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Review

Organic Supramolecular Assemblage Confined Photoluminescence

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Organic supramolecular hosts can selectively bond to small functional molecules with chromophores, inhibiting molecular motion and isolating quenching factors through spatial confinement, thereby enhancing fluorescence and phosphorescence emission and expanding their applications in chemistry, biology, and materials science. This review mainly focuses on supramolecular luminescent systems constructed from cucurbit[n]urils, cyclodextrins, and other macromolecules. It is very importance that cucurbit[n]urils and cyclodextrins both possesse rigid hydrophobic cavities, in which cucurbit[n]urils can bond to positively charged guest molecules due to the high negative potential of the carbonyl group at the port, while cyclodextrin tends to bond to negatively charged guest molecules and has abundant hydroxyl groups, providing numerous modification sites, and both can be further assembled with biomacromolecules through bonding or modification. Biomacromolecules such as hyaluronic acid and chitosan can multivalently bind to guest molecules through electrostatic interactions and hydrogen bonds. Supramolecular luminescent systems formed by these organic macrocyclic hosts or macromolecules and guest molecules have been widely used to construct intelligent supramolecular assemblies and have been successfully applied to near-infrared cell imaging, in situ photodynamic therapy, anti-counterfeiting, information encryption, logic gates, and other fields. With the continuous emergence of novel luminescent groups and new macrocycles, photoluminescence confined within the assembly of organic supramolecular systems will undoubtedly boost their further development in fields such as constructing chiral transfer amplification systems, novel organic light-emitting diodes, and in vivo imaging diagnostics.

1. Introduction

Supramolecular luminescent materials achieved by assembly confinement and cascade confinement strategies have attracted widespread interest in recent years due to their ability to effectively suppress nonradiative transitions and isolate quenching factors, thereby enhancing the emission intensity of luminescent groups[1-3]. Organic supramolecular self-assembly units primarily comprise macrocycles, such as cucurbit[n]uril (CB[n]) and cyclodextrin, as well as macromolecules like hyaluronic acid and chitosan. Cucurbit[n]uril is a type of cyclic molecule obtained by the condensation of glycoluril and formaldehyde[4]. It usually has 6-8 repeating units. Taking advantage of high negative potentials given by the carbonyl groups on the glycoluril units makes it have a high bonding constant for positively charged guest molecules[5]. Generally, CB[6] with smaller cavities tend to bond with aliphatic ammonium salts[6], CB[7] with medium cavities show high affinity for phenylammonium salts or pyridinium salts[7, 8], while CB[8] with larger cavities can accommodate adamantane, ferrocene derivatives, or two guest molecules to form a host-guest complex with a stoichiometric ratio of 1:2[9-12]. Unlike cucurbit[n]urils, cyclodextrins are cyclic molecules formed by α-D-glucanopyranose linked end-to-end by 1,4-glycosidic bonds[13]. The ends are hydrophilic while the inner walls are hydrophobic, giving them greater structural flexibility compared to cucurbit[n]urils. The abundance of hydroxyl groups also contributes to their good water solubility and modifiability[14-16]. Especially, the 6-OH group of cyclodextrins is relatively reactive, making it easy to modify with different functional groups or macromolecules. Different from molecular cages which possess encapsulation and isolation properties[17, 18], supramolecular macrocycles tend to recognize guest molecules, and their bonding is reversible. Therefore, they can be used to construct supramolecular assemblies with dynamically tunable stimulus responses[19, 20]. Hyaluronic acid, chitosan, and other natural polysaccharide macromolecules possess negative and positive charges due to their carboxyl and amino groups, respectively, allowing them to bond with guest molecules through multivalent electrostatic interactions[21-25]. Furthermore, the polysaccharide structure can form abundant hydrogen bonds, further confining the luminescent group (Table 1). However, despite numerous reviews on supramolecular photoluminescence in recent years, organic supramolecular confined luminescence has been rarely summarized in detail to the best of our known[2, 4]. In this review, we summarize recently reported organic supramolecular confined luminescence systems, mainly including (1) supramolecular luminescence systems constructed from cucurbit[n]urils (CB[n]s), (2) supramolecular luminescence systems constructed from cyclodextrins, and (3) supramolecular luminescence systems constructed from macromolecules (Scheme 1). We hope this

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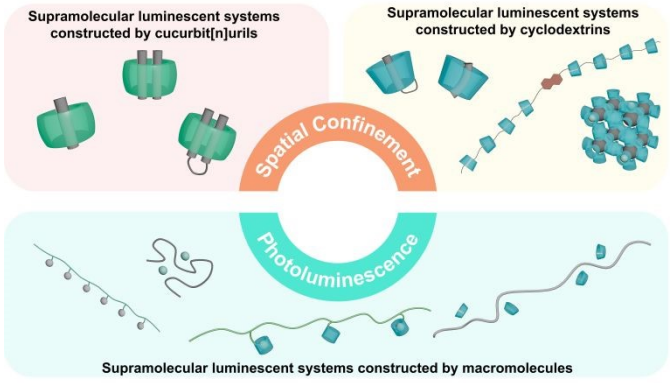
review will promote the application of novel supramolecular luminescent materials in chemistry, materials science, biology, and other fields.

