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# Luminescent lanthanide–macrocycle supramolecular assembly

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A series of macrocyclic compounds, including crown ether, cyclodextrin, cucurbituril and pillararene, bound to various specific organic/inorganic/biological guest molecules and ions through various non-covalent interactions, can not only make a single system multifunctional but also endow the system with intelligence, especially for luminescent materials. Due to their excellent luminescence properties, such as long-lived excited states, sharp linear emission bands and large Stokes shift, lanthanides have shown great advantages in luminescence, and have been more and more applied in the design of advanced functional luminescent materials. Based on reported research, we summarize the progress of lanthanide luminescent materials based on different macrocyclic compounds from ion or molecule recognition to functional nano-supramolecular assembly of the lanthanide–macrocycle supramolecular system including photo-reaction mediated switch of lanthanide luminescent molecules, multicolor luminescence, ion detection and cell imaging of rare-earth up-conversion of macrocyclic supramolecular assembly. Finally, we put forward the prospects of future development of lanthanide luminescent macrocyclic supramolecular materials.

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## 1. Introduction

Supramolecular chemistry uses a “bottom-up” approach to assemble sub-nanoscale small molecules into well-defined and highly ordered architectures and has received widespread attention in understanding and simulating biomolecules, such as proteins, DNA, and lipids, and also living organisms at the system level.<sup>1</sup> Different from traditional covalent bond chemistry, supramolecular chemistry mainly studies non-covalent interactions, including hydrogen bonding, metal coordination, hydrophobic forces, van der Waals force,  $\pi$ - $\pi$  stacking, electrostatic effects, *etc.*<sup>1a,2</sup> Among various supramolecular systems, it is noteworthy that macrocyclic supramolecular systems are more attractive because of their inherent advantages.<sup>3</sup> First of all, the

supramolecular interaction could be strengthened through a variety of weak non-covalent bond interactions between the macrocyclic host and the guest, which can achieve the covalent bond effect in a simple and convenient way, superior to the traditional complex organic synthesis of covalent systems. Secondly, the macrocyclic supramolecular system can combine a variety of functional groups together, which is expected to boost the performance of building blocks through comprehensive effects.

In the supramolecular system, the potential applications of macrocyclic compounds such as crown ethers, cyclodextrins, cucurbiturils and pillararenes have gained increasing interest. These macrocyclic compounds can bind various organic/inorganic/biomolecules and ions.<sup>1d,4</sup> For example, crown ethers, the first generation of macrocyclic hosts, have a strong binding ability to paraquat derivatives, secondary ammonium salt molecules, and alkaline earth metals.<sup>1d,4</sup> Cyclodextrin (CD), a type of cyclic oligosaccharide connected by  $\alpha$ -glucose units

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Yong Chen obtained his PhD degree in 2001 from Nankai University majoring in physical organic chemistry based on cyclodextrins. He has been a faculty member at the Institute of Chemistry, Chinese Academy of Science, and a post-doctoral fellow at Ecole Normale Supérieure (ENS, France). In 2003, he joined Prof. Yu Liu's group at Nankai University as an associate professor. His research interests are mainly focused on supramolecular chemistry of cyclodextrins.

through  $\alpha$ -1,4-glycosidic bonds, strongly binds with aromatic and/or adamantyl compounds mainly *via* hydrophobic interactions.<sup>1d,3,5</sup> Cucurbituril (CB), formed by condensation of different numbers of glycoluril units, can form host-guest inclusion complexes with positively charged organic and inorganic guest molecules as well as neutral organic guest molecules due to strong charge dipole, hydrogen bonding and hydrophobic interactions.<sup>1c,1d</sup> Pillararene, a type of rigid pillar architecture consisting of hydroquinone units connected by methylene bridges at the para position of the benzene ring, has electron-rich cavities with good binding ability to various electron-withdrawing or neutral molecules.<sup>1h</sup> Therefore, these macrocycles can be widely used not only as excellent receptors for molecular recognition, but also to construct functional materials of nanostructures including the photo-luminescent materials. In addition, the optical properties of supramolecular macrocyclic luminescent materials could realize the tunability of luminescent materials *via* the introduction of a variety of functional molecules or competitive binding molecules.

On the other hand, among many luminescent materials, lanthanide luminescent materials are widely applied in lighting, displays, laser, security ink and marking, pressure sensors, barcoding and biological applications due to their long-lived excited states, long wavelength emission, large Stokes shift and narrow emission bands.<sup>6</sup> Lanthanides (Ln III), also known as “rare earth elements”, have the electronic configuration [Xe] 4f<sup>n</sup>5d<sup>1</sup>6s<sup>2</sup> ( $n = 0-14$ ), and are located in group IIIB of the sixth period of the periodic table and comprise from lanthanum (atomic number 57) to lutetium (atomic number 71).<sup>7</sup> Their luminescence covers the entire spectral range, from ultraviolet light to visible light (400–800 nm) and even near infrared (NIR, 800–1700 nm): Eu<sup>3+</sup> (red light), Tb<sup>3+</sup> (green light), Sm<sup>3+</sup> (orange light), Tm<sup>3+</sup> (Blue light), and Dy<sup>3+</sup> (white light or close to white light) ions emit in the visible light region, while Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup> and other lanthanide ions all have near-infrared radiation.<sup>7,8</sup> Thus, the combination of rare earth elements with macrocycles will give luminescent materials with more characteristics and advantages including (1) rare earth systems with improved optical performance owing to the orderly, controllable and diverse assembly mode combined with macrocyclic supramolecular functional systems; (2) rare earth luminescent systems endowed with dynamic controllability and functional diversity to a certain extent.

In recent years, a variety of functional luminescent supramolecular systems have been successfully constructed through the combination of macrocyclic host compounds and lanthanide elements and have been further studied, demonstrating the rich research value of lanthanide luminescent materials based on macrocyclic supramolecular systems. Here, we review the recent

progress in combining lanthanides with macrocyclic compounds (including crown ether, cyclodextrin, cucurbituril and pillararene) and the applications of these luminescent systems in the fields of tunable multi-color light, smart materials, fluorescence sensing and up-conversion nanoparticles. The present challenges and opportunities for lanthanide luminescent materials based on macrocyclic compounds and the prospects of future development of this field are also discussed in this review.

## 2. Tunable multi-color luminescence

White-light emissive materials have attracted more and more attention due to the wide application in displays and lighting devices as well as sensors, which was realized through the combination of three primary colors (red (R), green (G), and blue (B)) or complementary mixing (blue and yellow)1a. According to the standard colorimetric regulations established by the Commission Internationale d'Eclairage (CIE) in 1931,<sup>9</sup> white light emission can be obtained by adjusting the ratio of three primary colors across the white light region. The white light emission of single molecules could be achieved by combining the red-emitting Eu<sup>3+</sup>, green-emitting Tb<sup>3+</sup>, and a blue emission ligand, which have a strong photoluminescence (PL) intensity, a special light damage threshold, and are very stable.<sup>10</sup>

Tian *et al.*<sup>11</sup> reported a multicolor fluorescent supramolecular hyper-branched polymer based on three symmetrical pillar[5]arene (MP5) hosts and terpyridine (TPY) modified triazole guest TAPN, where TAPN could form an assembly with pillar[5]arene through the host-guest interaction and TPY could coordinate with lanthanide ions. The multicolor orthogonal coordination complexation could be further formed upon addition of different lanthanide ions to the assembly (Fig. 1), and the fluorescence could be tuned by adding a competitive guest molecule.

Yang *et al.*<sup>12</sup> designed and synthesized a novel color-tunable fluorescent pillararene coordination polymer which was made up of di-carboxylatopillar[5]arene (DCP5) and lanthanide metal ions (Fig. 2). In this polymer, multicolor fluorescence containing white light was achieved through different ratios of europium (Eu<sup>3+</sup>) with red-color fluorescence, terbium (Tb<sup>3+</sup>) ions with green-color fluorescence, as well as DCP5 with blue emission. Furthermore, this white-color fluorescent pillararene-based polymer was utilized for detecting nitroaromatic pollutants not only under *in vitro* conditions (zebrafish and *Limnodrilus*) but also *in vivo* (vegetables) *via* an electron transfer mechanism.

