

## Light-Controlled Macrocyclic Supramolecular Assemblies and Luminescent Behaviors

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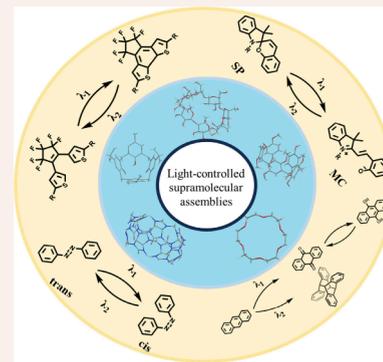
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**CONSPPECTUS:** Intelligent supramolecular assemblies can respond well to external stimuli such as pH, temperature, light, electricity, magnetism, and enzymes to achieve not only reversible topological morphology changes and assembly/disassembly processes but also special physical and chemical properties, which are successfully applied to biological imaging, cancer treatment, luminescent materials, anticounterfeiting, sensing, molecular switch in chemical, materials, as well as biological research fields. Among all stimuli-responsive supramolecular assemblies, light-controlled supramolecular assemblies have always attracted intense attention because light is a kind of clean and eco-friendly energy. In this Account, we focus on light-controlled supramolecular assemblies formed by four types of photoresponsive molecules and macrocyclic hosts such as cucurbit[n]urils, cyclodextrins, and crown ethers, and their regulations in luminescent materials and bioimaging. The assemblies and cascade assemblies between photoisomerization or photoreaction molecules and macrocyclic hosts mainly include: 1) light-controlled supramolecular assemblies based on macrocycles and diarylethene. As molecular switches, the open-ring and closed-ring configurations of diarylethenes can be reversibly controlled to achieve tunable fluorescence resonance energy transfer (FRET) process and further regulate luminescent behaviors to construct intelligent response cell-imaging, anticounterfeiting, and multicolor luminescence systems. 2) Light-controlled supramolecular assemblies based on macrocycles and spiropyran. Different from the diarylethenes, spiropyran can converse between positive charges in the ring-open merocyanic (MC) state, which is amphiphilic and easy to bond with macrocycles like cucurbit[n]urils, and neutral/negative charges in the ring-closed spiropyran (SP) state, which is more likely to self-assemble. Therefore, the differentiation of bonding affinities with macrocycles between MC and SP can achieve light-driven molecular machines. 3) Light-controlled supramolecular assemblies between macrocycles and azobenzene, whether azobenzene is modified to the macrocyclic hosts or functional guests, supramolecular assemblies are formed through host–guest interactions, and the topological morphology and luminescence behavior of the assemblies can be regulated by photoisomerization to apply in catalytic activity modulation, induction of microtubule (MT) assembly/disassembly, drug delivery, and others. 4) Light-controlled supramolecular assemblies based on macrocycles and anthracene, in which different bonding affinities between anthracene before and after photooxidation and macrocyclic hosts, as well as reversible dimerization, not only change the topological morphologies but also drive fluorescence phosphorescence dual imaging and the construction of photostimuli-driven luminescent lanthanide molecular switch. With the creation of macrocycles with novel building units and different modifications of photoresponsive molecules, we consider that the innovation and growth of light-controlled intelligent supramolecular materials should be more widely used in tunable material topological morphology conversion, real-time cell imaging, targeted drug delivery, organic optoelectronic materials, molecular machines, and photocatalysis reactions.



### 1. INTRODUCTION

Supramolecular intelligent materials based on macrocycles have received more and more widespread attention because of not only their applications in cell imaging, targeted drug delivery, and information encryption,<sup>1–5</sup> but also their combinations with polymers and biomacromolecules through noncovalent interactions such as hydrogen bonding and  $\pi$ – $\pi$  stacking to achieve tunable topological morphologies and crystalline states.<sup>6</sup> Possessing the hydrophobic cavities and modifiable functional groups, macrocyclic hosts can selectively bond guest molecules with responsive units through host–guest interactions to form intelligent supramolecular assem-

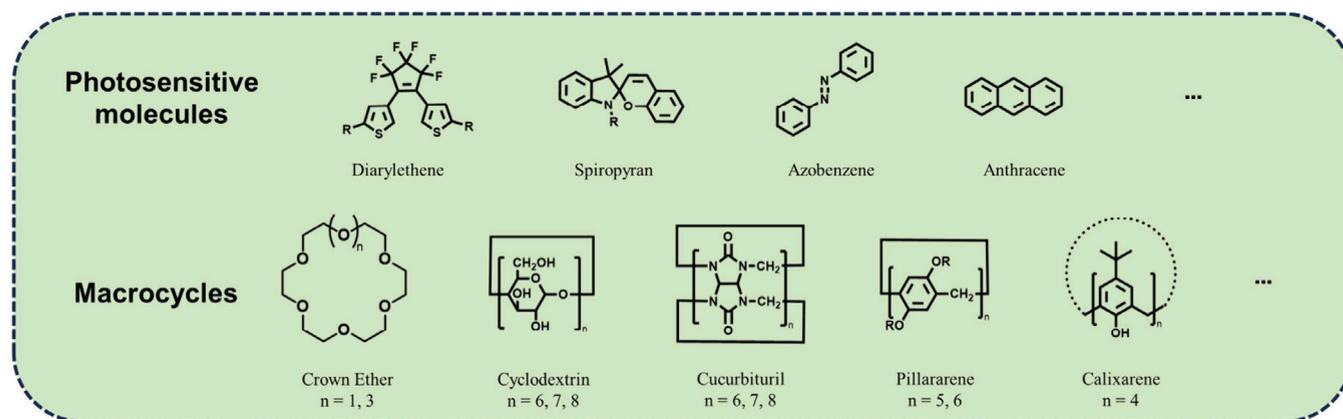
blies, which display good reversibility and special chemical/physical features under external stimuli such as light,<sup>7</sup> heat,<sup>8</sup> electricity,<sup>9</sup> and pH.<sup>10</sup> Among them, light, as a clean energy source, is widely used in stimulus-responsive supramolecular

