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Rotaxanes

A Doubly Alkynylpyrene-Threaded [4]Rotaxane That Exhibits Strong Circularly Polarized Luminescence from the Spatially Restricted Excimer**

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Abstract: *The Sonogashira coupling of γ-CD-encapsulated alkynylpyrenes with terphenyl-type stopper molecules gave a doubly alkynylpyrene-threaded [4]rotaxane. The rotaxane showed only excimer emission, with a high fluorescence quantum yield of $\Phi_f = 0.37$, arising from the spatially restricted excimer within the cavity of the γ-CD. The excimer emission suffered little from self-quenching up to a concentration of 1.5×10^{-5} M and was circularly polarized with a high g_{lum} value of -1.5×10^{-2}. The strong circularly polarized luminescence may result from the two stacked pyrenes existing in the rotaxane in an asymmetrically twisted manner.*

Materials capable of emitting circularly polarized luminescence (CPL)[1] have great potential for applications not only in 3D optoelectronic devices[2] but also for bio-probes.[3] Although chiral lanthanide complexes have so far held the spotlight in this field,[3,4] the use and waste of rare metals has resulted in a recent demand for CPL-active, purely organic fluorophores.[5] Aggregates with well-defined numbers of organic π fluorophores often demonstrate photophysical properties different from those when the π systems exist as singe units in dilute solutions. If even two achiral fluorophores are assembled in an asymmetrically twisted manner, the resulting chiral π systems could show the selective emission of right- and left-handed CPL.[6]

Since the 1980s, it has been known that pyrene and its derivatives interact with the large hydrophobic cavity of γ-cyclodextrins (γ-CDs) in water to generate an intense CPL emission as a result of the encapsulated pyrene excimers.[7] However, the stoichiometry of such inclusion complexes intrinsically depends on the measurement conditions, as several fluorescent species as well as monomeric ones usually coexist in the solutions. Of course, the transient complexes present in specific solvents could easily dissociate to their components in other media. To investigate the photophysical properties of the chiral excimers in a straightforward manner and to apply them in materials of optical interest, the labile inclusion complexes need to be elaborated into isolable species. Such a species is best represented by a rotaxane.

Although several kinds of rotaxanes have been synthesized with one axle and several wheel components, those with two axles are rare,[8] particularly those with emissive abilities.[8a] This is probably because two extremely bulky stopper molecules must react with the two terminal groups at the same end of the threaded axles to prevent unthreading. Indeed, no such rotaxanes with two pyrene-based axles have been reported, not even for pyrenes/γ-CD = 2:1, let alone the 2:2 series. Firstly, with the exception of our single alkynylpyrene-based [3]rotaxane,[9] rotaxanes have never been reported with pyrenes as an axle component. We have been studying a new class of pyrene derivatives, alkynylpyrenes, which have high fluorescence quantum yields in water even in the presence of oxygen.[10] Here we present the synthesis of a doubly alkynylpyrene-threaded [4]rotaxane and its optical properties, in particular the strong CPL arising from the spatially restricted, asymmetrically twisted excimer (Figure 1).

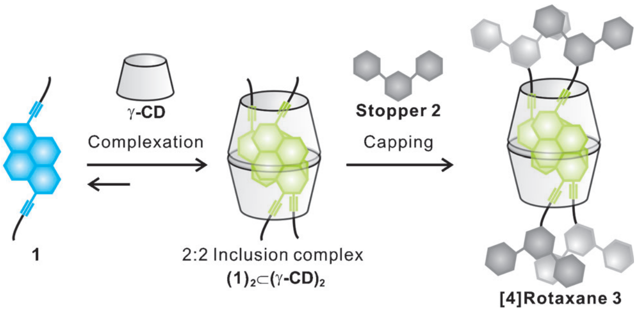

Figure 1. Schematic illustration of [4]rotaxane **3**.