Liu *et al.*<sup>13</sup> reported a two-dimensional (2D) lanthanide luminescent organic-inorganic hybrid material that was comprised of the anionic polyoxometalate Na<sub>9</sub>[EuW<sub>10</sub>O<sub>36</sub>]·32H<sub>2</sub>O (Eu-POM), mono-quaternary ammonium tetraphenylethene (MQATPE) and

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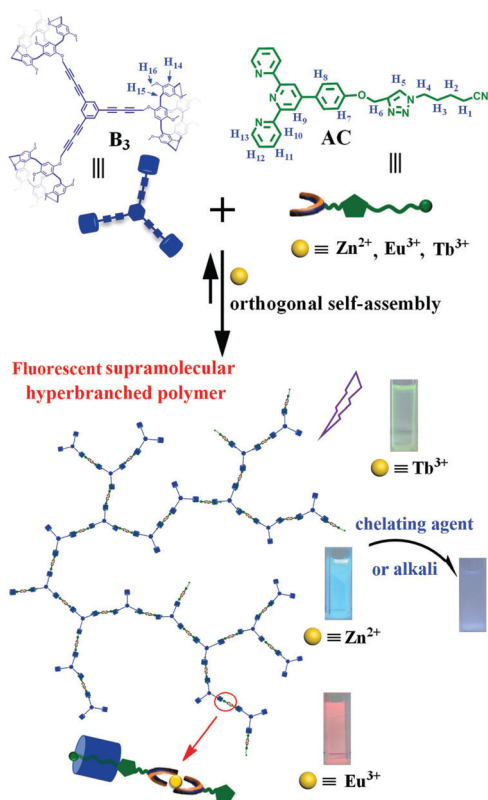


Fig. 1 Schematic illustration of construction of a multicolor luminescence supramolecular polymer based on MP5 and TAPN in coordination with lanthanide ions.<sup>11</sup> Copyright 2018, Wiley Online Library.

CB[7] via a two-step supramolecular assembly approach (Fig. 3). The supramolecular assembly formed multicolor (including white luminescence) single-layer films via mixing the red-emitting

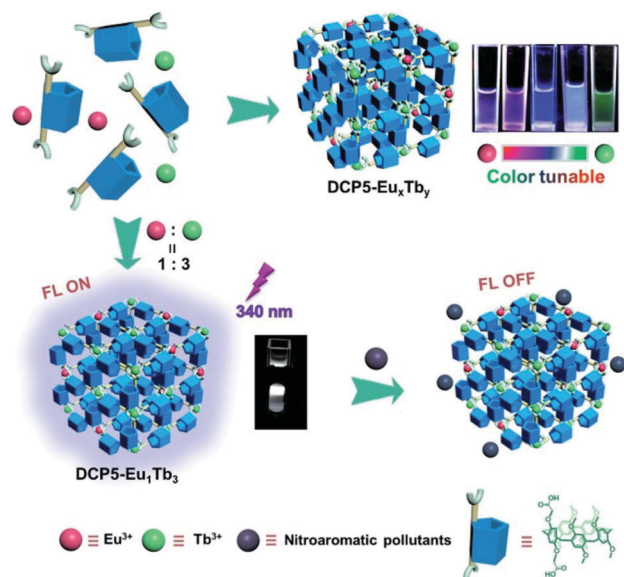


Fig. 2 Schematic illustration of the construction of the color-tunable luminescence polymer via DCP5 and lanthanide ions.<sup>12</sup> Copyright 2020, Royal Society of Chemistry.

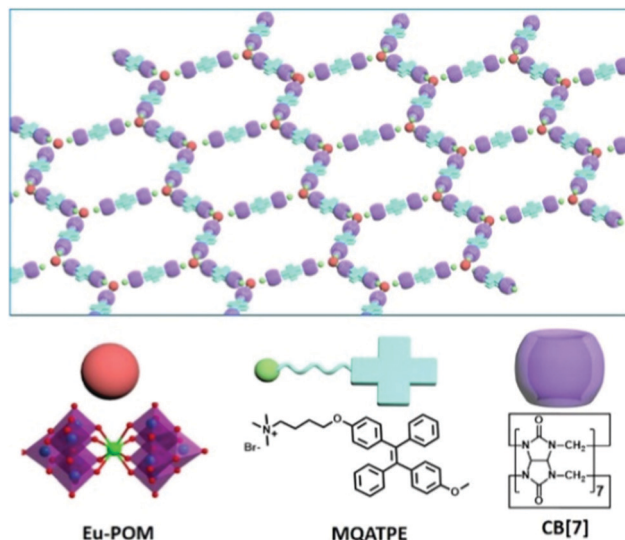


Fig. 3 Schematic illustration of the construction of a multicolor luminescence supramolecular assembly by the cationic MQATPE@CB[7] and the anionic Eu-POM.<sup>13</sup> Copyright 2020, American Chemical Society.

Eu-POM and the blue-emitting MQATPE@CB[7], where CB[7] can not only prevent the aggregation of MQATPE allowing it to retain its strong fluorescence, but also enable MQATPE to form a periodic assembly compared with that without CB[7]. Importantly, this 2D supramolecular lanthanide luminescence material could effectively regulate the activity of  $\alpha$ -chymotrypsin (ChT) because of the high surface area and more accessible active sites of the single-layer films. They also constructed a multi-color and solid-state lanthanide luminescence supramolecular assembly<sup>14</sup> based on CB[8], methylimidazole salt modified terpyridine and lanthanide ions, where CB[8] could form a stable 1:2 inclusion complex with the methylimidazole salt, and the terpyridine group could coordinate with and sensitize  $\text{Tb}^{3+}$  or  $\text{Eu}^{3+}$  for emitting green or red light, respectively (Fig. 4). Significantly, the luminescence intensity of the resulting solid-state lanthanide supramolecular assembly is 10 times higher than that of the corresponding system without CB[8], and the multi-colors including white light can be modulated through different molar ratios of blue light (terpyridine), red light ( $\text{Eu}^{3+}$ ) and green light ( $\text{Tb}^{3+}$ ).

### 3. Smart materials

Smart materials, also called stimulus-responsive functional materials, are inspired by natural biological systems (*e.g.*, the folding of mimosa plants and the skin tone change of cephalopods) which respond to various external stimuli (such as light, pH, chemicals, temperature, humidity, mechanical force, electrical field, and magnetic field) by changing their structures and/or chemical/physical properties.<sup>15</sup> Among these materials, smart fluorescent materials, due to their excellent sensitivity, high contrast, rapid response and other advantages, have more potential applications in the fields of smart logic circuit, biomedicine, optoelectronic equipment, *etc.*<sup>16</sup> Therefore, a simple and effective method to obtain fluorescent



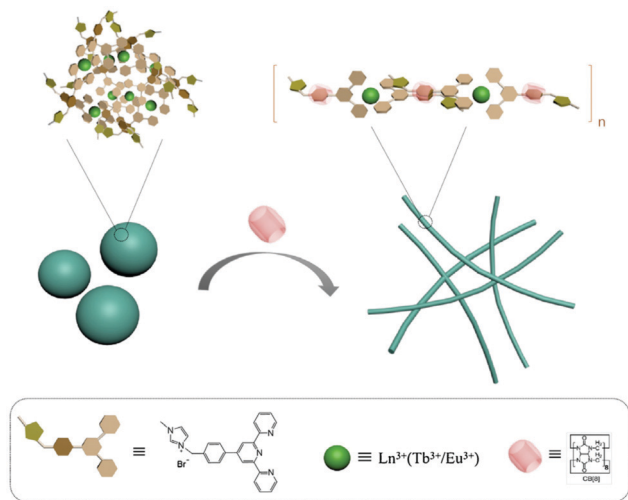


Fig. 4 Schematic illustration of the construction of a tunable luminescence solid-state supramolecular assembly by CB[8] and tripyridine derivatives in coordination with lanthanide ions.<sup>14</sup> Copyright 2019, Elsevier.

materials with excellent response performance and good luminescence performance is the direction that scientists are constantly pursuing.