Supramolecular Hosts	Advantages	Shortcomings
Cyclodextrins (CD)	Low prices, good water solubilities, easy in modification	Lower binding constant and confinement ability
Curcubit[n]urils (CB[n])	Rigid cavities to provide more efficient confinement, high affinities towards positively charged guests	Expensive, lower solubility, hard to modify
Linear Macromolecules (e.g. hyaluronic acid, chitosan)	Naturally acquired, good biocompatibility, easy to construct larger scale assemblies (~100 nm-500 nm)	Causing the solution to become excessively viscous at high concentrations

Table 1 Comparisons of different supramolecular hosts



Scheme 1 Schematic illustration of three types of organic supramolecular assemblage confined photoluminescence

2. Supramolecular luminescent systems constructed by cucurbit[n]urils

Cucurbit[n]urils have a high negative potential port carbonyl group, thus they have a strong bonding ability to positively charged guest molecules[26-28]. For example, bromobenzoimide, a phosphorescent group with an aliphatic ammonium structure, does not emit phosphorescence itself (Figure 1a)[29]. When it forms an assembly with CB[7] in a 1:1 stoichiometric ratio, where CB[7] can thread through the alkyl chain to form a pseudorotaxane structure. At the same time, its rigid cavity inhibits the vibration of the phosphorescent group, thereby inducing its room temperature phosphorescence at 505 nm. Further assembly with amphiphilic calixarene can greatly improve the intensity and lifetime of phosphorescence emission, so as to construct a phosphorescence resonance energy transfer system and use it for cell imaging. Coincidentally, CB[7] can also bond with bromophenylpyridinium modified with the side chain of polyacrylamide (Figure 1b)[30]. The assembled polymer exhibits dual emission of fluorescence at around 380 nm and phosphorescence at around 500 nm due to the combined effect of macrocyclic confinement and the rigid matrix of acrylamide. The phosphorescence lifetime can reach up to 2.2 seconds, which makes it possible to use it for phosphorescence resonance energy transfer to obtain long-lifetime multicolor delayed fluorescence, which can be used for time-resolved information encryption. Similarly, copolymerizing pyridium-modified [2.2]paracyclophane with acrylamide produces only weak phosphorescence[31]. However, when co-assembled with CB[8], the phosphorescence intensity is significantly enhanced, and it exhibits a large structure-dependent spectral shift, making it suitable for use in phosphorescence-based pure organic optical thermometers.

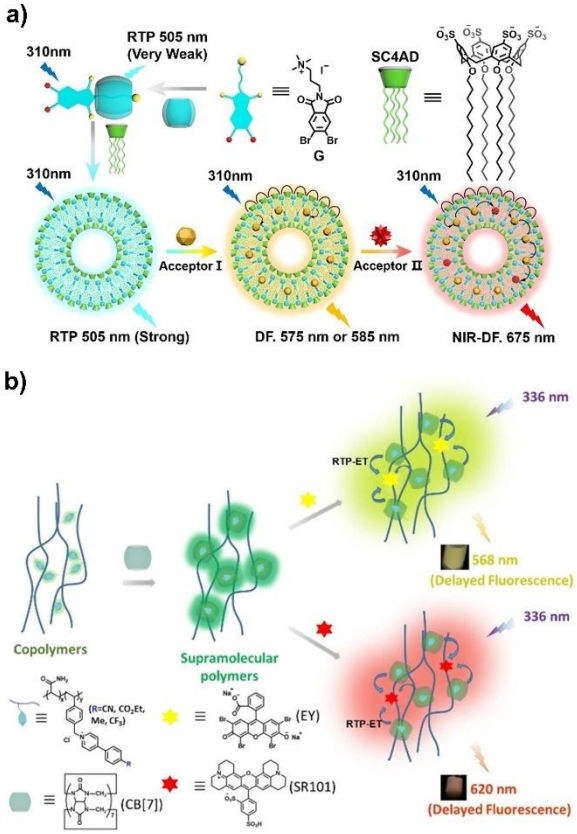


Figure 1 (a) Schematic illustration of the cascade phosphorescent resonance energy transfer system constructed by bromobenzoimide derivatives, CB[7], and SC4AD. This figure has been adapted from ref. 29 with permission from Wiley-VCH