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Scheme 1. Schematic Illustration of the Photosensitive Molecules and Host Macrocycles



systems, which have the advantages of good reversibility and high sensitivity, and have been receiving increasing attention.<sup>11,12</sup> Photoresponsive molecules, which constitute the core of light-controlled supramolecular systems, can usually undergo configuration changes or photochemical reactions under the irradiation of light of a certain wavelength and intensity.<sup>13</sup> Copolymerizing photochromic molecules into polymers is a general method for constructing light-responsive smart materials.<sup>14</sup> Changes in the microstructure of the polymer, such as collapse, expansion, and stretching, can affect the reactivity of the photochromic molecules and the efficiency of the FRET process, thereby achieving dynamic regulation.<sup>15</sup> On the other hand, a succinct strategy is to exploit the special host–guest recognition and bonding affinity in supramolecular chemistry to realize the amplification and morphological transformation. After the photoresponsive small molecule undergoes the process of encapsulation and dissociation of the host molecule under specific light conditions, the polarity and, thus, the hydrophilic and hydrophobic properties around the guest molecule change significantly, inciting changes in both the structural composition and the overarching performance of the supramolecular assemblies.<sup>16,17</sup> Feringa et al. and Yagai et al. have, respectively, reported supramolecular self-assemblies of amphiphilic photoisomeric molecules, which show tunable topological morphologies.<sup>18,19</sup> However, macrocyclic confined photoisomeric molecular assemblages can regulate not only supramolecular topological morphologies but also luminescence and combination with biomacromolecules.<sup>20</sup> This Account mainly focuses on four types of photoresponse functional units (diarylethene, spiropyran, azobenzene, and anthracene), which can be modified into guests or hosts—cyclodextrins (CDs), calix[n]arenes (CAs), pillar[n]arenes (PAs), and cucurbit[n]urils (CB[n]s)—to construct intelligent supramolecular assemblies (Scheme 1, Table 1), achieving light-controlled bioimaging, topological morphology transfer, targeted drug delivery, encryption, and interaction between biomacromolecules. We first describe diarylethene, which is a type of molecule with a cyclopentene core and aryl arms. Under short-wavelength ultraviolet (UV) light irradiation, the double bond in the aryl arm and cyclopentene undergo cyclization and transform into the closed-ring form; this process is usually accompanied by an obvious changing of color and will reversibly change into the open-ring form under the irradiation of long-wavelength visible light. The open/closed ring states can act as different energy transfer receptors, thereby regulating FRET/ phosphorescence

Table 1. Advantages and Drawbacks of the Macrocycles

Macrocycles	Structure	Advantages	Drawbacks
Crown Ether		High affinity with metal ions and ammoniums, easy for modification	Low yield in synthesis, toxic
Cyclodextrin		Non-toxic, cheap, easy for modification, high water solubility	Lack of rigidity, relatively low affinities
Cucurbituril		High affinity with positive ions (especially pyridium), rigid cavity	Expensive, poor water solubilities
Calixene/Pillararene	Or 	Easy for synthesis and modification, encapsulate guest molecule of different charges	Potential toxicity, benzene structure may cause unexpected charge transfer

resonance energy transfer (PRET) processes, leading to the intelligentization of the assemblies.<sup>21</sup> Then, we introduce spiropyran, which is a derivative of cyanine dyes, and the C–O bond formed by the carbon atoms of the spiro ring is easily broken under the action of a specific wavelength or macroscopic mechanical force, thereby becoming the opening form of MC; then, using different wavelength when exposed to light or heated, a reverse reaction can occur to form closed-ring SP.<sup>22</sup> By conjugating with charged functional groups, SP can have strong affinities with various macrocycles, and change in affinities by light is achieved through the charge transformation in ring-open/closed states, providing the possibility of light-controlled morphology changes and molecular machines.<sup>11,16</sup> Azobenzene, as a photoisomeric molecule, in which the nitrogen–nitrogen double (–N=N–) bond has a small isomerization energy barrier, thus it can change from *trans* to *cis* under the irradiation of short-wavelength light, and reverse under the irradiation of long-wavelength light.<sup>23</sup> The steric hindrance change caused by this process can change the bonding behaviors of the macrocyclic host and guest molecules, thereby regulating the luminescence

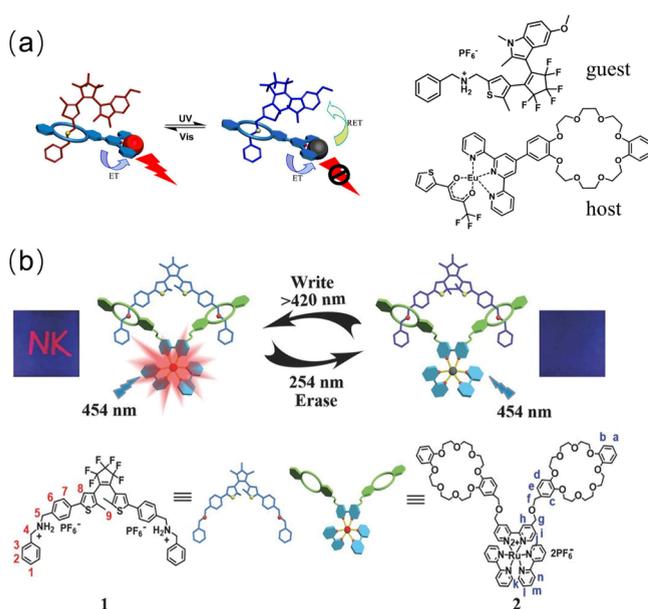
behaviors of the assemblies, and it can also change the stacking pattern between molecules to regulate topological morphologies. The final part discusses the photoreaction-driven supramolecular assembly and disassembly utilizing photo-oxidation or dimerization of anthracene, which has active hydrogen atoms at positions 9 and 10.<sup>24,25</sup> Through reversible conversion of anthracene and anthraquinone or dimers, the assemblies can achieve tunable cell-imaging and luminescent materials. From the four representative light-controlled supramolecular assemblies mentioned above, we can see their rapid development in chemistry, biology, and materials, and we also wish this Account could promote more application prospects of light-controlled macrocyclic supramolecular assemblies based on new macrocycles and photoresponsive molecules in intelligent materials.

## 2. LIGHT-CONTROLLED SUPRAMOLECULAR ASSEMBLIES BASED ON MACROCYCLES AND DIARYLETHENE

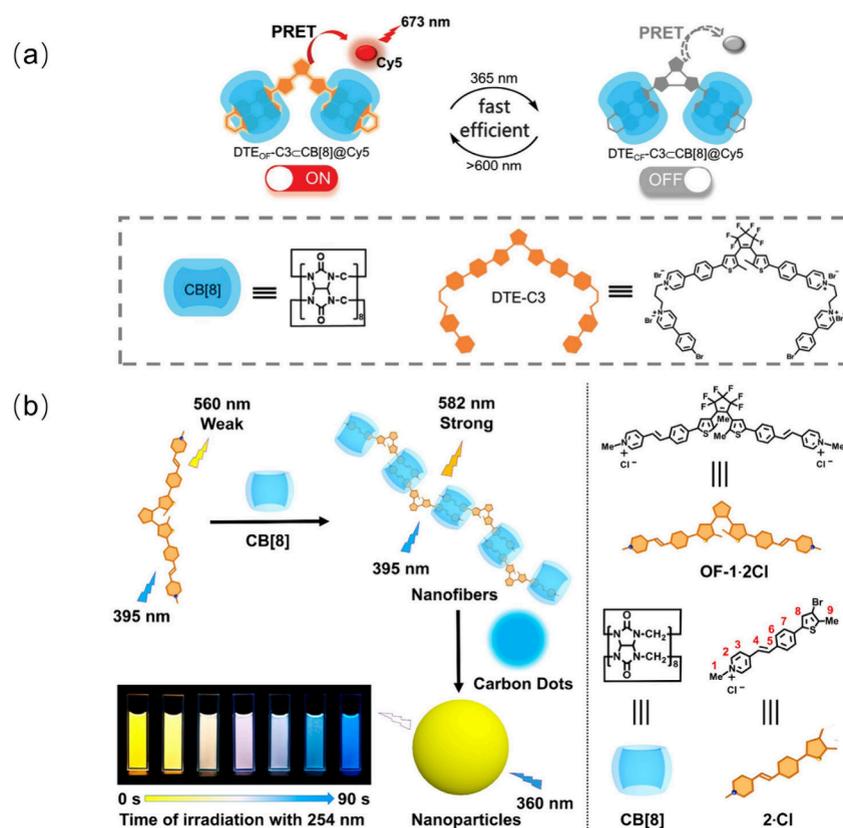
It is well-known that diarylethene is a type of molecule with a conjugated triene structure, which undergoes a reversible intramolecular ring-closing reaction under the irradiation of light of a specific wavelength. By modification of positively charged functional groups, it can be encapsulated into macrocycles which have a strong affinity with organic cations to form light-controlled supramolecular assemblies. For example, asymmetric benzylammonium-modified diarylethene and dibenzo-24-crown-8 conjugated tpy-Eu<sup>3+</sup> complex constructed a [2]pseudorotaxane through the host-guest interaction (Figure 1a).<sup>26</sup> When irradiated with 365 nm light, the fluorescence intensity of the system dropped by about 80%, accompanied by a decrease in lifetime and quantum yield (from 0.128 to 0.020) because of the FRET process from the tpy-Eu<sup>3+</sup> complex and closed-ring diary-

