

Reversibly Tunable White-Light Emissions of Styrylpyridiniums with Cucurbiturils in Aqueous Solution

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S Supporting Information

ABSTRACT: The different excimer emissions based on a series of host–guest complexes of dipolar dyes styrylpyridiniums (**An** and **Bn**) with cucurbit[*n*]urils (**CB[*n*]**) are reported. The *syn*- and *anti*- excimers due to the opposite stacking orientations have been well investigated both in experiments and DFT calculations. Furthermore, reversibly color-tunable luminescent supramolecular assemblies including near white-light emission with CIE coordinates (0.32, 0.29) were achieved by competitive inclusion of **An**-**CB[7]** with **ADA**.



Wavelength-tunable and switching “on/off” supramolecular organic luminescent materials have various applications in optical devices,¹ biological systems,² mechano-sensors,³ security inks,⁴ and chemical sensors.⁵ Generally, the luminescent properties of organic materials strongly depend on the molecular constitutions, the resource structure and conformation of molecules, and the aggregation of the molecules.⁶ Tuning the assembling structures of molecules for developing luminescence-tunable materials is an important research field in supramolecular chemistry.⁷ Several fluorescence-tunable supramolecular assemblies have been reported, which contain more than one kind of fluorophore,^{4,8} but using one kind of fluorophore to fabricate those materials remains challenging,⁹ especially covering the wider spectrum with the reversibility.

Excimer emission typically provides a broad spectrum with the maximum red-shifted around 100 nm compared to monomer emission.¹⁰ The minimum range of full-color spectrum is from 490 to 610 nm, which is from blue to red light, spanning 120 nm at least.^{1a} So tuning a single fluorophore’s photoluminescence from monomer to excimer emissions would be a promising way to fabricate luminescent-tunable materials covering a wide spectrum in visible light. The fluorophore emitting visible light usually is dipolar molecule, which consists of electro-donor and electro-acceptor in one molecule. The typical dipolar dyes are styrylpyridiniums (**SP**), which are easy access to different structures with various emission colors and have strong binding affinities with cucurbit[*n*]urils (**CB[*n*]**).¹¹ Two kinds of excimers for dipolar dyes might be involved (Figure 1), such as the *syn*-excimer (“head-to-head” pattern) and *anti*-excimer (“head-to-tail” pattern). Although the dimerization and isomerization of some **SP**-**CB[*n*]** complexes during photoirradiation have been reported,^{9b,12} the “*syn/anti*-excimer” formations were not investigated, especially for dipolar **SP**. Herein, we report the

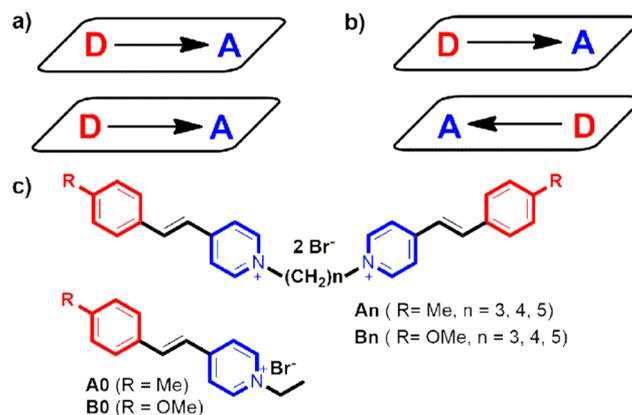


Figure 1. (a) *Syn*-excimers. (b) *Anti*-excimers. (c) Chemical structures of **SP**.

fluorescence properties of dipolar dyes **SP** (**An**, **Bn**) with **CB[*n*]** and that a “fluorescent chameleon” supramolecular system was achieved, which the emission color could reversibly change from blue (465 nm) to orange (607 nm), especially including white-light.

