Photochemistry

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Photoswitchable Exciton Coupling in Merocyanine–Diarylethene Multi-Chromophore Hydrogen-Bonded Complexes

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The use of phototriggered conformational change of photochromic molecules to tune the physical properties of functional molecules through noncovalent interactions is a challenging research topic[1] inspired by the sophisticated function in vision.[2] Aida and co-workers reported an elegant example in which the photoinduced conformational change of a scissorlike azobenzene–ferrocene–zinc porphyrin conjugated host is transmitted successfully to mechanical twisting of the guest molecule through two-fold axial ligation, thus enabling a remote photocontrol of the atropisomerism of the guest.[3] Andréasson and co-workers succeeded to transduce a photoinduced conformational change of diarylethene to the mechanical bending of diacetylene-tethered zinc porphyrin dimers through two-fold axial ligation, demonstrating a remote photocontrol of the absorption of the porphyrin dimer.[4] In these examples, conformations of chromogenic molecules are elaborately modulated by the structural change of the photochromic molecules through noncovalent interactions. On the other hand, exciton interactions of pigments play important roles in biological systems, through which they show distinct photochemical properties compared to the monomeric state.[5] However, none of the artificial photoresponsive supramolecular systems succeeded to control exciton interactions between pigments by using a conformational change of noncovalently bound photochromic molecules.[6]

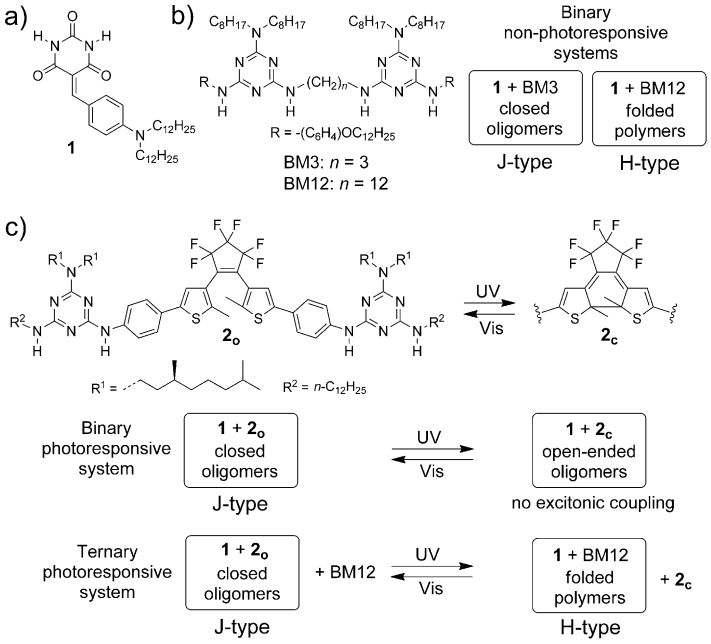

Figure 1. Structures of a) merocyanine **1**, b) bismelamine receptors BM3 and BM12, and c) diarylethene receptor **2** ($\mathbf{2}_o$: open form and $\mathbf{2}_c$: closed form). In b) and c), the complexation events are summarized.

We herein report a supramolecular system where exciton interactions of chromogenic components can be controlled through the conformational change of photochromic components. Previous our study on supramolecular complexation between merocyanine dye **1**[7] (Figure 1a) and bismelamine (BM) receptors[8] through multiple hydrogen bonds demonstrated that the oligomethylene linker length of the receptors can control the J- (BM3) and H-type (BM12) exciton interactions of **1** (Figure 1b).[9] From the spectroscopic and the NMR studies, it was suggested that the formation of discrete oligomers (**1** + BM3) and folded supramolecular polymers (**1** + BM12) are responsible for such contrasting exciton interactions. In the present study melamine-equipped diarylethene **2**[10] was used as a photoresponsive receptor for **1**. Chiral substituents[11] were introduced to melamine moieties to induce chiral exciton coupling, which is conveniently studied by circular dichroism (CD) spectroscopy. The phototriggered morphological change between the open-form $\mathbf{2}_o$ and closed-form $\mathbf{2}_c$ enabled "on/off" switching of chiral J-type exciton coupling between **1** in oligomeric species. Furthermore, a sufficiently large difference between the stabilities of the "on" and the "off" assemblies allowed a partial interconversion between J- and H-type exciton interactions by a ternary mixture including BM12 as "H-aggregation-inducer".[12]

