation. It is only when a system allows selective excitation of the energetically different species and relaxation of the fluorescent state is slow (hence, incomplete) that the excitation wavelength dependent emission can be expected. Therefore, the wavelength dependent fluorescence excitation and emission behavior stems from different isomeric distributions between the two translational isomers of rotaxane 1 that are populated in the excited state.

Temperature dependent fluorescence emission experiments revealed that the emission maxima of rotaxane 1 are shifted by 11 nm with respect to changing the temperature from 298 K down to 193 K for the excitation at longer wavelength, which is ascribed to the increasing population of pery co-conformer with decrease in temperature. Furthermore, observed changes in the fluorescence excitation spectra of rotaxane 1 provided additional information, complementary to the fluorescence emission spectral data, regarding the co-conformational equilibrium. Lowering the temperature results in both blue and red shifts in the excitation spectra depending on the detection wavelength. The excitation maximum of the species emitting on the blue side of the emission band shifts to shorter wavelengths, whereas it shifts to longer wavelengths for the species emitting on the red side of the emission band with decreasing temperature. This appears to be related to changes in the local populations of two co-conformers of rotaxane 1 in the excited state upon decreasing the temperature.

Time-dependent fluorescence studies of rotaxane 1 as a function of detection wavelength clearly point out the existence of two different emitting species having their own characteristic decay rates. The global analysis of these decays resulted in a short-lifetime component (~ 1 ns) for detection at the blue side of the emission band along with the long-lifetime component (~ 3 ns), whereas the detection at the red side of the emission band showed only the long-lived component. The faster decay time component can be assigned to the shuttling of the macrocycle from naphthalimide to perylene imide side in
the excited state. The decay time of the shorter-lived species increased at lower temperatures, while the values for the longer-lived species changed only slightly as the temperature decreased. On the other hand, in a solid matrix the fast component vanished and only the long decay time component was found irrespective of the emission wavelength. These findings could be attributed to the prohibition or slowing of the shuttle-like dynamic process in a solid matrix or by lowering the temperature, respectively.

Moreover, very efficient energy transfer from naphthalimide to perylene imide unit was detected. The experimental and calculated rate constants using \( R_0 \) are in fairly good agreement.

### 6.4 Experimental Section

**Materials:** Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. All reactions were carried out under an inert nitrogen or argon atmosphere. THF was dried and deoxygenated by distillation over sodium benzophenone under an atmosphere of argon. MeOH was distilled from Mg prior to use. MeCN was distilled over CaH₂. Flash column chromatography was carried out using Biosolve silica gel (particle size 32-63 µm). Analytical TLC was performed on precoated silica gel plates (0.20 mm thick, 60F254, Fluka). Oxygen-free solutions were obtained by bubbling for 20-30 min with a stream of argon in fluorescence cuvettes. The following compounds were prepared according to literature procedures: tert-butyl 3-hydroxy-3-carboxylate 3,2₄ 2-(acetic acid)-5,8-di-tert-butylbenzo[de]isoquinoline-1,3-dione 12⁷ and N-Boc-1,12-diaminododecane,²⁶ 8-bromo-2-(2,5-di-tert-butylphenyl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione 7.²⁵

**General Methods:** All \(^1\)H and \(^1\)C NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz for \(^1\)H, at a temperature of 298 K. Chemical shifts are reported in parts per million and were measured using solvent peaks. Coupling constants (\( J \)) are reported in hertz (Hz). The full assignment of the \(^1\)H NMR signals was performed using COSY (Correlation Spectroscopy) and ROESY (Rotating Frame Overhauser Effect Spectroscopy) experiments. Standard abbreviations indicating multiplicity were used as follows: \( s \) = singlet, \( m \) = multiplet, \( q \) = quartet, \( t \) = triplet, \( d \) = doublet, \( s \) = singlet, \( b \) = broad. Fast atom bombardment (FAB) mass spectra were obtained using a JEOL JMS SX/SX 102A four-sector mass spectrometer, equipped with Xenon primary atom beam, utilizing a 3-nitrobenzoyl alcohol (3-NOBA) matrix. Other abbreviations used: DMF = \( N,N' \)-dimethylformamide, Et₂O = Diethyl ether, MeOH = Methanol, tBuOH = tert-Butanol, TFA = Trifluoroacetic acid, \( \text{Pd}_2(\text{dba})_3 \) = Tris(dibenzylideneacetone)dipalladium(0), BINAP = (±)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl, NaOtfBu = Sodium tert-butoxide, Et₃N = Triethylamine, BOP = Benzotriazole-1-yl-oxy-tris(dimethylamino)-phosphonium.
hexafluorophosphate, DIPEA = N,N-Diisopropylethylamine, DIAD = Diisopropyl azodicarboxylate, Ph₃P = Triphenylphosphine.