The **SP** were obtained by the Knoevenagel condensation and characterized by ¹H NMR, ¹³C NMR, and HRMS (Figures S1–S16). Compared with the mono-**SP**, the maxima absorption bands were slightly red-shifted, which followed the order of (*n* = 3) > (*n* = 4) > (*n* = 5) > mono (Figures S17–S24). The maxima absorption peaks were generally blue-shifted as the solvent polarity increased, which were shown negative solvatochromism.¹³ The fluorescence spectra for those **SP**

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salts were also investigated in various solvents (Figures S25–S32). In the same solvent, the maxima fluorescence peaks of mono- and bis-SP were almost similar for **Bn** (Tables S2). But for **An** in aqueous solution, besides the same peaks around 450 nm for mono-SP's emissions, the bis-SP gave strong and broad emission bands with the peak values around 607, 579, and 551 nm for A3, A4, and A5, respectively (Figure 2). Furthermore,

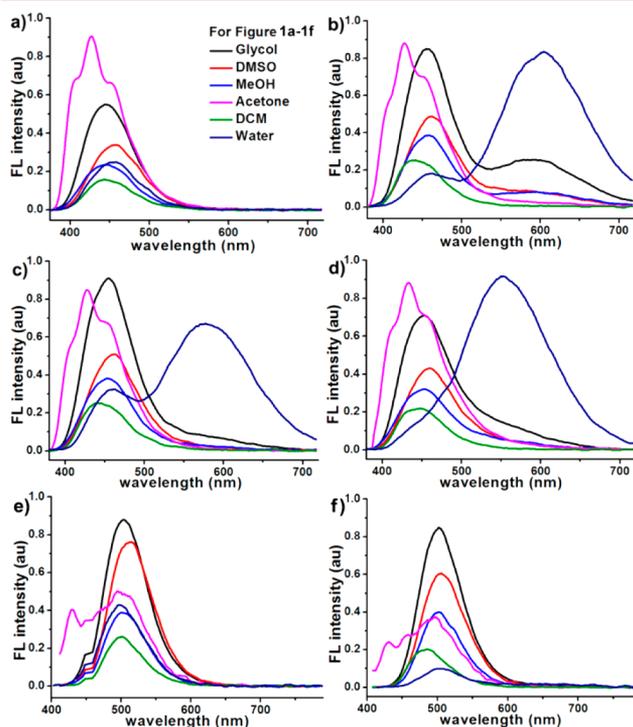


Figure 2. Fluorescence emission spectra of (a) **A0** (20.0 μM); (b) **A3** (10.0 μM); (c) **A4** (20.0 μM); (d) **A5** (20.0 μM); (e) **B0** (20.0 μM); (f) **B3** (10.0 μM) in various solvents.

the ratio of two emission peaks for **A3–5** did not change with the concentration changing from 1.0 to 38.0 μM (Figures S33–S38) that hint the excimer formations were more favorable to the intramolecular process, in which the two SP rings are undoubtedly stacked as “head-to-head” patterns. Those hydrophobicity induced excimer emission effects have also been reported for bis-pyrene and bis-anthracene systems which figured as pH-controlled fluorescent switches.¹⁴

Those aforementioned excimer formations were more favorable for the “head-to-head” pattern due to the folded configurations. By means of the host–guest interactions, both *syn*-excimers and *anti*-excimers were easily achieved (Figure 3a). Kaifer et al. have found that two **B0** could include in **CB[8]** as “head-to-tail” pattern but have not measured the fluorescence spectrum of **CB[8]** \supset **2B0**.¹⁵ In our studies, comparing with the fluorescence spectrum of **B0**, the spectrum of **CB[8]** \supset **2B0** was stronger and red-shifted (Figure S65), the maxima fluorescence peak of **B0** was 495 nm, and 536 nm for *anti*-excimer **CB[8]** \supset **2B0** (Figure 3). The *syn*-excimers of **Bn** also have been investigated by host–guest complexations with **CB[8]**. **B3–5** could be included in **CB[8]** to form 1:1 complex which have determined by the Job's plot (Figures S59–S61). In the presence of 1 equiv of **CB[8]**, the NMR signals of the aromatic hydrogens in **B3–5** were upfield shifted, which hints that the SP rings are located in **CB[8]**'s cavity (Figure S66). Our group has reported that bis-pyridiniums could be included