Merocyanine **1** ($c = 1.0 \times 10^{-5}$ M) exists as monomeric state in a nonpolar solvent such as cyclohexane, exhibiting a charge-transfer (CT) absorption band (M-band) at $\lambda_{max} =$ 456 nm (the full-width at half-maximum, FWHM, is about 1300 cm^{-1}). Upon adding aliquots of open-form DAE (diarylethene) receptor $\mathbf{2}_o$, a new band (J-band) grew at 495 nm at the expense of the M-band (Figure 2a). The pronounced red-shift (about 1730 cm^{-1}) of the maximum wavelength indicates the J-type exciton coupling of the dye in the hydrogen-bonded complexes $(\mathbf{1}\cdot\mathbf{2}_o)_n$. The intensity of the J-band increased almost linearly with the amount of $\mathbf{2}_o$ and leveled off at

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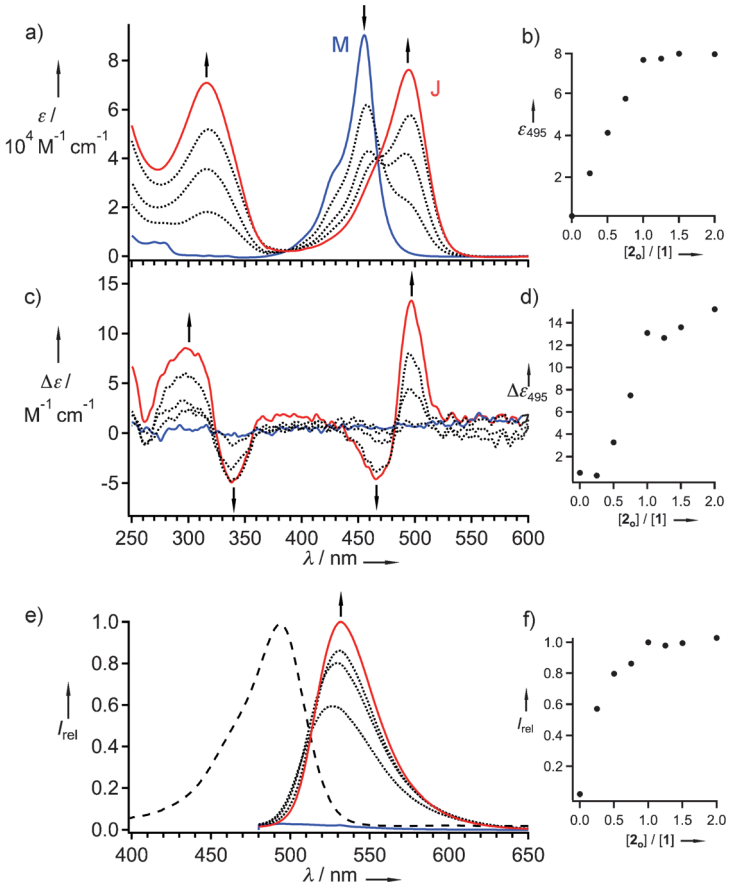

Figure 2. a,c,e) Changes of a) UV/Vis, c) CD, and e) fluorescence spectra of merocyanine **1** ($c = 1 \times 10^{-5}$ M) upon addition of 0 (blue) to 1 equiv (red) of $\mathbf{2_o}$ in cyclohexane. The dashed curve in (e) is the J-band normalized to the fluorescence spectrum of the 1:1 mixture. b,d,f) Plots of the respective spectral changes versus equivalent of [$\mathbf{2_o}$] (0 to 2 equiv).

a molar ratio of 1:1 (Figure 2b). This result suggests that the stoichiometric complexation is achieved at low concentration by the formation of stable assemblies. Although the FWHM of the J-band (about 2000 cm^{-1}) at 20 °C is greater than that of the M-band, the value is considerably smaller than that of the previously reported complex $(\mathbf{1}\cdot BM3)_n$ featuring a flexible trimethylene linker (FWHM of about 3000 cm^{-1}). This finding suggests that more uniform J-type exciton interaction is achieved upon complexation with $\mathbf{2_o}$ owing to a decrease in the conformational freedom of the linker moiety.

