Photoluminescent Crown Ether Assembly

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Contents

5.1 Introduction

Crown ether, as cyclic compound composed of several repeating ether units, is discovered by the winner of the Nobel Prize Pedersen in 1967 [1]. Subsequently, the concepts of supramolecular chemistry and host-guest chemistry were put

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forward. Traditional crown ether, containing repeating oligo-ethylene oxide units in a cyclic array, has high ability to bind alkali metal ions, alkaline-earth metals ions, ammoniums, and primary alkylammonium salts. Previously, researchers focused their attention on the molecular recognition based on crown ether. Since Stoddart first reported the complexation of bismetaphenylene-32-crown-10 derivative with paraquat and diquat in 1987 [2], the multifunctionalized supramolecular assemblies based on crown ether and organic guests have been fabricated. Nowadays, various synthetic novel crown ethers, which possess multi-cavity structures and multi-complexation modes, have been successively designed and synthesized to enrich their functions and applications through several decades of development, such as supramolecular polymers [3], artificial molecular machines [4], and drug delivery systems [5].

Photoluminescence is among the most fascinating characteristics of functional materials. Luminescent materials are applied for a wide variety of applications, such as chemical sensor [6], bio-imaging [7], drug delivery [8], phototherapy [9], and cell labeling [10]. Therefore, the integration of fluorophores into crown ether moieties is advantageous to construct specific responses or develop multistimuli-responsive photoluminescent crown ether assembly. Crown ether often reversibly binds guest molecules with high selectivity and could be fine-tuned chemically. So, the assemblies, based on crown ether, are sensitive to environmental changes and external stimuli like temperature, pH, light, or competitive guests. These features were successfully utilized to produce more sophisticated functions. In this chapter, we aim to illustrate the general concepts and structure-function-application relationships of photoluminescent crown ether assembly. First, we discuss some general luminescence system based on crown ether and organic dyes. Pseudorotaxanes and pseudopolyrotaxanes based on lanthanide luminescence are presented in the second part. In the last section, we highlight recent developments of supramolecular polymers based on crown ether with photoluminescence behavior. We hope to shed some light on the future work based on crown ether and inspire continuous endeavors in this emerging and exciting research area.

5.2 Luminescent Assemblies Based on Organic Dyes

The idea of introducing fluorophore into crown ether to construct fluorescent supramolecular materials has attracted tremendous attention in the past few decades because of their wide applications in sensors, fluorescence probes, organic light-emitting diodes, and solid-state lighting. In the following section, typical examples are used for briefly discussion and introduction of the construction of the luminescent assemblies based on crown ether and organic dyes.

Mechanically interlocked molecules have been investigated extensively due to their switchable ability in response to various external stimuli. In recent years, crown ether has always been used to construct the mechanically interlocked systems due to its easy modification [11, 12]. In 2012, Qu and coworker [13] designed and synthesized a bistable [2]rotaxane with high-contrast fluorescence output (Fig. 1a). The molecule shuttle, combining two ferrocene (Fc) groups as electron donors and DB24C8, could move between the dibenzylammonium (DBA) and N-methyltriazolium (MTA) recognition sites. The fluorescence of the 4-morpholin-naphthalimide (MA) stopper could be switched off when the shuttle moved to the MTA sites, suggesting a strong photoinduced electron transfer (PET) process from Fc to the excited MA, whereas the fluorescence of MA was switched on through controlling the shuttle to bind with DBA unit. Moreover, the shuttling motion of the molecule shuttle could be chemically dual-mode driven by not only pH stimuli but also addition/removal of the fluoride anion, revealing that the system has a potential application as a novel kind of fluorescent molecular sensing device. In 2013, a continuous work was reported by them [14]. They designed the dual-mode operation of a ferrocene-based bistable [1]rotaxane (Fig. 1b) so that a fluorescent emission "active" mode of the system could be controlled by the acid/

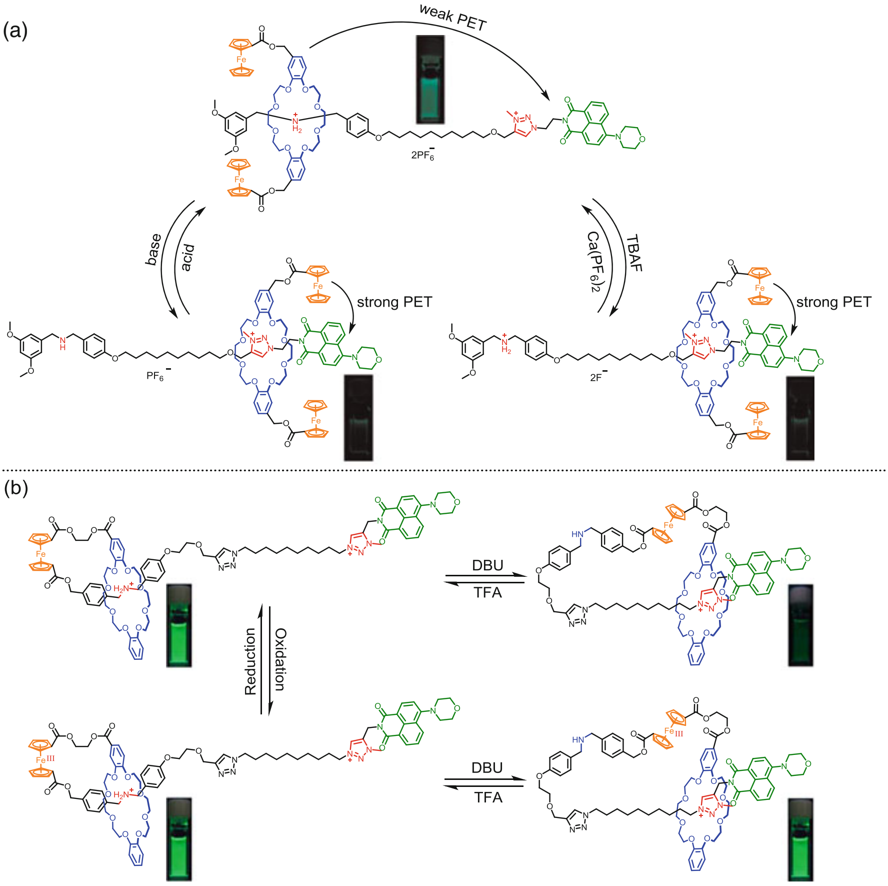

Fig. 1 Schematic illustration of the shuttling movement. (**a**) A bistable [2]rotaxane system [13]. (**b**) A bistable [1]rotaxane system [14]

base stimuli whereas the “silent” mode of the system could be regulated by the oxidation/reduction reaction of ferrocene unit. This study laid a solid foundation for the fabrication of advanced logic circuits with memories or sequential functions.

Most of the molecular machines with switchable fluorescent output were studied in the solution phase, which limited their practical applications. Therefore, Qu et al. [15] introduced the above bistable [2]rotaxane system into SiO_2 nanoparticles because of their chemical stability and optically transparent features (Fig. 2b). Intriguingly, the fluorescence intensity could be reversibly modulated by the acid/base stimuli in the solid state of the SiO_2 nanoparticles as well as in the solution state, thus paving a bright avenue for the construction of smart stimuli-responsive surfaces with tunable functions. Subsequently, they grafted the [2]rotaxane system into a polymer chain again and successfully constructed a fluorescent switch based on a polyrotaxane system, further expanding the application fields of solid-state fluorescent sensors (Fig. 2c) [16].

White-light-emitting devices have drawn wide attention in recent years, and these devices are now being considered to be a promising solid-state lighting source [17]. Tian and coworkers [18] reported a bistable [2]rotaxane with orthogonally tunable multicolor fluorescence features including white-light emission via combining a rotaxane-type molecular switch and traditional fluorescent switch (Fig. 3). A blue-light-emitting [2]rotaxane was constructed by N-propyl-1,8-naphthalimide (PNA) as the stopper and two Fc electron donor-decorated DB24C8 as the molecule shuttle. With the increase of base, the blue fluorescence intensity of the [2]rotaxane was continuously strengthened due to the weakened PET process between Fc unit and PNA group, accompanied by the decrease of yellow fluorescence intensity of the perylene bisimide derivative (PBI) owing to the aggregation of PBI molecule. Therefore, the emission color, containing white-light emission, could be reversibly regulated by simply changing pH. These systems provided a reliable method for the construction of multicomponent tunable fluorescence molecular systems.

Mechanochemistry, activated by mechanical force instead of conventional stimuli (i.e., pH, light, and heat), has been widely studied in the past few years. However, the conventional mechanophores activated by cleaving covalent bonds required a relatively high activation energy, and the process was usually irreversible [19]. Therefore, a linear polyurethane containing the rotaxane-based supramolecular mechanoluminophore with reversible on/off switching of its photoluminescence properties was reported by Weder and coworkers [20]. As shown in Fig. 4, the [2]rotaxane was fabricated via a 4,7-bis(phenylethynyl)-2,1,3-benzothiadiazole (BTH)-decorated 1,5-dinaphtho[38]crown-10 cycle and an electron-poor 1,4,5,8-naphthalenetetracarboxylic diimide (NpI) motif. Tri(*p*-*tert*-butylphenyl) phenylmethane stoppers were introduced into the system to lock in the structure. The free crown ether cycle could emit bright fluorescence, while the solution of [2]rotaxane showed no emission because the fluorescence of the BTH unit was quenched by the NpI moiety. Then, the [2]rotaxane was grafted into polymer chains through the reaction of two hydroxyl groups sites modified on the cycle and the