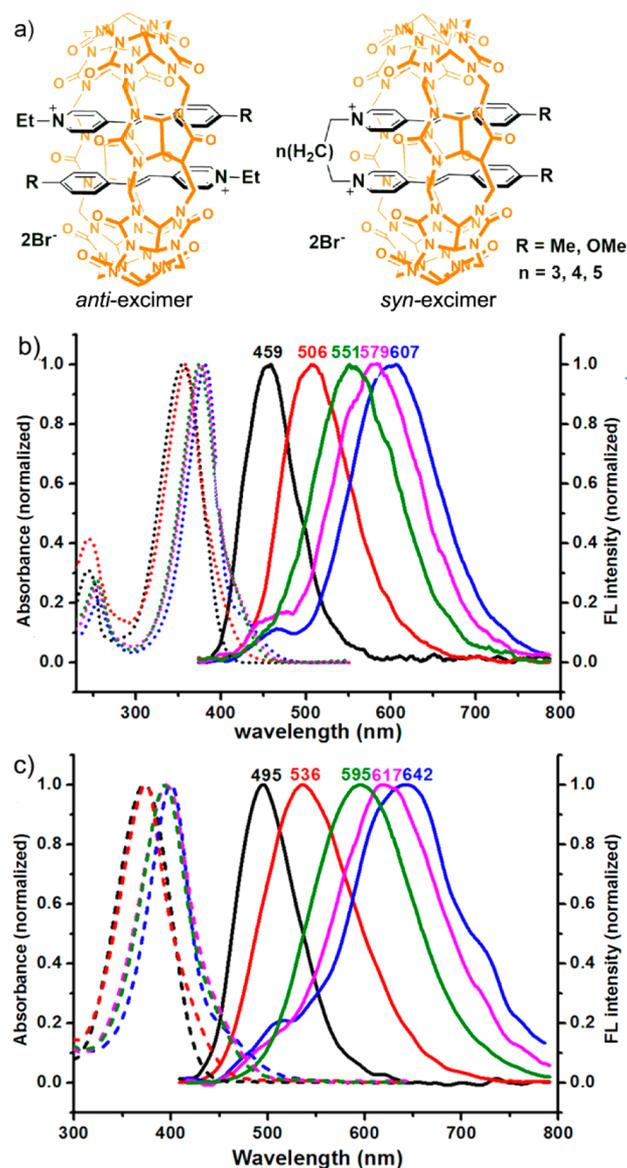


Figure 3. (a) Different including pattern of SP in **CB[8]**. (b) Normalized absorption and fluorescence spectra of **An** in absence/presence of 1.0 equiv of **CB[8]** in water. (c) Normalized absorption and fluorescence spectra of **Bn** in the absence/presence of 1.0 equiv of **CB[8]** in water. Dash lines are the absorption spectra (from left to right: **A0**, **CB[8]** \supset **2A0**, **CB[8]** \supset **A5**, **CB[8]** \supset **A4**, **CB[8]** \supset **A3**), and solid lines are the fluorescence spectra (from left to right: **B0**, **CB[8]** \supset **2B0**, **CB[8]** \supset **B5**, **CB[8]** \supset **B4**, **CB[8]** \supset **B3**).

in **CB[8]** as “head-to-head” patterns,¹⁶ so that **B3–5** also included in **CB[8]** as those patterns. The association constants K of **CB[8]** \supset **Bn** were measured by fluorescence spectral titration (Figures S62–S65) and are listed in Table S4. All of the constants were larger than 10^7 M^{-1} and followed the order **CB[8]** \supset **B5** > **CB[8]** \supset **B4** > **CB[8]** \supset **B3**.

The maximum fluorescence peaks of those *syn*-excimers were 642, 617, and 595 nm for **B3**, **B4**, and **B5**, respectively, which were more red-shifted than the *anti*-excimer emissions (Figure 3c and Table S4). Furthermore, in the presence of **CB[8]**, the red-shifted UV/vis spectra of **Bn** and different fluorescence excitation spectra (Figures S53) hinted that those excimers were “static excimers”, which are the dimers associated both in ground state and excited state.¹⁷ The fluorescence quantum

yield and lifetime (Φ_F, τ_F) of $\text{CB}[8] \supset \text{Bn}$ were measured (Figures S54–S58 and Table S4). Comparing with the monomer **B0**, the relatively higher τ_F were attributed to the host $\text{CB}[8]$ enhanced excimer emissions. Most Φ_F of $\text{CB}[8] \supset \text{Bn}$ were higher than the monomer **B0** except $\text{CB}[8] \supset \text{B3}$. More interestingly, the *anti*-excimer of $\text{CB}[8] \supset 2\text{B0}$ and the *syn*-excimer of $\text{CB}[8] \supset \text{B5}$ were quite similar without regard for emission peaks, and the Φ_F was followed the order as $\text{CB}[8] \supset 2\text{B0}$ ($\Phi_F = 3.99\%$) \approx $\text{CB}[8] \supset \text{B5}$ ($\Phi_F = 4.01\%$) $>$ $\text{CB}[8] \supset \text{B4}$ ($\Phi_F = 1.39\%$) $>$ $\text{CB}[8] \supset \text{B3}$ ($\Phi_F = 0.22\%$).

