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Fluorescence Control of Boron Enaminoketonate Using a Rotaxane Shuttle

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ABSTRACT

The effect of rotaxane shuttling on the fluorescence properties of a fluorophore was investigated by exploiting fluorophore-tethered [2]rotaxanes. A fluorescent boron enaminoketonate (BEK) moiety was introduced in a rotaxane via transformation of an isoxazole unit generated as a result of an end-capping reaction using a nitrile *N*-oxide. The rotaxane exhibited a red shift of the fluorescence maximum along with a remarkable enhancement of the fluorescence quantum yield through wheel translation to the fluorophore.

Boron enaminoketonates (BEKs) are a new type of boron-chelating dye.[1] Their optical properties feature a large Stokes shift and high-molar absorption coefficient (ε) that are quite similar to those of boron diketonates. Boron diketonates are useful in molecular probes,[2] lasers,[3] and in optical sensing devices,[4] which are capable of incorporating various organic backbones.

On the other hand, mechanically interlocked molecules, such as rotaxanes, catenanes, and polyrotaxanes, have attracted much interest as a new concept for improving the electro-optical properties of fluorophores via static encapsulation, because the method enables direct modification of such properties without any structural change in the fluorophore itself.[5,6] Considering such studies, we envisaged that the statistical and dynamic coverage of a fluorophore moiety on the rotaxane axle via wheel shuttling may diminish quenching to a certain extent by an

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external species and by energy transfer, even though the wheel cannot stay on the fluorophore.

We have previously reported a powerful and highly reliable catalyst-free click end-capping reaction of an alkyne-terminated pseudorotaxane with a stable nitrile *N*-oxide[7] to give a [2]rotaxane[8−10] accompanied by the formation of a promising isoxazole skeleton as a BEK precursor. Considering our previous work, we describe herein the fluorescence control of a BEK placed at the end of the rotaxane axle, which was demonstrated through a comparison between two types of BEKs with a through-space linkage: (i) a BEK-rotaxane with the wheel located at the far position and (ii) a BEK-rotaxane with the freely movable wheel. It was discovered that the high mobility of the wheel resulted in a red shift of the fluorescence maximum along with a remarkable enhancement of the fluorescence quantum yield (Φ_F), indicating that the mobile wheel stabilizes the excitation state of the fluorophore.

Scheme 1 shows the synthesis of [2]rotaxane **5**. Treatment of *sec*-ammonium salt **1** in the presence of dibenzo-24-crown-8-ether (DB24C8, **2**) gave pseudorotaxane **3** possessing an alkyne moiety at the terminus. A subsequent catalyst-free 1,3-dipolar cycloaddition reaction of the stable nitrile *N*-oxide **4** with **3** proceeded smoothly via isoxazole formation to give the corresponding [2]rotaxane **5** in an excellent yield (95% yield). The structure of **5** was determined by ^{1}H and ^{13}C NMR, IR, and ESI−TOF MS analysis, and **5** was confirmed to exist as a single regioisomer.[11]

The transformation of the isoxazole skeleton of **5** to a BEK functioning as a fluorophore was performed (Scheme 2). The selective N−O bond cleavage of the isoxazole moiety of **5** was performed using $Mo(CO)_6$ in a mixed solvent of CH_3CN-H_2O to give the β-enaminoketone, followed by the treatment with $BF_3 \cdot OEt_2$ in the presence of Et_3N to afford the BEK-containing [2]rotaxane **6**. Moreover, the removal of the hydrogen bonds in **5** was performed by acetylation of **5** to give the nonionic [2]rotaxane **7**. The sequential transformation of the isoxazole moiety of **7** to the BEK function was performed in the same manner to give **8**. The structures of **6** and **8** were determined by ^{1}H NMR, ^{19}F NMR, IR, and MALDI−TOF MS analysis.[11]