lethene. The fluorescence intensity gradually recovered when irradiated with 614 nm light. This process showed excellent reversibility, which can take more than 35 cycles without obvious fatigue. In the control experiment, the fluorescence of the tpy-Eu<sup>3+</sup> complex without crown ether can only be quenched by diarylethene by 9%, probably because the estimated distance between donor (Eu<sup>3+</sup>) and acceptor (diarylethene) was 20.2 Å due to the host-guest interaction ( $K_s = 1.2 \times 10^3 \text{ M}^{-1}$ ), which was shorter than the Förster radius (30.7 Å) to facilitate the FRET process. Additionally, another example was using [Ru(bpy)<sub>3</sub>]<sup>2+</sup> double-modified by dibenzo-24-crown-8 as the host and symmetric dialkylammonium-modified perfluorodiarylethene as the guest, which showed a closed-ring conversion rate of 95% (Figure 1b).<sup>27</sup> After being bonded to the host in a ratio of 2:1, under 254 nm UV light irradiation, the fluorescence emission of the assembly was gradually quenched by 91%, and the quantum yield also decreased from 0.076 to 0.027. The fluorescence can be restored by using 420 nm irradiation. This cycle can repeat more than ten times. Structural optimization calculations of the assembly showed that the center-to-center distance between the host and guest was 14.6 Å, which was shorter than the Förster energy transfer radius, proving that the mechanism of fluorescence quenching was a FRET process.

In addition, CB[n]s (n = 6, 7, and 8), as macrocyclic host molecules with a rigid hydrophobic cavity, can selectively bond positively charged guest molecules with different sizes through the host-guest induced fit complexation effect. Because of its small cavity, CB[7] can only encapsulate a single guest molecule to form 1:1 stoichiometric complexes, while CB[8] with a larger cavity can form single molecular folds or noncovalent polymers in dimer form, all of which can build light-controlled supramolecular assemblies. For example, CB[8] can encapsulate from both ends of the guest molecule at a stoichiometric ratio of 1:2 (Figure 2a),<sup>28</sup> forming a single molecular dual-fold structure ( $K_s = 7.96 \times 10^{12} \text{ M}^{-2}$  and  $2.09 \times 10^{12} \text{ M}^{-2}$ ), achieving phosphorescent emission at 600 nm. NMR experiments showed that its ring-opening/closing conversion rate was higher than 95%. Under irradiation with 365 nm light, the phosphorescence emission gradually disappeared, and the quenching efficiency was 99%. The phosphorescence emission was restored under the irradiation of >600 nm light, and this process can be repeated more than ten times. Furthermore, the coassembly with Sulfo-Cyanine5 (Cy5) dye achieved an energy transfer system with near-infrared (NIR) delayed fluorescence emission (673 nm) and was successfully used for cell imaging and information encryption. Besides, a chiral transfer supramolecular system was constructed based on the heterodimeric complex formed by the charge transfer effect of the CB[8] encapsulated naphthalene-modified L-phenylalanine dipeptide and bipyridinium-modified diarylethene,<sup>29</sup> and the reversible chiral transfer process was confirmed by the circular dichroism spectrum, which was also accompanied by changes in the morphology of the assembly. Different from heterodimers, homodimers formed by CB[8] encapsulated diarylethylene-bridged 3-methyl-2-phenylbenzothiazol-3-ium can not only form 1:1 end-to-end nanofibers ( $K_s = 3.19 \times 10^7 \text{ M}^{-1}$ ) but also activate photoreaction to generate photoisomerization by restricting the rotation of the benzothiazole, which can induce the on/off ring cycle to occur smoothly.<sup>30</sup> Interestingly, the nanofiber formed between vinylpyridium-modified diarylethene and CB[8] ( $K_a = 1.19 \times 10^7 \text{ M}^{-1}$ ) can effectively induce



**Figure 1.** (a) Schematic illustration of a dual-stimulus luminescent lanthanide molecular switch. Reproduced with permission from ref 26. Copyright 2013 American Chemical Society. (b) Schematic illustration of a reversibly photoswitchable supramolecular assembly. Reproduced with permission from ref 27. Copyright 2017 Wiley-VCH.



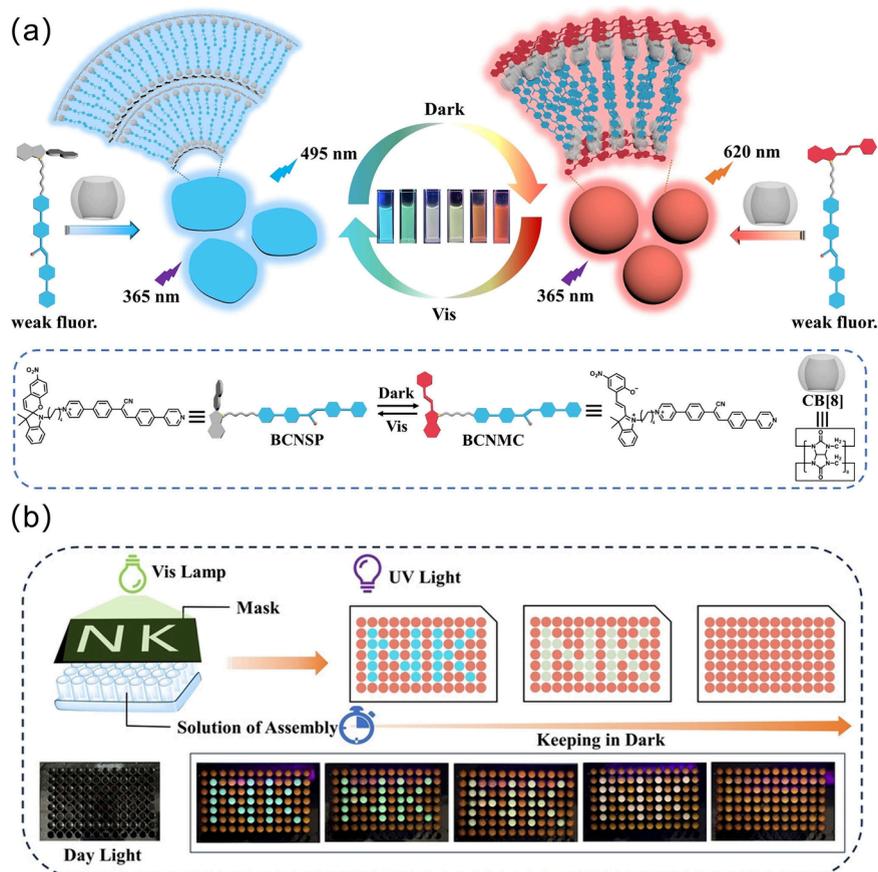
**Figure 2.** (a) Schematic illustration of a NIR phosphorescence supramolecular switch. Reproduced with permission from ref 28. Copyright 2022 The Authors. (b) Schematic illustration of a multicolor luminescence system based on carbon dot supported supramolecular assembly. Reproduced with permission from ref 31. Copyright 2019 American Chemical Society.