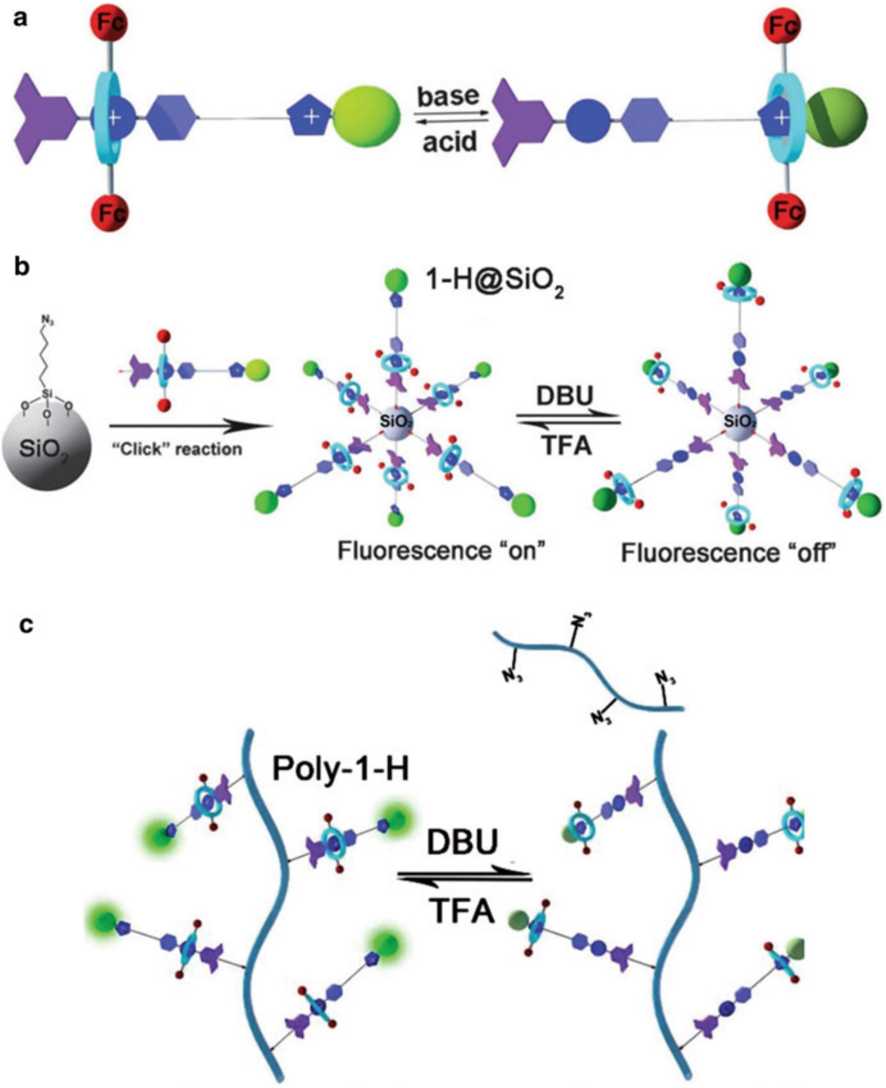

Fig. 2 Schematic illustration of (**a**) a bistable [2]rotaxane molecular shuttle, in which the relative shuttling movement could be driven by pH changes. (**b**) Immobilization of the [2]rotaxane onto SiO_2 nanoparticle surfaces [15]. (Adapted with permission [15]. Copyright 2015, Royal Society of Chemistry.) (**c**) Introduction of the [2]rotaxane into polymer chains [16]. (Adapted with permission [16]. Copyright 2016, Royal Society of Chemistry)

dumbbell with 4,4′ -methylenebis-(phenylisocyanate). The polymer chains contained [2]rotaxane were further made into thin films. Intriguingly, the films display the mechanoluminophore functions. The films exhibited the characteristic fluorescence of the BTH with the stress increase, owing to the spatial separation of

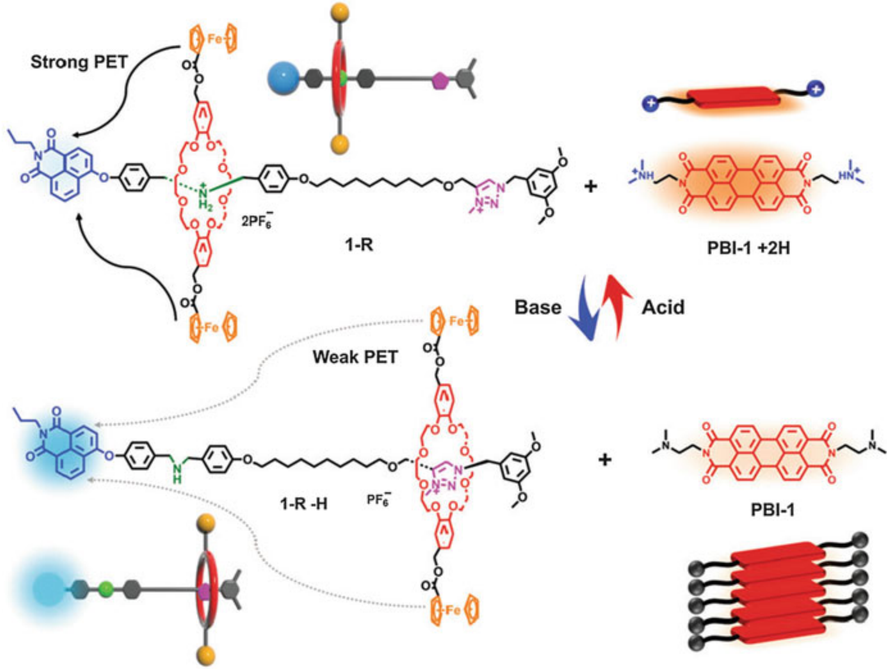

Fig. 3 Schematic illustration of the bistable [2]rotaxane with tunable multicolor fluorescence features [18]. (Adapted with permission [18]. Copyright 2018, Royal Society of Chemistry)

the BTH and NpI. Moreover, the activation process was reversible. As soon as the stress was released, the fluorescence of films was switched off.

As a continuous work, they reported another mechanoluminophore system taking advantage of the supramolecular approach, which the optical signal generated could readily be tailored by a simple and rational method (Fig. 5) [21]. Three mechanoresponsive polyurethanes containing blue-, green-, and orange-light-emitting rotaxanes were constructed through varying only the fluorophore (i.e., pyrene, anthracene, or 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) incorporated in the crown ether cycle unit. The photoluminescence of the fluorophores in the systems was suppressed by the NpI group when the systems were in the unactivated state, whereas the fluorescence of each of the fluorophores was switched on and exhibited strong optical signal upon the application of mechanical force, suggesting that each polymer could exhibit instantly reversible, strain-dependent on/off switching of its photoluminescence. In addition, the photoluminescence color containing white-light-emitting of such motifs could be successfully tailored by variation of the fluorophore and also by combining several mechanophores in one system. The results demonstrated that adaptability is a key advantage of supramolecular approaches to construct mechanoresponsive materials.

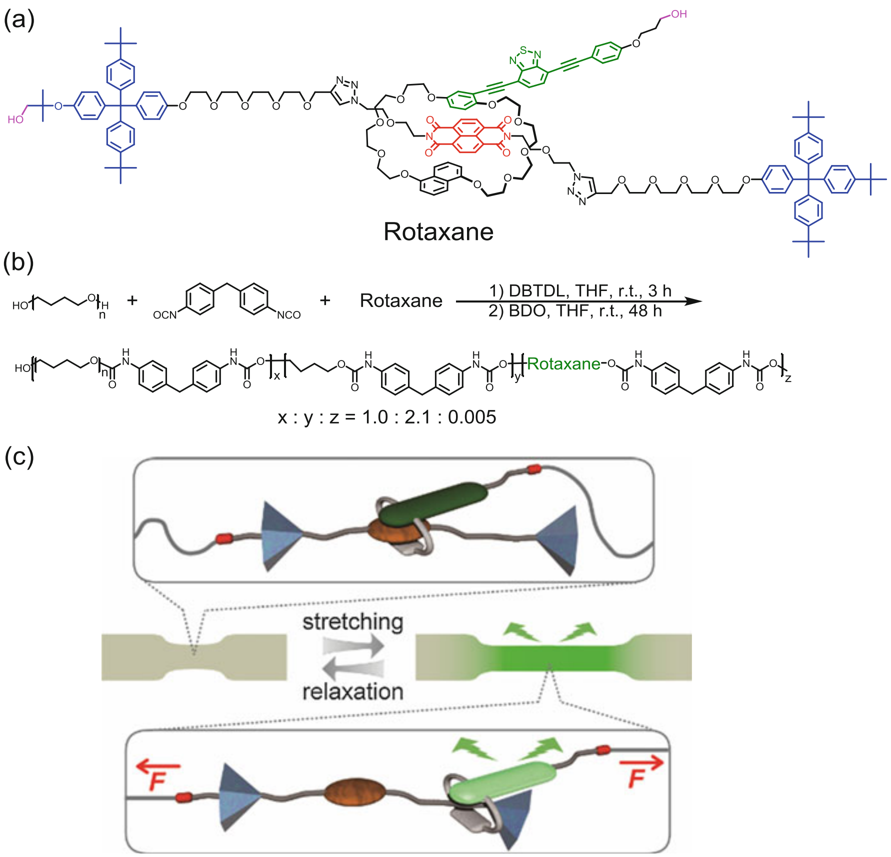

Fig. 4 (**a**) Molecular structure of rotaxane. (**b**) Synthesis of the mechanophore-containing polyurethane. (**c**) Schematic illustration of rotaxane-based mechanoluminophores [20]. (Adapted with permission [20]. Copyright 2018, American Chemical Society)

5.3 Crown Ether Assembly Based on Lanthanide Metal

Among the various functional materials, lanthanide-luminescence-based ones have attracted considerable attention in recent years, owing to their unique photo-physical characteristics [22–25]. Their characteristic sharp emission and clearly defined bands have been applied within a number of technologies, such as organic light-emitting diodes [26], sensors [27], novel display devices [28], and biological applications [29]. In addition, they could also be used to the time-gated detection techniques due to their long lifetimes [30]. The obvious features of lanthanide metals make them ideal and highly desirable candidates for integration into luminescent supramolecular assembly, resulting in the emission signals that could be modulated by an external stimulus, including ions, pH, light, temperature, vapors, redox, small molecules, etc.