Water-soluble alkynylpyrenes that emit bright luminescence, such as **1**, were employed as the axle component of a [4]rotaxane (Figure 2). γ-CD was selected as the wheel because its cavity is large enough to accommodate the two pyrene rings to afford a doubly threaded inclusion complex.[11] In advance of constructing the rotaxanes, the complex-forming ability of γ-CD with **1a** was examined by NMR

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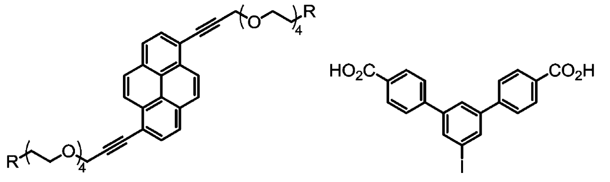

Water-soluble alkynylpyrenes **1**
1a: R = NH_2
1b: R = $OCH_2C{\equiv}CH$

Stopper **2**

Figure 2. Structures of the water-soluble alkynylpyrenes **1** and stopper **2**.

spectroscopic titrations in aqueous solutions. Amphiphilic **1a** readily assembled in aqueous solution into a typical face-to-face aggregate through stacking of the aromatic pyrene ring system. The ^{1}H NMR spectrum of **1a** in D_2O $(3.0\times10^{-3}\,\text{M})$ thus showed the aromatic proton signals to be shifted significantly upfield to around $\delta=7$ ppm, compared with those at $\delta=8.1$ and $\delta=8.6$ ppm in $CDCl_3$ (Figure 3a). The addition of γ-CD resulted in a new set of signals appearing at $\delta=7.5$–8.2 ppm, thus in the region between those of **1a** alone in D_2O and $CDCl_3$. When the molar ratio of γ-CD/**1a** reached 1:1, the original proton signals of **1a** disappeared completely. Further addition of γ-CD hardly affected the new set, which means that **1a** and γ-CD form an *n*:*n* complex. The newly emerging signals can be assigned to **1a** encapsulated in the γ-CD and seem rather complicated by the presence of smaller signals than would be expected for a single species of **1a**. Thus, one might assume the presence of conformational isomers of **1a** in the cavity and/or of diastereomeric inclusion complexes based on both enantiomers arising from the right- and left-handedly twisted **1a** pairs.[7,12] Their chemical shifts implied that the alkynylpyrenes exist neither alone nor in highly aggregated states in the complexes. Furthermore, the two-dimensional diffusion-ordered NMR (DOSY) spectrum of a 1:1 mixture of **1a** and γ-CD $([\mathbf{1a}]=[\gamma\text{-CD}]=6.0\times10^{-3}\,\text{M})$ demonstrated a single diffusion constant (see Figure S1 in the Supporting Information).

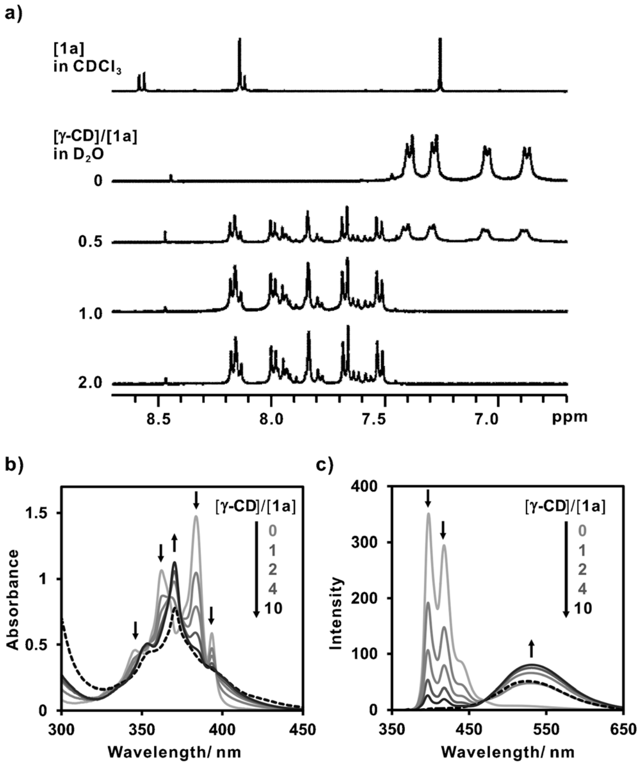

Figure 3. a) ^{1}H NMR spectra of **1a** $(3.0\times10^{-3}\,\text{M})$ upon addition of increasing amounts of γ-CD at 25 °C in D_2O. b) Absorption and c) fluorescence spectra of **1a** $(3.0\times10^{-5}\,\text{M})$ upon addition of increasing amounts of γ-CD in H_2O (gray and black line, respectively) and of [4]rotaxane **3** $(1.5\times10^{-5}\,\text{M}$, black dashed line) in a small amount of ammonia-containing H_2O at ca. pH 9.5 at 25 °C. For (c), $\lambda_{ex}=370$ nm.