intramolecular charge transfer (ICT) to enhance the fluorescence, and the emission peak showed a significant red shift due to assembly-induced J-aggregation. It can take secondary assemblage with carbon dots and achieve multicolor luminescence with white light emission, which can be used for light-controlled lysosome-targeted imaging (Figure 2b).<sup>31</sup> The photochemical behavior can be improved by bonding with CB[n]s, as well. For example, CB[7] encapsulated quaternary ammonium-modified diarylethene formed a supramolecular assembly, achieving excellent antifatigue properties and light-controlled super-resolution imaging of MT through the host-guest interactions with CB[7].<sup>12</sup>

Compared with crown ethers and CB[n]s, PAs can modify various functional groups at both ends of their cavities to form amphiphilic macrocyclic hosts and construct host-guest complexes through electrostatic interactions. Typically, a full-color lanthanide supramolecular photoswitch based on the coordination of Ln<sup>3+</sup> and 2,6-pyridinedicarboxylic-acid-modified pillar[5]arenes and further encapsulated quaternary ammonium-modified diarylethene ( $K_s = 2.99 \times 10^4 \text{ M}^{-1}$ ) was constructed,<sup>7</sup> which had a network structure to effectively isolate the coordination of external water and the collision of oxygen, greatly improving the emission performance of Ln<sup>3+</sup>. The inherent blue light emission of pillar[5]arene can be mixed with Ln<sup>3+</sup> in different proportions to achieve multicolor luminescence with white light emission. Furthermore, the absorption band of the closed-ring diarylethene overlapped well with the emission of Ln<sup>3+</sup>. When irradiated with UV light at 254 nm, the polychromatic luminescence of the system gradually changed to the blue emission of the pillar[5]arene.

Using a wavelength >450 nm, the polychromatic luminescence gradually recovered, and can be used for anticounterfeiting or information encryption.

Supramolecular polymers, constructed by in situ polymerization where the macrocycles and rigid matrix can restrict molecular motion, lead to the decrease in nonradiative transition and show great enhancement in emission intensity, quantum yield, and phosphorescence lifetime. For one case, a highly efficient and tunable room temperature phosphorescence system based on bromonaphthylpyridinium (BrNP) polymer was constructed by copolymer p-BrNP-diarylethene assembling with SBE- $\beta$ -CD, in which the quantum yield reached 71.3%.<sup>32</sup> Under 254 nm light irradiation, the lifetime and phosphorescence intensity of the terpolymer at 550 nm were significantly reduced, and the quenching rate can reach 52.9%. After visible light irradiation, the phosphorescence intensity and lifetime can be restored, and this process can be repeated for multiple cycles without obvious light fatigue, which can be used to create stimulus-responsive inks. Moreover, macrocycles can noncovalently connect light-controlled groups to construct a multicolor phosphorescent switch consisting of coumarin-modified 24-crown-8 and diarylethene,<sup>33</sup> which showed good reciprocating performance. Due to its visible afterglow effect, a time-resolved encryption system was constructed in this work.



**Figure 3.** (a) Schematic illustration of a light-driven supramolecular shuttle. Reproduced with permission from ref 11. Copyright 2023 Wiley-VCH. (b) Schematic illustration of a photocontrolled, reversibly chiral-ordered assembly. Reproduced with permission from ref 11. Copyright 2023 Wiley-VCH.

### 3. LIGHT-CONTROLLED SUPRAMOLECULAR ASSEMBLIES BASED ON MACROCYCLES AND SPIROPYRAN

As a photochromic molecule, the C–O bond in spiroopyran can reversibly be broken and recover under external stimulations. In open-ring state MC, the phenoxy anion easily combines with hydrogen ions to show positive electricity,<sup>34</sup> which can assemble with CB[n]s, sulfonated CAs, and other hosts as an energy acceptor to build light-controlled cascade energy transfer systems, while the closed-ring state SP shows the increased hydrophobicity leading to changes in assembly mode. As Figure 3a shows,<sup>11</sup> a supramolecular shuttle that achieves single-molecule bidirectional reversible multicolor luminescence was constructed through the confinement of a single molecule (spiroopyran-modified cyanostilbene) by CB[8] to form a pseudorotaxane ( $K_s = 7.21 \times 10^6 \text{ M}^{-1}$ ), which caused the significant enhancement of fluorescence intensity at 495 nm and quantum yield (from 0.05% to 6.24%). With increasing time placed in the dark, the closed-ring SP in the assembly gradually transformed into the open-ring MC, causing the fluorescence emission to change from blue to white, and then to red within 120 min, which was caused by the FRET process between cyanostilbene and MC. Under the irradiation of visible light, MC gradually transformed into SP while the red fluorescence returned to blue. The supramolecular shuttle was successfully used to achieve dynamic information loading and information decryption (Figure 3b). On the other hand, spiroopyran can also be used as an acceptor in cascade assembly.

For example, CB[7] encapsulated 6-bromoisoquinoline derivatives to perform cascade assembly with amphiphilic sulfonated calix[4]arenes (SC[4]A[4]) and SP, which can switch between macrocycle-confined induced room temperature phosphorescence and delay fluorescence.<sup>35</sup> When the assembly was irradiated with 254 nm light, SP gradually transformed into the phosphorescence energy transfer acceptor MC, the phosphorescence intensity of isoquinoline at 540 nm decreased significantly, and a delayed fluorescence peak appeared at 635 nm. Irradiation with visible light caused the delayed fluorescence to gradually disappear, showing the phosphorescent emission of isoquinoline. This process can be carried out alternately many times and showed excellent resistance to photobleaching.

