

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

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A [2]rotaxane has been constructed from a di-pyrene appended pillar[5]arene wheel, a pyridinium axle, and a perylene stopper. It shows efficient Förster resonance energy transfer from pyrene to perylene by formation of a mechanically interlocked [2]rotaxane.

Mechanically inter-locked molecules (MIMs)¹ including rotaxanes, catenanes, polyrotaxanes and polycatenanes have been extensively studied in the development of mechanically bonded molecular machines, such as shuttles,² 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**¹² (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

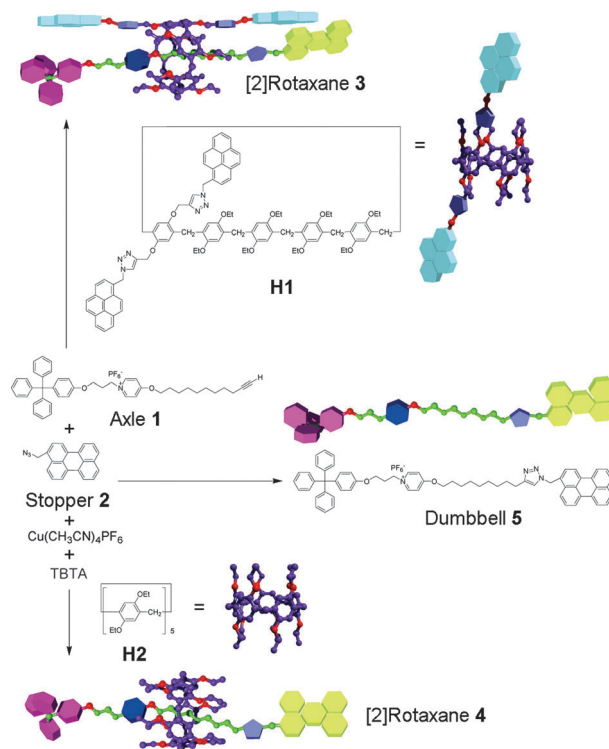


Fig. 1 Synthesis of [2]rotaxanes (**3** and **4**) consisting of perethylated pillar[5]arene (**H2**) and A1–A2 di-pyrene appended pillar[5]arene (**H1**).

Thus, a pyridinium derivative **1** (Fig. 1), bearing an alkyne at one end and a bulky trityl 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 $(1.01 \pm 0.21) \times 10^4 \text{ M}^{-1}$.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 $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ and tris-[(1-benzyl-1*H*-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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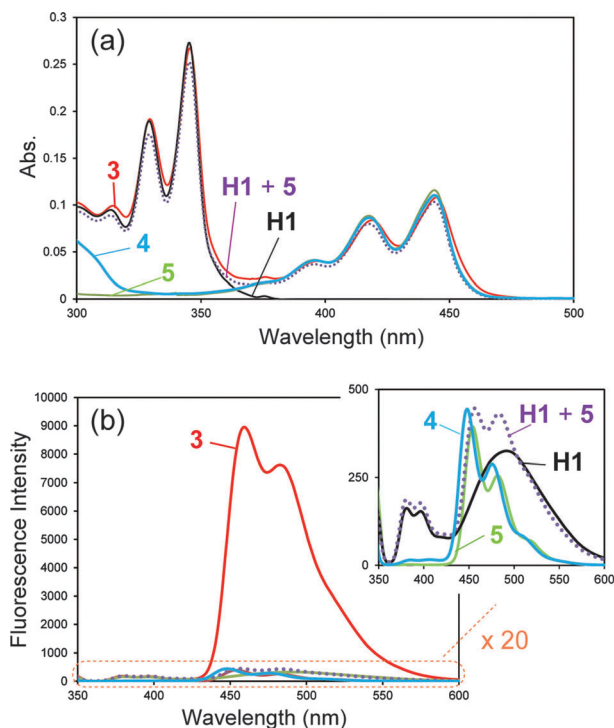


Fig. 2 (a) Absorption and (b) emission spectra (excited at 345 nm) of **H1** (black line), [2]rotaxane **3** (red line), [2]rotaxane **4** (blue line), dumbbell **5** (green line), and a mixture of **H1** and **5** (purple dashed line), all at 4.0×10^{-6} M in chloroform.