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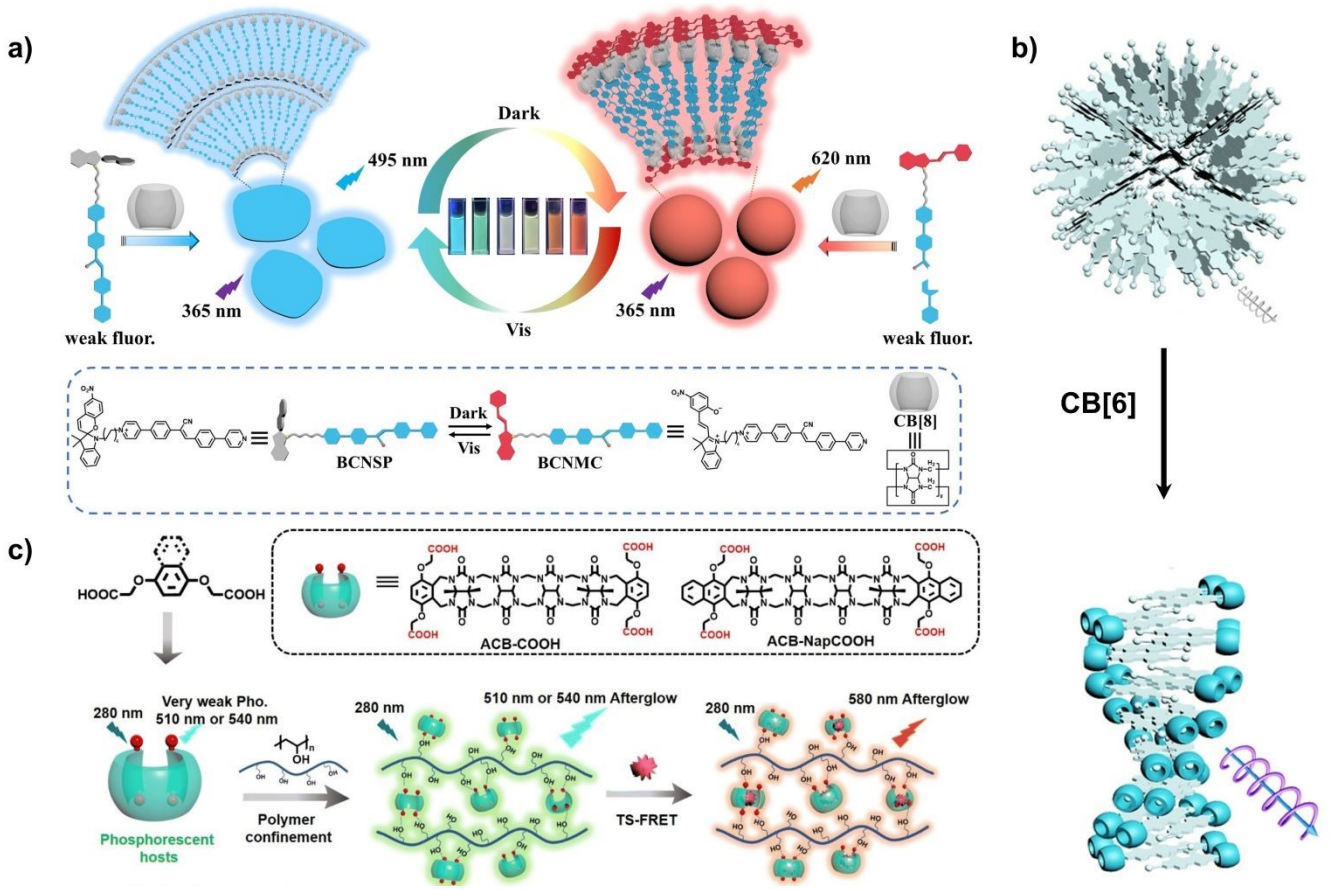

Figure 2 (a) Schematic illustration of the supramolecular shuttle constructed by spiropyran derivatives and CB[8]. This figure has been adapted from ref. 32 with permission from Wiley-VCH GmbH, copyright 2023. (b) Schematic illustration of the CB[6] induced chiral transfer amplification. This figure has been adapted from ref. 35 with permission from Wiley-VCH GmbH, copyright 2024. (c) Schematic illustration of the phosphorescence of acyclic cucurbituril (ACB) induced by rigid matrix. This figure has been adapted from ref. 38 with permission from the authors, copyright 2024.

Interestingly, photoisomerization of spiropyran can change the electrical properties of the molecule, thereby altering its assembly mode with cucurbit[n]urils. For example, spiropyran modified with cyanostyl styrene derivatives is a dicationic salt in the open-ring state (MC) and a monocationic salt in the closed-ring state (SP) (Figure 2a)[32]. Utilizing the high affinity of CB[8] for cations, a light-controlled supramolecular shuttle can be assembled: in the closed-ring state, only cyanostyl styrene exhibits blue fluorescence under 365 nm excitation. When the assembly is placed in darkness, spiropyran gradually changes from SP to MC, followed by intramolecular fluorescence resonance energy transfer from cyanostyl styrene to MC, causing the fluorescence to gradually change from blue to green, and finally to orange. Irradiating the assembly with visible light can reverse this process. Similarly, when sulfonic acid-modified spiropyran is added to the linear supramolecular polymer composed of CB[8] and pyridinium-modified diarylethene, its closed-ring SP is negatively charged, thus it can cascade assembly with positively charged supramolecular polymers to form nanorods or nanospheres, while the open-ring MC is neutral and cannot be further assembled with supramolecular polymers[33]. Furthermore, the emission wavelength of this assembly can be orthogonally modulated by three wavelengths, thus enabling its use in multi-dimensional information encryption. Spiropyran derivatives modified with styrene derivatives can assemble with CB[7] and CB[8][34]. After assembly with CB[7], the emission of the assembly gradually changes from blue to orange when placed in the dark. When assembled with CB[8], because CB[8] can bond to styrene units in a 1:2 stoichiometric ratio, forming a π-π stacked structure, the emission of the assembly redshifts. When placed in the dark, the emission gradually changes from yellow to red. This