Similarly, addition of 1 equiv of $\text{CB}[8]$ to **A3–5** could enhance fluorescence emissions at different levels (Figures S46–S48) without shifting the maxima fluorescence peaks, which also indicated that the bis-SP included in $\text{CB}[8]$ as “head-to-head” stacking (*syn*-excimers). The maxima fluorescence peak of *anti*-excimer $\text{CB}[8] \supset 2\text{A0}$ was around 506 nm, which was also larger than the monomer’s peaks (459 nm) and smaller than the *syn*-excimers’ (Figure 3b).

DFT calculations were performed on the **An** and **Bn** to obtain insight into the fluorescent properties for the different excimers. The ground-state geometries of complexes $\text{CB}[8] \supset 2\text{An}$ and $\text{CB}[8] \supset 2\text{Bn}$ were optimized. The results showed that the geometries of the dyes **An** and **Bn** were folded. And then, the $\text{CB}[8]$ s were removed from the optimized geometries to gain the purely dimeric geometries for **An** and **Bn**, which could simplify the single point energy calculations for the excimers (Table S5). The LOMO of two aromatic rings in **A3** were much overlapped than other excimers, and meanwhile, the HOMO–LUMO gap ($\Delta E_{\text{LUMO-HOMO}}$) of **A3** was much smaller than that of others. With the lower $\Delta E_{\text{LUMO-HOMO}}$, the dyes often exhibited the longer emission wavelengths in the fluorescent spectra.¹⁸ As shown in Table S4, the $\Delta E_{\text{LUMO-HOMO}}$ values for the excimers followed the order of $2\text{A0} > \text{A5} > \text{A4} > \text{A3}$ and $2\text{B0} > \text{B5} > \text{B4} > \text{B3}$, which were agreement with the experimental data.

Considering that **An** gave monomer emission in glycol and excimer emission in water, the fluorescent spectra of **An** in different ratio of water and glycol were studied. Interestingly, near white-light emission with CIE coordinates (0.32, 0.32) and (0.33, 0.30) could be achieved by **A4** in water/glycol = 6:4 and **A3** in water/glycol = 7:3 (Figures S39–S44). These color-tunable properties are attributed to different ratios of monomer and *syn*-excimer emissions. To further achieving the reversibly tunable emissions, a supramolecular method was also involved. The monomer **A0** showed good affinities with $\text{CB}[7]$ with the binding constant $K = (5.70 \pm 0.64) \times 10^6 \text{ M}^{-1}$ (Figure S67). So addition $\text{CB}[7]$ to **A3–5** in aqueous solution could separate two SP rings, which led to weaken the *syn*-excimer formations. For example, the *syn*-excimer fluorescence peak (607 nm) of $10.0 \mu\text{M}$ **A3** was gradually weakened until disappeared and monomer emission (460 nm) was enhanced in the presence of 0 to 2.0 equiv. $\text{CB}[7]$ (Figures S68 and S69). The 1931 CIE chromaticity coordinate changes of **A3–5** in the presence of $\text{CB}[7]$ are summarized in Figure 4b. The color of **A3** and **A4** changed from orange to blue, which included the near white-light regions with the chromaticity coordinates in (0.32, 0.29) and (0.32, 0.32), and the color of **A5** changed from yellow to blue covered the near white-light emission (0.30, 0.34) (Figure 4d). Owing to the stronger affinities for 1-adamantanamine hydrochloride (**ADA**) with $\text{CB}[7]$ ($4.2 \times 10^{12} \text{ M}^{-1}$),¹⁷ addition **ADA** to the $\text{CB}[7] \supset \text{An}$ solution could make **An** out of $\text{CB}[7]$ ’s cavity and recover the *syn*-excimers emissions (Figure 4c). Then, addition $\text{CB}[7]$ to the above solution could also