The conversion between SP and MC can reversibly combine/release protons, which is regulated by light; these molecules are also called photoacids. By regulating the release of protons, the affinity between the guest molecule and the macrocyclic host can be adjusted, further regulating assembly and disassembly. For example, the electrically neutral tetrakis-4-pyridylphenylethene cannot assemble with the amphiphilic sulfonated calix[4]arene (SC[4]A[8]) and exhibited characteristics of aggregated emission.<sup>36</sup> After the addition of the sulfonic-group-modified spiroopyran (photoacid MEH), and under irradiation of 420 nm light, MEH gradually became a closed-ring SP and released protons, causing pyridine to protonate and form an assembly with SC[4]A[8] due to electrostatic interaction, and the fluorescence emission was

also red-shifted to 540 nm. The process was reversed in darkness. Coincidentally, the molecular chain, which was constructed by CD-4,4'-bipyridine pseudorotaxane and metallic ions,<sup>37</sup> can also be regulated by MEH.<sup>38</sup> As MEH became closed-ring SP under visible light irradiation, hydrogen ions were released, and the protonated bipyridine lost its coordination ability for  $Zn^{2+}$ , resulting in the disintegration of the pseudorotaxane. It can be observed in TEM images that the long nanofibers were broken into small nanorods, while the reformation of nanofibers was observed in darkness. Furthermore, an aqueous-phase photoactivated dissipative molecular machine was achieved by coassembly of pyridinium-modified MEH (EPMEH) and CB[8] in a ratio of 2:1 ( $K_1 = (4.42 \pm 0.37) \times 10^7 M^{-1}$ ,  $K_2 = (1.58 \pm 0.83) \times 10^6 M^{-1}$ ).<sup>16</sup> Under 420 nm light, EPMEH gradually transferred to EPSP, which induced the stoichiometric ratio with CB[8] to change to 1:1 ( $K_s = (5.94 \pm 0.09) \times 10^4 M^{-1}$ ) due to the steric effect, accompanied by the significant change in the micro-morphology of the assembly. The process from EPSP to EPMEH was a thermal relaxation process, which is highly sensitive to optical power and temperature, and can achieve precise control of the EPSP's half-life. In addition, spiropyran can be noncovalently modified onto the polymer using host-guest interactions. For one case, adamantane was introduced into the side chain of the polymer and bonded to the spiropyran-modified CD through molecular recognition ( $K_s = 95 M^{-1}$ ) where the copolymerized pillar[5]arene derivative can effectively encapsulate the AIE molecule N-DSA-CN ( $K_s = 160 M^{-1}$ ) as an FRET donor.<sup>39</sup> The luminescence behavior of the polymer can be switched back and forth under irradiation of 365 nm UV light and visible light >420 nm, showing the yellow-green fluorescence of N-DSA-CN and the red fluorescence of spiropyran, respectively. Likewise, the non-covalently cross-linked polymer network obtained through the bonding ability of nitriles and pillar[5]arenes, in which spiropyran was covalently modified in the polymer, can achieve tailorable fading rates.<sup>40</sup> When the degree of cross-linking was high, the photochromic process went slower because spiropyran was in an aggregated state. Adding adiponitrile, which had a larger bonding constant with pillar[5]arenes, caused the degree of cross-linking to decrease due to the competition effect. The degree of aggregation of spiropyran units decreased, showing a fast photochromic process, thus achieving time-resolved encrypted inks.

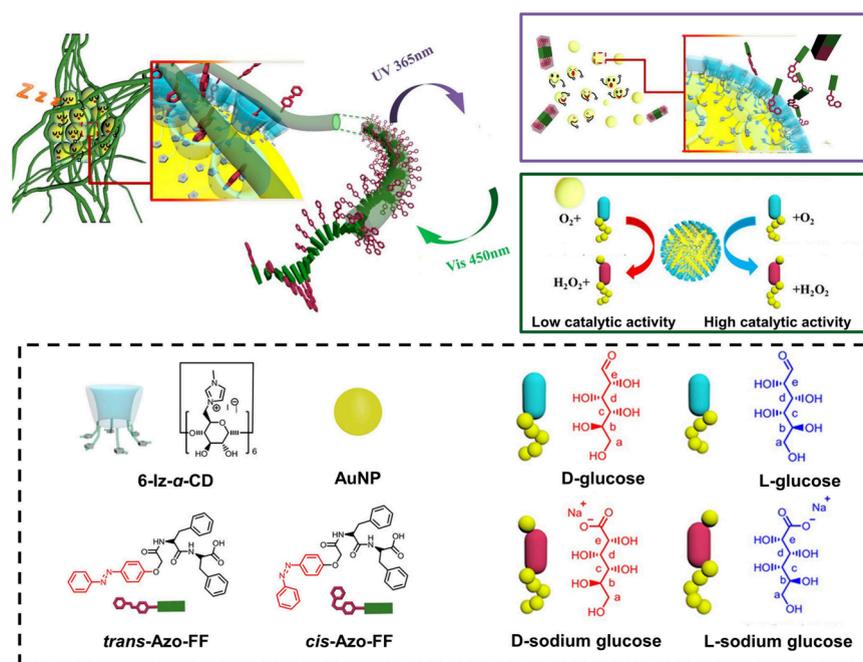
Spiropyran can not only regulate the luminescence behavior and morphology change but also control the generation of singlet oxygen, which is a type of reactive oxygen species (ROS). For example, a light-controlled ROS generation system was constructed, in which the host diphenylethylene-modified pillar[5]arene served as a donor of FRET, the guest triazole-modified sulfonated spiropyran served as an acceptor of FRET, and Nile blue (NiB) acted as the secondary energy transfer acceptor.<sup>41</sup> The excitation spectrum of the ring-opened spiropyran had a good overlap with the emission spectrum of pillar[5]arene, and the FRET process can smoothly occur while generating a fluorescence emission of 625 nm, which was further harvested by NiB and ROS. Pillar[5]arenes can greatly improve the ROS generation efficiency of spiropyran and NiB. At the same time, the ROS production of this system can be activated by 365 nm light and turned off by light of more than 500 nm, avoiding unnecessary cytotoxicity.