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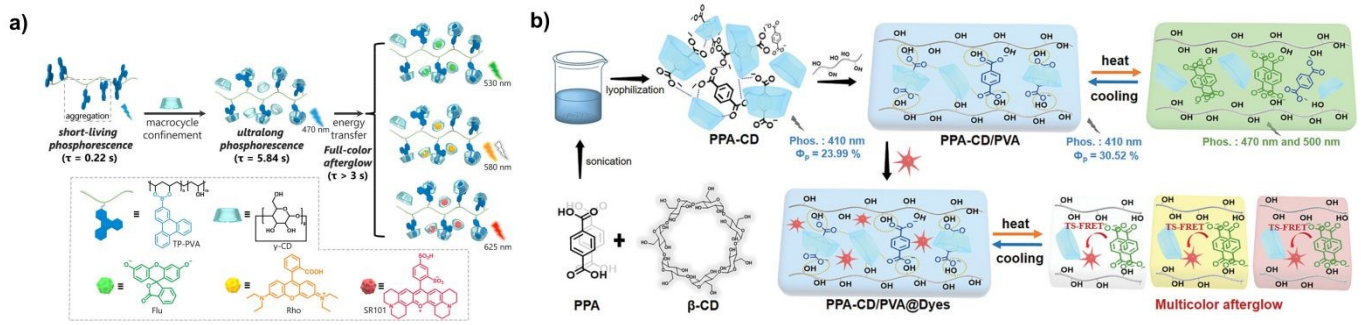
bidirectional molecular shuttle can be used for information encryption and cell imaging.

Figure 3 (a) Schematic illustration of the ultra-long lifetime phosphorescence in PVA film achieved by phenylboronic acid



derivatives and γ-CD. This figure has been adapted from ref. 41 with permission from the authors, copyright 2023. (b) Schematic illustration of the thermal-activated reversible phosphorescence. This figure has been adapted from ref. 19 with permission from Wiley-VCH GmbH, copyright 2024.

Furthermore, by utilizing the molecular recognition between CB[6] with smaller cavities and chiral ammonium modified luminescent group guests, supramolecular assemblies with chiral stacking patterns can be constructed, inducing strong CD signals and enhancing the luminescence intensity of the guest molecules (Figure 2b)[35]. While CB[7] with larger cavities can also form supramolecular assemblies, it cannot induce chiral stacking patterns.

CB[8] with larger cavities can bond two guest molecules in a 1:2 stoichiometric ratio. For example, tetracation-modified phenothiazine derivatives can form supramolecular organic frameworks (SOFs) with CB[8] and emit red light at 710 nm[36]. Adding a D/L phenylalanine tripeptide to the system as a chiral source allows it to bond with CB[8] at the framework edge, where non-covalent crosslinking nodes have not formed, inducing circularly polarized luminescence throughout the framework. It is noteworthy that heating causes the assembly to disintegrate, thus losing its inducible chirality, while cooling restores the chiral luminescence. CB[8] can also be assembled with bromophenylpyridinium modified with aniline derivatives. When the aniline derivative is N, N-dimethylaniline with less steric hindrance, it can bond with CB[8] in a 2:2 stoichiometric ratio, avoiding intramolecular twisted charge transfer (TICT) and promoting space charge transfer (TSCT), thereby obtaining enhanced near-infrared delayed fluorescence/phosphorescence dual emission[37]. However, N, N-diphenylaniline with larger steric hindrance can only form an assembly with CB[8] in a 2:1 stoichiometric ratio, and there is no phosphorescence emission due to TICT.

Interestingly, acyclic cucurbituril (ACB) itself can also act as a luminescent group. For example, ACB with port-modified phenylcarboxylic acid derivatives exhibits long-lifetime room-temperature phosphorescence emission in polyvinyl alcohol films (Figure 2c)[38]. The rigid coiled configuration of the cucurbituril tetramer restricts the movement of phenylcarboxylic acid, while the abundant hydrogen bonds in the PVA film provide further confinement, ultimately resulting in long-lifetime phosphorescence with a lifetime of 2.12 seconds. Furthermore, the cavity of ACB has the ability to bond to various dyes and drugs, making it suitable for drug detection and phosphorescent resonance energy transfer.

3. Supramolecular luminescent systems constructed by cyclodextrins

Cyclodextrins are a class of cyclic polysaccharide molecules with hydrophobic cavities, exhibiting strong affinity for negatively charged or neutral guest molecules[39, 40]. For example, in the rigid matrix of polyvinyl alcohol (PVA), γ-cyclodextrin can bond to phenylboronic acid derivatives grafted onto PVA, effectively inhibiting the aggregation of luminescent groups and significantly enhancing its phosphorescence lifetime (Figure 3a)[41]. Further doping with dyes such as rhodamine and SR101 allows them to be encapsulated within the cavities of γ-cyclodextrin, achieving phosphorescence resonance energy transfer to obtain multicolor afterglow longer than 50 seconds. In aqueous solution, β-cyclodextrin can still bond to 4-phenylphenylboronic acid, inducing room-temperature phosphorescence with a lifetime of up to 1.03 seconds through the synergistic effect of macrocyclic confinement and intermolecular hydrogen bonding[42]. Notably, only after ultrasonic treatment to encapsulate 4-phenylphenylboronic acid with β-cyclodextrin can room-temperature phosphorescence emission be induced. In the PVA matrix, β-cyclodextrin can bond with terephthalic acid, inducing blue phosphorescence emission at 410 nm through spatial confinement and the rigid matrix (Figure 3b)[19]. Interestingly, as the temperature increases, the bonding effect of β-cyclodextrin with terephthalic acid weakens, causing the terephthalic acid to leave the cyclodextrin cavity and accumulate, resulting in a redshift of the phosphorescence emission to 500 nm. Furthermore, the phosphorescence emission after heating shows good overlap with the excitation of rhodamine and SR101, while the phosphorescence emission before heating shows poor overlap with the excitation of the two dyes. Therefore, a thermally activated phosphorescence resonance energy transfer system can be constructed for multi-level anti-counterfeiting and information encryption.