Next, UV/Vis and fluorescence titration experiments were performed to further deduce the state of the inclusion complex in H_2O. A dilute solution of alkynylpyrene **1a** in H_2O $(3.0\times10^{-5}\,\text{M})$ showed absorption bands at 390, 385, and 360 nm, which are attributed to the $\pi\rightarrow\pi^*$ transitions of the pyrene chromophore.[10] Titration with γ-CD resulted in a new broad band appearing at around 370 nm, while the intensity of the original bands decreased (Figure 3b, black and gray lines, respectively). This new absorption band could be due to the transannular interaction between the two pyrene planes in the cavity of the γ-CD. A highly dilute solution (100 times more dilute than in the NMR experiments) of **1a** alone, namely in the absence of γ-CD, emitted monomeric blue light between 390 and 450 nm. This monomeric emission peak was accompanied by a small and structureless one around 528 nm, which must originate from the excimer of the alkynylpyrene (Figure 3c, gray and black line).[10a] The addition of γ-CD resulted in the emission from the monomer decreasing and that from the excimer increasing. In the presence of γ-CD at $3.0\times10^{-4}\,\text{M}$, the yellow-green excimer emission became exclusive, and further addition of γ-CD had little influence on the spectrum.[13] From consideration of the NMR, UV/Vis, and fluorescence data, we concluded that the 2:2 inclusion complex $(\mathbf{1a})_2{\subset}(\gamma\text{-CD})_2$ had formed, in which the two axles of **1a** are encapsulated by the two γ-CD wheels (Figure 1).

Now we progressed to isolate the [4]rotaxane-type fluorophore by adding four stopper molecules to the dissociable and transient $(\mathbf{1a})_2{\subset}(\gamma\text{-CD})_2$. Extremely bulky stoppers needed to be used to prevent unthreading of the pyrenes through the large γ-CD cavity. Unfortunately, formation of an amide bond between the terminal amino groups in **1a** and the carboxy groups of various stopper molecules failed. After exhaustive attempts, we finally succeeded in forming a rotaxane through Sonogashira coupling[14] between the newly synthesized acetylene-terminated alkynylpyrene **1b**[15] and 4,4″-biscarboxy-5′-iodo-1,1′:3′,1″-terphenyl (**2**)[16] in water (Figure 2). A mixture of **1b**, **2**, palladium catalyst, and γ-CD was stirred for 72 h at 30 °C, acidified, and filtered. The resulting precipitate was purified by reverse-phase HPLC to afford the first pyrene-based [4]rotaxane **3** in 5 % yield. The purity of **3** was established by HPLC and MALDI-TOF-MS (see Figures S4 and S5 in the Supporting Information), although the presence of conformational and diastereomeric isomers could not be excluded. Rotaxane **3** was fairly soluble in a small amount of ammonia-containing H_2O at about pH 9.5.

The ^{1}H NMR signals of the [4]rotaxane **3** were significantly broadened, probably because of its molecular size and motion, and overlapped with one another owing to the presence of stereoisomers and the four stopper molecules. Since the chemical shifts of γ-CD and the pyrene core in **3** are similar to those in the inclusion complex $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$, we first used the well-resolved signals of $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$ for the assignment of the ^{1}H NMR spectrum. A cluster of signals corresponding to the C2, C3, and C4 protons was distinguished from the corresponding one for the C5 and C6 protons of γ-CD on the basis of the COSY spectrum of $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$ (see Figure S6 in the Supporting Information). The C3 proton signal significantly shifted upfield by about 0.4 ppm compared to that for γ-CD alone in D_2O (ca. $\delta =$ 3.9 ppm). The diamagnetic anisotropy of the encapsulated pyrenes strikingly influenced the C3 proton that exists inside the cavity. We found strong NOE interactions between the pyrene protons and the cluster of C2, C3, and C4 protons for γ-CD in the NOESY spectrum of **3**. On the other hand, only weak interactions were found between the pyrene protons and other γ-CD protons at C1, C5, and C6 (see Figure S7 in the Supporting Information). This finding means that the pyrene cores exist near the two wider rims of two γ-CD molecules and face each other, as shown in Figure 1.