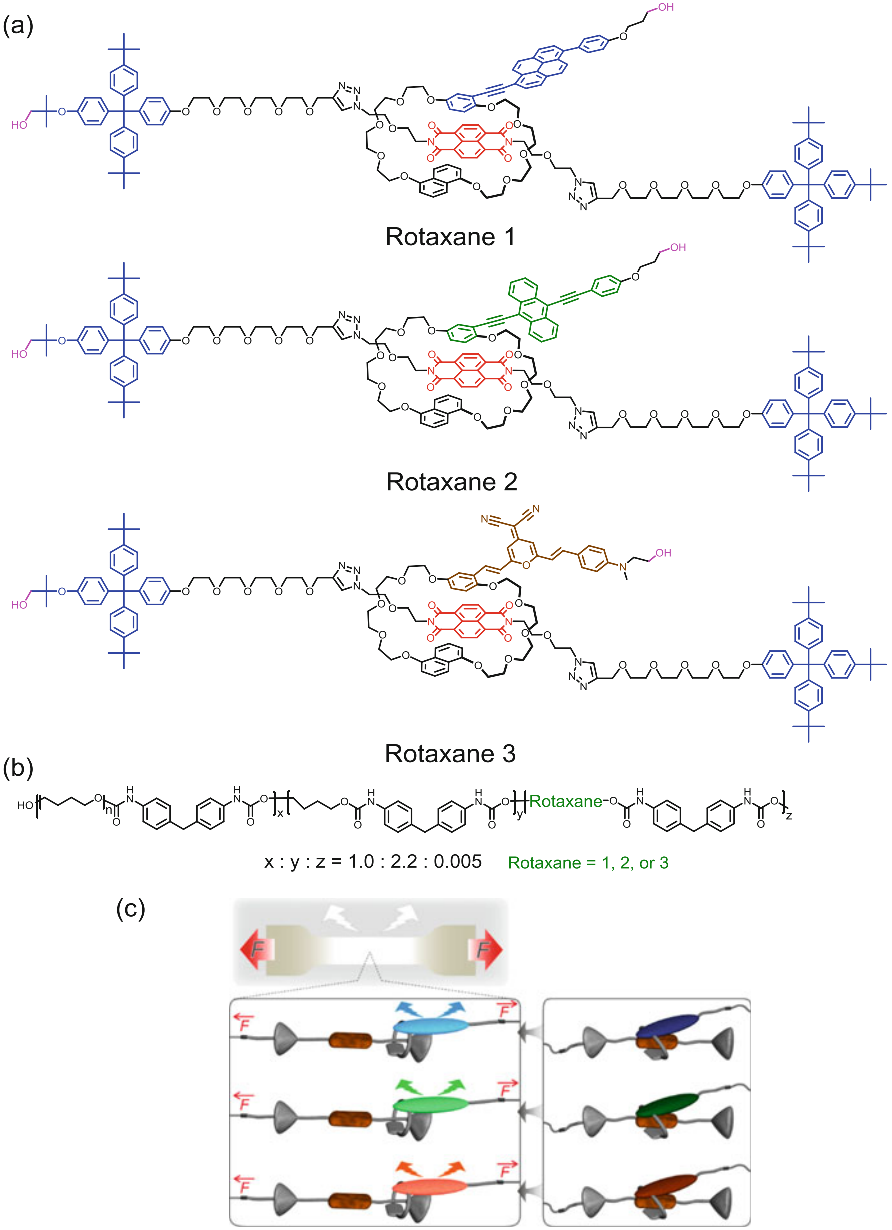

Fig. 5 (**a**) Molecular structures of rotaxanes 1, 2, 3. (**b**) Molecular structures of the mechanophore-containing polyurethanes. (**c**) Schematic illustration of rotaxane-based mechanoluminophores with white-light-emitting characteristic [21]. (Adapted with permission [21]. Copyright 2019, American Chemical Society)

Therefore, the elaborate designed supramolecular assembly containing lanthanide metals could function as molecular switches, sensing platforms, and molecular machines. In the following part, we will briefly introduce the recent progresses on functions and applications of the lanthanide luminescent crown ether assembly.

5.3.1 A Highly Selective Luminescent Sensor

How to build a platform for the sensitive and selective detection of potassium to achieve the accurate clinical disease diagnosis (such as hypertension, stroke, and seizures) is still a considerable challenge.

Pierre [31] reported a luminescent sensor for the time-gated detection of K^+ with enhanced selectively based on a diaza-18-crown-6 and Tb^{3+} ion system (Fig. 6). They chose azaxanthone as the antenna since it was demonstrated to be an efficient sensitizer of Tb^{3+}. Then, the Tb·DOTA chelate and azaxanthone were separated via a diaza-18-crown-6 coordination site and flexible linker. In the "off" state, the fluorescent intensity of Tb was weak, deriving from large separation between the Tb^{3+} and its sensitizing azaxanthone. Capturing K^+ by the crown ether coordination site favors a cation-π interaction with the aryl ether unit, resulting in the formation of assembly where the antenna is significantly closer to Tb^{3+} center. Consequently, the luminescence of Tb was increased due to the efficiency of energy transfer from the azaxanthone to the Tb. Moreover, the system showed excellent selectivity for K^+, with a 93-, 260-, 105-, and 61-fold selectivity over Na^+, Li^+, Mg^{2+}, and Ca^{2+}. Furthermore, the luminescence intensity at 545 nm was increased 22-fold by the addition of 10 mM K^+ (the clinically useful range of K^+ was 0–10 mM), and the signal could be stable for several hours.

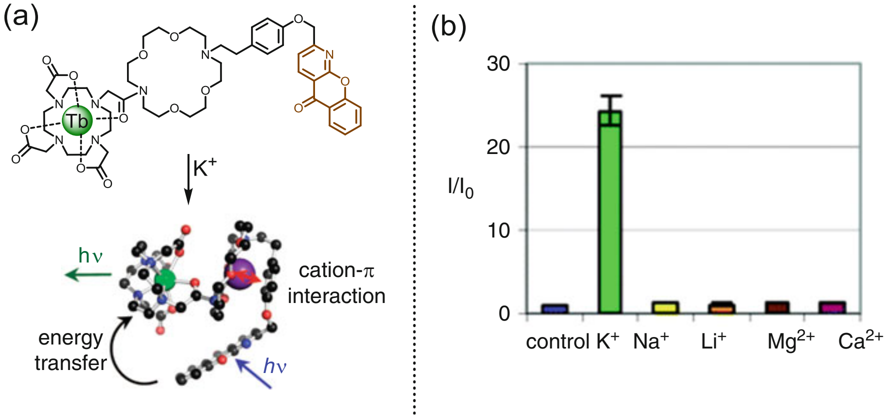

Fig. 6 (**a**) Schematic illustration of the K^+ sensor based on a diaza-18-crown-6 and Tb^{3+} complex. (**b**) Selectivity of the complex to various cations [31]

The group of Tang [32] has also focused on developing sensing systems based on crown ether and lanthanide metal, allowing for highly selective detection of Hg^{2+}. They designed and synthesized a benzo crown ether host, 4,5-bis{[(2′-benzylaminoformyl)-phenoxyl]-methyl}benzo-15-crown-5. The zigzag coordination polymeric chains were formed through the synergistic effect of the coordination interaction with Tb^{3+} and the π-π interaction between the phenyl groups of the two side arms of the neighboring hosts (Fig. 7). The Tb^{3+} complex exhibited excellent luminescence at 490, 546, 584, and 619 nm, corresponding to $^5D_4 \rightarrow {}^7F_n$ (n = 6, 5, 4, 3) transition. Moreover, the complex showed a highly selective and sensitive response to Hg^{2+}. The results showed that the luminescence emission of Tb^{3+} complex was switched off by the addition of Hg^{2+}, which not just because the crown ether will bind with Hg^{2+} but also because the fluorescent reporter played a vital role in the binding with Hg^{2+}. Therefore, the energy transfer from the ligand to Tb^{3+} was prevented. While the alkali, alkaline-earth, and transition metal cations (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+, Cd^{2+}, Mn^{2+}, Zn^{2+}, and Pb^{2+}) were added into the Tb^{3+} complex solution, the fluorescence emission intensity of the Tb^{3+} was slightly influenced by these cations. This Hg^{2+}-recognized system based on lanthanide metal and crown ether provided a novel way to develop a range of chemosensors for the detection of heavy metals.

Similar investigations were reported by Gunnlaugsson [33, 34] and Wong [35]. Gunnlaugsson and coworkers [33] constructed novel luminescent switches through

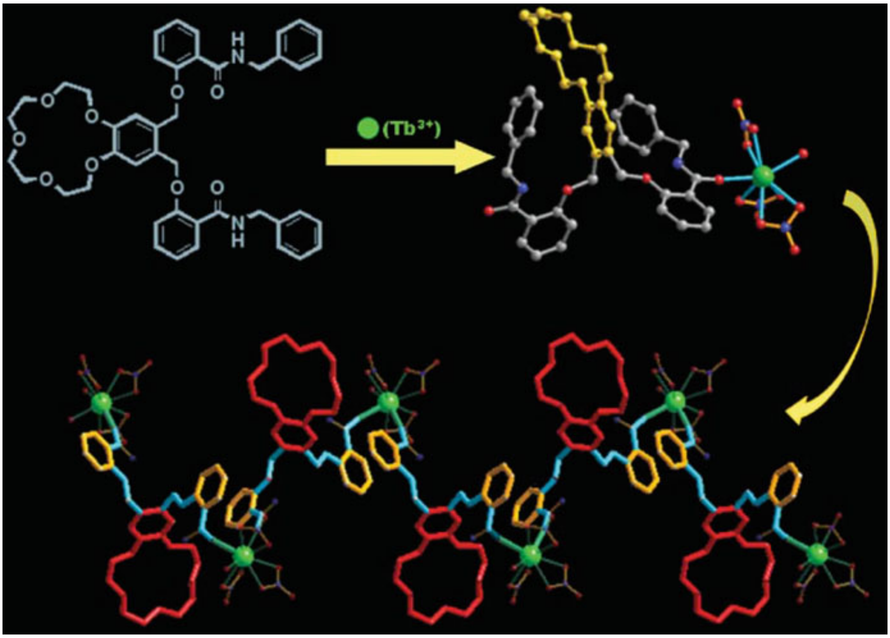

Fig. 7 Molecular structures of crown ether-containing ligand and the structure of the Tb^{3+} complex [32]. (Adapted with permission [32]. Copyright 2010, Royal Society of Chemistry)

the combination of cyclen and diaza-aromatic crown ether (Fig. 8a). The aromatic crown ether not only could work as receptors for Na^+ and K^+ but also could act as antenna for the sensitization of the lanthanide ions. While the pH of the Tb^{3+} complex solution was 7.4, the system could detect accurately Na^+ and K^+ upon the change of the fluorescence emission intensity of the Tb^{3+} complex. In related work by the same group [34], a novel stable dinuclear Eu^{3+} conjugating through tethering a mono-aza-18-crown-6 moiety to a cyclen macrocyle was designed as a luminescent lanthanide sensor for dicarboxylates (Fig. 8b). The sensor showed its ability to bind small dicarboxylic acids such as aspartic, malonic, succinic, and glutaric acids in pH 6.5 solutions, while just malonic acid gave rise to selective Eu^{3+} luminescence enhancements, as the emission intensity was reduced for the other acids. This work provides new thought for the development of luminescent sensing of other biologically important structures. Wong and coworkers [35] also