In 2008, we constructed a reversible lanthanide luminescent switch based on dibenzo-24-crown-8 (DB24C8) modified pyridine-2,6-dicarboxylic acid (DPA), a ferrocenyl-modified dialkylammonium salt, and lanthanide ions, where DPA could be used as an excellent chelator and antenna for  $\text{Tb}^{3+}$ , and DB24C8 could bind the dialkylammonium group of the guest molecule for the regulation of optical properties (Fig. 5).<sup>17</sup> In this tris[2]pseudorotaxane, fluorescence was quenched significantly

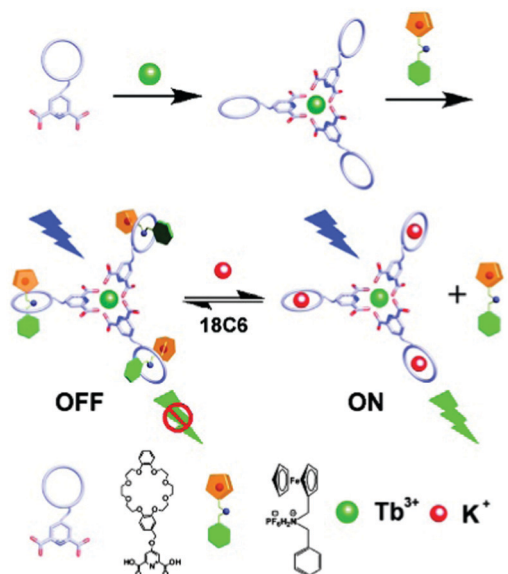


Fig. 5 Schematic illustration of the construction of the controlled luminescence supramolecular assembly by ferrocenyl-modified dialkylammonium salts and DPA/DB24C8 in coordination with lanthanide ions.<sup>17</sup> Copyright 2008, American Chemical Society.

due to the photoinduced electron transfer (PET) from the lanthanide ion to the ferrocene. However, when  $\text{K}^+$ , which can more easily bind DB24C8 than the dialkylammonium salt, was added to the assembly, the dialkylammonium salt was displaced to prevent PET, and the fluorescence was restored. Further, when we added the competing host molecule 18-crown-6 (18C6), which has a stronger binding ability with  $\text{K}^+$ , the fluorescence was quenched again. Then, we constructed another molecular switch using a DB24C8 derivative bearing a terpyridine unit, a fullerene-containing ammonium salt and lanthanide ions (Fig. 6).<sup>18</sup> In this assembly, the PET process can also be regulated by the way of competitive bonding between  $\text{K}^+$  and 18C6, so as to reversibly regulate the luminescence of lanthanide ions. These two molecular switches are realized by the way of host-guest competitive bonding.

On the basis of previous work, terpyridine modified DB24C8 was used as the host and diarylethene modified dialkylammonium salt (DAE)<sup>19</sup> as the guest (Fig. 7). DAE is an excellent light-responsive molecule that can realize the isomerization reactions of ring-closing and ring-opening by alternating UV and visible light, and also has outstanding fatigue resistance.<sup>20</sup> In an assembly constructed of DB24C8, DAE and lanthanide ions, the luminescence of  $\text{Eu}^{3+}$  can be regulated not only by the competitive bonding of  $\text{K}^+$  and 18C6, but also, most importantly, through the alternation of UV and visible light which controls the resonant energy transfer (RET) from the excited lanthanide ion to the photochromic DAE owing to the perfect spectral overlap between the  $\text{Eu}^{3+}$  emission and the DAE absorption. This multi-stimulus responsive, especially light-driven, highly efficient luminescence switch may provide a novel perspective for the development of smart materials.

In a following work, other photo-controlled groups were selected to design and prepare functional molecular switches. It is well-known that anthracene is a very good photo-responsive group, which can not only realize dimerization/depolymerization by UV or visible light irradiation,<sup>21</sup> but can also realize the reversible conversion process by reacting with singlet oxygen on heating.<sup>22</sup> Therefore, DB24C8, terpyridine, anthracene and lanthanide ions were employed to construct a molecular switch, where modified terpyridines were attached at

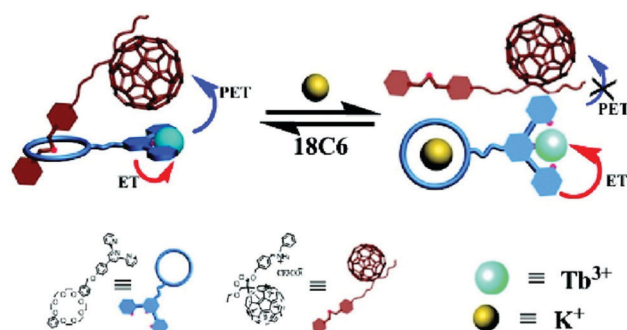


Fig. 6 Schematic illustration of the construction of the controlled luminescence supramolecular assembly by fullerene-containing ammonium salt and terpyridine-modified DB24C8 in coordination with lanthanide ions.<sup>18</sup> Copyright 2011, American Chemical Society.



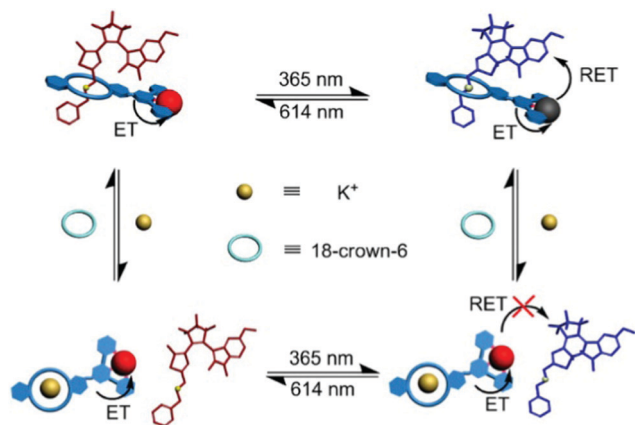


Fig. 7 Schematic illustration of the construction of the dual-stimulus luminescence supramolecular assembly via DAE and tribipyridine-modified DB24C8 in coordination with lanthanide ions.<sup>19</sup> Copyright 2013, American Chemical Society.

the 9 and 10 positions of anthracene and two-arm DB24C8s were modified at both ends of anthracene (Fig. 8).<sup>23</sup> In this molecular switch, terpyridine can form a 2 : 1 complex with Eu<sup>3+</sup> or Tb<sup>3+</sup>. However, the large  $\pi$  conjugated group on the antenna molecule terpyridine cannot excite Eu<sup>3+</sup> or Tb<sup>3+</sup> for luminescence as the lowest triplet energy of the ligand does not match with the first excited state of lanthanide ions. On the other hand, because the anthracene's 9 and 10 positions are modified with aromatic groups, the anthracene can react with singlet oxygen to generate endoperoxides (EPOs) which could destroy the big conjugated system to achieve energy level matching for the luminescence of Eu<sup>3+</sup> or Tb<sup>3+</sup> after UV light irradiation and this process could be restored by heating. In addition, DB24C8 can complex with alkali earth metal ions in solution to prevent their quenching effect on Eu<sup>3+</sup> or Tb<sup>3+</sup> luminescence. This method based on photo/thermo-controlled lanthanide luminescence supramolecular assembly will provide a new idea for multi-stimulus responsive molecular machines and logic gate applications. Furthermore, the photo-controlled molecule DAE was introduced (Fig. 9),<sup>24</sup> and the resultant assembly can not only regulate the luminescence of Eu<sup>3+</sup> or Tb<sup>3+</sup> through the transformation of UV light to heat for the oxidation and deoxidation of anthracene, but can also realize the switching of the luminescence of Eu<sup>3+</sup> or Tb<sup>3+</sup> based on the regulation of

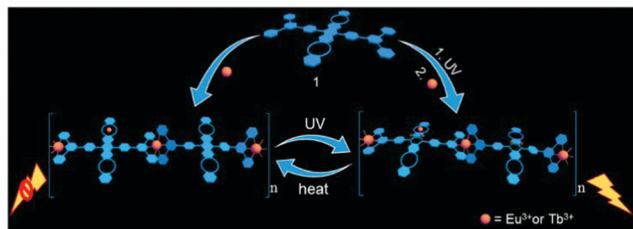


Fig. 8 Schematic illustration of the construction of the photo-oxidation regulation luminescence supramolecular assembly based on anthracene/DB24C8/tribipyridine and lanthanide ions.<sup>23</sup> Copyright 2017, American Chemical Society.