Circular dichroism spectroscopy provided further support for the exciton coupling in $(\mathbf{1}\cdot\mathbf{2_o})_n$. Upon mixing $\mathbf{2_o}$ to the monomeric solution of **1**, a bisignate CD signal was induced in the CT absorption region (Figure 2c), the intensity of which once levelled off at a molar ratio of 1:1 (Figure 2d). The zero-crossing point locates at 482 nm, which is blue-shifted by 13 nm from the maximum wavelength of the J-band. This might be attributed to the presence of other small CD signals in the same region. The positive and negative CD signs from longer wavelength indicate the *P*-type (clockwise) chiral exciton coupling occurring in excess between transition dipoles of **1**. Notably, another bisignate CD signal was observed in the absorption region of $\mathbf{2_o}$ despite the fact that free $\mathbf{2_o}$ is CD inactive. Because the absorption band of $\mathbf{2_o}$ could be attributed to the π–π* transition of the phenylenethienylene moieties, its induced CD signal strongly suggests that this molecule adopts the parallel conformation[13] upon complexation with **1**. The complexation-induced CD signal of $\mathbf{2_o}$ was not observed when nonchromophoric *N*-dodecylcyanurate[10] was used as a guest, indicating that the J-type aggregation of **1** is responsible for the formation of the specific assemblies.

Monomeric **1** is almost nonemissive due to nonradiative deactivation through a bond twist in the excited states. However, a clear fluorescence was observed at 532 nm upon exciting the J-band of $(\mathbf{1}\cdot\mathbf{2_o})_n$ (Figure 2e). The fluorescence intensity maximized at a molar ratio of 1:1 (Figure 2f). A relatively small Stokes shift of 37 nm (about 1400 cm^{-1}), and a mirror-image relationship between the absorption and the fluorescence bands are both characteristic of J-type aggregates.[14]

With the above evidence for the J-type exciton coupling of **1** upon complexation with $\mathbf{2_o}$ in hand, we performed light-irradiation experiments of the 1:1 complex. When a cyclohexane solution was irradiated at around 313 nm, the progress of the ring-closure reaction was indicated by the growth of the absorption bands at 395 and 606 nm with the bleaching of the band at 316 nm (Figure 3a). The photostationary state (PSS) was achieved with 6 minutes of irradiation under the applied conditions (see the Supporting Information), resulting in the quantitative conversion of $\mathbf{2_o}$ to $\mathbf{2_c}$. The ring-closure reaction was accompanied by a decrease of the J-band of **1** at 495 nm, which is compensated by a new band at 475 nm (M_{2c}-band). The M_{2c}-band is red-shifted from the M-band (456 nm) by 19 nm, which could be ascribed to the electronic effect of hydrogen-bonding interaction on the barbituric acid moiety.[9b] The tunable exciton interaction of **1** upon ring-closure reaction was supported by CD spectroscopy. At the PSS, the bisignate CD signal of **1** was significantly weakened, and the maximum molar circular dichroism (Δε) value of the positive CD sign decreased from 13 to 3.0 $M^{-1}cm^{-1}$. Notably, the bisignate CD signal arising from the diarylethene scaffold completely disappeared (Figure 3b). This observation strongly supports the hypothesis that $\mathbf{2_o}$ indeed adopts the parallel conformation in $(\mathbf{1}\cdot\mathbf{2_o})_n$ (Figure 3e). Under a dynamic equilibrium between aggregated and monomeric state, however, $\mathbf{2_o}$ can adopt the antiparallel conformation even in the presence of **1**, and thereby the ring-closure photoreaction can take place. The resulting rigid receptor $\mathbf{2_c}$ spatially separates the bound guests, allowing only weak exciton coupling.

As expected, the fluorescence of **1** was quenched upon ring-closure of $\mathbf{2_o}$ probably due to the loss of J-type exciton coupling (Figure 3c). In the present system, however, the possibility of energy transfer from **1** to $\mathbf{2_c}$ was indicated by the following experiment. When the complex $(\mathbf{1}\cdot\mathbf{2_c})_n$ was irradiated at the absorption maximum of **1** (475 nm) at which $\mathbf{2_c}$ alone did not show ring opening, an efficient ring-opening