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Multicharged cyclodextrins prepared by modifying cyclodextrins with different functional groups can bond guest molecules via electrostatic interactions[43, 44]. For example, a copolymer of bromonaphthylpyridinium with phosphorescence and fluorescence dual emission with acrylamide can be assembled with sulfobutylether-β-cyclodextrin (SBE-β-CD), enhancing the polymer's yellow room-temperature phosphorescence at 550nm through spatial confinement (Figure 4a)[45], which mix with the blue fluorescent emission at 425 nm to achieve strong white light emission. By copolymerizing the photo-switching molecule diarylethylene with monomers and controlling the ratio of yellow phosphorescence to blue fluorescence, white light emission can be obtained, which can be used for data encryption and white LEDs. Similarly, a copolymer of cyano-substituted 4-phenylpyridinium derivatives with acrylamide can also be assembled with SBE-β-CD[46]. SBE-β-CD not only acts as a non-covalent crosslinking node but also effectively improves the polymer's phosphorescence lifetime. This phosphorescence exhibits reversible responsiveness to light and heat; the phosphorescence intensity and lifetime decrease sharply after irradiation with a 275 nm UV lamp, while heating reverses this process, thus enabling its application in intelligent UV detection. SBE-β-CD can also form a sheet-like nanostructure by electrostatic interaction with the primary assembly of tetraphenylethylene derivative and CB[8], which significantly enhances its yellow light emission at 600 nm[47]. However, when assembled with a single tetraphenylethylene derivative, a spherical nanostructure is formed, but the lack of macrocyclic confinement results in insignificant luminescence enhancement. After adding the near-infrared dye aluminum phthalocyanine sulfonate to the sheet-like secondary assembly, fluorescence resonance energy transfer occurs, and near-infrared fluorescence emission is obtained at 691 nm with an efficiency of 75%. In addition, sulfonic acid-modified β-cyclodextrin can be assembled with the pH probe DPy-6C by electrostatic interaction[48]. Under acidic conditions, the assembly exhibits weak red fluorescence, while under alkaline conditions, the stacking mode of the assembly is disrupted, resulting in a slight blue shift and significant enhancement of luminescence, which has been successfully used for the quantitative detection of volatile organic amines in liquid and gas phases.

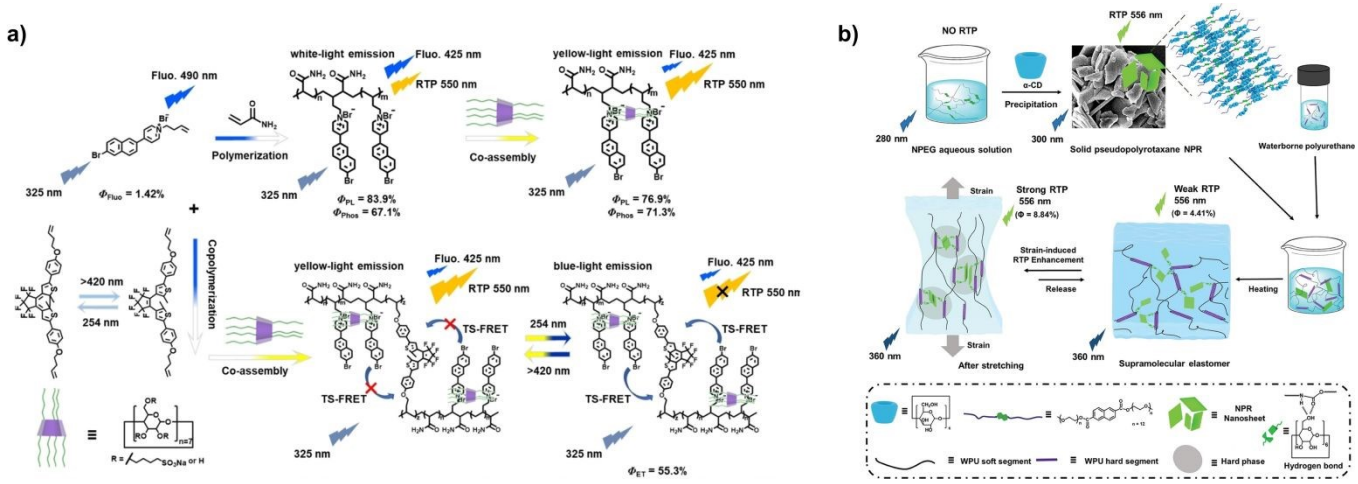

Figure 4 (a) Schematic illustration of the SBE-β-CD enhanced phosphorescence. This figure has been adapted from ref. 45 with permission from Wiley-VCH GmbH, copyright 2022. (b) Schematic illustration of the elastomer with stress-responsive luminescence constructed by polyurethane and α-CD polypseudorotaxane. This figure has been adapted from ref. 53 with permission from the authors, copyright 2024.