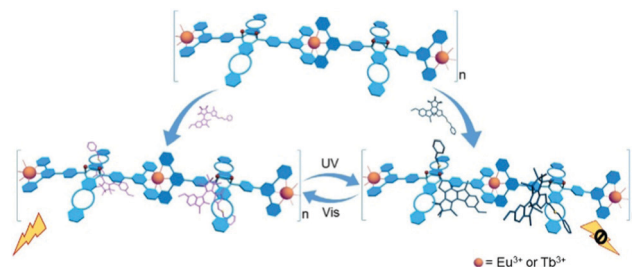


Fig. 9 Schematic illustration of the construction of the dual-photoresponsive luminescence supramolecular self-assembly based on DAE/anthracene/DB24C8/tribipyridine and lanthanide ions.<sup>24</sup> Copyright 2018, Elsevier.

the closed form and open form of DAE under ultraviolet and visible light irradiation alternately. This kind of supramolecular switching based on dual-light-stimuli-driven luminescent lanthanides provides a new way for smart materials. In a following research study, water-soluble cyclodextrin was employed to construct a molecular switch in water. It is well documented that anthracene tends to undergo photo-dimerization reaction when there are functional groups in other positions. For example,  $\gamma$ -CD binds two anthracenes in water, which can increase the solubility of anthracene and accelerate the anthracene dimerization reaction.<sup>25</sup> When a DPA moiety is introduced at the 2 position of anthracene,<sup>26</sup> a pseudo[3]rotaxane could be formed between  $\gamma$ -CD and anthracene with a 1 : 2 molar ratio in aqueous solution, and DPA simultaneously coordinates with Eu<sup>3+</sup> or Tb<sup>3+</sup> with a 3 : 1 stoichiometry (Fig. 10). In this supramolecular assembly, the energy level of the ligand does not match that of the rare earth ion so that the rare earth ions do not emit because of the large  $\pi$  conjugated group of anthracene. However, when the conjugated group was destroyed by the dimerization reaction of anthracene under UV light, the luminescence of rare earth ions in water could be observed. More

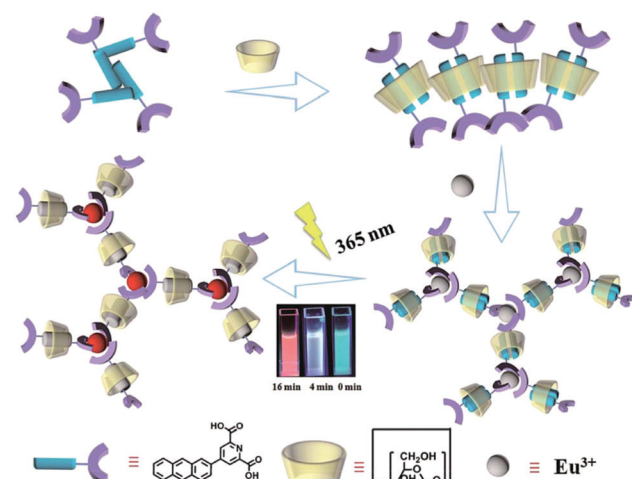


Fig. 10 Schematic illustration of the photo-cyclodimerization supramolecular assembly by  $\gamma$ -cyclodextrin/Eu<sup>3+</sup>/anthracene.<sup>26</sup> Copyright 2019, Royal Society of Chemistry.

interestingly, the conversion of multicolor fluorescence including white light could be realized by adjusting the light irradiation time, and this multicolor fluorescence emission is also available in a variety of environments such as solid films and cells.

Azobenzene is also a photoisomerized molecule with very good reciprocity by UV and visible light, and its isomers have very large binding ability differences with  $\alpha$ -CD.<sup>27</sup> That is, the E-type isomer of azobenzene has a strong binding ability with  $\alpha$ -CD up to  $10^4 \text{ M}^{-1}$ , but the Z-type isomer does not bind  $\alpha$ -CD. Therefore, the  $\alpha$ -CD/azobenzene pair is also a good candidate to construct smart luminescence materials by combining with rare earth ions. Li *et al.*<sup>28</sup> constructed an organic–inorganic hybrid supramolecular luminescence hydrogel with a high  $G'$  value and photo-controlled properties from the long alkyl chain DPA modified  $\alpha$ -CD (2), guanidinium-azobenzene (Guazo), sodium polyacrylate exfoliated LAPONITE<sup>®</sup> nanosheets (SPLNs), and rare earth ions (Fig. 11). In this supramolecular assembly, the positively charged guanidinium group associated with the negatively charged SPLNs to form hydrogels through electrostatic interactions, azobenzene and CD were used as photo-regulating components, and DPA was coordinated with rare earth ions as a luminescence center. This supramolecular lanthanide luminescent hydrogel could achieve photo-switchable sol–gel phase conversion under the irradiation of UV light.

## 4. Fluorescence sensing

Fluorescence sensing responds to the presence of target analytes with changes in the luminescence signal (such as fluorescence enhancement or quenching, the movement of the fluorescence characteristic peak position, the change of fluorescence lifetime, the change of fluorescence polarization, *etc.*) and could realize

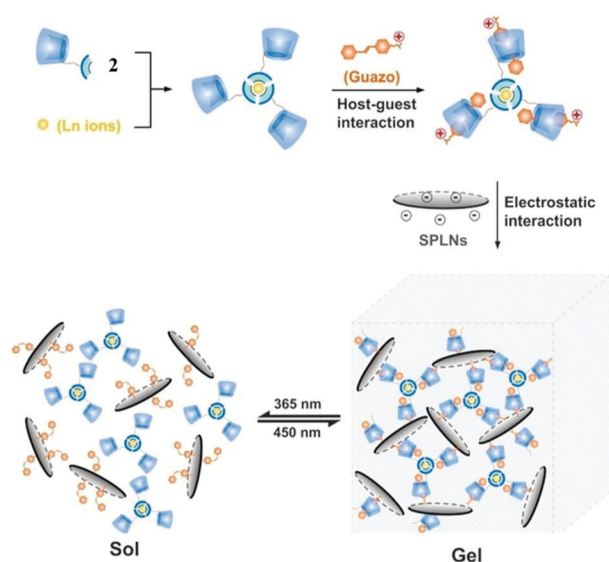


Fig. 11 Schematic illustration of the photoresponsive supramolecular hydrogels for sol–gel phase transition by DPA- $\alpha$ -cyclodextrin/Guazo/lanthanide ions and SPLNs.<sup>28</sup> Copyright 2018, Wiley Online Library.

the specific selective recognition of molecules or ions.<sup>29</sup> Fluorescence sensing has become a recent research hotspot in the field of chemical and biological analysis due to its high sensitivity, easy operation, and low cost. For the lanthanide ion complex, the luminescence can be adjusted to achieve the sensing effect through three aspects:<sup>30</sup> (1) water molecules that quench the fluorescence can compete with other molecules or ions in the inner coordination sphere leading to changes in the optical properties of the lanthanide ion complex; (2) the photophysical properties of the ligand can be changed by the electron or charge transfer processes; (3) the detected substance can act as either an antenna molecule to sensitize lanthanide ions or a quencher to compete with lanthanide ions for coordination.

Nocera *et al.* prepared a series of luminescent lanthanide macrocyclic compounds based on CDs. Among them, two macrocyclic ligands have good sensitizing luminescence effects (Fig. 12 and 13). One is 4,10,13-tetraoxa-7,16-diazacyclooctadecane (aza)-modified  $\beta$ -CD (aza- $\beta$ -CD) and the other one is diethylenetriaminepentaacetic acid (DTPA)-modified  $\beta$ -CD (DTPA- $\beta$ -CD).<sup>31</sup> For aza- $\beta$ -CD@Eu, because of the size matching between the cyclodextrin cavity and aromatic compounds, benzene formed an inclusion complex with  $\beta$ -CD in  $\text{D}_2\text{O}$ , and then absorption-energy transfer-emission (AETE) from benzene to  $\text{Eu}^{3+}$  occurred for the enhancement of the fluorescence of  $\text{Eu}^{3+}$ , leading to the detection ability towards benzene. However, this detection ability could not be achieved in  $\text{H}_2\text{O}$  due to the swing of the aza ligand and the coordination of water molecules with  $\text{Eu}^{3+}$ . On the other hand, the cradle-like macrocyclic complex DTPA- $\beta$ -CD could provide  $\text{Tb}^{3+}$  with more coordination sites for preventing the possibility of  $\text{H}_2\text{O}$  molecule coordination, which realizes the high-sensitivity detection of polycyclic aromatic hydrocarbons through the cavity of CD.<sup>32</sup>

DPA, as the main component of the protective layer of *Bacillus* spores, is of vital importance for accurate, rapid, sensitive and highly selective detection of *Bacillus* spores, because this can be utilized to effectively prevent the occurrence of fatal acute anthrax.<sup>33</sup> Reinhoudt and Huskens *et al.*<sup>34</sup> developed a supramolecular method for high sensitivity/selectivity detection of DPA with low detection limit (Fig. 14). Firstly,

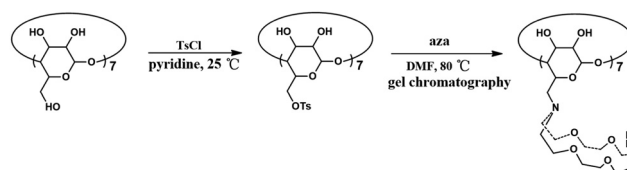


Fig. 12 The synthesis route toward aza- $\beta$ -CD.