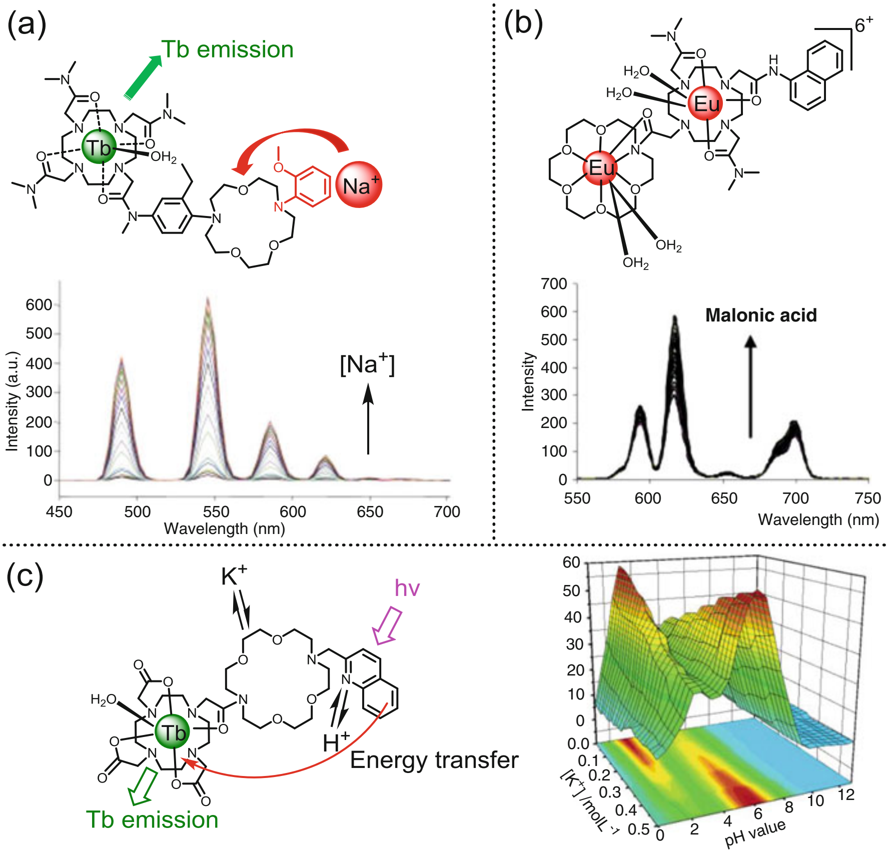

Fig. 8 (**a**) Molecular structure of the Na^+ and K^+ sensors based on a Tb^{3+} complex [33]. (**b**) Structure of fluorescence sensor for dicarboxylates [34]. (**c**) Structure of fluorescence probe for the dual-component recognition of H^+ and K^+ [35]

reported a luminescent Tb^{3+} complex with pendant quinoline-alkylated diaza-18-crown-6 (Fig. 8c). The system showed dual-component recognition of concentrations of H^+ and K^+ at four independent pH ranges, especially in the physiological pH window. In addition, it exhibited pH- and $[K^+]$-independent long-lived lanthanide luminescent lifetimes in aqueous solution.

Recently, Li and coworkers [36] constructed a novel luminescent and self-calibrating sensor for K^+ constructed by Ln^{3+}-directed supramolecular self-assembly through the coordination of Eu^{3+} and Tb^{3+} with a crown-connected bis-terpyridine (Fig. 9). The 18-crown-6 moiety could efficiently regulate the lanthanide luminescence behavior through the binding of potassium ions via K^+-crown cation-π interaction, resulting that the supramolecular assembly could be used as a potential luminescent sensor for selective and quantitative detection of K^+. Moreover, the results also showed that the K^+ concentration was linearly correlated with the emission intensity ratio of $^5D_4 \rightarrow {}^7F_5$ transition (Tb^{3+}) to $^5D_0 \rightarrow {}^7F_2$ transition (Eu^{3+}) of the Eu^{3+}/Tb^{3+} assembly and the detection limit was down to 1 μM. Therefore, this luminescent lanthanide supramolecular assembly could open a window for the construction of novel sensing materials.

5.3.2 Luminescent Lanthanide Assemblies Based on Pseudorotaxanes/Pseudopolyrotaxanes

The fabrication of mechanically interlocked supramolecular architectures as integral components of molecular switches, data storage, and sensor is currently an area of

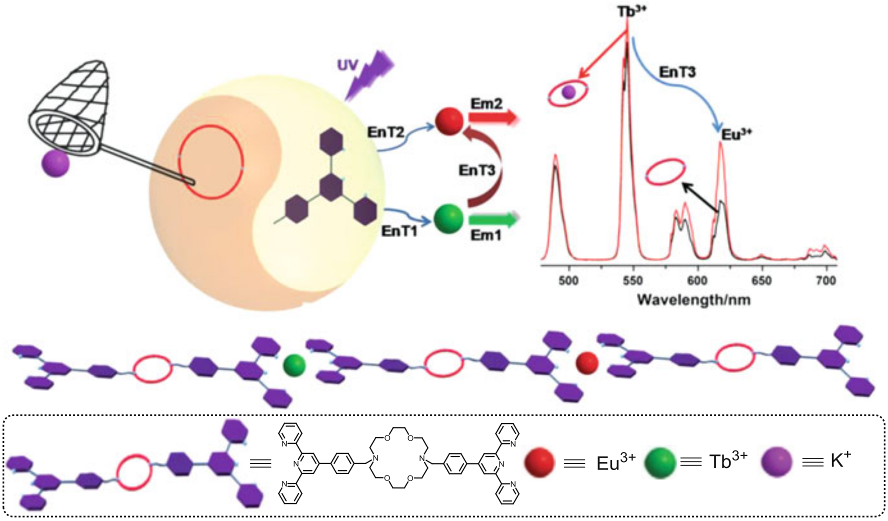

Fig. 9 Schematic illustration of the construction of lanthanide metal complex and its self-calibrating detection of K^+ [36]. (Adapted with permission [36]. Copyright 2018, Royal Society of Chemistry)

intense research activity. Integrating luminescent lanthanide series into these systems will make the spatial configurational change, chemical binding, or triggered molecular motion to be monitored through the change of fluorescent emission intensity. The Beer group [37] design and synthesize an anion-templated assembly of a d–f heterobimetallic [2]pseudorotaxane (Fig. 10). The host molecule possesses two functional moieties, which consists of a transition metal rhenium(I) bipyridyl metal sensitizer and isophthalamide-based anion recognition site. By chloride anion template, the [2]pseudorotaxane was constructed through threading into an axle, containing an imidazolium cation and lanthanide luminescent neodymium complex. The [2]pseudorotaxane could exhibit excellent near IR emission through the energy transfer between rhenium(I) and neodymium metal fragments by exciting the rhenium(I) bipyridyl metal antenna.

With the rapid development of the lanthanide materials, reversible regulation the luminescence of lanthanide complexes has become one of the researching hotspots in molecular switches currently. Recently, our group constructed a supramolecular assembly of tris[2]pseudorotaxane via the coordination of a host molecule and Tb^{3+} ion (Fig. 11) [38]. The host molecule possesses a dibenzo-24-crown-8 (DB24C8), suspending a pyridine-2,6-dicarboxylic acid (DPA) ligand. The DPA can form a stable 3:1 luminescent complex with Tb^{3+} at a high association constant. Therefore, the Tb^{3+} complex, containing three DB24C8 units, could show the characteristic emission of Tb^{3+}. Then, threading of a guest, modifying a dialkylammonium in the ferrocene (Fc), into the DB24C8, the fluorescence emission of the Tb^{3+} complex was significantly quenched, due to an intramolecular photoelectron transfer (PET) process from the Fc units to the DPA moieties. Intriguingly, the luminescence of Tb^{3+} could be reversibly switched on/off by addition of KPF_6 and 18-crown-6 (18C6), attributed to the competitive bonding between DB24C8 and 18C6 with K^+. This new synthetic strategy of an excellent reversible luminescent lanthanide switch through

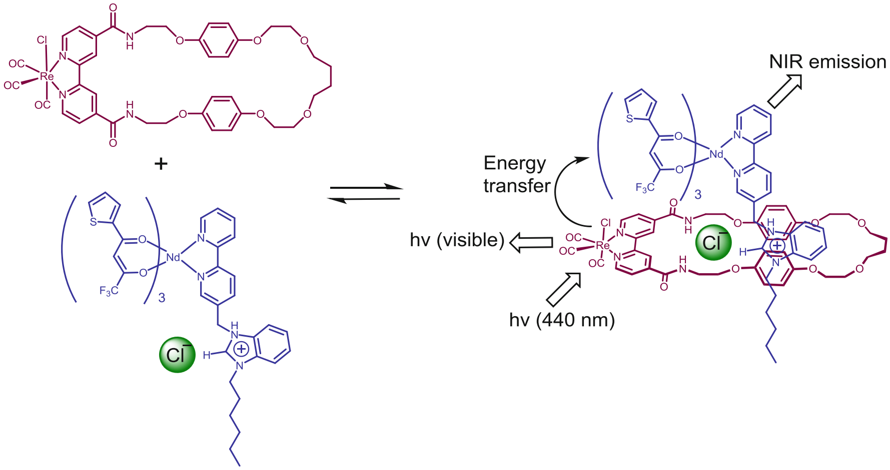

Fig. 10 Schematic illustration of an anion-templated [2]pseudorotaxane assembly. [37]

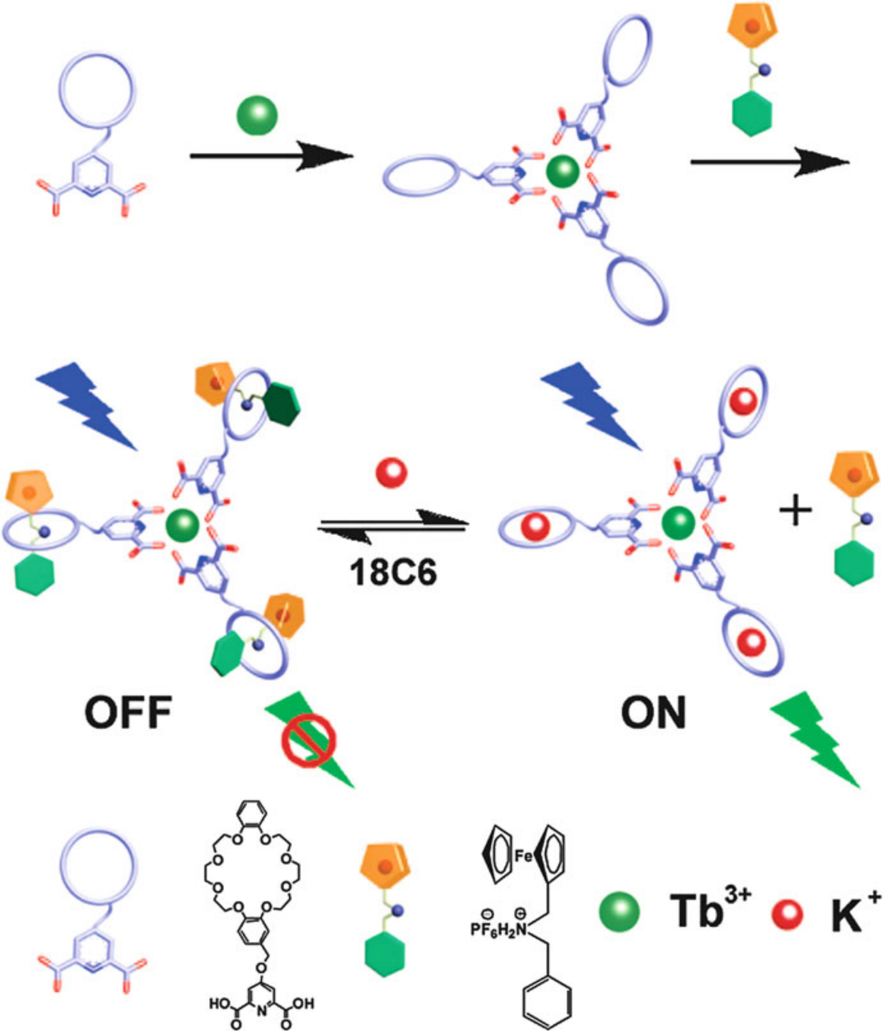

Fig. 11 Schematic illustration of the fabrication of tris[2]pseudorotaxane assembly [38]. (Adapted with permission [38]. Copyright 2008, American Chemical Society)

electron transfer showed potential application in the fabrication of new molecule-based devices.