**Temperature Control:** Measurements at low temperatures were performed using an Oxford Instrument liquid nitrogen cryostat DN 1704 with an ITC4 control unit. The samples were degassed by at least three freeze-pump-thaw cycles and allowed to thermally equilibrate for at least 30 min prior to data collection.

**Solid Matrix:** Sucrose octaacetate (SOA) was purchased from Aldrich and purified by the following procedure. To remove slightly colored polar impurities, a concentrated SOA chloroform solution (typically 100 g/200 mL) was passed through a pad of silica gel column and eluted with more chloroform. After removing the solvent under reduced pressure, the white powder was recrystallized several times from absolute ethanol and dried in a desiccator at reduced pressure overnight. The purified SOA (white crystals), which had a melting point of 83-85 °C, was stored away from moisture.

The solid glass samples were prepared for spectroscopic measurements by thoroughly mixing 300 µL of stock solution (0.5 mM compound in dichloromethane) with SOA powder (4.0 g) and heating the mixture to ~100 °C in a small beaker, after which the melt was transferred into 1 cm × 1 cm quartz cells. The sample was then allowed to cool down to room temperature with the cell in a vertical position to avoid excessive surface shrinkage. The sample cells were sealed (with Parafilm) from air after cooling and were stored in the dark. Fluorescence measurements on solid matrices were performed under front-face conditions.

**UV-Vis 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 Varian Cary 3E (range 190-900 nm) spectrophotometer.

**Steady State Fluorescence Emission:** Steady state emission spectra were obtained using a Spex Fluorolog 3 spectrometer, equipped with two monochromators (excitation and emission) and corrected for the wavelength response of the detection system. Quantum yields of compounds were determined by employing N,N’-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene bisimide (Φ₁ = 0.96 in CHCl₃)²⁹ or quinine bisulfate (Φ₁ = 0.55 in 0.5 M H₂SO₄)³⁸ as a reference. The concentrations of the solutions were kept as low as 10⁻⁶ M.

**Time-Resolved Fluorescence Emission:** Fluorescence lifetimes were measured by a time-correlated single photon counting apparatus. Experimental details are described in Chapter 5. The fluorescence decays recorded at different wavelengths were fitted using global analysis with the computer program Fluofit (PicoQuant).
**tert-butyl 3-(4-tritylphenoxy)pyrrolidine-1-carboxylate (4)**

To a solution of tert-butyl 3-hydroxy pyrrolidine-1-carboxylate 3 (0.250 g, 1.33 mmol) and Ph₃P (0.523 g, 1.99 mmol) in THF (10 mL) was added 4-tritylphenol (0.447 g, 1.33 mmol). This suspension was cooled to 0 °C and DIAD (338 µL, 1.99 mmol) was added. The mixture was warmed to room temperature and stirred overnight. After the solvents were removed under reduced pressure, the residue was purified by column chromatography on silica gel with a solvent gradient of acetone/CH₂Cl₂ (20%) to get a colorless solid. Yield 0.504 g (75%); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.29-7.19 (m, 15H, H₈), 7.12 (AA’BB’ system, H₇+ H₇’), 6.75 (AA’BB’ system, H₆+ H₆’), 4.48 (m, 1H, H₃), 3.61 - 3.51 (m, 4H, H₂+ H₂’+ H₅+ H₅’), 2.23-2.18 (m, 1H, H₄), 2.13-2.04 (m, 1H, H₄’), 1.49 (s, 9H, H₁); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 155.0 (CO), 154.4 (ArC), 146.8 (ArC), 139.3 (ArC), 132.1 (ArCH), 130.9 (ArCH), 127.3 (ArCH), 125.7 (ArCH), 114.0 (ArCH), 79.1 (CH), 64.1 (C₆), 54.1 (C₆), 51.4 (2 x CH₃), 43.8 (CH₃), 28.5 (CH₃). FAB-MS (3-NOBA matrix): m/z = 506.3 [M+H]+ (Calcd for C₃₄H₃₅NO₃ + H+: m/z = 506.3).