Combining two photoisomerization molecules, spiropyran and diarylethene, can achieve multiwavelength-controlled

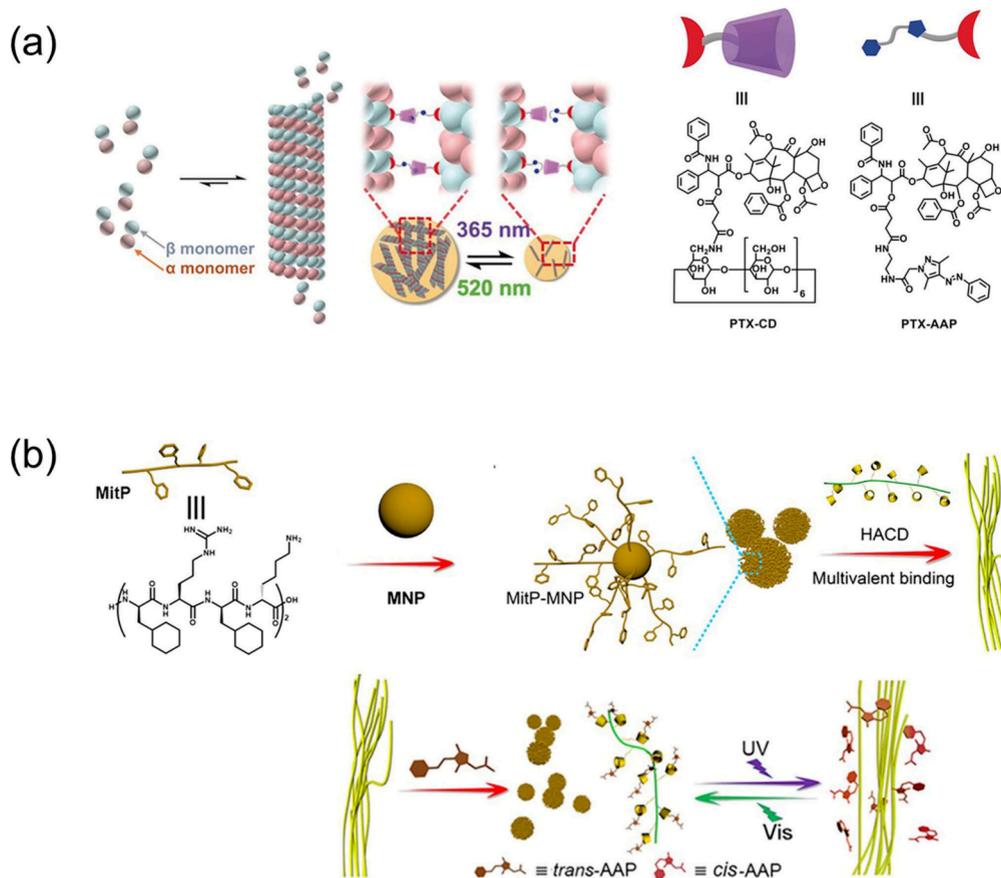
supramolecular cascade assemblies that can be used for multi-information encryption. An orthogonal three-wavelength light-controlled supramolecular assembly where CB[8] and pyridinium-modified diarylethene formed a one-dimensional noncovalent polymer ( $K_s = (1.23 \pm 0.34) \times 10^5 M^{-1}$  in open-ring form and  $(1.55 \pm 0.75) \times 10^6 M^{-1}$  in closed-ring form) can switch different colors under the illumination of 254, 420, and 650 nm.<sup>17</sup> Due to the different electrical properties of SP and MC, the microscopic morphology switched between amorphous droplets, nanospheres, and nanorods. Combinations of spiropyran and diarylethenes with different open/closed ring states can achieve yellow, green, and blue fluorescence emissions as well as entire quenching, thereby enabling an encryption method that hides multiple pieces of information under dual signal emission. Besides, a supramolecular polymer with photoswitchable multistate fluorescence was constructed through noncovalent bonding of spiropyran-modified  $\beta$ -CD by recognition with adamantane attached to the polymer, while disulfonylethylene was modified onto the polymer via copolymerization.<sup>42</sup> The ring-closed state of dithiosulfone ethylene SDTE-c emitted green fluorescence, and can further lead the system to emit red fluorescence of the open-ring state of spiropyran CDSP-o through the FRET process. Because it can regulate the luminescence in 495 and 655 nm, this system was used for anticounterfeiting and multilayer information encryption.

#### 4. LIGHT-CONTROLLED SUPRAMOLECULAR ASSEMBLIES BASED ON MACROCYCLES AND AZOBENZENE

Possessing the  $-N=N-$  bond, azobenzene can not only be encapsulated in macrocyclic hydrophobic cavities in the *trans* structure, which the *cis* structure cannot, so that photosensitization can drive the release and inclusion to regulate assembly and disassembly but also connect to macrocyclic hosts, which can take photoisomerization, leading to topological and luminescent behavior transformation. When azobenzene bridged dibenzo-24-crown-8 complexation with the secondary ammonium in chiral guests cholesterol derivative, nanoscale macroscopic chirality changes were observed under different lighting irradiations, in which snowflake-like clockwise helical supramolecular assemblies were formed in the *trans* state and became nonhelical upon UV irradiation, while the circular dichroism signal in the azobenzene region disappeared.<sup>43</sup> Taking advantage of the strong interaction between the permethyl- $\beta$ -CD and negatively charged porphyrin derivatives, azobenzene bridged-bis-(permethyl- $\beta$ -CD) constructed the supramolecular assemblies with amphiphilic porphyrin molecules for well-reversible and reproducible light-controlled structural transformation between long nanotubes and nanoparticles after light irradiation at 450 and 365 nm,<sup>44</sup> the apparent binding constant between guest and *trans*-/*cis*-host was  $2.37 \times 10^6 M^{-1}$  and  $8.54 \times 10^6 M^{-1}$ , showing 30-fold enhanced fluorescence which was originally quenched by porphyrin's H-aggregation in aqueous solution. The azobenzene-bridged bis( $\beta$ -CD) also can encapsulate adamantyl-modified diphenylalanine to realize the reversible conversion of 2D nanosheets and 1D nanotubes under different light irradiation ( $K_s = 5.32 \times 10^4 M^{-1}/5.18 \times 10^4 M^{-1}$  for *trans*-/*cis*-host). Different assembly morphologies had different fluorescence enhancement capabilities; after loading with Nile Red, the fluorescence intensity of 2D nanosheets was much stronger than that of nanotubes.<sup>45</sup>



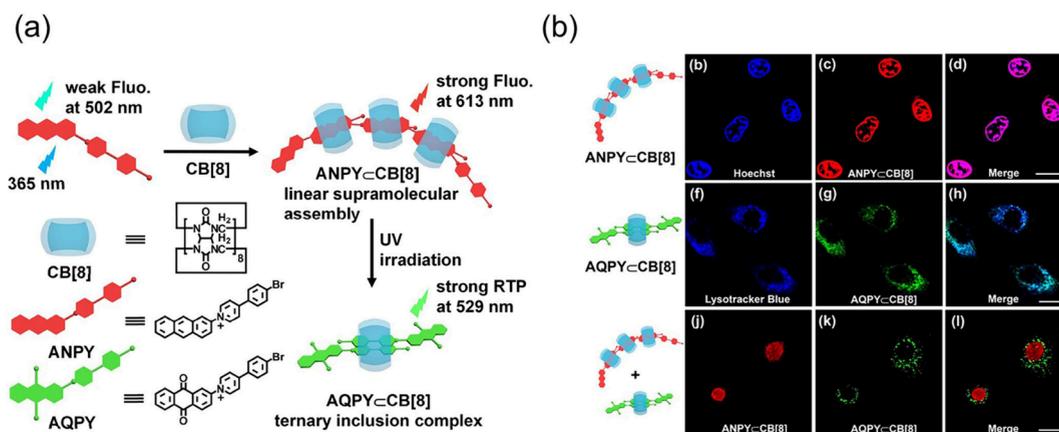
**Figure 4.** Schematic illustration of a supramolecular system for the photocontrollable catalysis and recognition of chiral monosaccharides. Reproduced with permission from ref 47. Copyright 2021 Wiley-VCH.