The [4]rotaxane **3** exhibited a similar UV/Vis spectrum as the inclusion complex $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$ under the conditions that most of **1a** was encapsulated by γ-CD (Figure 3b, black dashed line). It is noteworthy that the pure excimer emission was seen in the fluorescence spectrum of **3** even at a concentration of 7.5×10^{-10} M,[17] while monomer emission became predominant for the dissociable $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$ below a complex concentration of 2.3×10^{-5} M (see Figure S9 in the Supporting Information). The rotaxane, which cannot dissociate, would force the two pyrenes to be close in the cavity regardless of the concentration, and therefore only excimer emission is seen (Figure 3c, black dashed line). The excitation spectrum of **3** monitored at the excimer emission wavelength (528 nm) was similar to the corresponding absorption spectrum, thus confirming that the excimer emission must result from the stacked pyrenes (see Figure S10 in the Supporting Information). The emission intensity was found to obey a linear relationship with the concentration up to as high as 1.5×10^{-5} M (see Figure S11 in the Supporting Information). The linearity means there is no interaction between one excited rotaxane and another one, usually in the ground-state, even at 10^{-5} M. The "γ-CD-isolated" excimer no longer suffers from the unfavorable self-quenching of their excited states. These characteristics as well as its high fluorescence quantum yield of $\Phi_f = 0.37$[18] are likely to be important when considering its application in optical materials.

The circular dichroism spectrum of [4]rotaxane **3** showed strong Cotton effects in the absorption region of the pyrenes (Figure 4a). According to exciton coupling theory, when two chromophores with a left-handed sense are located nearby, they show bisignated Cotton effects with negative and positive signs in the longer and shorter wavelength regions, respectively.[19] However, bisignated Cotton effects are often confused with normal induced circular dichroisms (ICDs), the presence of which sometimes complicates the accurate assignment of the chirality. In **3**, the positive Cotton effect ranging from 407 to 329 nm might be amplified by the normal ICD, since our single alkynylpyrene-based [3]rotaxanes also revealed a positive Cotton effect in the same wavelength region.[9] No circular dichroism appeared above 407 nm for the [3]rotaxanes, while a negative Cotton effect was seen in the case of [4]rotaxane **3**. If this assumption is correct, we could predict that the two pyrenes are arranged or at least biased with a left-handed chirality because of the continuous bisignated Cotton effects with negative and positive signs ranging from 503 to 275 nm. This arrangement coincides with the stable conformation of the two alkynylpyrene cores in **3** found by MacroModel-based Monte Carlo simulations followed by B3LYP/6-31G (Figure 5). The computational prediction of Cotton effects in the simulated core was performed by time-dependent density functional theory (TD-DFT) and proved to qualitatively agree with the experimental data (see Figure S12 in the Supporting Information).[20] The Kobayashi and Kano research groups have also reported the same order of Cotton effects with two parent pyrenes encapsulated in γ-CD, thus suggesting a left-handed chirality for the arrangement of the pyrenes in their inclusion complexes.[7]

The rotaxane architecture fixed a pair of alkynylpyrene molecules in a spatially restricted and asymmetrically twisted

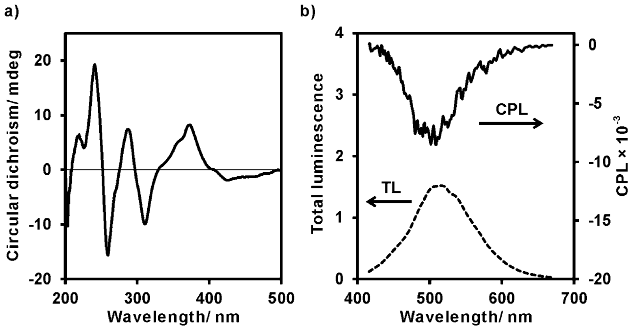

Figure 4. a) Circular dichroism and b) CPL (black line) as well as total luminescence (black dashed line) spectra of [4]rotaxane **3** in a small amount of ammonia-containing H_2O at ca. pH 9.5 at 25 °C. For a), $[\mathbf{3}] = 1.5\times10^{-5}$ M and for (b), $[\mathbf{3}] = 4.5\times10^{-5}$ M, $\lambda_{ex} = 370$ nm.