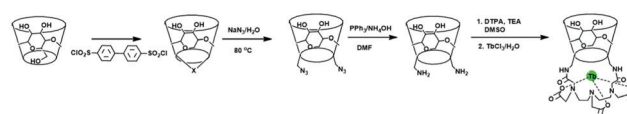


Fig. 13 The synthesis route toward DTPA- $\beta$ -CD.





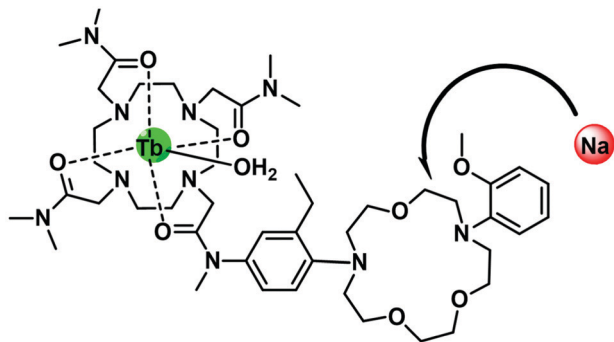


Fig. 17 Schematic illustration of the molecular structure of the  $\text{Tb}^{3+}$  complex sensor for  $\text{Na}^+$  and  $\text{K}^+$ .

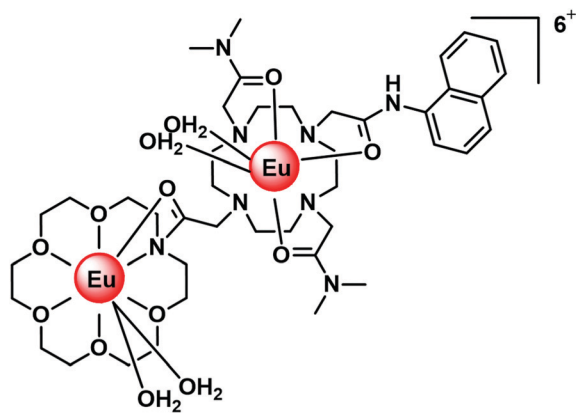


Fig. 18 Schematic illustration of the molecular structure of the sensor for dicarboxylates.

$\text{Eu}^{3+}$ . This luminescent binuclear complex could selectively detect malonic acid in a buffer solution at pH 6.5 *via* competitive coordination of  $\text{Eu}^{3+}$  with the water ions on the binuclear complex, leading to an increased fluorescence, while other small dicarboxylic acids such as aspartic, succinic, or glutaric acid would cause the fluorescence quenching of the luminescent complex. This method of combining crown ether and luminescent lanthanide ions to detect small biologically important dicarboxylic acids will provide a new idea for the detection of some biologically important structures.

Wong *et al.*<sup>39</sup> reported a sensor consisting of diaza-18-crown-6, quinoline as the antenna molecule and the cyclen/ $\text{Eu}^{3+}$  complex as the luminescence center (Fig. 19). This sensor not only showed the response to  $\text{H}^+$  due to the pH changes causing the heteroaryl nitrogen and tertiary amine to undergo protonation and deprotonation, but also presented the response to  $\text{K}^+$  because of the change of conformation and rigidity before and after the complexation of crown ether with  $\text{K}^+$ . Therefore, the sensor exhibited the dual response to  $\text{H}^+$  and  $\text{K}^+$  at four independent pH ranges especially in the physiological pH. In this sensor, the lifetime of fluorescence of lanthanide  $\text{Tb}^{3+}$  didn't change with the variation of pH and  $\text{K}^+$  concentration in aqueous solution. Pierre *et al.*<sup>40</sup> improved the selectivity and detection limit of  $\text{K}^+$

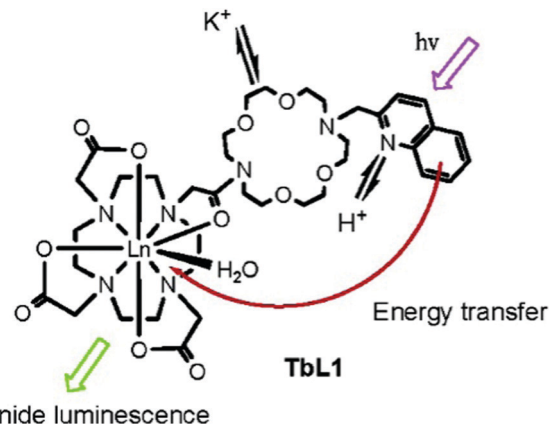


Fig. 19 Schematic illustration of the molecular structure of the sensor for  $\text{H}^+$  and  $\text{K}^+$ .<sup>39</sup> Copyright 2004, American Chemical Society.

recognition by using cationic- $\pi$  interaction (Fig. 20). They introduced the  $\text{Tb}^{3+}$  chelator and the antenna molecule phenyl-azaxanthone at both sides of diaza 18-crown-6 receptors. In this system, the antenna molecule and the  $\text{Tb}^{3+}$  luminescence center were separated by the crown ether ring, which could not effectively sensitize the  $\text{Tb}^{3+}$  luminescence resulting in the sensor to be in the "off" state with a weak  $\text{Tb}^{3+}$  luminescence. When the crown ether in the sensor was complexed with  $\text{K}^+$ , the cationic- $\pi$  interaction between  $\text{K}^+$  and the benzene ring on azaxanthone shortened the distance between the antenna molecule azaxanthone and the luminescence center of  $\text{Tb}^{3+}$  realizing the energy transfer from azaxanthone to  $\text{Tb}^{3+}$ , which led to increased fluorescence. The important thing was that the sensor was suitable for application in the clinical detection concentration range (0–10 mM). In the presence of 10 mM  $\text{K}^+$ , the fluorescence of the sensor was increased by 22 times and it showed high selectivity for  $\text{K}^+$ , but no obviously improved effect for other ions such as  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , *etc.*

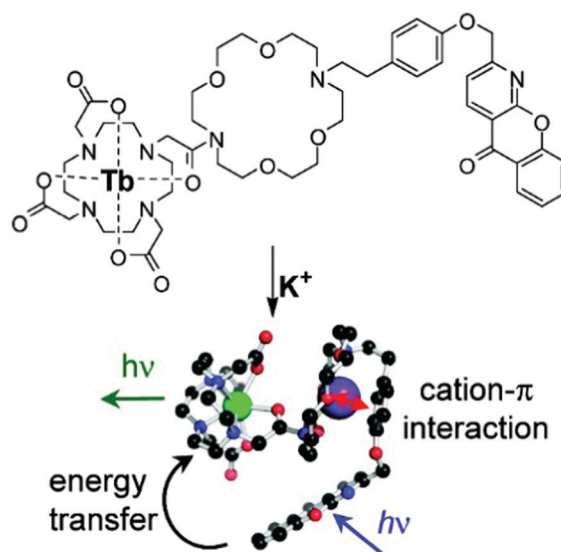


Fig. 20 Schematic illustration of the structure and mode of the sensor for  $\text{K}^+$ .<sup>40</sup> Copyright 2009, American Chemical Society.

Li *et al.*<sup>41</sup> reported a sensor that responded to  $K^+$  ions on the surface of a silicon plate based on the coordination of the crown ether-connected bisterpyridine (L1) and  $Ln^{3+}$  ions (Fig. 21). The ligand L1 coordinated with  $Ln^{3+}$  ions, and 18C6 strongly bound  $K^+$  ions. Therefore, this sensor effectively detected  $K^+$  through the fluorescence enhancement of the light-emitting assembly which stemmed from the enhancement of the triplet state energy level of the ligand L1 after 18C6 binding  $K^+$  and the energy transfer from  $Tb^{3+}$  ions to  $Eu^{3+}$  ions. In addition, the energy transfer of the bimetal in the sensor could be adjusted according to the  $K^+$  ion concentration, and its detection limit reached  $1\ \mu M$ . This lanthanide supramolecular assembly presented a promising way for the construction of sensing materials.

Tang *et al.*<sup>42</sup> constructed a pendant benzocrown ether ligand benzo-15-crown-5 through the reaction of the macrocyclic receptor 4,5-dibromomethylbenzo-15-crown-5 with *N*-benzylsalicylamide, which formed a one-dimensional (1-D) zig-zag luminescent lanthanide polymeric chain *via* coordination with  $Tb^{3+}$  (Fig. 22). The luminescent supramolecular chain could detect  $Hg^{2+}$  with high selectivity *via* fluorescence quenching attributed to the interaction of ligands, especially crown ethers, and  $Hg^{2+}$ , which hindered the energy transfer between antenna molecules and  $Tb^{3+}$ .