**3-(4-tritylphenoxy)pyrrolidine (5)**

To a stirred solution of tert-butyl 3-(4-tritylphenoxy)pyrrolidine-1-carboxylate 4 (0.100 g, 0.197 mmol) in anhydrous CH₂Cl₂ (10 mL) was added TFA (1 mL) and the solution was allowed to stir at room temperature for 2 h. The resulting solution was reduced in volume and the excess TFA was removed under reduced pressure to obtain a colorless solid. Then, it was dissolved in CH₂Cl₂ (20 mL), washed with 1N NaOH (2x10 mL), and brine and dried over MgSO₄. The solvent was removed to give a colorless solid (0.079 g, 99%); ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.29-7.19 (m, 15H, H₈), 7.12 (AA’BB’ system, H₇+ H₇’), 6.75 (AA’BB’ system, H₆+ H₆’), 4.48 (m, 1H, H₃), 3.61-3.51 (m, 4H, H₂+ H₂’+ H₅+ H₅’), 2.23-2.18 (m, 1H, H₄), 2.13-2.04 (m, 1H, H₄’); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 154.5 (ArC), 147.3 (ArC), 139.6 (ArC), 132.6 (ArCH), 131.3 (ArCH), 127.6 (ArCH), 126.1 (ArCH), 114.6 (ArCH), 77.5 (CH), 64.6 (C₆), 53.0 (CH₃), 45.5 (CH₃), 32.9 (CH₃). FAB-MS (3-NOBA matrix): m/z = 406.3 [M+H]+ (Calcd for C₂₉H₂₇NO + H+: m/z = 406.2).
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2-(2,5-di-tert-butylphenyl)-8-(3-(4-tritylphenoxy)pyrrolidin-1-yl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (8)

An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with dry toluene (10 mL), Pd$_2$(dba)$_3$ (1.30 mg, 0.5 mol%), BINAP (1.77 mg, 1 mol%) and NaOtBu (0.038 g, 0.399 mmol). 9-Bromo-[N-(2,5-di-tert-butylphenyl)]-3,4-dicarboxyimidoperylene 7 (0.168 g, 0.285 mmol) and 3-(4-tritylphenoxy)pyrrolidine (0.140 g, 0.342 mmol) were successively added. The reaction mixture was heated at 100 °C for 24 h. After cooling to room temperature, water (50 mL) and Et$_2$O (100 mL) were added and the phases were separated. The aqueous phase was extracted with more Et$_2$O and the combined organic phases were dried over MgSO$_4$. Removal of the solvent under reduced pressure followed by column chromatography on silica gel eluting with CH$_2$Cl$_2$ / acetone (94:6) afforded 8 as a blue solid (0.195 g, 75%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.62 (d, $J = 7.8$, 2H, H$_1$), 8.58 (d, $J = 8.4$, 1H, H$_{10}$), 8.47 (d, $J = 7.8$, 1H, H$_2$), 8.37 (dd, $J = 8.4$, $J = 2.8$, 1H, H$_5$), 8.32 (d, $J = 8.4$, 1H, H$_3$), 8.23 (d, $J = 8.4$, 1H, H$_{13}$), 7.60 (d, $J = 8.4$, 1H, H$_{12}$), 7.56 (t, $J = 7.5$, 1H, H$_9$), 7.44 (dd, $J = 8.4$, $J = 2.3$, 1H, H$_{11}$), 7.29-7.19 (m, 15H, H$_{21}$), 7.07 (d, $J = 2.3$, 1H, H$_{10}$), 6.84 (AA'BB' system, 4H, H$_{19}$ + H$_{19'}$), 6.74 (d, $J = 8.4$, 1H, H$_4$), 5.10 (bs, 1H, H$_{16}$), 4.90-4.05 (m, A-part of AB system, 1H, H$_{15}$), 4.01-3.97 (m, B-part of AB system, 1H, H$_{15'}$), 3.82-3.78 (m, A-part of AB system, 1H, H$_{16}$), 3.69-3.62 (m, B-part of AB system, 1H, H$_{16'}$), 2.45-2.40 (m, 2H, H$_{17}$), 1.34 (s, 9H, H$_{13}$), 1.30 (s, 9H, H$_{14}$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) = 164.9 (CO), 155.1 (ArC), 150.5 (ArC), 149.9 (ArC), 146.9 (ArC), 144.1 (ArC), 135.7 (ArC), 135.5 (ArC), 133.9 (ArC), 132.1 (ArCH), 131.7 (ArCH), 131.3 (ArCH), 130.7 (ArCH), 130.6 (ArC), 129.4 (ArC), 129.3 (ArC), 128.9 (ArC), 128.5 (ArC), 128.1 (ArCH), 127.9 (ArCH), 127.3 (ArCH), 126.4 (ArC), 125.8 (ArCH), 125.6 (ArCH), 125.5 (ArCH), 124.6 (ArCH), 124.4 (ArCH), 120.4 (ArC), 120.3 (ArC), 119.1 (ArCH), 118.5 (ArC), 117.7 (ArCH), 114.1 (ArCH), 111.4 (ArCH), 111.3 (ArC), 75.9 (CH), 63.9 (C$_{10}$), 58.4 (CH$_3$), 50.6 (CH$_3$), 31.9 (CH$_3$), 31.2 (CH$_3$), 30.8 (CH$_3$). FAB-MS (3-NOBA matrix): $m/z = 913.4$ [M+H]$^+$ (Calcd for C$_{65}$H$_{54}$N$_2$O$_3$ + H$: m/z = 913.4$).
8-(3-(4-tritylphenoxy)pyrrolidin-1-yl)benzo[5,10]anthra[2,1,9-def]isochromene-1,3-dione (9)