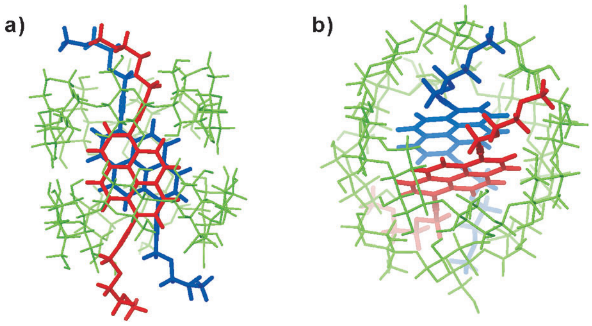

Figure 5. One of the stable conformations of two alkynylpyrenes in the cavity of γ-CD as found by MacroModel-based Monte Carlo simulation. The structure was further optimized by using B3LYP/6-31G. γ-CDs: green, alkynylpyrene-based axles: red and blue. a) Side view, b) top view.

manner. This was confirmed by examining the fluorescence and circular dichroism spectra at high temperature and comparing them with those of $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$. In the fluorescence spectra, [4]rotaxane **3** showed only eximcer emission even at 80 °C, and the Cotton effects remained almost unchanged. On the other hand, a switch from excimer to monomer emissions was observed for $(\mathbf{1a})_2\subset(\gamma\text{-CD})_2$ on raising the temperature. This change accompanied the disappearance of the Cotton effects, thus demonstrating the dissociation of the transient chiral complex (see Figure S13 in the Supporting Information). The chirality from the asymmetrically twisted alkynylpyrene pair in **3** should be preserved in the excited state. Indeed, the strong right-handed CPL signal (415–650 nm) was observed in the excimer emissive region of the spectrum for a pyrene core (Figure 4b and Figure S14 in the Supporting Information).[21] The dissymmetry factor of luminescence (g_{lum}), a parameter indicating chirality in the excited state, is defined as $2(I_L-I_R)/(I_L+I_R)$, where I_L and I_R denote the intensity of left and right circularly polarized emissions, respectively. The g_{lum} value of **3** was -1.5×10^{-2} at 480 nm, which is one of the highest g_{lum} values for CPL-active, purely organic fluorophores.[5] The negative sign for the g_{lum} value denotes the excess emission of right-handed CPL from the excimer in **3**, and was consistent with the corresponding circular dichroism band at the longest wavelength (407–503 nm). This means the CPL band arose from the same chiral source as the circular dichroism band,[22] so that the handedness may similarly exist in the excited state because of the restricted rotational motion of the two alkynylpyrene molecules. Thereby, the left-handed chirality of the pyrene excimer in **3** exhibited the right-handed CPL.

In summary, we designed and synthesized a doubly alkynylpyrene-threaded [4]rotaxane-type fluorophore that showed strong yellow-green excimer emission with a high fluorescence quantum yield in aqueous solutions. The excimer emission survived unquenched up to a concentration as high as 10^{-5} M and was found to be strongly CPL-active. Although only one-handed CPL was presented in this study, the opposite CPL is bound to exist, providing that the antipode of natural γ-CD was used. Thus, the rotaxane approach could be a new strategy for creating novel CPL-emitting molecules for future optical technologies.

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Keywords: chirality · circularly polarized luminescence · cyclodextrins · excimer emission · rotaxanes

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i.e., monomeric alkynylpyrene and its excimer, during the titration. Therefore, the binding isotherm fitted well to a 1:1 complexation model, from which the apparent K_a value of $6.6\times 10^4\,\text{M}^{-1}$ was determined (see Figure S3 in the Supporting Information).

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