Beer and Faulkner<sup>43</sup> reported a lanthanide appended rotaxane responsive to  $Cl^-$ , which was prepared by using a

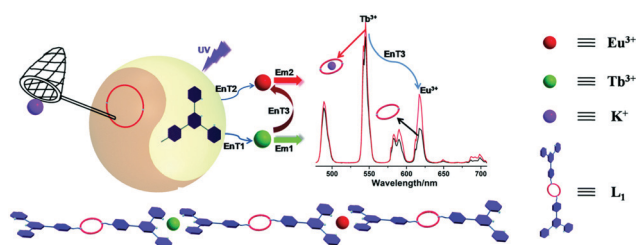


Fig. 21 Schematic illustration of the construction of supramolecular assembly  $Ln \cdot L1$  and detection of  $K^+$ .<sup>41</sup> Copyright 2018, Royal Society of Chemistry.

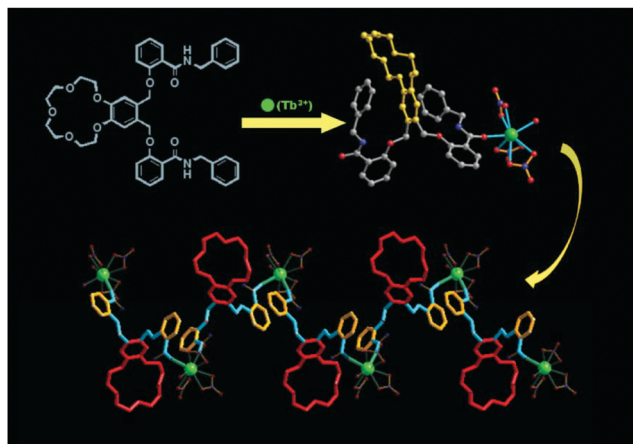


Fig. 22 Schematic illustration of the molecular structure of the crown ether/terbium complex.<sup>42</sup> Copyright 2010, Royal Society of Chemistry.

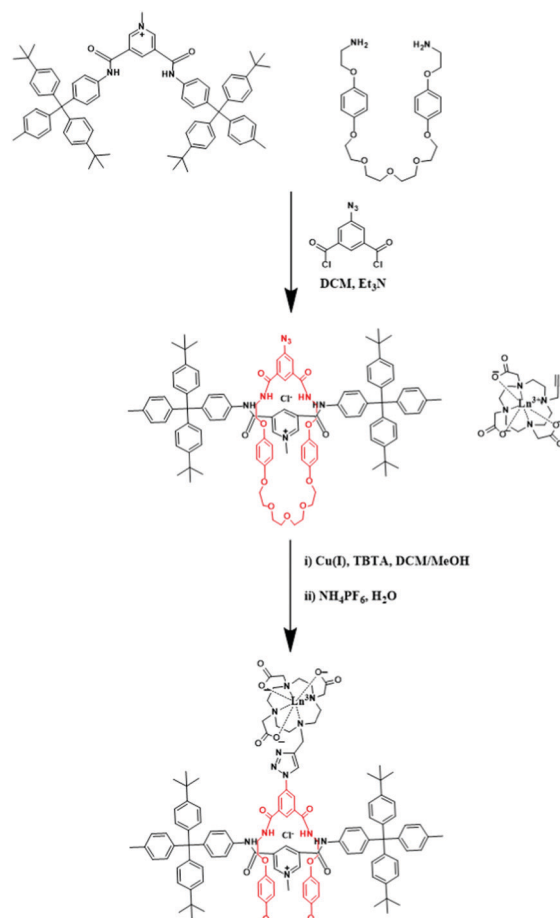


Fig. 23 Schematic illustration of the construction of a lanthanide appended rotaxane in response to  $Cl^-$ .<sup>43</sup>

chloride anion templated condensation clipping reaction of a pyridinium chloride axle, a diamine macrocycle precursor and 5-azidoisophthaloyl chloride, followed by the click reaction with the lanthanide complexes and washing with aqueous ammonium hexafluorophosphate (Fig. 23). With the continuous addition of  $Cl^-$ , the fluorescence of this lanthanide appended rotaxane quenched initially and then recovered, which was attributed to the binding of  $Cl^-$  to the ninth (axial) donor site on the lanthanide complex the binding of  $Cl^-$  from the the ninth (axial) donor site on the lanthanide complex to the rotaxane pocket accompanied by solvation. This lanthanide luminescent supramolecular rotaxane can act as a sensor to detect solvation through the fluorescence changes due to structural changes as it is combined with  $Cl^-$ .

## 5. Up-conversion luminescence

Lanthanide-doped up-conversion nanoparticles (UCNPs) exhibit anti-Stokes luminescence in that they could generate higher energy outcome photons (*e.g.* ultraviolet, visible and NIR) from low-energy continuous-wave (CW) near-infrared (NIR) photons (*e.g.*, 808 nm or 980 nm laser) through successive photon

absorption and a more efficient energy transfer from their low-lying energy levels.<sup>44</sup> These NIR excited UCNPs not only have the advantages of large Stokes shift, high tissue penetration depth, high signal-to-noise ratios and low photo-damage, but also have the advantages of excellent chemical stability, superior photostability, high resistance to photobleaching and low auto-fluorescence background compared with other up-conversion nanoparticles.<sup>44</sup> Therefore, they have a wider range of application value in biological sciences.

González-Béjara and Pérez-Prieto *et al.*<sup>45</sup> reported a nanohybrid scaffold for excitation in the near infrared (NIR: 980 nm) light which was prepared by the sonication of CB and the naked UCNPs ( $\text{NaYF}_4\text{:Yb}^{3+}$  (18%),  $\text{Er}^{3+}$  (2%)) in water (Fig. 24). In this scaffold, CB could bind functional molecules with size matching *via* the host-guest interaction to shorten the distance from UCNP surface, which may not only prevent the accumulation of fluorescent molecules to enhance fluorescence emission, but also increase the solubility in water. Taking this advantage, they studied the effects of different CB modified UCNPs ( $\text{UCNP@CB}$ ) on the luminescence of the assembly with methylene blue (MB) and pyronin Y (PYY). Interestingly,  $\text{UCNP@CB}[n]\text{@MB}$  and  $\text{UCNP@CB}[n]\text{@PYY}$  ( $n = 6$  and  $7$ ) nanohybrids formed exclusion complexes *via* the interaction of the CB carbonyl free portal and the dyes to achieve efficient energy transfer from the UCNP to the dyes. Finally, they discussed the singlet oxygen generation of  $\text{UCNP@CB}[7]\text{@MB}$  under NIR excitation (980 nm).

Subsequently, they used an efficient cementing strategy to combine  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  perovskite nanoparticles and naked  $\text{NaYF}_4\text{:Yb}^{3+}$ ,  $\text{Tm}^{3+}$  nanoparticles to construct the near-infrared excited up-conversion perovskite nanohybrid nanoparticles by the binding of CB[7]'s two portals (Fig. 25).<sup>46</sup> Therein, methylammonium bromide (MABr), adamantylammonium bromide (ADABr),  $\text{PbBr}_2$  and CB[7] were mixed together and

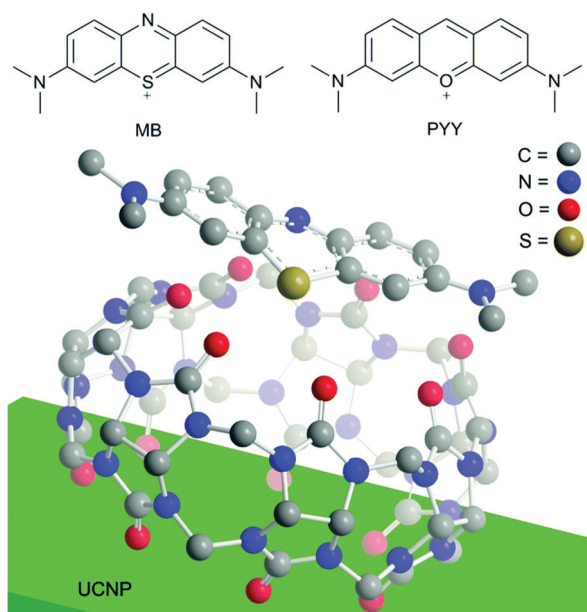


Fig. 24 Schematic illustration of the interaction between the UCNPs, CB[7] and MB.<sup>45</sup> Copyright 2015, Royal Society of Chemistry.