A solution of 8 (150 mg, 0.206 mmol) and KOH (0.809 g, 14.4 mmol) in tBuOH (25 mL) was heated to reflux. After stirring for 3 h, the reaction mixture was poured into a mixture of acetic acid (30 mL) and 1N HCl (20 mL) and stirred overnight at room temperature. The resulting mixture was poured into a biphasic mixture of CH₂Cl₂ (100 mL) and H₂O (50 mL). After separation, the organic layer was washed with brine (100 mL) and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was subjected to column chromatography (silica gel, eluent: CH₂Cl₂ to CH₂Cl₂/EtOAc = 50/1) to give compound 9 (0.075 g, 50%) as a blue solid; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.32 (d, J = 8.4, 1H, H₁), 8.26 (d, J = 7.8, 1H, H₉), 8.19 (d, J = 8.4, 1H, H₂), 8.11 (d, J = 8.0, 1H, H₇), 8.00 (m, 2H, H₃+ H₅), 7.76 (d, J = 7.8, 1H, H₈), 7.51 (t, J = 8.0, 1H, H₆), 7.33-7.19 (m, 15 H, H₁₆), 7.16 (AA’BB’ system, 2H, H₁₅+ H₁₅’), 6.86–6.84 (m, 3H, H₁₄+ H₁₄’+ H₄), 5.15 (bs, 1H, H₁₁), 4.18–4.15 (m, A-part of AB system, 1H, H₁₀), 4.10-4.06 (m, B-part of AB system, 1H, H₁₀’), 3.85 (d, J = 10.7, 2H, H₁₃), 2.49–2.45 (m, 2H, H₁₂).

tert-butyl 2-(1,3-dioxo-8-(3-(4-tritylphenoxy)pyrrolidin-1-yl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinolin-2(3H)-yl)acetate (10)

Anhydride 9 (0.090 g, 0.123 mmol) and glycine tert-butyl ester hydrochloride (0.042 g, 0.249 mmol) were dissolved in DMF (15 mL). Then, K₂CO₃ (0.069g, 0.495 mmol) was added and the reaction mixture was stirred at 100 °C overnight. DMF was removed under reduced pressure and the solid residue was redissolved in CH₂Cl₂ (100 mL). The resulting solution was washed with water (3 × 50 mL) and dried over MgSO₄. The crude product was purified by column chromatography on silica gel (eluent: CH₂Cl₂/ MeOH gradient from 99/1 to 95/5) to give 10 as a blue solid (0.088 g, 85%); ¹H NMR (CDCl₃): δ = 8.30-8.14
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(1H, H1+ H9+ H2), 7.82 (d, J = 7.8, 1H, H3), 7.44 (t, J = 7.6, 1H, H6), 7.29–7.22 (m, 15H, H18), 7.20 (AA'BB’system, 2H, H17+ H17'), 6.89 (m, 3H, H16 and H16+ H1), 5.13 (bs, 1H, H11), 4.82 (s, 2H, H16), 4.11–4.08 (m, 2H, H12), 4.01–3.97 (m, 3H, H14), 3.79 (d, A-part of AB system, J = 10.3, 1H, H12), 3.69 (bs, B-part of AB system, 1H, H13), 2.46–2.41 (m, 2H, H14), 1.54 (s, 9H, H11); 13C NMR (100 MHz, CDCl3): δ = 167.4 (CO), 163.2 (CO), 163.1 (CO), 155.1 (ArC), 150.0 (ArC), 139.4 (ArC), 138.1 (ArC), 137.6 (ArC), 132.1 (ArCH), 131.9 (ArCH), 131.2 (ArCH), 130.7 (ArCH), 129.8 (ArC), 128.8 (ArC), 128.5 (ArC), 127.7 (ArC), 127.3 (ArCH), 127.2 (ArCH), 125.9 (ArC), 125.8 (ArC), 125.7 (ArCH), 125.6 (ArCH), 124.3 (ArCH), 124.1 (ArCH), 119.8 (ArC), 119.0 (ArC), 118.6 (ArCH), 117.2 (ArC), 117.1 (ArCH), 114.1 (ArCH), 111.3 (ArCH), 81.5 (Cq), 75.9 (CH), 64.1 (Cq), 58.4 (CH2), 50.5 (CH2), 41.7 (CH2), 31.4 (CH3), 27.5 (CH3). FAB-MS (3-NOBA matrix): m/z = 838.4 [M+H]+ (Calcld for C57H46N2O5 + H+: m/z = 838.9).