**Figure 5.** (a) Schematic illustration of a supramolecular assembly of photomodulated microtubule self-assembly morphology. Reproduced with permission from ref 48. Copyright 2018 Wiley-VCH. (b) Schematic illustration of supramolecular assemblies with dual control of magnetism and light. Reproduced with permission from ref 20. Copyright 2018 The Authors.

On the other hand, *cis/trans* azobenzene units can selectively bind with CDs. For example, azobenzene functional-group-

modified phenylalanine dipeptide molecule (**Azo-FF**) was assembled with  $\alpha$ -CD to culminate a supramolecular assembly



**Figure 6.** (a) Schematic illustration of a photooxidation-driven supramolecular assembly with two-color luminescence. Reproduced with permission from ref 24. Copyright 2021 American Chemical Society. (b) Schematic illustration of a dual cellular imaging targeting nuclei and lysosomes. Reproduced with permission from ref 24. Copyright 2021 American Chemical Society.

with photoregulated structural transmutation and chiral modulation.<sup>46</sup> The *cis*-Azo-FF self-assembled into nano-squares, and after a brief 365 nm irradiation, *trans*-Azo-FF spontaneously organized into nanofibers. Upon further assembly with  $\alpha$ -CD, the *trans* form showed right-handed helical pitch-enhanced nanofibers, while the *cis* form preserved its original nanosquare structure because of the poor bonding ability of *cis*-Azo-FF with CDs. Azo-FF@ $\alpha$ -CD can also be used to precisely photocontrol the catalytic activity. Polycationic  $\alpha$ -CD modified by imidazolyl groups interacted well with gold nanoparticles via electrostatic interactions at negative surface potentials and introduced Azo-FF to compete with the reactive substrate for encapsulation (Figure 4).<sup>47</sup> The hydrophobic cavities of CDs served as chiral channels for substrate molecules to contact the catalytic center, and the binding capacity of CDs to *cis/trans* azobenzene varies so that the catalytic activity can be accurately and dynamically tuned by alternating UV and visible light irradiation. Furthermore, the chiral cavities of CDs enabled chiral recognition, which allowed for the selective catalytic oxidation of glucose with different configurations.

The reversible inclusion of CDs and azobenzene derivatives can achieve light regulation of the self-assembly morphology of MT (Figure 5a).<sup>48</sup> The modification of paclitaxel to  $\beta$ -CD and photoisomerized azole group enabled the interconnection with MT and a wide range of morphological changes from nanofibers and nanobelts to spherical nanoparticles of different sizes can be observed under TEM, which was successfully applied to intracellular MT assembly and disassembly. Through cell staining experiments, it was evident that the host-guest assembly induced morphological changes in MT and a relatively high cytotoxicity. Furthermore, we constructed two-dimensional supramolecular nanomaterials for inducing mitochondrial aggregation, which consisted of  $\beta$ -CD-grafted graphene oxide (GOCD) as the host, and mitochondria-targeting peptide (MitP), azobenzene, polylysine, and polyethylene glycol-covalently modified transferrin as guest (TPM-Azo).<sup>49</sup> Since GO has the property of absorbing light in the NIR region, the assembly was tested and found to have better photothermal therapeutic effects and was essentially nontoxic to normal cells. Therefore, the synergistic therapy of the TPM-AzoGOCD supramolecular assembly combining mitochondrial dysfunction and photothermal therapy is promising in the field of cancer therapy. Supramolecular assemblies with dual

control of magnetism and light have been also used to induce mitochondrial dysfunction. Biocompatible ferromagnetic nanoparticles encapsulated with MitP and  $\beta$ -CD-grafted hyaluronic acid (HACD) were assembled into supramolecular nanofibers, which further featured arylazo pyrazole carboxylates as competing guest molecules, and not only exhibited reversible light-induced assembly and disassembly under irradiation at different wavelengths but also underwent growth along the direction of the magnetic field induced by a weak geomagnetic field (Figure 5b).<sup>20</sup> Due to the cancer-cell-targeting property of HA, this ternary supramolecular assembly based on HACD showed good biocompatibility, which can respond to weak geomagnetic fields to develop novel stimulus-responsive biomaterials that reduce tumor cell metastasis and decrease mortality by inducing mitochondrial dysfunction and intercellular aggregation in cancer cells, and inhibiting tumor cell invasion and metastasis in vitro and in vivo.

Based on a simple supramolecular strategy, in which the luminescence of the assemblies was quenched by modifying azobenzene on the guest molecule with its light-quenching ability, a hypoxia-responsive fluorescence activation system was constructed, in which guest molecules of azobenzene derivatives modified by cationic imidazole moieties and hydrophobic alkyl chains formed aggregates with sulfonated CDs via electrostatic interactions, upon further doping with Rhodamine 123, the fluorescence of the dyes was quenched, and after the addition of sodium bisulfite (SHS, a chemical reductant mimicking the azoreductase enzyme) to the solution, the fluorescence intensity was gradually restored with the fracture of azobenzene which was successfully used to activate cellular imaging.<sup>50</sup> In the construction of supramolecular lanthanide photoswitching materials, azobenzene derivatives based on 2,6-pyridinedicarboxylic acid modification can coordinate lanthanide ions ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ), and the photoluminescent supramolecular assemblies formed with  $\alpha$ -CD underwent a tight host-guest complex under 365 nm irradiation ( $K_s = 1.1 \times 10^4 \text{ M}^{-1}$ ), which effectively reduced the nonradiative energy loss of azobenzene to activate the intrinsic emission of the lanthanide complexes, whereas the fluorescence of the disassembly was completely quenched after the irradiation of light at 450 nm.<sup>51</sup>

The properties of conductive materials can also be controlled by utilizing the *cis/trans* isomerism of azobenzene. Lin et al. reported a conductive supramolecular composite gel

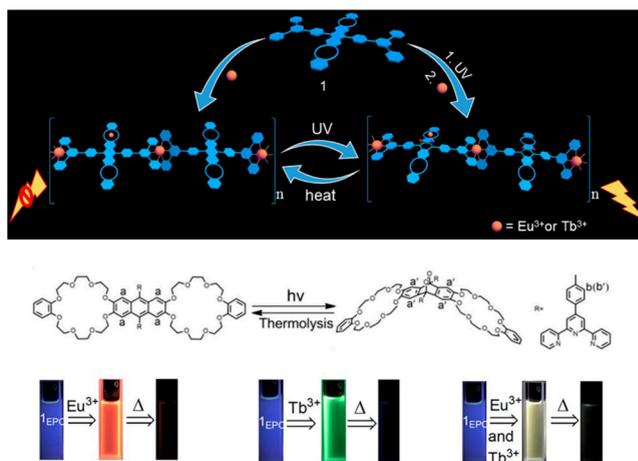
system based on the photoresponsive phase transition coassembled by  $\alpha$ -CD-encapsulated long alkyl-chain-linked azobenzene and MXene, which can be used as a light switch in solid-state circuits, showing excellent reversible phase transition and charge transfer path.<sup>52</sup>