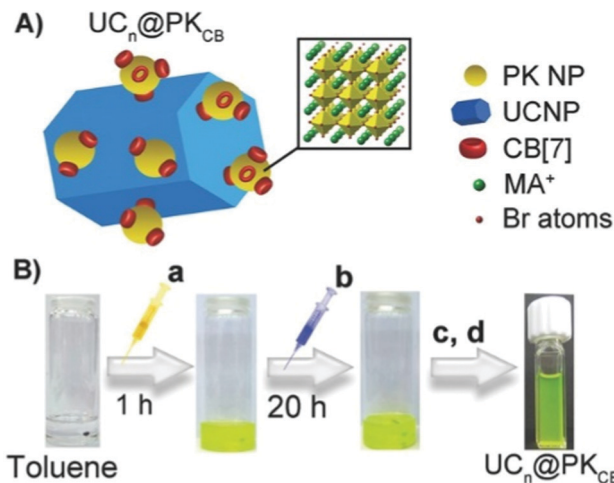


Fig. 25 Schematic illustration of (A) the proposed structure for the  $\text{UC}_n\text{@PK}_{\text{CB}}$  nanohybrids; (B) the preparation process of the  $\text{UC}_n\text{@PK}_{\text{CB}}$  toluene solution.<sup>46</sup> Copyright 2016, Wiley Online Library.

stirred in toluene solution. Then, the DMF solution of UCs was added to the above solution during the process, followed by precipitation and separation. This construction method realized the energy transfer from UCs to the perovskite under near-infrared excitation, and the important thing is that the transfer efficiency reached 100%. Furthermore, multiphoton laser scanning confocal microscopy was used to evaluate luminescence lifetime and visualize the homogeneity of the emission of the assembly.

Yang *et al.*<sup>47</sup> constructed a pH-responsive and near-infrared (NIR) excited oral drug delivery system based on phosphoryl-functionalized pillar[5]arene (PP5) and  $\beta\text{-NaYF}_4\text{:Yb/Er}$  upconversion nanoparticles (UCNPs) *via* a facile ligand exchange method. Rhodamine B (RhB) was loaded in this system as a kind of drug model compound through the host-guest interaction for exploring the stability and optical properties of the system under different physiological pH conditions.

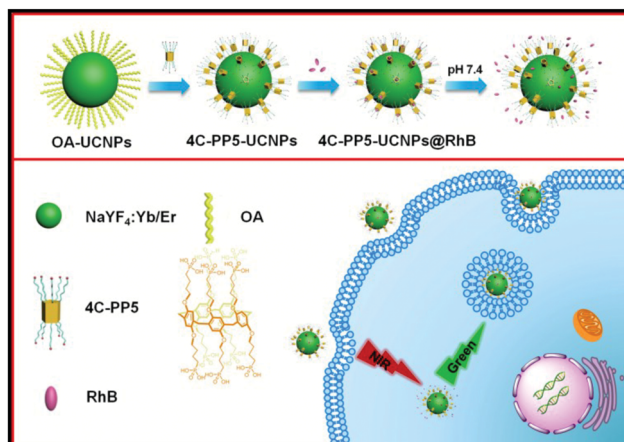


Fig. 26 Schematic illustration of the construction of the 4C-PP5-UCNPs@RhB nanosystem and UCL cell imaging.<sup>47</sup> Copyright 2018, Royal Society of Chemistry.



Subsequently, cell imaging experiments were carried out and was evaluated by both an anti-inflammatory drug named 5-amino-salicylic acid (5-ASA) and RhB loaded in the system under the excitation of a 980 nm laser (Fig. 26).

Li and Yi *et al.*<sup>48</sup> reported a simple, fast and efficient method for the synthesis of water-soluble UCNPs (Fig. 27), where adamantane acetic acid and upconversion nanoparticles ( $\text{NaYF}_4:18\%\text{Yb}, 2\%\text{Er}$ ) were used to prepare adamantane acid-modified upconversion nanoparticles (UCNPs-Ad) through a thermal decomposition procedure. Then UCNPs-Ad was dispersed in a  $\text{CHCl}_3/\text{H}_2\text{O}$  mixed solution, and  $\beta$ -CD was added to the assembly with the adamantane on the surface of UCNPs-Ad for drawing UCNPs to the water phase. It is noteworthy that the assembly exhibited not only good bioimaging capabilities to collect 520–560 nm light in the cell through the excitation of near-infrared light at 980 nm but also low cytotoxicity. This kind of water-soluble UCNP constructed through the host-guest interactions will provide a new way for the application of UCNPs' luminescence in biology.

Early detection of changes in the structural and functional properties of biological living systems plays a key role in human health.<sup>49</sup> For instance, mercury ion ( $\text{Hg}^{2+}$ ), a highly toxic ion, accumulation in the human body can cause serious nervous system damage. Therefore, it is of great significance to monitor  $\text{Hg}^{2+}$  in the human body efficiently and sensitively. However, the shortcomings of traditional luminescent materials such as difficult to be distinguished from background fluorescence in living bodies due to their short emission lifetime (less than 100 ns), the inability to penetrate human skin by UV excitation, high cytotoxicity, and a short circulation half time restrict their biological applications. Zhang *et al.*<sup>50</sup> combined CD and water-soluble UCNPs *via* the host-guest interaction between  $\alpha$ -CD and oleic acid-coated UCNPs ( $\text{NaYF}_4:20\%\text{Yb}, 1.8\%\text{Er}, 0.5\%\text{Tm}$ ). Subsequently, the UCNPs were loaded with thiazole derivatives

responsive to  $\text{Hg}^{2+}$ , and their luminescence intensity ratio ( $I_{540}/I_{803}$ ) at 540 nm and 803 nm was used as the detection signal under NIR excitation. Without  $\text{Hg}^{2+}$ , the fluorescence at 540 nm disappeared owing to the luminescence resonance energy transfer (LRET) process between UCNPs and the triazole dye. When the amount of  $\text{Hg}^{2+}$  increased, the intensity at 540 nm gradually recovered, which was thus applied to  $\text{Hg}^{2+}$  detection in living cells (Fig. 28).

Photodynamic therapy (PDT) is a Food and Drug Administration (FDA)-approved cancer treatment which could generate reactive oxygen species (ROS), especially singlet oxygen ( $^1\text{O}_2$ ), that are toxic to the cancer cells by light sensitive photosensitizers (PSs) under light irradiation.<sup>51</sup> However, most of the PSs are excited by visible light or even ultraviolet (UV), have poor tissue-penetration capacities and could produce photodamage. This greatly hampers the application of PDT to treat large or internal tumors. Zhou and Wei *et al.*<sup>52</sup> modified  $\text{COOH-}\beta$ -CD onto the UCNP surface *via* the coordination between the  $\text{COOH}$  group and the Ln (III) ions as well as the assembly of adamantane modified phthalocyanine (Ad-ZnPc) with  $\beta$ -CD (Fig. 29). Most importantly, the resonance energy transfer (FRET) process was achieved from UCNPs to ZnPc which could produce  $^1\text{O}_2$  under NIR (980 nm) excitation to show PDT activity towards the cancer cells *in vitro*.

A common problem of PDT is the low accumulation of contrast agents in the lesion area and high uptake in the reticuloendothelial system (RES) which could be improved through the formation of the assembly of nanoparticles. However, the uncontrolled assembly also occurs in the liver and spleen due to the absorption of nanoparticles by the RES, which may result in more serious health hazards and a higher bio-imaging background hampering the clinical applications. Among all the controlled methods, photo-control with relatively high spatial and temporal accuracy was favored by scientists, but it is still a challenge because of the light damage from the UV excitation of most of the PSs.<sup>53</sup> Zhang *et al.*<sup>54</sup> used azobenzene-modified UCNPs (10%Y, 25%Yb, 0.5%Tm@NaGdF<sub>4</sub>) and  $\alpha$ -CD-modified down-conversion nanoparticles (DCNPs:

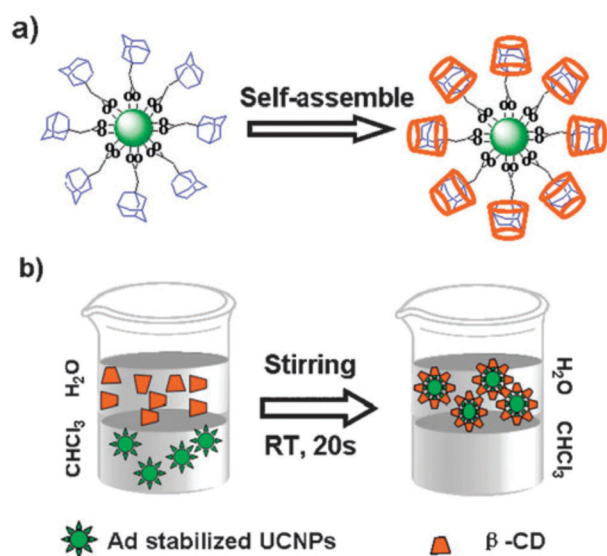


Fig. 27 Schematic illustration of (a) the construction of a supramolecular assembly and (b) phase transfer from the chloroform phase to the aqueous phase.<sup>48</sup> Copyright 2010, Royal Society of Chemistry.