Then, our group designed a novel kind of [2]pseudorotaxane assembly taking advantage of host-guest binding between DB24C8 derivative, which decorated a terpyridine unit as ligand for lanthanide ions, and fullerene-containing ammonium salt (Fig. 12) [39]. Sensitized by terpyridine, the complex showed strong and unique emission properties of Tb^{3+} ion in the case of the unthread macrocycle. The phenomenon of fluorescence quenching was observed after the addition of

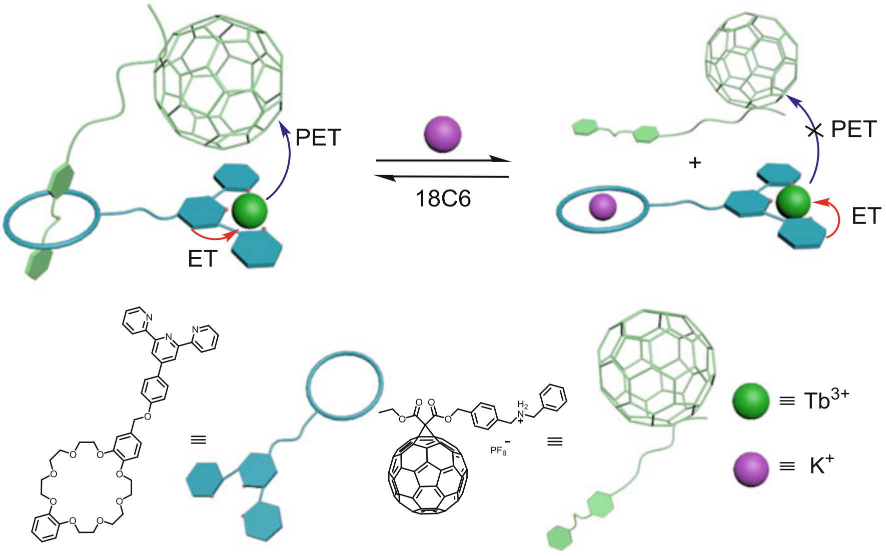

Fig. 12 Competitive bonding-driven reversible luminescent lanthanide switch with the PET-ET processes [39]

fullerene-containing ammonium salt, attributed to an intramolecular PET process from the excited singlet state of Tb^{3+} complex to C_{60} moiety. Similarly to the above findings, the luminescence of [2]pseudorotaxane could be reversibly switched on/off by the alternating addition of K^+ and 18C6.

The capability to operate the structure and function of nanodevices via external stimuli is becoming a most attractive candidate for developing multifunctional materials. Light stimulus represents a preferred external physical and chemical tool for manipulating the function of the materials owing to its unique advantages of instant action, high spatial and temporal resolution, and cleanness. Photochromic materials are known to undergo reversible transformations by light between two states with distinct properties [40–45]. Therefore, the integration of photochromism into various devices has endowed the materials with intriguing photoresponsive behaviors and more sophisticated functions. Possessing the ability of excellent thermal stability and prominent fatigue resistance, diarylethene derivatives have been extensively introduced into many systems for constructing optically responsive materials [46]. Our group have successfully developed a [2]pseudorotaxane via combining an unsymmetrical diarylperfluorocyclopentene (DAE) and a Eu^{3+}-containing complex of terpyridinyldibenzo-24-crown-8 (Fig. 13) [47]. The guest molecule could exhibit reversible and stable photochromic properties, achieving the interconversion between the ring-opened and ring-closed forms under alternate UV-vis light irradiation. Benefiting from the excellent luminescence properties of Eu^{3+}, the assembly displayed satisfactory luminescence, while the guest molecule kept the ring-opened form. Exposing the pseudorotaxane to 365 nm UV light, ~80% of the fluorescence intensity of Eu^{3+} was quenched, revealing an initiated resonance energy

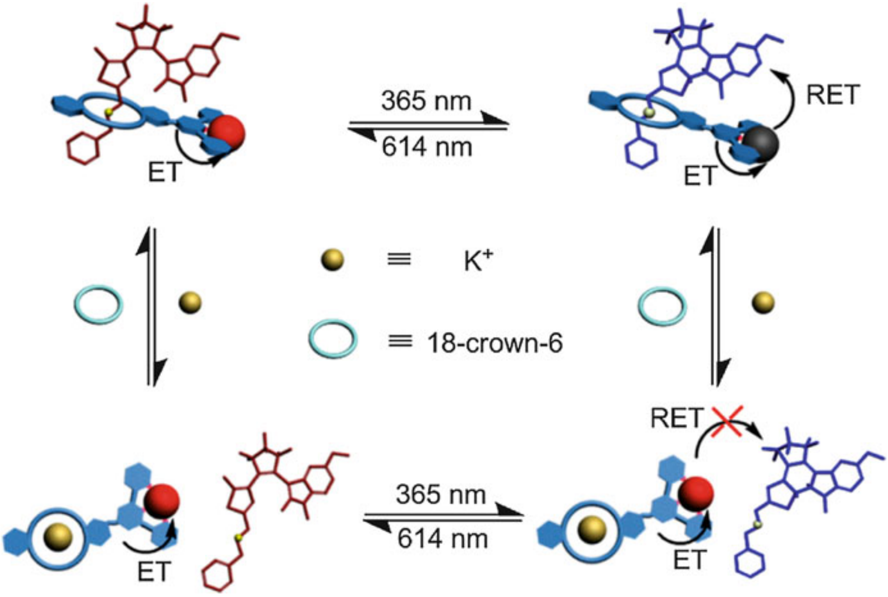

Fig. 13 Schematic illustration of the light-modulated molecular switch [47]. (Adapted with permission [47]. Copyright 2013, American Chemical Society)

transfer (RET) from the Eu^{3+} ion to the ring-closed formed diarylperfluorocyclopentene acceptor. The reversible optically modulation of the fluorescence of the pseudorotaxane could be achieved upon alternating UV and visible-light irradiation. Furthermore, by introducing the K^+ and 18C6 into the [2] pseudorotaxane, we could also reversibly regulate the fluorescence of the assembly through the competitive bonding. The present results may provide an attractive paradigm for the fabrication of multistimuli-driven molecular switch, logic gates, and molecular machines.

As we all know, anthracenes are also photoresponsive units, which can be reversibly transformed into dimerization [48] or trap singlet oxygen to form stable endoperoxides (EPOs) [49] upon UV light irradiation and heating. Yuan et al. [50] reported a Eu^{3+} complex-based luminescence probe for efficient detection of singlet oxygen via the rapid reaction between anthracene and singlet oxygen, resulting in remarkable luminescence enhancement. Inspired by this finding, we developed a tunable luminescent lanthanide supramolecular assembly based on photoreaction of anthracene (Fig. 14) [51]. The macrocyclic component consists of a 9,10-diphenylanthracene (ant) core with photosensitivity, terminal terpyridine (tpy), and two-arm DB24C8. Upon supramolecular assembly formation via the coordination of the macrocyclic host and lanthanide metal ions, irradiation of the systems at 365 nm leads to photoreaction of the ant core and unique lanthanide emission. Intriguingly, the existence of two crown ether rings is to prevent the influence of alkali and alkaline-earth metal ions on luminescence of the Ln^{3+}. Significantly, the

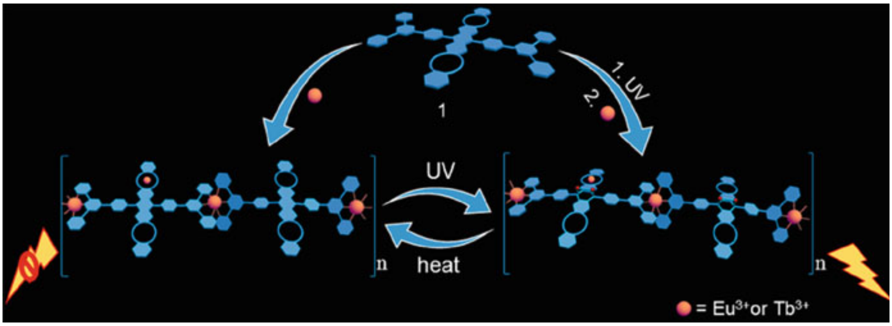

Fig. 14 Schematic illustration of the lanthanide luminescence driven by the process of reversible photoreaction [51]. (Adapted with permission [51]. Copyright 2017, American Chemical Society)

luminescence of the assembly could be reversibly switched on and off through a regulable photoreaction upon light irradiation or heating. Subsequently, threading a guest, which incorporated a dialkylammonium binding site and a DAE moiety, into the DB24C8, resulted in the formation of the poly[2]pseudorotaxane (Fig. 15) [52]. By switching between closed-form and open-form states of the DAE using UV and visible-light irradiation alternately, the lanthanide luminescence of poly[2]pseudorotaxane can be reversibly modulated.

5.4 Luminescent Supramolecular Polymers Based on Crown Ether

Supramolecular polymers, fabricated via the noncovalent interactions, such as hydrogen bonding, π-π stacking, metal coordination, and host-guest interactions, possess interesting and fascinating physical/chemical properties, including stimuli responsiveness, self-healing, and self-adjusting abilities. Therefore, supramolecular polymers have found a wide range of applications, including light harvesting, drug delivery, and catalysis [53]. By the combination of the fluorophores and dynamic noncovalent connections of supramolecular polymers, supramolecular polymers display the dynamic features attributing to the noncovalent bonds and also exhibit a tunable fluorescent ability through various external stimuli.