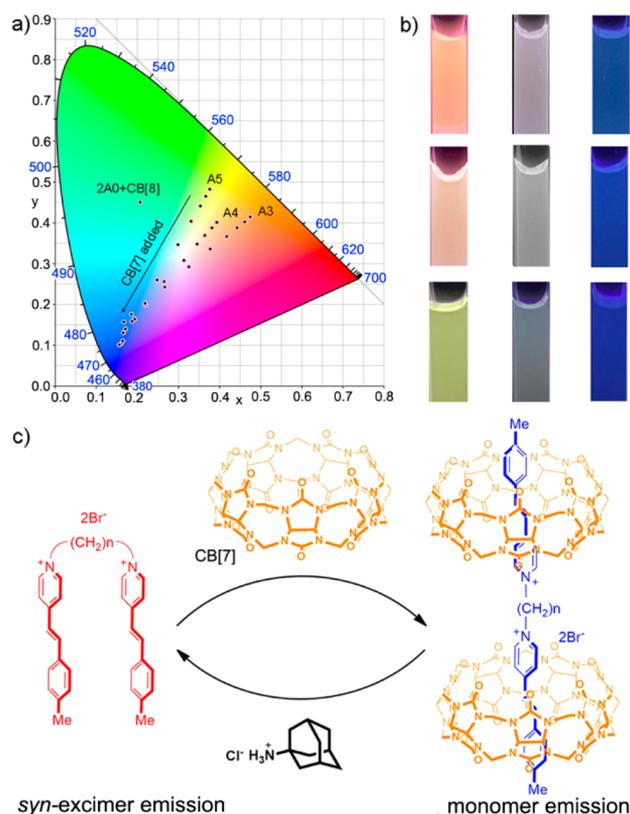


Figure 4. (a) 1931 CIE chromaticity coordinate changes of **A3** ($10.0 \mu\text{M}$), **A4** ($10.0 \mu\text{M}$), and **A5** ($10.0 \mu\text{M}$) in the presence of $\text{CB}[7]$ (0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 2.0 equiv). (b) Examples of fluorescence photographs with CIE coordinate (from left up to right bottom): $10.0 \mu\text{M}$ **A3** with 0.0, 1.0, and 2.0 equiv of $\text{CB}[7]$ (0.47, 0.41; 0.32, 0.29; 0.17, 0.16), $10.0 \mu\text{M}$ **A4** with 0.0, 0.8, and 2.0 equiv of $\text{CB}[7]$ (0.39, 0.40; 0.32, 0.32; 0.16, 0.13), $10.0 \mu\text{M}$ **A5** with 0.0, 0.8, and 2.0 equiv of $\text{CB}[7]$ (0.38, 0.48; 0.30, 0.34; 0.15, 0.10). (c) Schematic representation of reversibly tuning emissions from monomer to *syn*-excimer.

make the emission color blue-shifted again and these emission color changeable processes could repeat three times (Figures S74–S76). But the fluorescence intensities were obviously weak after three times because of those chemical stimulus might cause byproducts or waste and make the concentration higher than the initial state which resulted in fluorescence quenching.

In summary, owing to the hydrophobicity induced excimer emissions of bis-SP **An** and the competitive binding behaviors of **ADA/An** with $\text{CB}[7]$, the reversibly color-tunable luminescent supramolecular assemblies with wide-spectrum (460 to 607 nm for **A3**, spanning 147 nm) including near white-light emission (0.32, 0.29) were achieved. These wide-spectrum changes were attributed to *syn*-excimers, of which the emission peaks are nearly 100 nm red-shifted compared with *anti*-excimers. The differences between *syn*- and *anti*-excimers have been well investigated by comparisons of the fluorescent properties of host–guest complex $\text{CB}[8] \supset \text{An}$ and $\text{CB}[8] \supset \text{Bn}$ both in experiments and DFT calculations. Those color-tunable luminescent supramolecular assemblies and the differences of *syn*-/*anti*-excimers formations provided a convenient and powerful method for constructing smart luminescent materials which have potential applications in light-emitting materials and information technology.

■ ASSOCIATED CONTENT**■ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03377.

Detailed experiments, additional spectroscopic data, and computational simulation details (PDF)

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Notes

The authors declare no competing financial interest.

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