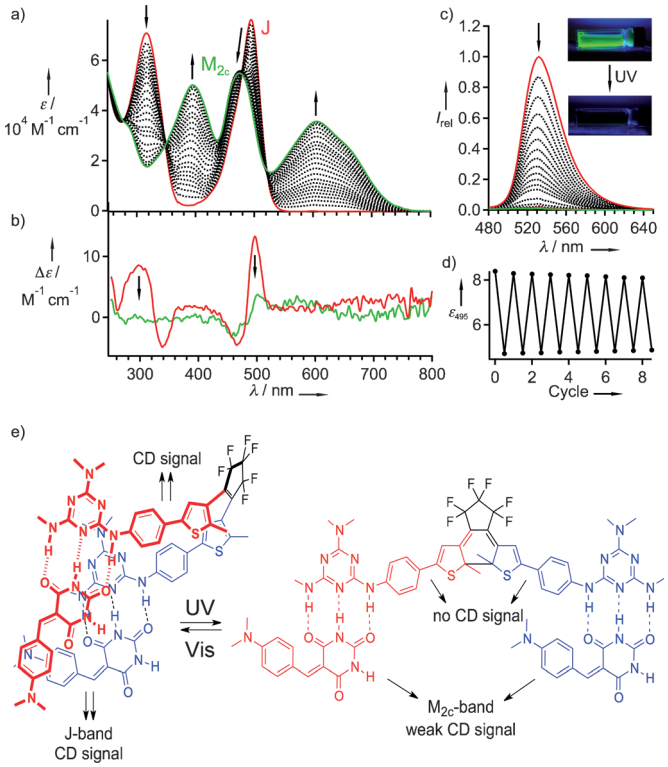

Figure 3. a–c) Changes of a) UV/Vis, b) CD, and c) fluorescence spectra of the 1:1 complex of **1** ($c = 1\times10^{-5}$ M) and $\mathbf{2_o}$ ($c = 1\times10^{-5}$ M) upon UV irradiation at around 313 nm for 6 minutes at 20 °C. The inset in c) shows photographs of the solution before and after UV irradiation. d) Change of the molar extinction coefficient (ε) at 495 nm (J-band of **1**) upon UV and visible light irradiation cycle. e) Proposed photo-triggered structural change of the complexes. Only the local binding structures were shown.

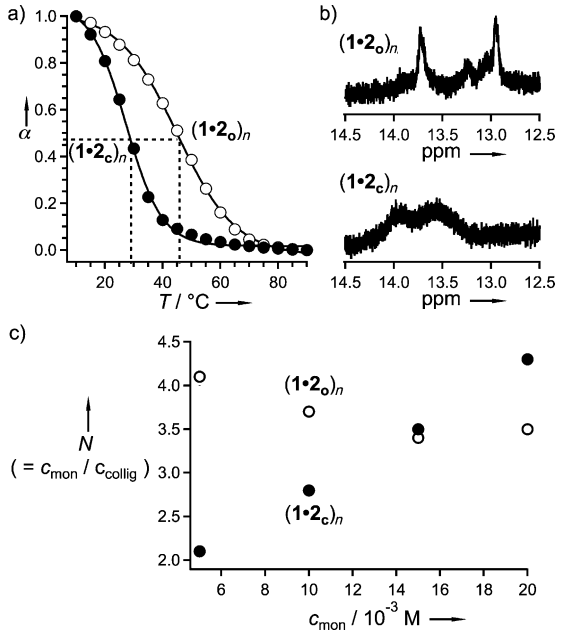

Figure 4. a) Plots of mole fraction of aggregates (α) versus temperature for variable temperature UV/Vis spectra of $(\mathbf{1\cdot2_o})_n$ (○) and $(\mathbf{1\cdot2_c})_n$ (●) in methylcyclohexane ($c = 1\times10^{-5}$ M). b) Comparison of ^{1}H NMR spectra of $(\mathbf{1\cdot2_o})_n$ in [D_{12}]cyclohexane ($c = 5\times10^{-4}$ M) before (upper panel) and after UV irradiation (lower panel). c) Plots of the aggregation number N ($= c_{mon}/c_{collig}$) determined by VPO versus stoichiometric concentrations (c_{mon}) of the components for $(\mathbf{1\cdot2_o})_n$ (○) and $(\mathbf{1\cdot2_c})_n$ (●).