2-(1,3-dioxo-8-(3-(4-tritylphenoxy)pyrrolidin-1-yl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinolin-2(3H)-yl)acetic acid (11)

To a cooled solution of compound 10 (0.160 g, 0.198 mmol) in anhydrous CH2Cl2 (10 mL) at 0 °C was added TFA (2 mL). After stirring for 3 h at room temperature, the reaction mixture was evaporated to dryness. The residue was diluted with CH2Cl2 and concentrated under reduced pressure several times to afford 9 as a blue solid (0.146 g, 99%); 1H NMR (400 MHz, CDCl3): δ = 8.30–8.14 (m, 3H, H1+ H9+ H2), 8.04–7.98 (m, 2H, H7+ H5), 7.82 (d, J = 7.8, 1H, H3), 7.44 (t, J = 7.6, 1H, H6), 7.29–7.22 (m, 15H, H18), 7.22–7.18 (AA’BB’ system, 2H, H17+ H17'), 6.89–6.87 (m, 3H, H16+ H16+ H1), 5.13 (bs, 1H, H11), 4.82 (s, 2H, H16), 4.11–4.08 (m, A-part of AB system, 1H, H12), 4.01–3.97 (m, B-part of AB system, 1H, H12), 3.79 (d, A-part of AB system, J = 10.3, 1H, H13), 3.69 (bs, B-part of AB system, 1H, H13), 2.46–2.41 (m, 2H, H14).
**tert-butyl (12-(2-(5,8-di-tert-butyl-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)acetamido)dodecyl)carbamate (13)**

To a stirred solution of 2-(acetic acid)-5,8-di-tert-butyl-benzo[de]isoquinoline-1,3-dione 12 (0.300 g, 0.816 mmol) in DMF (15 mL) under nitrogen was added BOP (0.541 g, 1.24 mmol) in one portion. The reaction mixture was stirred for 30 min at room temperature. Then, DIPEA (1.1 mL, 5.71 mmol) and N-Boc-1,12-diaminododecane (0.270 g, 0.897 mmol) were added to the reaction mixture. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The resulting solid was dissolved in CH$_2$Cl$_2$ and extracted with water (2 × 100 mL), brine (2 × 100 mL), dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with CH$_2$Cl$_2$/Acetone (95:5), affording the title compound as a white solid (0.401 g, 90%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.68 (d, $J$ = 2.0 Hz, 2H, H$_2$), 8.17 (d, $J$ = 2.0 Hz, 2H, H$_3$), 5.76 (t, $J$ = 6.4, 1H, H$_5$), 4.87 (s, 2H, H$_4$), 4.51 (bs, 1H, H$_{10}$), 3.31 (td, $J$ = 6.8, $J$ = 6.4, 2H, H$_6$), 3.11 (td, $J$ = 6.4, $J$ = 5.6, 2H, H$_9$), 1.49 (bs, 2H, H$_7$+H$_8$+H$_1$), 1.46 (s, 9H, H$_{11}$), 1.29-1.25 (m, 16H, CH$_2$ alkyl chain); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.4 (CO), 167.8 (CO), 164.3 (CO), 164.1 (CO), 150.1 (ArC), 131.8 (ArC), 129.6 (ArCH), 129.5 (ArCH), 124.9 (ArC), 121.5 (ArC), 43.0 (CH$_2$), 39.6 (CH$_3$), 35.1 (C$_q$), 34.4 (CH$_2$), 33.7 (CH$_2$), 31.0 (CH$_3$), 29.9 (CH$_3$), 29.7 (CH$_3$), 29.6 (CH$_3$), 29.4 (CH$_2$), 29.3 (CH$_2$), 29.1 (CH$_2$), 29.0 (CH$_3$), 28.3 (CH$_3$), 26.8 (CH$_2$), 26.7 (CH$_2$).