## 5. LIGHT-CONTROLLED SUPRAMOLECULAR ASSEMBLIES BASED ON MACROCYCLES AND ANTHRACENE

The hydrogen atoms at the ninth and tenth positions of anthracene are significantly photoreactive, readily photooxidize to anthraquinone, and undergo reversible photodimerization under specific light irradiation. Therefore, by connecting anthracene to macrocyclic hosts or guest molecules, it can serve as a switch to regulate the luminescence of single or multiple components of supramolecular assemblies for information encryption, luminescence material, and targeted cell imaging. For example, as a guest molecule, anthracene-conjugated bromophenyl pyridinium salt was confined in the CB[8] cavity to form a “head-to-tail” linear polymer ( $K_s = 2.78 \times 10^6$  and  $2.34 \times 10^6 \text{ M}^{-1}$ ), where the anthracene group is oxidized to anthraquinone under UV irradiation (Figure 6a),<sup>24</sup> driving the disassembly to form a “head-to-head” stoichiometric 1:2 complex ( $K_s = 3.13 \times 10^{12}$  and  $6.98 \times 10^{11} \text{ M}^{-2}$ ) accompanied by red fluorescence changing to the intense green phosphorescence, and was successfully applied to the dual nucleus- and lysosome-targeted cellular imaging (Figure 6b).

While anthraquinone units modified to macrocyclic hosts  $\beta$ -CD (AQ-CD), AQ-CD self-assembled into linear nanofibers through anthraquinone encapsulated in another  $\beta$ -CD cavity, displaying reversible photoluminescence behavior ( $K_s$  of AQ- $\beta$ -CD is 135).<sup>53</sup> Under UV exposure, the hydrophobic cavity of the CDs provided a shielding effect to oxygen molecules, enabling the anthraquinone group to rapidly reduce to 9,10-anthracenediol, leading to strong yellow luminescence. However, with the bubbling of air into the aqueous solution, 9,10-anthracenediol was reoxidized to anthraquinone, achieving reversible color conversion, and was successfully employed in information encryption as fluorescence inks. Interestingly, anthracene conjugated two tripyridine and two dibenzo 24-crown-8 as a bridge formed a linear assembly through complexation with  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions, which showed reversible on/off of lanthanide luminescence by the photooxidizing properties of anthracene, and the presence of the crown ethers can efficaciously prevent the effects of alkali and alkaline earth metal ions, thus better actualizing the reversible response of the lanthanide luminescence for the assembly (Figure 7).<sup>54</sup> Utilizing the photooxidation properties of anthracene, a supramolecular photolyzable system was constructed through tightly packed supramolecular assemblies of amphiphilic 9-alkoxy-substituted anthracene (AnPy) and *p*-sulfonatocalix[4]arene (SC4A) ( $K_s = 4.22 \times 10^5 \text{ M}^{-1}$ ), in which AnPy was photoreactive and slowly decomposed to anthraquinone and alkanol under UV irradiation, and SC4A not only inhibited fluorescence quenching caused by AnPy self-aggregation but also facilitated photosensitization, and after the introduction of Eosin Y as an exogenous photosensitizer, the supramolecular assembly exhibited effective photolysis in the visible light.<sup>55</sup>

The photodimerization of anthracene can cross-link and fix the assembly, enhancing the stability of the structure and imparting a wealth of properties to the supramolecular assemblies. This dynamic process holds profound significance



**Figure 7.** Schematic illustration of lanthanide supramolecular assemblies with reversible photoluminescence behavior. Reproduced with permission from ref 54. Copyright 2017 American Chemical Society.

in the realms of host–guest recognition and the construction of stimulus-responsive materials. For example, Ma et al. prepared anthracene-containing copolymers, and assembled with  $\gamma$ -CD for further cross-linking, enabling a conversion between blue and cyan phosphorescence through reversible regulation of anthracene’s photodimerization reaction by different light exposure.<sup>56</sup>

## 6. CONCLUSION AND OUTLOOK

In this Account, we summarized the recent research progress on light-controlled supramolecular assemblies of four photoisomerization molecules (diarylethenes, spiropyran, azobenzenes, and anthracene derivatives) formed with several macrocyclic hosts and applications in chemistry, biology, and materials. Possessing double-arm units, diarylethene can be modified by single/two functional groups or macrocycles to form derivatives, constructing nanofibers, nanoparticles, or 2D nanosheets through host–guest interaction and realizing tunable luminescent behaviors. Different from diarylethene, spiropyran has different hydrophilic properties in the ring-open and -closed states and can reversibly bind/release protons under the control of light as a photoacid, both leading to the alterations in its affinity to the host, exhibiting significant changes in the assembly mode and subsequent modifications to the topological morphologies. Open-ring MC can act as a FRET/PRET receptor for energy transfer while closed-ring SP cannot, thus realizing photochromic behavior in the assembly and achieving multicolor luminescence for information security. Azobenzene can bridge two macrocycles or be modified into guest molecules, utilizing its photoisomerization characteristics to achieve tunable topological conversion of nanotubes, nanospheres, and nanosheets for use in photocontrolled supramolecular catalytic systems, inducing organelle aggregation and cell imaging. With the property of being easily photooxidation and photodimerization reactions, anthracene can also connect macrocyclic hosts or guest molecules, resulting in assemblies with different physical and chemical properties for the construction of dual-organelle imaging and multicolor luminescent materials. In addition, macrocyclic hosts can significantly enhance the fatigue resistance and luminescence intensity of photoisomerization molecules and hosts modified on polymers or biomacromolecules can

assemble with guests to achieve adjustable topological morphologies.

From the above Account, we can see that light-controlled supramolecular systems are widely used in the fields of cell imaging, targeted drug delivery, photodynamic therapy, anticounterfeiting, information encryption, and optoelectronic devices.<sup>57,58</sup> With the continuous development of new photoisomerization molecules such as tetraphenylethylene that can undergo intramolecular cyclization, vinylpyridine that is prone to photodimerization, etc.,<sup>59,60</sup> the construction of new macrocycles and guest derivatives as frameworks and the new self-assembly mode of amphiphilic photoisomeric molecules have brought more opportunities and challenges for the new light-controlled supramolecular assemblies, including molecular motors, molecular rotors, and logic devices. We hope that this Account will promote the development of light-controlled macrocyclic supramolecular assemblies as well as the coassembly of photoresponsive molecules with macrocycles, biomacromolecules, and polymers, to realize their broad applications in 3D printing, soft robots, wearable devices, photodynamic agents, force-responsive luminescence, and other fields.

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<sup>#</sup>The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. S.-Q. S. and H.-Z. Z. contributed equally to this work. **Shuangqi Song** writing—original draft (lead); **Hengzhi Zhang** writing—original draft (equal); **Yu Liu** supervision (lead).

### Notes

The authors declare no competing financial interest.

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