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 ^1H , ^{13}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 PF_6^- anion. This is consistent with the formation of the [2]rotaxanes **3** and **4**. Fig. 2 shows the absorption and fluorescence spectra of wheel **H1**, dumbbell **5**, an equimolar mixture of wheel **H1** and dumbbell **5**, and [2]rotaxanes **3** and **4**.

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]rotaxane **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

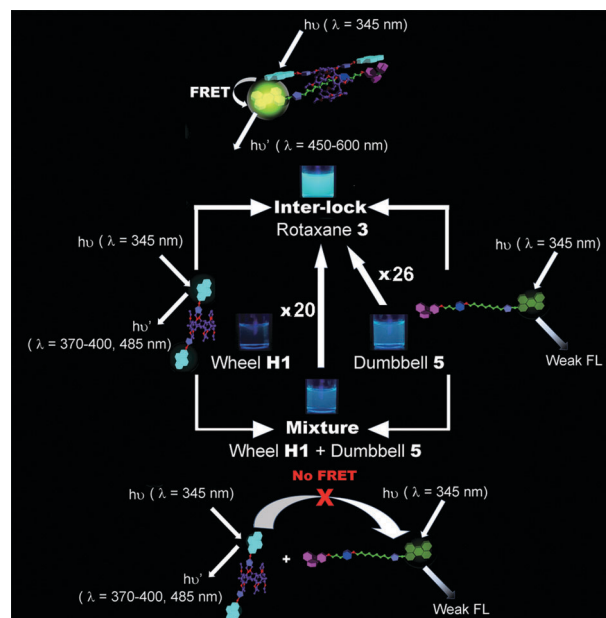


Fig. 3 Schematic illustration of the photophysical properties of wheel **H1**, dumbbell **5** and [2]rotaxane **3**.

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 $\sim 25\times$ 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).¹⁴ 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 pyrene absorption band ($\Phi_f = 0.50$) with that obtained by exciting in the perylene absorption band ($\Phi_f = 0.82$). 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 $\sim 75\%$. The Förster radius was estimated to be $R_0 = 1.8$ nm using the pyrene emission and the dumbbell absorption bands.¹⁵ Energy transfer may, however, also originate from the excimer.¹⁶ 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 $\sim 0.8R_0 = 1.6$ 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 $\tau = 4.6$ ns, the dumbbell **5** shows two components with $\tau_1 = 3.7$ ns (85% of the integrated intensity) and $\tau_2 = 6.0$ ns (15%). A possible

Table 1 Photophysical properties of [2]rotaxane **3**, wheel **H1** and dumbbell **5**

Compound	$\lambda_{\text{abs}}^{\text{max}}$ (nm)	λ_{em}^a (nm)	Φ_f^b
Wheel H1	345	376, ^c 396 ^{c,e} 490 ^{d,e}	0.01 0.06
Dumbbell 5	445	453 ^f	0.82
[2]Rotaxane 3	345	376, ^c 396 ^{c,e} 456 ^c	< 0.01 0.50
	445	459 ^f	0.83

^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 perylene absorption band.

explanation is that electron transfer occurs from the excited perylene to the pyridinium unit, in a reversible fashion. The [2]rotaxane **3**, when excited in the long-wavelength band, *i.e.* the perylene absorption, gives rise to an emission spectrum that is not identical to that of the dumbbell **5**, and three-exponential decay is observed with short components $\tau_1 = 1.3$ ns and $\tau_2 = 3.4$ ns that predominate at short wavelength (Fig. S9, ESI[†]) and a longer decay time $\tau_3 = 8.3$ ns, the contribution of which peaks at 482 nm. A tentative explanation for this observation is that interaction between the excited perylene (emission maximum 450 nm in the dumbbell) and the pyrene unit leads to an exciplex or heteroexcimer.

Excitation of the pyrene absorption band in the wheel **H1** or in the [2]rotaxane **3** gives rise to complicated wavelength dependent multiexponential decays. The weakness of the pyrene emission band ($\Phi_f < 1\%$), quenched by excimer formation and FRET, makes it impossible to perform an accurate quantitative analysis. In the wheel, a decay component of ~ 1 ns at 396 nm (a pyrene peak) 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.¹⁷ 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 pillararene wheel. We plan to synthesize [2]rotaxanes having longer spacers between the pyridinium cation station and the perylene stopper to tune the FRET efficiency and to investigate the shuttling process of the pillar[5]arene wheel within [2]rotaxanes.

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