Scheme 1. Synthesis of [2]Rotaxane **5**

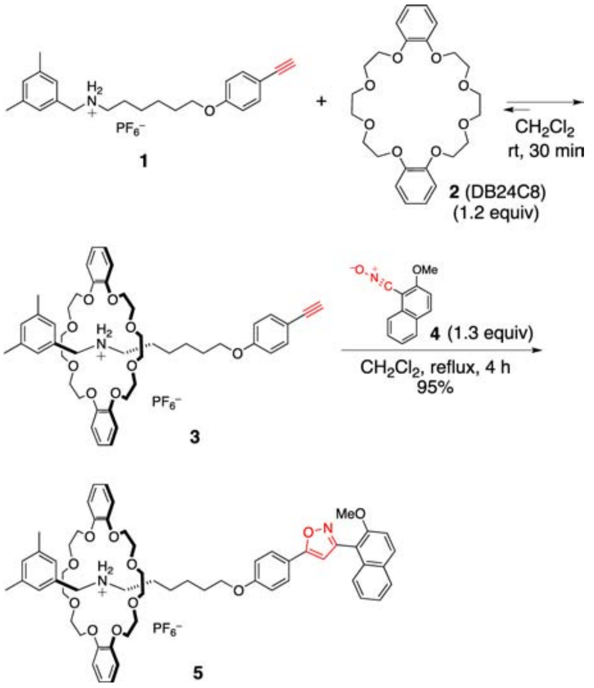

Figure 1 shows ^{1}H NMR spectra of **6** and **8**. In spectrum (A), the characteristic signals of the benzyl protons (c and d) of the axle component of **6** appear as broad peaks due to geminal coupling, supporting the assignment of the interlocked structure of **6**, in which the ammonium moiety is localized at the center of the crown ether moiety in accordance with the literature.[12] As can be seen in spectrum (B), the signals of the benzyl protons (c and d) are upfield-shifted, and the signals of the acetyl group can be observed, confirming the *N*-acetylated structure of **8**. In addition, certain signals of the axle portion of the molecule are shifted due to the ring current effect from **2**, and these shifts provide critical information about the increased

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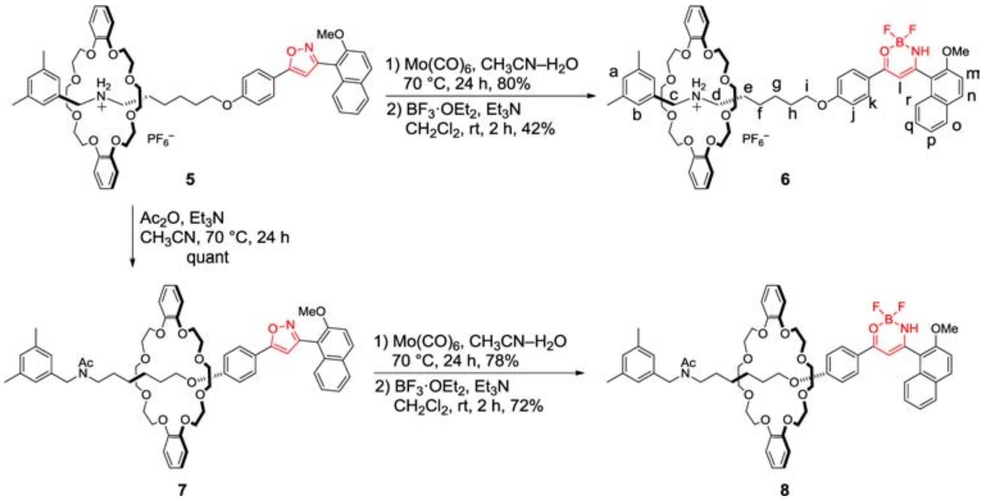
Scheme 2. Synthesis of Fluorescent [2]Rotaxanes via Selective Transformation of Different Isoxazoles to BEK



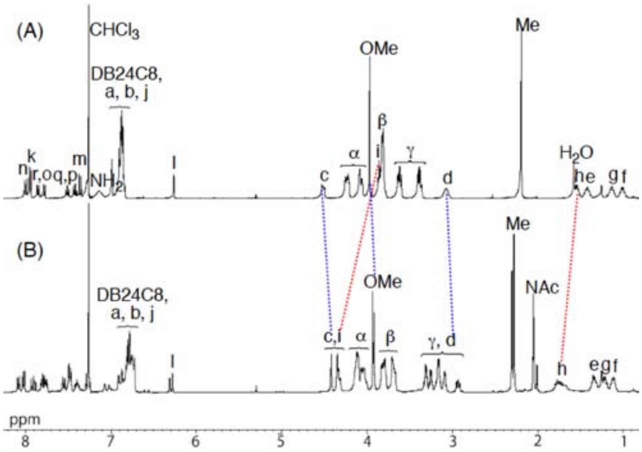


Figure 1. ^{1}H NMR spectra of (A) **6** and (B) **8** (400 MHz, $CDCl_3$, 298 K).

mobility of the wheel component that is separated from the ammonium moiety. Signals h and i are downfield-shifted, indicating deshielding of these protons from the aromatics of **2**. In contrast, the methoxy signal (OMe) is upfield-shifted, implying CH$-\pi$ interactions of the methoxy group with the π-plane of the wheel aromatic substituents. It should be noted that **8** is a nonstationary rotaxane consisting of the wheel that is capable of free movement along the axle, because **8** does not have any strong interaction between the components.[8,13]