reaction was observed at the same reaction rate as that rate obtained for direct irradiation of $\mathbf{2_c}$ at 600 nm. The ring-opening reaction caused the recovery of the J-band of **1** together with the green fluorescence and the bisignate CD signal. A plausible explanation for this result is that fluorescence resonance energy transfer (FRET) takes place from weakly exciton-coupled **1** to $\mathbf{2_c}$ in $(\mathbf{1\cdot2_c})_n$.[15] As another possibility, we must consider energy transfer from nonfluorescent **1** to $\mathbf{2_c}$.[16] Although further studies are needed to disclose the mechanism, it is worth noting that "non-photochromic" merocyanine **1** show "photochromic fluorescence" through the supramolecular complexation with **2**. The switching of the J-type exciton coupling of **1** could be repeated at least 10 times (Figure 3d).

To gain insight into the present photoresponsive assemblies, the stabilities of $(\mathbf{1\cdot2_o})_n$ and $(\mathbf{1\cdot2_c})_n$ were compared by variable-temperature (VT) UV/Vis measurements in methylcyclohexane. Both assemblies ($c = 1.0\times10^{-5}$ M) showed reversible changes in the absorption band of **1** between aggregated (495 nm with $\mathbf{2_o}$; 475 nm with $\mathbf{2_c}$) and monomeric states (456 nm) upon varying the solution temperatures between 10 and 90 °C (see Figure S1 in the Supporting Information). Plots of the fraction of aggregated molecules (α) versus temperature gave dissociation curves (Figure 4a), from which melting temperatures (T_m, 50% of molecules form complexes) of 45 °C and 27 °C were determined for $(\mathbf{1\cdot2_o})_n$ and $(\mathbf{1\cdot2_c})_n$, respectively, by fitting with the Boltzmann equation $[\alpha = 1/(1+\exp[(T-T_m)\Delta T])]$. A pronouncedly higher stability of $(\mathbf{1\cdot2_o})_n$ relative to that of $(\mathbf{1\cdot2_c})_n$ despite its higher entropic penalty associated with the flexible open-form diarylethene core implies the formation of cyclic supramolecular assemblies.[17]

The ^{1}H NMR spectrum of $(\mathbf{1\cdot2_o})_n$ ($c = 5\times10^{-4}$ M) in [D_{12}]cyclohexane showed two major resonances between 12–14 ppm, ascribable to the hydrogen-bonded NH proton atoms of **1** (upper, Figure 4b). The relatively sharp resonances suggest the formation of well-defined supramolecular assemblies. Upon converting $\mathbf{2_o}$ to $\mathbf{2_c}$ with UV irradiation, these resonances displayed significant broadening (Figure 4b, bottom). This observation suggests the formation of complex mixtures composed of various hydrogen-bonded assemblies with different aggregation numbers and supramolecular structures.[18]

Vapor pressure osmometry (VPO) was used to further analyze the properties of $(\mathbf{1\cdot2_o})_n$ and $(\mathbf{1\cdot2_c})_n$. For this purpose, solutions of $(\mathbf{1\cdot2_o})_n$ and $(\mathbf{1\cdot2_c})_n$ were prepared separately at four total concentrations of monomers ($c_{mon} = [\mathbf{1}] + [\mathbf{2}]$): $c_{mon} = 5.0\times10^{-3}$, 1.0×10^{-2}, 1.5×10^{-2}, and 2.0×10^{-2} M. In the case of $(\mathbf{1\cdot2_o})_n$, the colligative concentrations measured by VPO (c_{collig}) were 1.2×10^{-3}, 2.7×10^{-3}, 4.5×10^{-3}, and 5.8×10^{-3} M for the above stoichiometric concentrations, respectively. From these results, aggregation numbers N ($= c_{mon}/c_{collig}$) were calculated to be 4.2, 3.7, 3.4, and 3.5 for the above four concentrations, respectively (Figure 4c). A relatively

concentration-insensitive number N with an average value of 3.7 indicates the formation of closed [2+2] assemblies $[(\mathbf{1}\cdot\mathbf{2_o})_2]$. In striking contrast, the c_{collig} values of $(\mathbf{1}\cdot\mathbf{2_c})_n$ were measured as 2.4×10^{-3}, 3.6×10^{-3}, 4.3×10^{-3}, and 4.7×10^{-3} M, for the four stoichiometric concentrations, providing N values of 2.1, 2.8, 3.5, and 4.3, respectively (Figure 4c). An increase of N upon increasing of concentration illustrates the formation of open-ended oligomeric species.[19]