Utilizing the bonding effect of cyclodextrin cavities on negatively charged dyes can enhance the efficiency of phosphorescent resonance energy transfer (PRET). For example, copolymerizing double-bond modified β-cyclodextrin and carbazole with acrylamide allows the rigid polyacrylamide to induce room-temperature phosphorescence emission of carbazole[49]. Compared to copolymers without β-cyclodextrin, the terpolymer better enriches the dye, increasing the PRET efficiency from 27.3% to 97.4%.

The cavity size of α-cyclodextrin matches that of polyethylene glycol (PEG) chains, making it easy to thread through the PEG chains to form pseudorotaxane structures[50-52]. Adding α-cyclodextrin to PEG-modified naphthalene esters results in pseudorotaxanes that produce green room-temperature phosphorescence (Figure 4b)[53]. Further incorporating these pseudorotaxanes into polyurethane elastomers results in stress-enhanced phosphorescence emission because the hard segments of the polyurethane exert a stronger confinement effect on the pseudorotaxanes under stress.

Interestingly, supramolecular luminescent systems can also be constructed using cyclodextrins in some novel solid materials. For example, adding aromatic boric acid to a MOF formed by γ-CD and potassium ions allows γ-cyclodextrin to effectively bond with the aromatic boric acid, resulting in blue room-temperature phosphorescence emission from the MOF crystals[54]. Adding different dyes can effectively generate phosphorescence resonance energy transfer, producing multicolor afterglow. Randomly methylated β-cyclodextrin and p-hydroxybenzoic acid can be hot-pressed to construct

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transparent supramolecular glasses with good transmittance and high fracture stress[55]. Adding tetraphenylethylene derivatives and luminescent groups such as BODIPY to this glass can prepare supramolecular transparent luminescent materials. Furthermore, grafting monomers containing adamantyl groups onto the surface of a hydrogel, when treated with a solution containing naphthalimide-modified cyclodextrin, causes the naphthalimide units originally self-encapsulated within the cyclodextrin cavity to leave due to the competitive bonding of adamantylane, promoting π-π stacking and producing green fluorescence emission[56]. This can be used for the detection of aromatic hydrocarbon derivatives and multi-level information encryption.

4. Supramolecular luminescent systems constructed by linear macromolecules and other macrocycles

Biomacromolecules, such as hyaluronic acid (HA) and chitosan (CS), can also be used to construct supramolecular confined luminescence systems. Among them, hyaluronic acid is a natural polysaccharide with a negatively charged carboxyl group on its surface, so it can bond guest molecules through electrostatic interactions[25]. At the same time, it can be easily modified with various functional groups[57, 58]. For example, using hyaluronic acid (HACD) with a side chain modified with cyclodextrin as the host of secondary assembly to bond the primary assembly of dodecyl-bridged 6-bromoisoquinoline and CB[7], the cyclodextrin cavity can effectively encapsulate the primary assembly, and the positively charged primary assembly and the negatively charged HACD can also be assembled through electrostatic interactions[59]. Secondary assembly increases the luminescence intensity by 8 times and the phosphorescence lifetime from 59 μs to 581 μs. After incorporating near-infrared dyes such as Nile Blue or sulfonated porphyrin, near-infrared delayed fluorescence can be obtained through phosphorescence resonance energy transfer. In addition, due to the targeting of hyaluronic acid to tumor cells, the assembly has been successfully applied to near-infrared targeted imaging of live tumor cells. HACD can also effectively bond to the assembly of tetracation macrocycle and doxorubicin, promoting intermolecular photoelectron transfer (Figure 5a)[60]. Under light irradiation, the assembly can generate singlet oxygen species with a high quantum yield of 185%, which enables it to perform efficient photodynamic therapy. The assembly exhibits good tumor cell targeting in vitro and in vivo, and shows excellent antitumor activity. HACD can also bond to the xanthracene part of the primary assembly of indole-bridged xanthracene derivative and CB[8], thereby providing further confinement, which increases the quantum yield of the assembly by 22 times (Figure 5b)[61]. The cavity of β-cyclodextrin can also bond to the inclusion complex of phosphorescent donor sulfonic acid modified bromophenylpyridinium and CB[8] to achieve phosphorescent resonance energy transfer with an efficiency of 84.49%. The assembly also exhibits upconversion properties and can achieve three-photon excitation at 940 nm, thereby achieving targeted imaging that penetrates deep tissues. HACD can undergo secondary assembly with a ternary supramolecular complex formed by bromophenylpyridium modified tetraphenylethylene and CB[7]/CB[8] with a donor-acceptor structure, and simultaneously activate the intramolecular phosphorescent resonance energy transfer from bromophenylpyridine to tetraphenylethylene, thereby obtaining near-infrared delayed fluorescence at 700 nm, which can be used for mitochondrial targeted imaging of tumor cells[62]. In addition, HACD can further confine the two-dimensional SOF network formed by CB[8] and bis(triphenylamine) derivatives to enhance its red fluorescence at 810 nm[63]. Adding the bromophenylpyridium derivative and CB[8] to this assembly as a phosphorescent donor can obtain near-infrared delayed fluorescence, which can be used for targeted near-infrared cell imaging and information encryption.

