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Förster resonance energy transfer by formation of a mechanically interlocked [2]rotaxane†

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Mechanically interlocked molecules (MIMs)† including rotaxanes, catenanes, polyrotaxanes and polycatenanes have been extensively studied in the development of mechanically bonded molecular machines, such as shuttles,7 switches3 and even muscles.4 Several extensive studies have reported on Förster resonance energy transfer (FRET) in such systems which can contain multiple chromophoric units either in the axle or in the wheel components.5 Rotaxanes are ideal platforms to place donors and acceptors in a close proximity for FRET.

Pillararenes,6–12 which were first reported by our group in 2008,6 can be exploited as hosts in the creation of many supramolecular assemblies. To date, two kinds of pillararenes, pillar[5]arenes and pillar[6]arenes, containing five or six repeating units, respectively, have been used in the construction of supramolecular assemblies. We reported high-yield syntheses of planar-chiral pillar[5]arene-based [2]- and [3]rotaxanes, and a first pillar[6]arene-based [2]rotaxane.8,9 In this study, we report an efficient FRET system by formation of [2]rotaxane 3 (Fig. 1) constructed from an A1–A2 di-pyrene functionalized pillar[5]arene wheel H1 (Fig. 1) and an axle with a perylene stopper.

The A1–A2 di-pyrene appended pillar[5]arene H1 and a perethylated pillar[5]arene H2 (Fig. 1) were used as wheels. Pillar[5]arene derivatives form host–guest complexes with cationic molecules such as the pyridinium and viologen cations.13

Thus, a pyridinium derivative 1 (Fig. 1), bearing an alkyne at one end and a bulky triyl moiety at the other, was used as an axle. The stoichiometry of the H2·1 complex determined from a job plot was 1:1 and the association constant was found to be (1.01 ± 0.21) × 104 M−1.9 The copper(i)-catalyzed Sharpless azide–alkyne click reaction was used to synthesize the [2]rotaxanes. An azide-terminated perylene stopper 2 was added to a mixture of the wheel H1 and axle 1, together with Cu(CH2CN)4PF6 and tris-[[1-benzyl-1H-1,2,3-triazol-4-yl]methyl]amine (TBTA). Purification of the crude products from the reaction mixtures by silica gel chromatography afforded the wheel H1-based [2]rotaxane 3 in high yield (72%). The click reaction of axle 1 with stopper 2 in

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† Electronic supplementary information (ESI) available: Experimental section, characterization data, excitation spectrum, molecular structure, emission spectra of [2]rotaxane 3 with the different components from the decay time measurements and time profiles of the fluorescence decay. See DOI: 10.1039/c3cc42612b
the presence of non-functionalized wheel H2 was carried out under the same reaction conditions, and [2]rotaxane 4 was isolated in a yield of 80%. As a reference compound, the dumbbell-shaped molecule 5 was also synthesized using the same conditions as those for the preparation of the [2]rotaxanes in the absence of the pillar[5]arene wheel. The chemical structures of these compounds were fully characterized using H, C, and 2D NMR spectroscopies, and high-resolution electrospray ionization mass spectrometry (HRESIMS). The HRESIMS spectrum of [2]rotaxanes 3 and 4 contained peaks at m/z = 2354.1352 and 1819.9752, respectively, corresponding to the loss of one PF6 anion. This is consistent with the formation of the [2]rotaxanes at 345 nm and 4.0 × 10⁻⁶ M in chloroform.