**N-(12-aminododecyl)-2-(5,8-di-tert-butyl-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)acetamide (14)**

Procedure as for acid 11, starting from amide 13 (0.150 g, 0.231 mmol), gave amine 12 as a white solid (0.126 g, 99%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.68 (d, $J$ = 2.0 Hz, 2H, H$_2$), 8.17 (d, $J$ = 2.0 Hz, 2H, H$_3$), 5.76 (bs, 1H, H$_5$), 4.87 (s, 2H, H$_4$), 4.51 (bs, 1H, H$_{10}$), 3.30 (td, $J$ = 7.2, $J$ = 6.4, 2H, H$_6$), 3.11 (td, $J$ = 7.2, 2H, H$_9$), 1.51-1.46 (m, 2H, H$_7$+H$_8$+H$_1$), 1.29-1.25 (m, 16H, CH$_2$ alkyl chain); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.8 (CO), 166.9 (CO), 164.3 (CO), 150.1 (ArC), 131.9 (ArC), 129.6 (ArCH), 129.5 (ArCH), 124.8 (ArC), 121.5 (ArC), 43.0 (CH$_2$), 39.6 (CH$_3$), 35.1 (C$_q$), 34.9 (CH$_2$), 33.7 (CH$_3$), 31.0 (CH$_3$), 29.9 (CH$_3$), 29.7 (CH$_3$), 29.6 (CH$_3$), 29.4 (CH$_2$), 29.3 (CH$_2$), 29.1 (CH$_2$), 29.0 (CH$_3$), 28.3 (CH$_3$), 26.8 (CH$_2$), 26.7 (CH$_2$).
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\[(\text{CH}_3), 29.3 (\text{CH}_2), 29.1 (\text{CH}_3), 29.0 (\text{CH}_2), 26.8 (\text{CH}_2), 26.7 (\text{CH}_2).\]

FAB-MS (3-NOA matrix): \(m/z = 550.4\) [M+H]+ (Calcd for \(\text{C}_{88}\text{H}_{98}\text{N}_5\text{O}_7 + \text{H}^+\): \(m/z = 550.4\)).

**2-(5,8-di-tert-butyl-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)-N-(13-(2-(1,3-dioxo-8-(3-(4-tritylphenoxy)pyrrolidin-1-yl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinolin-2(3H)-yl)acetamido)tridecyl)acetamide-Thread 2**