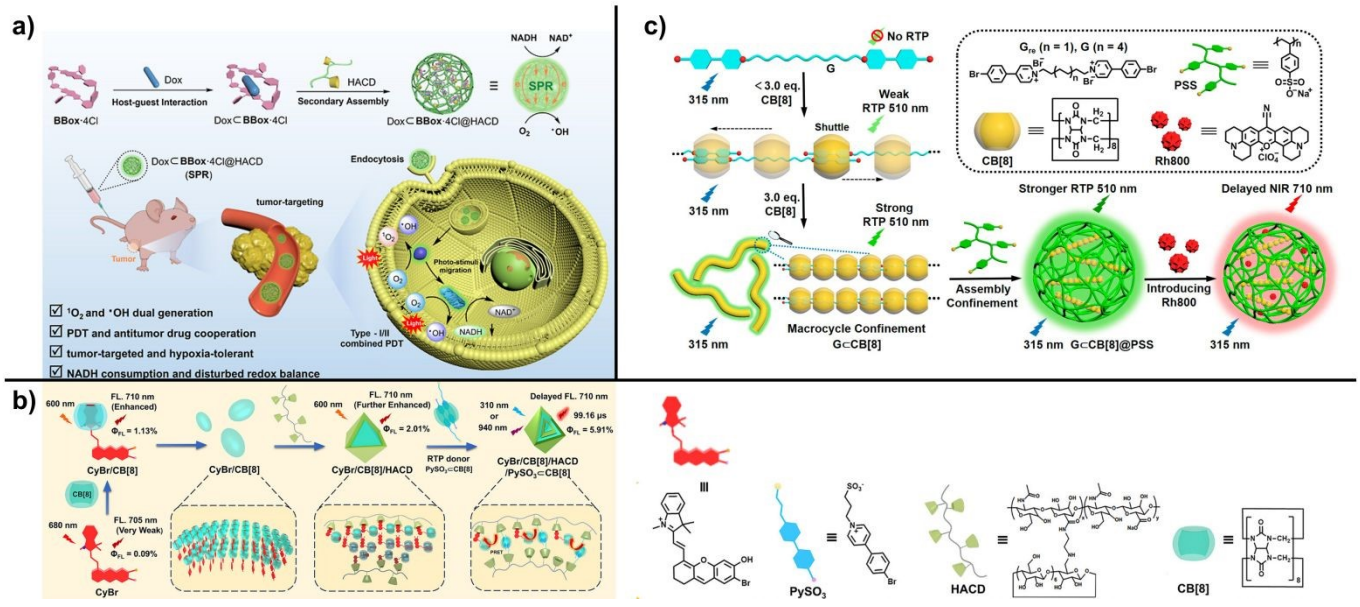

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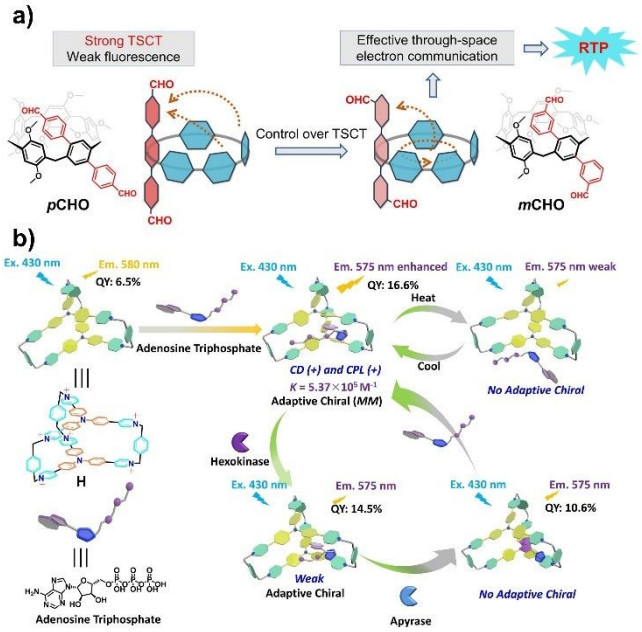
Figure 5 (a) Schematic illustration of the HACD co-assembled photodynamic therapy system. This figure has been adapted from ref. 60 with permission from American Chemical Society, copyright 2025. (b) Schematic illustration of the HACD co-assembled upconversion near-infrared emission. This figure has been adapted from ref. 61 with permission from Wiley-VCH GmbH, copyright 2025. (c) Schematic illustration of the PSS co-assembled supramolecular phosphorescence resonance energy transfer system. This figure has been adapted from ref. 68 with permission from the authors, copyright 2024.

HA can also be modified by guest molecules containing other functional groups. For example, HA modified with mitochondrial-targeting peptides and bromophenylpyridine salts can wrap around mitochondria[64]. When CB[8] is added, it can bond bromophenylpyridium in a 1:2 stoichiometric ratio, driving mitochondrial aggregation and emitting strong room-temperature phosphorescence at 500 nm. This mitochondrial aggregation can effectively enhance the antitumor efficiency of cisplatin. HA modified with bromophenylpyridium alone can also bond CB[8] in a 2:1 stoichiometric ratio, producing green room-temperature phosphorescence emission and constructing a phosphorescence resonance energy transfer system[65].