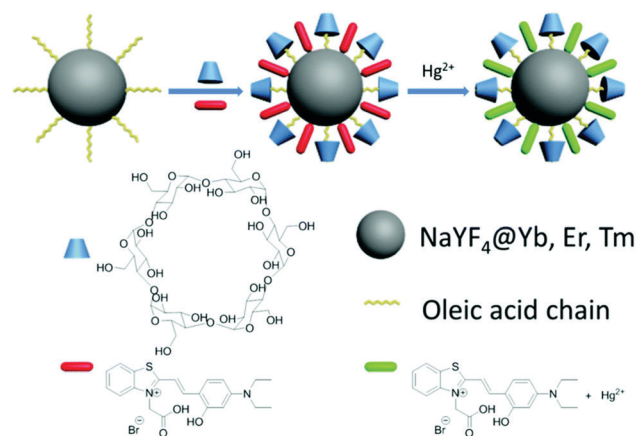


Fig. 28 Schematic illustration of the construction of UCNPs' supramolecular assembly and the detection  $\text{Hg}^{2+}$ .<sup>50</sup> Copyright 2016, Royal Society of Chemistry.

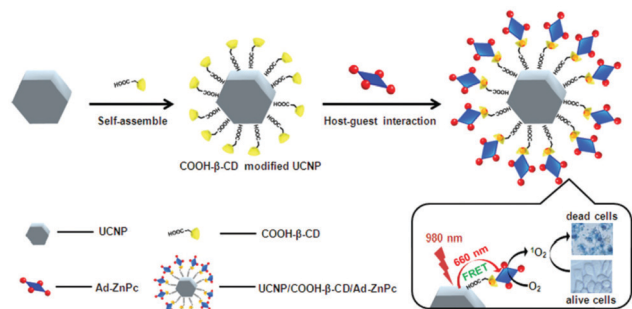


Fig. 29 Schematic illustration of the construction of the COOH-β-CD/UCNPs/Ad-ZnPc supramolecular assembly and the NIR-triggered PDT through FRET.<sup>52</sup> Copyright 2016, Royal Society of Chemistry.

5%Nd@NaGdF<sub>4</sub>) through the host-guest interaction of CD and azobenzene to construct a NIR (980 nm) excitation supramolecular assembly in which assembly and disassembly was controlled by the conversion of the *trans* and *cis* isomers of azobenzene (Fig. 30). The 1060 nm emission with high tissue permeability and low tissue autofluorescence interference in second near-infrared (1000–1700 nm) was realized by exciting DCNPs with 808 nm excitation. This supramolecular assembly way can greatly increase the time for the nanoprobe to accumulate in the tumor compared with that of the single-injection way. Meanwhile, the residence time in the liver can be controlled through the disassembly with 980 nm irradiation which reduces the biological toxicity.

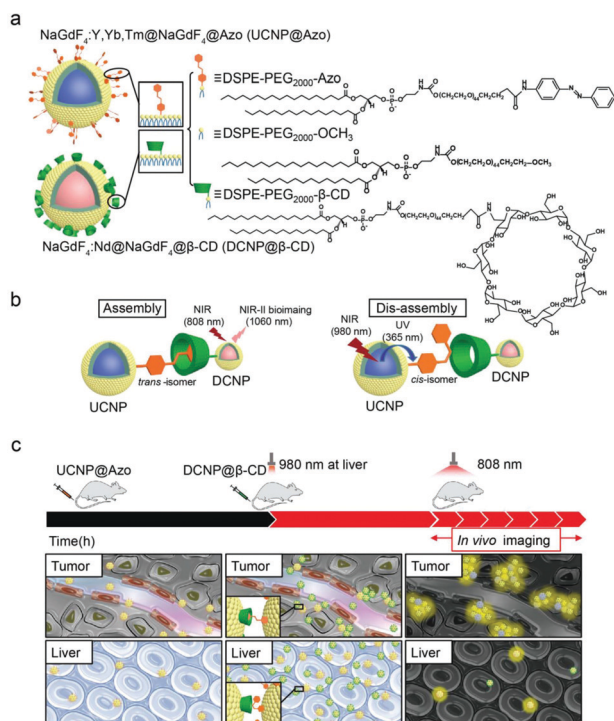


Fig. 30 Schematic illustration of (a) the construction of azobenzene (Azo) modified NaGdF<sub>4</sub> UCNPs and β-CD modified NaGdF<sub>4</sub> DCNPs; (b) the photo-controlled supramolecular assembly and disassembly; (c) NIR imaging *in vivo*.<sup>54</sup> Copyright 2018, Wiley Online Library.

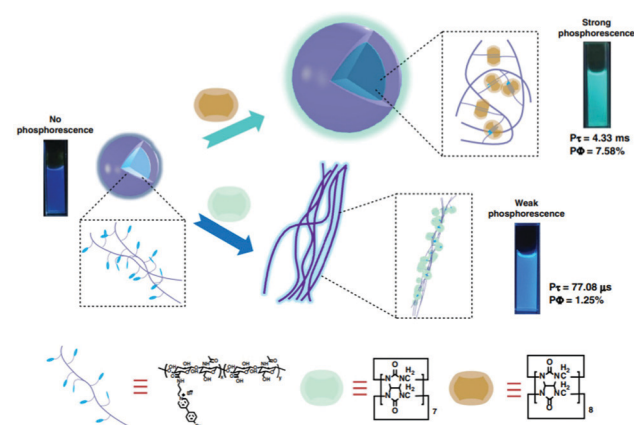


Fig. 31 Schematic illustration of the behavior of CBs/HA-BrBP phosphorescent supramolecular polymers in aqueous solution.<sup>55</sup>

More recently, we reported a supramolecular assembly based on up-conversion nanoparticles and successfully applied to phosphorescence cell imaging for cancer cell targeting in water.<sup>55</sup> This phosphorescent supramolecular assembly with a long lifetime and high quantum yield was first constructed from the host CB[8] and 4-(4-bromophenyl)pyridine-1-ium bromide (BrBP) phosphor modified tumor-targeted hyaluronic acid (HA) polymer chain which realized the phosphorescence imaging of cancer cell mitochondria in near-infrared through the co-assembly with the UCNPs in aqueous solution (Fig. 31).

## 6. Summary and outlook

From the above study, we can see that the luminescent lanthanide-macrocycle supramolecular assembly relies on the bonding of functionalized macrocyclic host or guest molecule derivatives to rare earth ions, and this multidimensional and multi-level assembly provides an intelligent control of light, pH, temperature, *etc.* In addition, due to the rich energy levels of lanthanides and the transitions between different energy levels, lanthanides show many unique and excellent luminescence properties, such as long-lived excited states, relatively narrow emission, and large Stokes shift and thus are widely used in biosensing, biological imaging, anti-counterfeit and other aspects. The use of the supramolecular assembly means to combine macrocyclic compounds with lanthanides will endow luminescent materials with more excellent performance, which not only simplifies the complicated synthesis steps, but also improves the luminous efficiency, the reduction of photobleaching, the material stability and recyclability, and the dynamic and reversible control performance of lanthanide luminescent materials. Therefore, the combination of macrocycles and lanthanide elements to construct supramolecular luminescent materials has become a frontier hotspot in this field. We can believe that with the functional design and synthesis of various macrocyclic compounds and guest molecule derivatives, supramolecular assemblies coordinated with rare earth ions will show more

applications in multi-color luminescence, smart materials, cell imaging, fluorescence sensing, etc.

## Conflicts of interest

The authors declare no competing financial interest.

## Acknowledgements

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