To a stirred solution of 2-(acetic acid)-5,8-di-tert-butyl-benzo[de]isoquinoline-1,3-dione compound 11 (0.060 g, 0.077 mmol) in an anhydrous DMF (10 mL) under nitrogen was added BOP (0.051 g, 0.116 mmol) in one portion. The reaction mixture was stirred for 30 min at room temperature. Compound 14 (0.096 g, 0.189 mmol) and DIPEA (499 µL, 1.20 mmol) were added sequentially and the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, followed by redissolving of the blue residue in \(\text{CH}_2\text{Cl}_2\) (100 mL), which was washed with water, and then dried over MgSO\(_4\). Removal of the solvent gave a blue solid from which the product was isolated by column chromatography (SiO\(_2\), eluent: 95:5 \(\text{CH}_2\text{Cl}_2\)/Acetone) as a dark blue solid (0.081 g, 80%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.65\) (d, \(J = 1.7\), 2H, \(H_2\)), 8.48–8.42 (m, 3H, \(H_2\), \(H_{13}+H_{20}\)), 8.35 (d, \(J = 8.1\), 2H, \(H_{14}\)), 8.25–8.20 (m, 2H, \(H_{16}+H_{18}\)), 8.13 (d, \(J = 1.7\), 2H, \(H_3\)), 8.06 (d, \(J = 8.4\), 1H, \(H_{19}\)), 7.50 (\(J = 7.9\), 1H, \(H_{17}\)), 7.35–7.18 (m, 15H, \(H_{27}\)), 7.15 (A-part of AA’BB’ system, 2H, \(H_{26}+H_{26}’\)), 6.96 (d, \(J = 8.1\), 1H, \(H_{13}\)), 6.82 (B-part of AA’BB’ system, 2H, \(H_{25}+H_{25}’\)), 6.02 (t, \(J = 5.6\), 1H, \(H_5\)), 5.87 (t, \(J = 5.9\), 1H, \(H_{10}\)), 5.08 (bs, 1H, \(H_{22}\)), 4.86 (s, 2H, \(H_4\)), 4.84 (s, 2H, \(H_11\)), 4.06–4.04 (dd, A-part of AB system, \(J = 13.8\), \(J = 4.3\), 1H, \(H_{21}\)), 3.97 (dd, B-part of AB system, \(J = 13.8\), \(J = 8.5\), 1H, \(H_{21}\)), 3.76 (d, A-part of AB system, \(J = 11.2\), 1H, \(H_{23}\)), 3.67–3.57 (m, B-part of AB system, 1H, \(H_{23}\)), 3.30–3.18 (m, 4H, \(H_6+H_9\)), 1.56–1.51 (m, 4H, \(H_7+H_8\)), 1.47 (s, 18H, \(H_1\)), 1.30–1.22 (m, 16H, \(CH_2\) alkyl chain); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 167.3\) (CO), 167.1 (CO), 164.5 (CO), 164.0 (CO), 163.9 (CO), 155.1 (ArC), 150.5 (ArC), 150.2 (ArC), 146.9 (ArC), 139.6 (ArC), 138.7 (ArC), 138.3 (ArC), 132.4 (ArC), 132.3 (ArCH), 132.2 (ArCH), 132.0 (ArC), 131.7 (ArCH), 131.0 (ArCH), 130.4 (ArC), 129.7 (ArCH), 129.6 (ArCH), 129.3 (ArC), 129.0 (ArC), 128.2 (ArCH), 127.4 (ArCH), 126.5 (ArC), 126.2 (ArC), 126.0 (ArCH), 125.9 (ArCH), 125.0 (ArC), 124.8 (ArCH), 124.5 (ArCH), 121.6 (ArC), 120.6 (ArC), 119.5 (ArC), 119.2 (ArCH), 117.7 (ArCH), 117.6 (ArC), 114.1 (ArCH), 111.7 (ArCH), 75.9 (CH), 64.3 (C), 48.8 (CH_2).
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43.7 (CH₃), 43.4 (CH₂), 43.1 (CH₂), 39.8 (CH₂), 39.7 (CH₂), 35.2 (C₆), 34.1 (CH₂), 33.4 (CH₂), 31.9 (CH₂), 31.7 (CH₂), 29.7 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 29.0 (CH₂), 26.7 (CH₂). FAB-MS (3-NOBA matrix): m/z = 1328.6 [M+H]⁺ (Calcd for C₈₈H₉₈N₅O₇ + H⁺: m/z = 1328.7).

2-(1,4,7,14,17,20-Hexaaza-2,6,15,19-tetraoxo-3,5,9,12,16,18,22,25-tetra benzoclohexacosane)-2-(5,8-di-tert-butyl-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)-N-(13-(2-(1,3-dioxo-8-(3-(4-tritylphenoxy)pyrrolidin-1-yl)-1H-benzo[5,10]anthra[2,1,9-def]isoquinolin-2(3H)-yl)acetamido)tridecyl)acetamide-Rotaxane 1