Unlike HA, CS has numerous amino groups on its polysaccharide chain, which allows it to be protonated and thus carry a positive charge, enabling it to assemble with negatively charged guest molecules. In addition, amino groups can coordinate with metal ions or undergo Schiff base reactions[66]. For example, β-cyclodextrin derivatives containing aldehyde groups can form hydrogels with chitosan through Schiff base reactions, producing fluorescence emission at 315 nm due to aggregation[67]. The gel has good injectability and can achieve multicolor luminescence based on fluorescence resonance energy transfer by doping with triphenylamine derivatives.

Interestingly, artificially synthesized macromolecules can also serve as the host for secondary assembly to further enhance confinement. For example, sodium poly(p-phenylenesulfonate) (PSS) can be further assembled with bromophenylpyridinium and CB[8] via electrostatic interactions to form uniform spherical nanoparticles, thereby further enhancing phosphorescence lifetime (Figure 5c)[68]. Adding Rhodamine 800 to the assembly can yield near-infrared delayed fluorescence of 710 nm through phosphorescence resonance energy transfer. This can be used for cell imaging.

In addition, novel macrocyclic compounds such as pillararenes can also serve as the host for supramolecular confined luminescence[69, 70]. For example, m-formylphenyl-substituted pillar[5]arenes can produce millisecond-level room-temperature phosphorescence emission through effective space charge transfer (TSCT), while formylphenyl-substituted columnar[5]arenes cannot produce long-lifetime phosphorescence emission due to excessively strong TSCT (Figure 6a)[71]. The bonding of guests with heavy atoms (such as bromoethane) can improve quantum yield by promoting ISC, while shortening phosphorescence lifetime, thus being applied to the detection of volatile organic compounds. The hexacation cage constructed with triphenylamine has a rotatable rigid framework that can effectively bond nucleotides (Figure 6b)[72]. When bonded with adenosine triphosphate (ATP), the fluorescence intensity and quantum yield are significantly enhanced, while exhibiting circularly polarized luminescence caused by chiral transfer. This circularly polarized luminescence not only exhibits thermal responsiveness but also gradually disappears under the stepwise hydrolysis of ATP by hexokinase and adenosine triphosphate diphosphorylase. This chiral supramolecular transfer container has been successfully used for chiral logic gates and multi-level information encryption. Furthermore, the π-extended triphenylamine tetracation macrocycle not only enables photodynamic therapy with a high



singlet oxygen quantum yield, but its cavity can also effectively bind the antitumor drug pemetrexed[73]. This synergistic therapy achieved a good antitumor efficacy of 93.4% in a mouse model.

Figure 6 (a) Schematic illustration of the room temperature phosphorescence of pillar[5]arene derivatives induced by through-space electron communication. This figure has been adapted from ref. 71 with permission from American Chemical Society, copyright 2023. (b) Schematic illustration of the biofuel-driven step-chiral transfer system. This figure has been adapted from ref. 72 with permission from Wiley-VCH GmbH, copyright 2024.

Conclusions

In this review, we mainly summarize the applications of supramolecular assembly confined luminescence strategies based on cucurbit[n]urils, cyclodextrins, and other macromolecules in enhancing luminescence, extending phosphorescence lifetime, as well as cell imaging, photodynamic therapy, and anti-counterfeiting. Although cucurbit[n]urils and cyclodextrins both have rigid cavities, cucurbit[n]urils can bind to various positively charged

molecules due to the negative potential on its edge, while cyclodextrins with different functional groups can bind guest molecules with positive or negative charge, both can effectively restricts molecular motion and isolates it from external quenching factors, thereby enhancing the phosphorescence or fluorescence emission of the luminescent group. Meanwhile, hyaluronic acid, a negatively charged linear polysaccharide, can assemble with not only guest molecules but also host-guest complexes through electrostatic interactions, enhancing its luminescence through multi-level confinement. Chitosan, also a linear polysaccharide, readily protonates due to its amino groups, resulting in a positive charge. This allows it to assemble with negatively charged guest molecules. Furthermore, the amino groups can condense with aldehyde groups to form dynamic chemical bonds. Artificially synthesized multi-charged polymers, such as PSS, can also enhance the luminescence of guests through electrostatic interactions. Novel hosts, such as pillararenes and triphenylamine-based polycationic macrocycles, can bond with different guests to achieve applications in bioimaging, synergistic therapy, and volatile organic compound detection. Despite the remarkable progress made in the supramolecular assembly confined luminescence systems described above, further applications in the biomedical field still face challenges in terms of economic cost, in vivo stability, controllable release, and clinical trial data, which also face the drawbacks of fatigue resistance and environmental tolerance in fields such as anti-counterfeiting and organic light-emitting diodes. We believe this review will promote the application of emerging macrocycles and novel luminescent groups in luminescent systems constructed through supramolecular confinement in in vivo imaging, synergistic therapy, smart materials, multi-level anti-counterfeiting, and encryption, and will also advance the development of supramolecular chemistry.

Author contributions

H. Z. searched the literature and wrote the manuscript. Y. L. edited and modified the manuscript.

Conflicts of interest

There are no conflicts to declare.

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Data availability

Data availability is not applicable to this article as no new data was created or analyzed in this study