In wheel H1 (Fig. 2a, black line), absorption bands were observed at 320–360 nm, which can be assigned to the pyrene moiety. Dumbbell 5 (Fig. 2a, green line) and [2]rotaxane 4 (Fig. 2a, blue line) showed absorption bands at 380–460 nm, which are related to the perylene moiety. Both absorption bands were found for [2]rotaxanes 3 (Fig. 2a, red line) as it contains both pyrene and perylene moieties. The absorption spectrum of a 1:1 mixture of wheel H1 and dumbbell 5 (Fig. 2a, purple dashed line) is identical to that of [2]rotaxane 3 (Fig. 2a, red line). When the wheel H1 was excited at 345 nm (Fig. 2b, black line), two emission peaks at 376 and 396 nm and a broad band with a maximum at ~490 nm were observed, and were assigned as monomer and excimer emissions from the pyrene moiety, respectively. Excitation of dumbbell 5 (Fig. 2b, green line) and non-functionalized [2]rotaxane 4 (Fig. 2b, blue line) at 345 nm gave fluorescence bands for the perylene moiety (440–550 nm). These emissions are extremely weak because the perylene moiety has only a small absorbance at 345 nm. In contrast, when [2]rotaxane 3 was excited at 345 nm, a strong emission from the perylene moiety was observed (Fig. 2b, red line). The emission intensity of [2]rotaxane 3 at 457 nm was ~25× that of dumbbell 5 or [2]rotaxane 4. When a 1:1 mixture of dumbbell 5 and wheel H1 with concentrations of 4.0 × 10⁻⁶ M (Fig. 2a, purple dashed line) was excited at 345 nm, the emission was essentially a superposition of those of the two components. These results provide clear evidence that in [2]rotaxane 3 efficient Förster energy transfer occurs from the pyrene in the wheel to the perylene of the dumbbell (Fig. 3, top). In the mixture of dumbbell 5 and wheel H1 in dilute concentration, the average distance between the chromophores is too large for the Förster-type energy transfer to occur (Fig. 3, bottom).

The efficiency of the FRET process can be estimated by comparing the quantum yields (Table 1) of the fluorescence of the [2]rotaxane 3 with excitation of the perylene absorption band (Φf = 0.50) with that obtained by exciting in the perylene absorption band (Φf = 0.82). Alternatively, the intensities of these bands in the excitation spectrum detected in the pyrene emission can be compared to the absorption intensities (Fig. S7, ESI†). From these analyses we conclude that the efficiency of energy transfer is ~75%. The Förster radius was estimated to be R0 = 1.8 nm using the perylene emission and the dumbbell absorption bands. Energy transfer may, however, also originate from the excimer. When the entire emission band of the wheel is used, the Förster radius is estimated to be 2.2 nm. The FRET yield corresponds with an effective transfer distance of ~0.8R0 = 1.6 nm, which is in good agreement with the molecular structure (Fig. S8, ESI†).

Time-resolved fluorescence measurements indicated that the photophysical behavior of the systems studied is more complex than expected (time profiles are shown in Fig. S10–S13, ESI†). Whereas perylene has a simple mono-exponential decay with τ = 4.6 ns, the dumbbell 5 shows two components with τ1 = 3.7 ns (85% of the integrated intensity) and τ2 = 6.0 ns (15%). A possible
Table 1  Photophysical properties of [2]rotaxane 3, wheel H1 and dumbbell S

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{abs}}^\text{max}) (nm)</th>
<th>(\lambda_{\text{em}}^\text{o} \text{ (nm)})</th>
<th>(\Phi_t^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheel H1</td>
<td>345</td>
<td>376, 396</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>495</td>
<td>0.06</td>
</tr>
<tr>
<td>Dumbbell</td>
<td>445</td>
<td>453</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>[2]Rotaxane 3</td>
<td>345</td>
<td>376, 396</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>456</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>445</td>
<td>459</td>
<td>0.83</td>
</tr>
</tbody>
</table>

a Emission maximum. b Absolute fluorescence quantum yield of emission. c Pyrene monomer emission. d Pyrene excimer emission. e Excitation of the pyrene absorption band. f Excitation of the pyrene absorption band.

The weakness of the pyrene emission spectrum corresponds to a rising component in the excimer emission. Other components are present, however, which may arise from the existence of different conformations or from the reversibility of excimer formation. Upon excitation of the pyrene chromophore in the rotaxane 3 a rising component of ~0.2 ns can be discerned, which is likely to correspond to the FRET, but the overall time profile is too complicated to allow a reliable analysis.

In conclusion, we have successfully constructed an efficient FRET system by the formation of a mechanically interlocked [2]rotaxane 3. To the best of our knowledge, this is the first example of a pillararene-based rotaxane consisting of a functionalized pillarene wheel. We plan to synthesize [2]rotaxanes having longer spacers between the pyridinium cation station and the pyrene stopper to tune the FRET efficiency and to investigate the shuttling process of the pillar[5]arene wheel within [2]rotaxanes.

Notes and references