Self-assembly of molecular units into more complex and multifunctional superstructures is ubiquitous in nature. The number of fascinating superstructures prepared via multilevel self-assembly of artificial nanoscale units is also increasing rapidly. Stang and coworkers [54] designed and constructed a supramolecular oligomer with the concentration-dependent tunable emission properties by threading a fluorescent bis-ammonium salt into the phenanthrene-21-crown-7 (P21C7)-containing rhomboidal organoplatinum(II) metallacycle via the host-guest interactions (Fig. 16). Intriguingly, the assemblies, combining the orange-emissive metallacycle and the blue-emissive bis-ammonium linker, could exhibit a controllable emission from orange to blue as the concentration decreases, whereas white-light

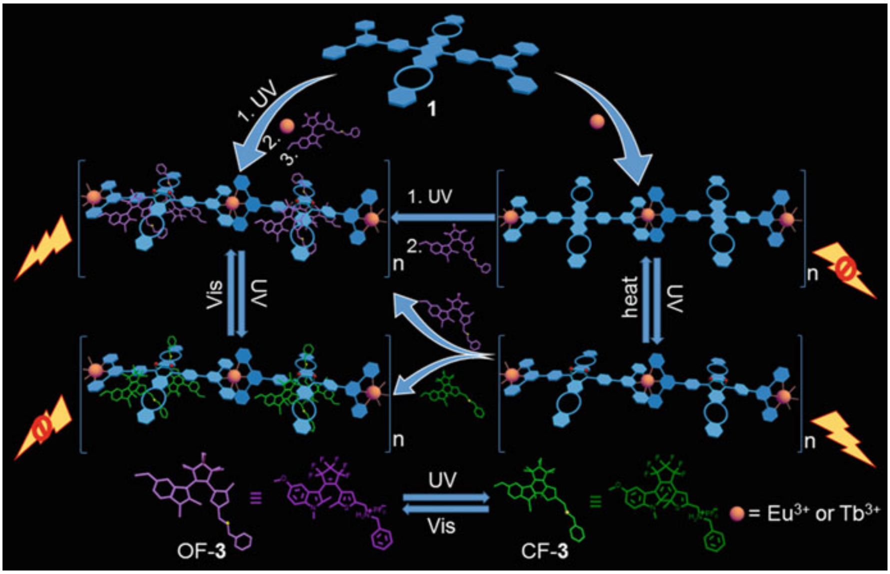

Fig. 15 Schematic illustration of the luminescent lanthanide switch based on a poly[2]pseudorotaxane [52]

emission was obtained at a concentration of 29 μM (Fig. 16c). This study provided an effective strategy for the fabrication supramolecular assemblies with tunable emissive properties. Subsequently, they reported a novel kind of supramolecular polymers taking advantage of host-guest binding between P21C7-containing metallacycles and bis-ammonium salt (Fig. 17) [55]. By modification of the substituents on the metallacycle precursor, the supramolecular polymers showed extraordinary abilities to regulate the fluorescent emission. Then, when coating a yellow-emitting supramolecular polymer thin film onto a blue-light LED, a white-light-emitting LED was obtained (Fig. 17c), indicating the potential of the supramolecular polymers for the construction of photoelectronic materials.

Recently, luminescent supramolecular polymer gels, which combine the elasticity of solid, the fluidity of liquid, and the inherent optoelectronic properties, have become an interesting research field. Significant work on luminescent supramolecular polymer gel has been reported by the group of Wong and coworkers [56]. The assembly of three metal ligands, appended to a benzo-21-crown-7 (B21C7) macrocycle, resulted in a Zn^{2+} complex exhibiting a strong yellow fluorescence (Fig. 18). Threading of a guest, including a bis-ammonium salt binding site, into the B21C7, resulted in the formation of a [3]pseudorotaxane with weak blue fluorescence. The supramolecular polymer gels were constructed successfully by threading of the bis-ammonium salt into the Zn^{2+} complex, accompanying with weak yellow fluorescence. Moreover, the supramolecular polymer gels showed an excellent multi-responsive performance. The reversible sol-gel transition could be triggered by temperature, pH, and cation. Therefore, the gel could display diverse fluorescent

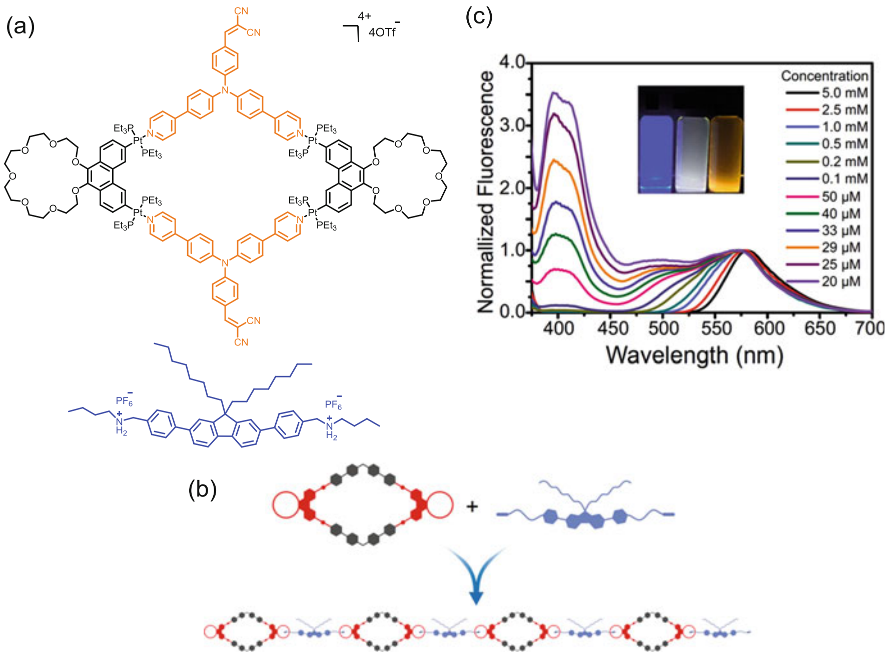

Fig. 16 (**a**) Molecular structures of crown ether-containing metallacycle and guest molecule. (**b**) Schematic illustration of the construction of supramolecular oligomers. (**c**) Emission spectra of supramolecular oligomers at different concentrations [54]. (Adapted with permission [54]. Copyright 2017, National Academy of Sciences (USA))

switching phenomena through controlling the self-assembly process in different ways, suggesting its potential application as advanced intelligent materials.

Huang et al. [57] fabricated a novel supramolecular cross-linked network via the host-guest interactions between the pendent DB24C8 units of a conjugated polymer and a bis-ammonium cross-linker (Fig. 19). However, the supramolecular cross-linked network showed a weak fluorescence, compared with conjugated polymer, originating from the aggregation of polymer chains, whereas the fluorescence intensity of this network increased obviously through inputting external stimulus signals, containing potassium cation, chloride anion, pH increase, and heating, attributed to the disassembly process of the supramolecular cross-linked network. In addition, the thin films were prepared by spin-coating the solution of the supramolecular cross-linked network. Interestingly, the fluorescence intensity of the thin films showed an obvious increase when the film was exposed to the vapor of ammonia. This system will pay the way for designing multiple fluorescent sensor materials.

The abovementioned supramolecular polymers not only possess the dynamic characteristic but also regulate their fluorescence by various external stimuli. However, all of them undergo an inescapable process of aggregation-caused quenching (ACQ) due to the formation of excimers and exciplexes, which seriously limits their

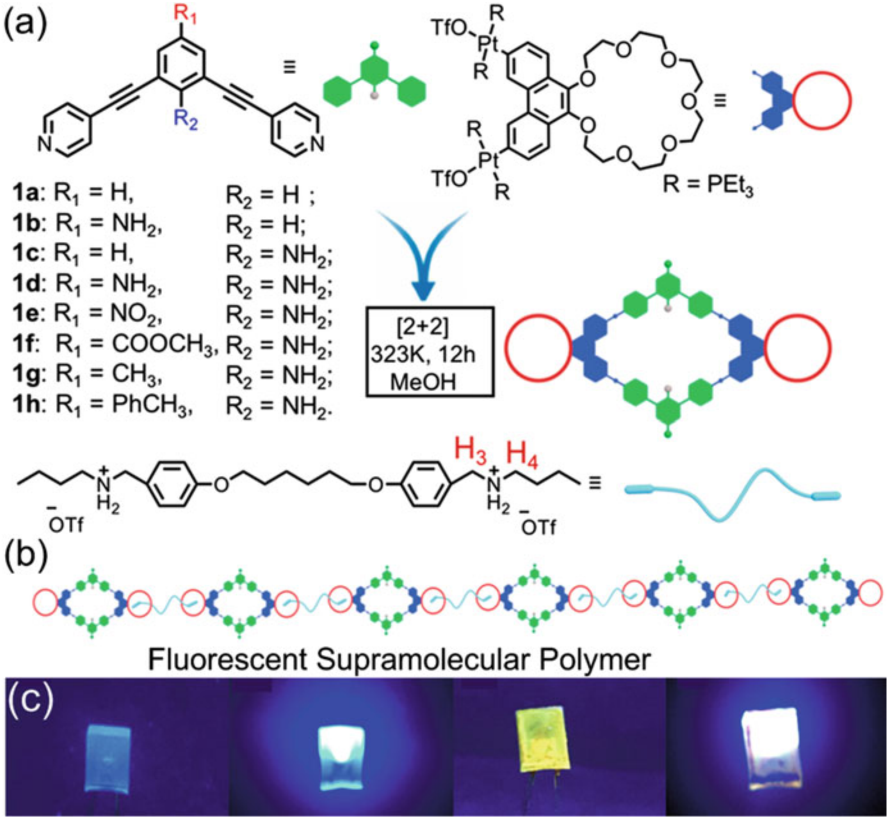

Fig. 17 (**a**) Schematic illustration of the construction of metallacycle. (**b**) The formation of fluorescent supramolecular polymer from metallacycle and guest molecules. (**c**) Photos from LED [55]. (Adapted with permission [55]. Copyright 2018, American Chemical Society)

practical applications. In 2001, the concept of aggregation-induced emission (AIE) was first put forward [58]. Luminescent materials with AIE can efficiently solve the self-quenching problem of traditional fluorescent materials. AIE has received considerable attention due to their potential applications for photoelectronic devices, chemo- and biosensors, and bio-imaging. Tetraphenylethene (TPE) is a typical AIE-active molecule. The marriage of TPE and crown ether system provides new smart function materials with unique fluorescent properties. Liu and coworkers [59] reported a highly sensitive and selective K^+ probe, constructed via AIE and host-guest molecular recognition. Four benzo-15-crown-5 (B15C5) macrocycles were docked with TPE molecule, endowing the system with the AIE-active motif and supramolecular K^+-recognizing functionalities. Supramolecular polymer was obtained by the formation of K^+/B15C5 1:2 sandwich complex, accompanied by the turned-on fluorescence via AIE effect, whereas the fluorescence emission changes were negligible in the presence of competitive ions (Li^+, Na^+, NH_4^+, Ca^{2+},