Thread 2 (0.100 g, 0.075 mmol) and Et₃N (0.253 µL, 1.8 mmol) were dissolved in chloroform (75 mL), and stirred vigorously whilst solutions of p-xylylene diamine (0.122 g, 0.90 mmol) and isophthaloyl dichloride (0.182 g, 0.90 mmol) in CHCl₃ (20 mL) were simultaneously added over a period of 4 hours using a motor-driven syringe pump. The resulting suspension was stirred overnight and filtered through a pad of Celite to afford the crude product. The solvent was removed and the residue was subjected to column chromatography (silica gel, CH₂Cl₂: Acetone (8:2) to yield unreacted thread 2 (0.082 g, 82%) and rotaxane 1 (0.016 g, 12%) as a blue solids; ¹H NMR (400 MHz, CD₂Cl₂): Δ = 8.55 (d, J = 1.5, 1H, H₂), 8.35 (d, J = 7.7, 1H, H₁₂), 8.26–8.14 (m, 9H, H₁₃+ H₁₄+H₂₀+ H₁₇), 7.61–7.41 (m, 3H, H₂₆+ H₂₇), 7.03 (s, 8H, H₆), 6.94 (d, J = 8.7, 1H, H₁₆), 6.84–6.81 (m, 3H, H₂₃+ H₁₉), 6.61 (t, J = 5.8, 1H, H₅), 5.09 (s, 1H, H₂₁), 4.44 (dd, A-part of ABX system, J = 13.6, J = 4.5, 4H, H₂₃), 4.39 (s, 2H, H₄), 4.28 (dd, B-part of ABX system, J = 13.6, J = 3.7, 4H, H₂₃), 4.07 (dd, A-part of AB system, J = 10.1, J = 4.2, 1H, H₂₁), 3.99 (dd, B-part of AB system, J = 17.2, J = 10.1, 1H, H₂₁), 3.89 (s, 2H, H₄₁), 3.79 (d, A-part of AB system, J = 11.1, 1H, H₂₃), 3.64 (bs, 1H, H₂₃), 2.91 (td, J = 4.8, J = 5.8, 1H, H₄), 2.83 (td, J = 4.8, J = 5.2, 1H, H₄), 1.43 (bs, 22H, H₁₊ H₁₊ H₁), 1.09–1.05 (m, 16H, CH₂ alkyl chain); ¹³C NMR (100 MHz, CD₂Cl₂): Δ = 166.8 (CO), 166.5 (CO), 166.4 (CO), 165.6 (CO), 164.6 (CO), 164.3 (CO), 155.0 (ArC), 150.0 (ArC), 149.9 (ArC), 146.8 (ArC), 139.4 (ArC), 137.2 (ArC), 137.1 (ArC), 136.2 (ArC), 134.2 (ArC), 133.4 (ArC), 132.2 (ArC), 132.1 (ArCH), 132.0 (ArCH), 131.9 (ArCH), 131.8 (ArC), 131.4 (ArC), 130.7 (ArCH),
130.6 (ArCH), 129.6 (ArC), 129.5 (ArCH), 129.1 (ArCH), 128.9 (ArCH), 128.4 (ArCH), 128.3
(ArCH), 127.5 (ArC), 127.4 (ArCH), 127.3 (ArCH), 126.9 (ArC), 125.6 (ArCH), 125.2
(ArCH), 125.1 (ArCH), 124.8 (ArC), 124.5 (ArCH), 122.5 (ArCH), 121.5 (ArC), 120.8 (ArC),
119.8 (ArC), 117.1 (ArC), 116.2 (ArCH), 114.0 (ArCH), 111.9 (ArCH), 75.6 (CH), 64.1 (Cq),
46.3 (CH2), 44.4 (CH2), 42.4 (CH2), 39.4 (CH2), 34.9 (CH2), 31.7 (CH2), 30.7 (CH2), 30.5 (CH2),
29.5 (CH2), 29.3 (CH2), 29.2 (CH2), 29.0 (CH2), 28.9 (CH2), 28.8 (CH2), 28.7 (CH2), 28.6 (CH2),
26.4 (CH2), 26.3 (CH2). FAB-MS (3-NOBA matrix): m/z = 1861.0 [M+H]+ (anal. Calcd for
C120H117N9O11 + H+: m/z = 1860.9).

6.5 Appendix

Figure 32. Normalized fluorescence emission spectra of rotaxane 1 A) in CH2Cl2; B) in acetone; C) in
acetonitrile as a function of excitation wavelength. Arrow indicates the spectral changes upon increasing
excitation wavelength.
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Figure 33. Normalized fluorescence emission spectra of thread 2 A) in CH₂Cl₂ and B) in acetone as a function of excitation wavelength. Arrow indicates the spectral changes upon increasing excitation wavelength.

Figure 34. Temperature dependence of the fluorescence emission spectra of thread 2 at A) 273 K; B) 253 K. All spectra are scaled to the same intensity. Arrow indicates the spectral changes upon increasing excitation wavelength.

Figure 35. Changes of relative amplitudes of short (dashed) and long decay time components (dotted) of rotaxane 1 at different detection wavelengths (obtained from global analysis) as a function of temperature.
6.6 References