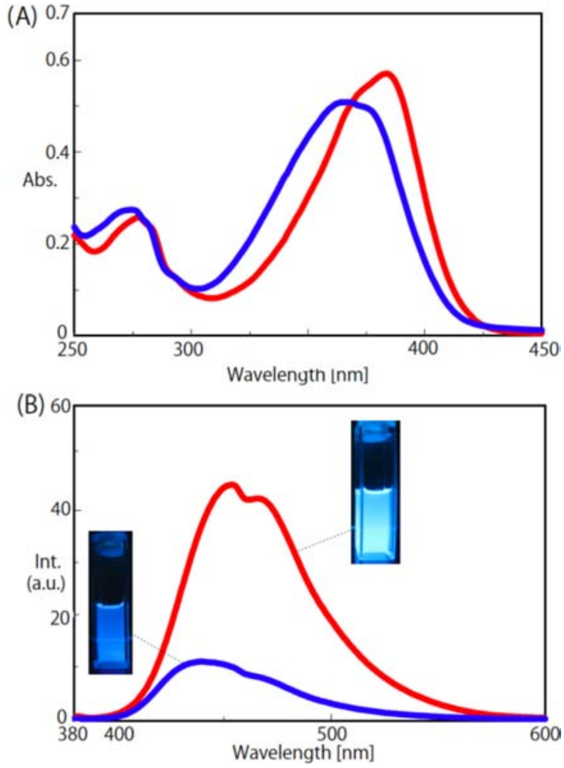


Figure 2. UV–vis (A) and fluorescence spectra (B) of **6** (blue line) and **8** (red line) (CH_2Cl_2, 293 K, 20 μM). The excitation wavelengths of **6** and **8** at (B) are 364 and 384 nm, respectively.

To evaluate the effect of the wheel mobility on the optical properties of compound **8**, the UV–vis absorption spectra of **6** and **8** in CH_2Cl_2 were measured (Figure 2A). The absorption spectrum of **6** exhibits a maximum at 364 nm, while the absorption maximum of **8** appears at 384 nm. The 20 nm red shift of the absorption maximum of

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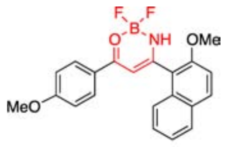
8 from that of **6** can be assumed to be the result of the increasing conjugation length of the BEK moiety and/or $\pi-\pi$ stacking between the BEK and crown ether moieties. The ε values of **6** and **8** were 2.5×10^4 and 2.9×10^4 $M^{-1}\cdot cm^{-1}$, respectively.

The fluorescence emission spectra of **6** and **8** when excited at their absorption maxima are shown in Figure 2 B. The fluorescence maxima of **6** and **8** appear at 440 and 454 nm, indicating that the Stokes shifts are sufficiently large (1.3×10^5 and 1.4×10^5 cm^{-1}, respecitvely) and similar to that of conventional boron diketonates. The Φ_F's of **6** and **8** were determined on the basis of the fluorescent intensity of 9,10-diphenylanthracene as a reference standard ($\Phi_F = 97\%$).[14] As a result, **8** was found to exhibit an enhanced Φ_F ($\Phi_F = 12\%$) that is approximately 4-fold higher than that of **6** ($\Phi_F = 3\%$). The model compound **9** containing a partical structure of the rotaxanes was also synthesized as a control sample (Figure 3). It turned out that the UV−vis and fluorescence spectra of **9** were in good accordance with those of **6**[11] and the Φ_F of **9** was determined to be a similar value to that of **6** (**9**: $\Phi_F = 4\%$). This result suggests that the reason for the dramatic change of the optical properties of **8** originates not from the absence of the ammonium group but from the statistical existence of the crown ether moiety.



9 ($\Phi_F = 4\%$)

Figure 3. Structure and Φ_F of model compound **9**.

To clarify that the enhancement of Φ_F accompanies increased wheel mobility, the energy-minimized structure of **8** was calculated using the density-functional theory (DFT) at the B3LYP/6-31G level.[1,11] The calculated structure of **8** indicates increased rigidity around the BEK moiety of **8** in the excited state with the support of the wheel translation, which restricts the conformational freedom of the fluorophore. In addition, the naphthalene skeleton of **8** barely affected the π-extension of the emissive framework because of the distorted structure. The improved Φ_F of **8** with respect to **6** appears to be the result of the steric protection of the fluorophore by the mobile wheel.[15] Although this work has focused on the synthesis of the fluorescence control system, future studies will concentrate on the evaluation of the steric protection effect of the mobile wheel on the optical properties of fluorophore.

In conclusion, we have described the usefulness of a statistical stabilization method using a rotaxane system through a comparison of the fluorescence properties between two types of BEKs with a through-space linkage. The rotaxane-based BEKs were readily prepared via sequential transformation of an isoxazole-containing rotaxane synthesized via a stable nitrile *N*-oxide-based click end-capping reaction. The statistical stabilization can be clearly distinguished from conventional stabilization methods, such as thermodynamic and kinetic stabilization. The present achievement will provide crucial insights for not only supramolecular chemistry but also polymer chemistry, because the sequential transformation from isoxazole to BEK would be versatile and the concept of dynamic steric protection should be applicable to the construction of unprecedented polymers with chemically unstable functionalities. The development of stimuli-responsive fluorescent switching materials exploiting a combination of this system with polyrotaxane network chemistry will be an important subject for future work.

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Supporting Information Available. Full experimental details for all new compounds are provided, including ^1H NMR, ^{13}C NMR, IR, UV−vis, and fluorescence spectra of the rotaxanes. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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