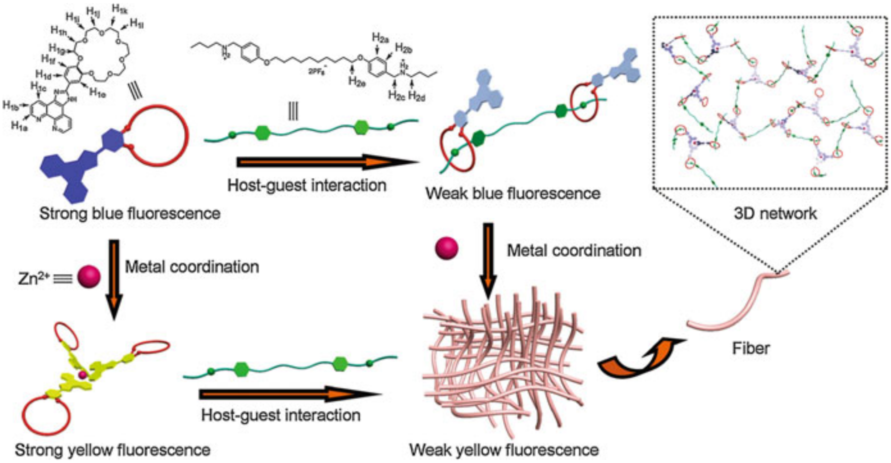

Fig. 18 Molecular structures of host and guest molecules and schematic illustration of the supramolecular polymer with multiple fluorescent features [56]. (Adapted with permission [56]. Copyright 2016, Royal Society of Chemistry)

Mg^{2+}, and Pb^{2+}), suggesting that the system could be used as an excellent selectivity sensor for K^+ ion (Fig. 20a). Tang et al. [60] constructed an AIE-active supramolecular polymer via the interactions of DB24C8-modified TPE derivatives with dibenzylammonium-containing TPE derivatives (Fig. 20b). Upon acidification or basification of the system, the fluorescence of linear supramolecular polymers could be reversibly switched on and off, owing to the self-assembly and disassembly of the system.

Yin and coworkers [61] designed a novel fluorescent supramolecular polymer for Pd^{2+} detection (Fig. 21a). The supramolecular polymer was fabricated via the host-guest interactions with dibenzo[24]crown-8-contained TPE and a bis-ammonium salt, which exhibited much higher fluorescence emission than its monomer due to the restriction of the intramolecular rotation of the TPE unit. Moreover, the 1,2,3-triazole moiety could form metal-ligand complex with Pd^{2+} ion, resulting in significant loss of the fluorescence intensity of supramolecular polymer, attributed to an energy transfer process from the TPE units to Pd^{2+} ions. Thus, the results suggest that the supramolecular polymer can be used to detect Pd^{2+} ions. Subsequently, they constructed a hyperbranched fluorescent supramolecular polymer based on metal-ligand coordinating interactions and host-guest interactions (Fig. 21d) [62]. Two functional monomers were designed and prepared by combining DB24C8 and terpyridine with an alkyl chain and modifying a TPE unit with four dibenzylammonium salts (DBAS). Based on the host-guest interactions of DB24C8 with DBAS and the metal-ligand coordinating interactions of terpyridine with Zn^{2+}, the hyperbranched supramolecular polymer was obtained. Benefiting from AIE effect of TPE, the system displayed strong fluorescent emission. In addition, the supramolecular polymer was able to respond to various stimuli, including temperature, deprotonation/protonation of the ammonium units, the addition/removal of K^+ or

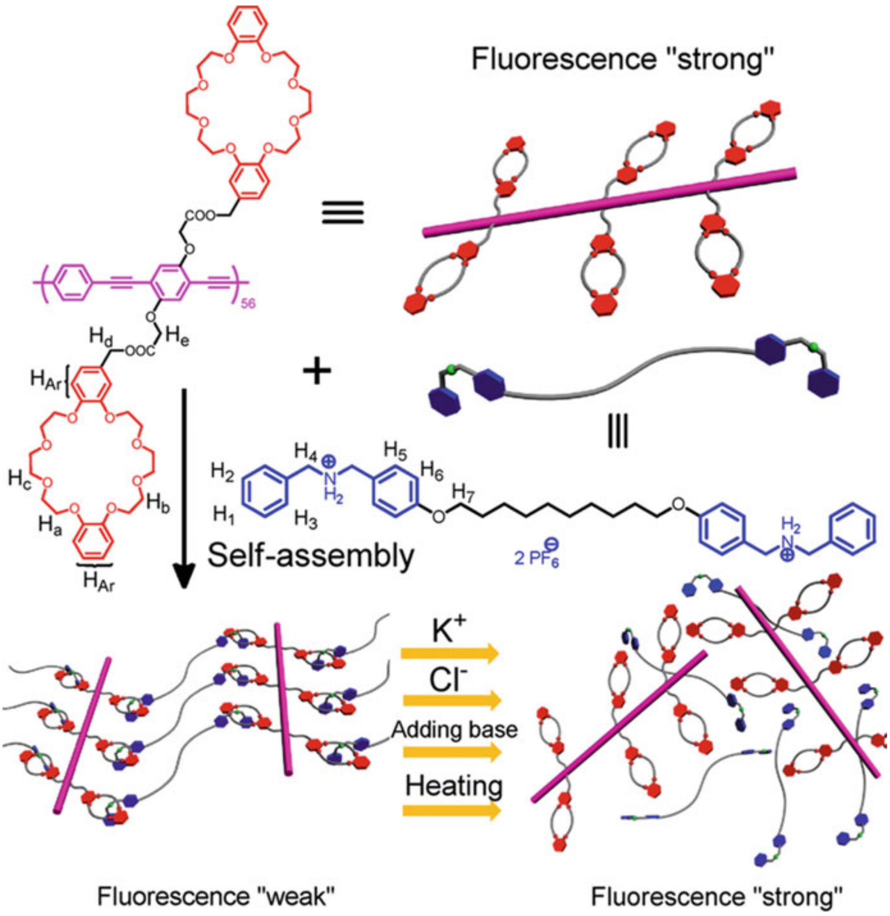

Fig. 19 Schematic illustration of the fabrication of supramolecular cross-linked polymer network [57]. (Adapted with permission [57]. Copyright 2013, American Chemical Society)

Cl^-, and 1,4,7,10-tetraazacyclododecane (cyclen). The results revealed that this system will have a potential application value in the fabrication of the smart and adaptive luminescent materials.

Further research was reported by the same group [63]. A polystyrene backbone with coumarin units and DBAS moieties as functional groups was prepared by polymerization reaction. The TPE-containing host molecule was synthesized by modifying DB24C8 and terpyridine. Then, a cross-linked supramolecular polymer network with two emission bands was constructed via the orthogonal self-assembly of host-guest and metal-ligand coordination interactions of functional polymer chain with TPE-containing host molecule and Zn^{2+} (Fig. 22a). The system could exhibit different fluorescent emission signals at 390 and 460 nm owing to the emission of coumarin and TPE, and the fluorescence intensities at these two wavelengths could

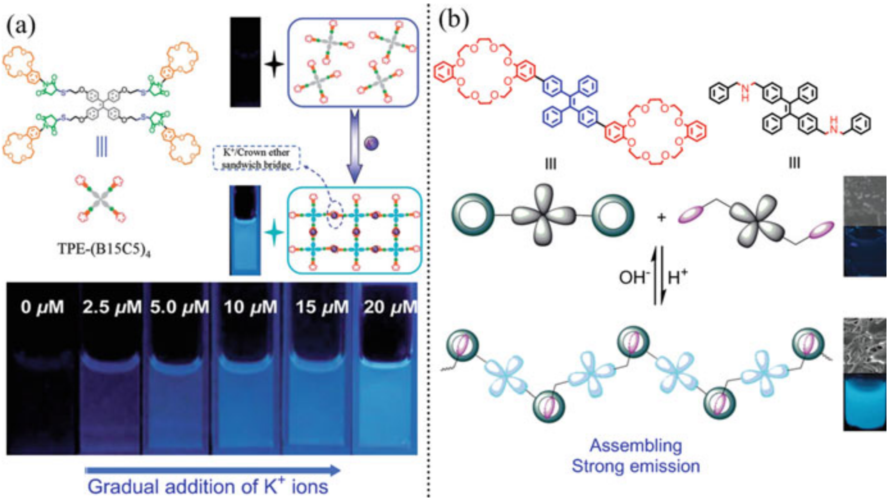

Fig. 20 (**a**) Schematic illustration of the construction of fluorescence probe for K^+ based on TPE-(B15C5)$_4$, induced by supramolecular recognition between K^+ ions and B15C5 moieties [59]. (Adapted with permission [59]. Copyright 2012, Royal Society of Chemistry.) (**b**) Illustration of the self-assembly via host-guest interaction with pH-responsive properties [60]. (Adapted with permission [60]. Copyright 2015, Royal Society of Chemistry)

be reversibly modulated by the addition and removal of cyclen, Cl^-, or pH changes, revealing that the supramolecular polymer network could act as a multiple ratiometric fluorescent sensor. In addition, supramolecular gels were formed with the increase in concentration of the supramolecular polymer network, and the gels displayed stimuli-responsive gel-sol transition and good self-healing behaviors. Huang and coworkers [64] also constructed a dual-stimuli-responsive fluorescent supramolecular cross-linked polymer gel combining a polystyrene chain with dialkylammonium salt units and four-arm benzo-21-crown-7 (B21C7)-contained TPE derivative (Fig. 22b). Originating from the host-guest interactions of B21C7/dialkylammonium salt and the TPE-based AIE effect, the fluorescence intensities of supramolecular polymer gel could be reversibly regulated by thermal stimuli and pH variations, accompanied with the reversible gel-sol transitions. This fluorescence tunable supramolecular gel based on host-guest interactions provided a novel way to construct responsive light-emitting materials.