All the above spectroscopic and VPO studies demonstrate that the present multi-chromophore assemblies can change the supramolecular structures between closed $[(\mathbf{1}\cdot\mathbf{2_o})_2]$ and open-ended oligomeric state $[(\mathbf{1}\cdot\mathbf{2_c})_n]$ in response to UV and visible light. This structural change enables the "on/off" switching of the J-type exciton interaction of **1**. To expand this system to a J⇄H interconvertible system, we incorporated BM12 to the binary system of **1** and **2**. This attempt is based on the fact that the T_m value of $(\mathbf{1}\cdot\mathrm{BM12})_n$ at 1.0×10^{-4} M is 52 °C, which is in between those of $(\mathbf{1}\cdot\mathbf{2_o})_2$ (63 °C) and $(\mathbf{1}\cdot\mathbf{2_c})_n$ (48 °C). The low stability of $(\mathbf{1}\cdot\mathbf{2_c})_n$ compared to $(\mathbf{1}\cdot\mathbf{2_o})_2$ could enable selective conversion of the former assemblies to $(\mathbf{1}\cdot\mathrm{BM12})_n$ that organizes into folded supramolecular polymers by intrachain H-type aggregation of **1**.[9b,c] We thus prepared a 1:1:1 ternary mixture $\mathbf{1}+\mathbf{2_o}+\mathrm{BM12}$ with the concentrations of all the components at 1.0×10^{-4} M. As shown by the red curve in Figure 5, the addition of BM12 resulted in

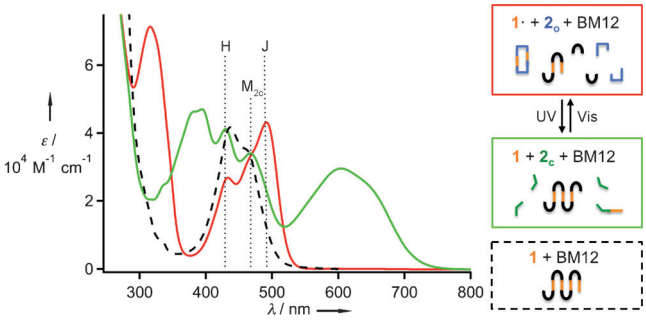

Figure 5. UV/Vis spectral change of the 1:1:1 ternary mixture of **1**, **2**, and BM12 upon UV irradiation. Concentrations of all the components are 1×10^{-4} M. Red curve: the spectrum recorded before UV irradiation; green curve: the spectrum recorded at PSS; dashed curve: the spectrum of the binary mixture of **1** and BM12 (H-aggregates). On the right, pictures of the three states.

the emergence of an absorption peak at 433 nm, which is ascribable to the H-band of **1**. From the decrease of the J-band, it was estimated that about 50% of **1** coordinates with BM12 to form H-type aggregates ([J-**1**]:[H-**1**] = 50:50). Upon UV irradiation, the J-band was completely bleached, and only the H- and the M_{2c}-bands could be observed. The ratio [H-**1**]:[M_{2c}-**1**] at the PSS was calculated to be 77:23, indicating that about 25% of **1** changed their exciton interactions from J- to H-type. Although the perfect J⇄H interconversion remains challenging, the present system demonstrates that two representative modes of exciton interaction can be controlled in a dynamic system by an external light stimulus.

In summary, we have constructed a merocyanine–diarylethene multichromophore hydrogen-bonded complex where J-type exciton coupling between the merocyanine components could be switched reversibly "on/off" by irradiation with UV and visible light. The "on" state of the J-type exciton coupling was confirmed by the red-shifted absorption band, the bisignate CD signals, and the enhanced fluorescence. ^{1}H NMR and VPO studies revealed that distinct types of supramolecular assemblies are interconverted by the ring-closure/ring-opening photoreactions of the diarylethene units. Furthermore, a relatively large change in the stabilities of these assemblies allowed the extension of the "on/off" switching property to the J/H switchable functionality by using a third component, BM12, that can convert the "off" state to the H-aggregated state. The present study thus demonstrates that dynamic molecular assemblies based on rational designs of building blocks could realize complicated stimuli-responsive systems similar to those found in natural systems.

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