Multiple orthogonal noncovalent interactions were utilized to fabricate new supramolecular polymers with the more sophisticated functions. Recently, Stang et al. [65] reported an efficient strategy to construct fluorescent supramolecular polymer network by the multiple interactions within a single process, including metal-ligand coordination, hydrogen bonding, and host-guest interactions (Fig. 23a). Firstly, they fabricated a hexagonal metallacycle from a 120° B21C7-containing di-Pt (II) acceptor and 2-ureido-4-pyrimidinone (UPy)-decorated 120° bis-pyridyl donor through the coordination of the pyridyl with organoplatinum. Then, the

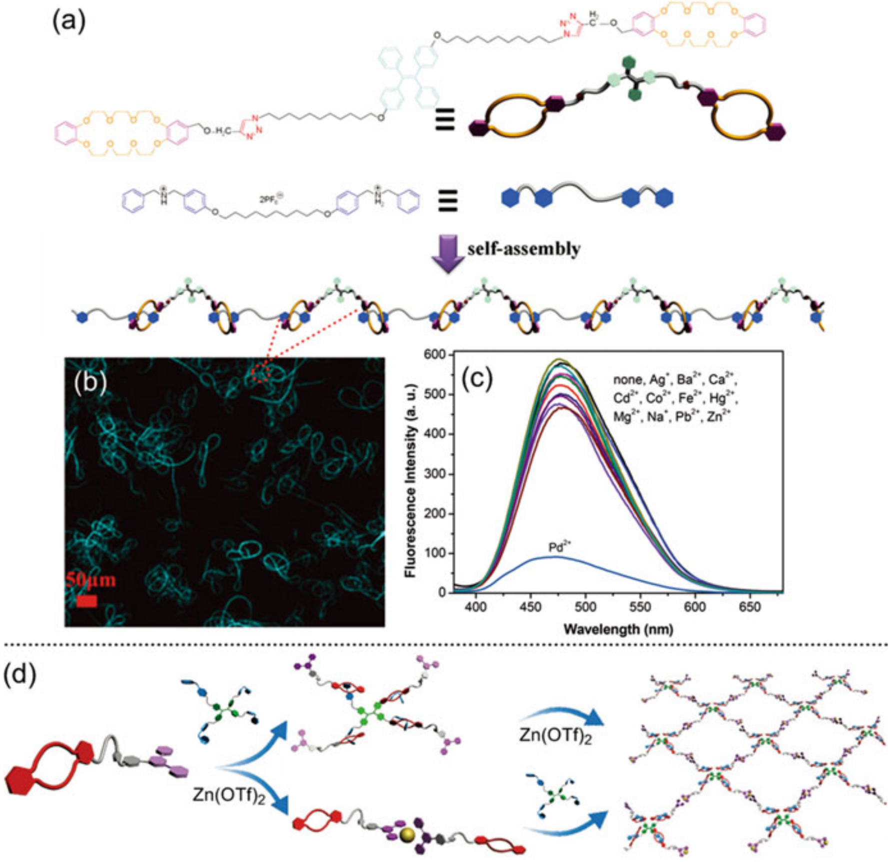

Fig. 21 (**a**) Construction of supramolecular polymers for Pd^{2+} detection based on host-guest interactions between DB24C8 and ditopic linkers. (**b**) 350 nm fluorescence emission-irradiated photo of the electrospun supramolecular polymer nanofibers. (**c**) Emission spectra of supramolecular polymer with different metal ions in the solid state [61]. (Adapted with permission [61]. Copyright 2015, Royal Society of Chemistry.) (**d**) Schematic illustration of the construction of hyperbranched fluorescent supramolecular polymer [62]. (Adapted with permission [62]. Copyright 2016, Royal Society of Chemistry)

supramolecular polymer network was achieved via a self-assembly process driven by hydrogen-bonding interactions with the UPy units. The remained B21C7 moieties could offer a platform for further introducing a guest via host-guest interaction. For example, TPE-functionalized dialkylammonium salt and perylene-decorated dialkylammonium salt were incorporated into supramolecular polymer network to obtain two light-emitting supramolecular polymers by taking advantage of B21C7/dialkylammonium complexation. Moreover, the network could form supramolecular gels at high concentrations or upon solvent swelling. This orthogonal strategy based on noncovalent bond provides a simple yet highly efficient method to achieve

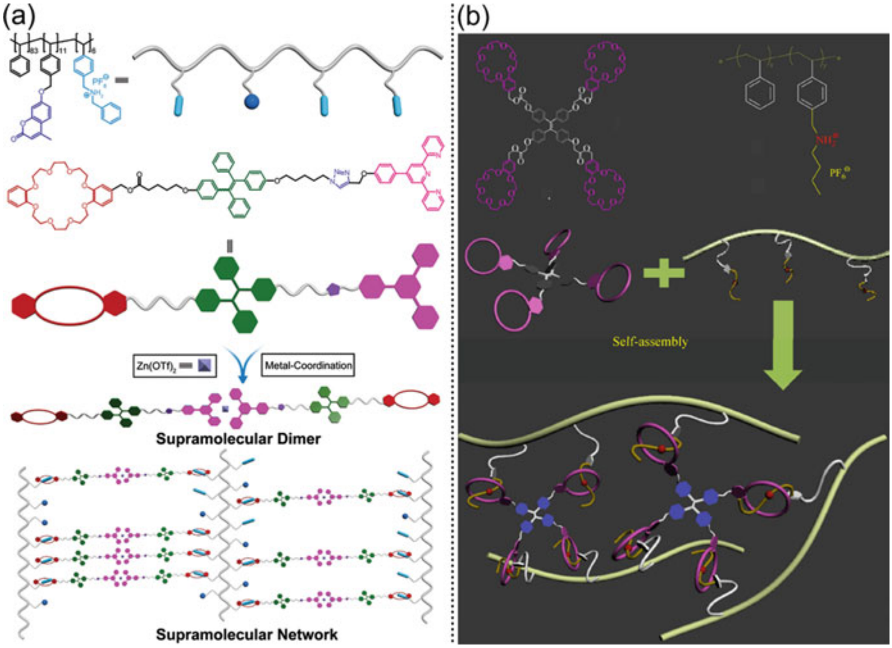

Fig. 22 (**a**) Molecular structures of polymer chain and host molecule and schematic illustration of the formation of supramolecular network [63]. (Adapted with permission [63]. Copyright 2018, Royal Society of Chemistry.) (**b**) Illustration of the fluorescent supramolecular cross-linked polymer gel formed by the self-assembly of B21C7 and polymer chains [64]. (Adapted with permission [64]. Copyright 2015, Springer)

modular functional supramolecular polymer materials. Likewise, Stang et al. [66] recently reported the fabrication of a multifunctional metallacage-core supramolecular gel via orthogonal metal-coordination-driven self-assembly of cis-Pt(PEt$_3$)$_2$-(OTf)$_2$, TPE-based sodium benzoate ligands and linear dipyridyl ligands containing 21C7 units (Fig. 23b). Threading a guest, incorporating a dialkylammonium binding site, into the free 21C7 moieties within the metallacage by host-guest interactions, resulted in the formation of a supramolecular polymer network, which further formed a supramolecular gel at relatively high concentrations. Interestingly, the supramolecular polymer gel showed an excellent fluorescence emission, deriving from the AIE properties of TPE derivatives. The employment of noncovalent bond to construct supramolecular polymer gel suggested that the gel network could respond to multiple stimuli and possess outstanding self-healing properties. Moreover, rheological results revealed that the rigidity of the metallacages enhanced the stiffness of the gel. This novel multiple-functional supramolecular polymer network based on orthogonal self-assembly could open an avenue for the fabrication of supramolecular gels with stimuli-responsive and self-healing properties as smart materials.

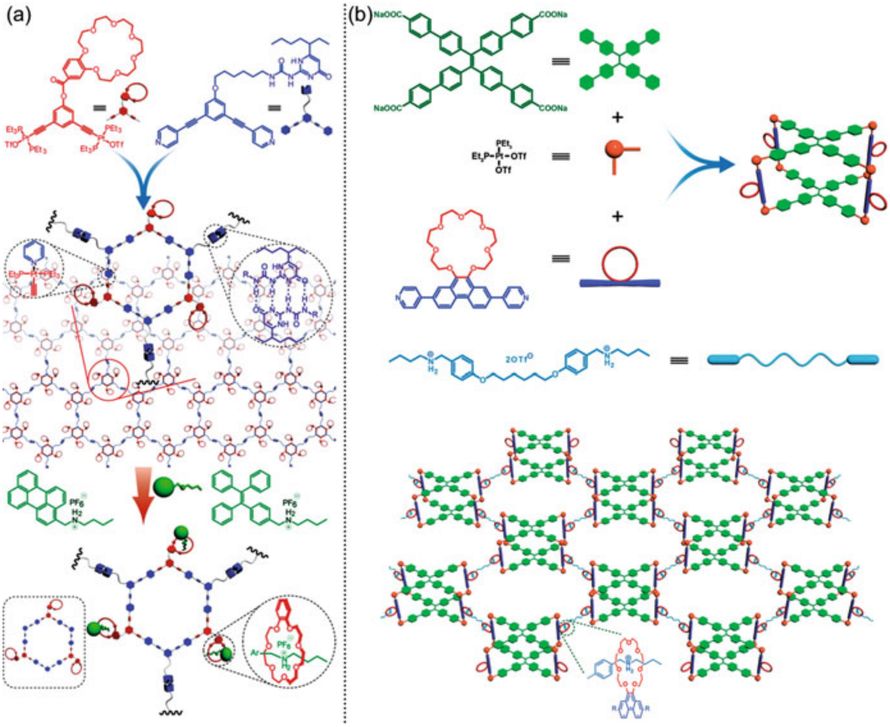

Fig. 23 (**a**) Schematic illustration of the construction of a cross-linked 3D supramolecular polymeric network from hierarchical self-assembly [65]. (Adapted with permission [65]. Copyright 2016, American Chemical Society.) (**b**) Illustration of the fluorescent supramolecular polymer network formed by the self-assembly of metallacage and bis-ammonium salt [66]. (Adapted with permission [66]. Copyright 2018, American Chemical Society)

5.5 Conclusion

In conclusion, recent developments in the designation and construction of photoluminescent crown ether assembly have been discussed. These complicated structures fabricated via self-assembly at the molecular scale provided many opportunities for the preparation of new smart luminescent supramolecular materials. Various noncovalent interactions, such as metal-ligand coordination, hydrogen bonding, and host-guest interactions, were the essential characteristics of these materials. Ingeniously, the combination of functional units (i.e., DAE, TPE, and anthracene) and the dynamic noncovalent interactions endowed the luminescent materials with multistimuli-responsive and self-healing features. The fluorescence intensity of the systems could be reversibly modulated upon external stimuli, like light, pH, temperature, etc. Moreover, these luminescent materials could be further used in sensors, light harvesting, and bio-imaging.

Although luminescent crown ether assemblies have played a crucial role in numerous fields in the current research, some uncharted terrains still need chemists to explore. For example, in the field of biological field, how to develop the biocompatible and NIR luminescence systems that can be introduced into cells, even living organisms, is a large unexplored area. In the field of solid-state lighting, how to solve the problems of the low stabilities and low fluorescence quantum yields of these systems also needs to be further investigated. In the field of luminescent supramolecular polymers, how to construct a supramolecular polymer with high mechanical strength, self-healing, and excellent fluorescence characteristics still remains a major difficulty. In a word, this is just the beginning of the journey to prepare ever more sophisticated and complex structures for application in the luminescent materials based on crown ether assembly. Future developments involving crown ether assembly are unconceivable, and we firmly believe that photoluminescent crown ether assembly will play an irreplaceable role in the near future.

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