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Supramolecular Purely Organic Room-Temperature Phosphorescence

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III Metrics & More

CONSPECTUS: In recent years, purely organic room-temperature phosphorescence (RTP) has aroused wide concern and promotes the development of the supramolecular phosphorescence. Different from organic crystallization, polymerization, or matrix rigidification, supramolecular strategy mainly takes advantage of the synergy between supramolecular co-assembly and strong binding by macrocyclic host compounds (cucurbit[n]urils, cyclodextrins, etc.) to overcome deficiencies such as poor processability and water solubility and improves RTP materials' quantum efficiency and lifetime in the solid state or in an aqueous solution. Meanwhile, it expands application, especially in aqueous solution, in cell imaging. Therefore, supramolecular phosphorescence will become a new growth point and will have broad application prospects in chemistry, biology, and material science.

This Account focuses on the uniquely synergetic advantages of co-assembly and host-guest interaction from macrocyclic hosts for enhancing RTP. This Account starts with a brief introduction of the recent development of organic RTP materials as well as the host-guest interaction and co-assembly. Then, we introduce a supramolecular solid-state RTP strategy involving an ultrahigh



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phosphorescent quantum yield via the tight encapsulation of macrocyclic host cucurbit[6]uril, an ultralong lifetime via changing the substituents of phosphors, and long-lived and bright RTP by the synergy of host-guest interaction and polymerization. Meanwhile, the applications of solid-state RTP materials for anti-counterfeiting and data encryption are presented. The third part will be the water-phase supramolecular phosphorescence systems constructed by water-soluble macrocyclic host cucurbit[8]uril. Host-guest interaction and polymerization worked together toward efficient phosphorescence in aqueous solution, and the multi-stage assembly promoted phosphorescent applications such as cell targeted imaging and energy transfer. A humidity sensor and data encryption by the conversion of supramolecular hydrogels and xerogels are also involved. In the summary section, we present perspectives and possible research directions for supramolecular phosphorescence.

Furthermore, on the basis of previous research, we would like to conclude and propose the developing concept of "macrocycles enhance guest's phosphorescence", and this concept not only means that the macrocyclic host limits the movement of the guest compound or promotes interactions between guest compounds but also involves the synergetic enhancement centered on macrocyclic compounds via multi-stage supramolecular assembly which further improves the efficiency of RTP, water solubility, and biocompatibility. And we believe that this concept will be able, together with theory of "assembly-induced emission" and "aggregation-induced emission", to accelerate the development of purely organic RTP materials.

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- Zhang, Z.-Y.; Liu, Y. Ultralong room-temperature phosphorescence of a solid-state supramolecule between phenylmethylpyridinium and cucurbit[6]uril. Chem. Sci. **2019**, 10, 7773–7778.² Ultralong RTP ($\tau = 2.62$ s) is achieved by a solid-state supramolecule between a cucurbit[6]uril (CB[6]) host and a heavy-atom-free phenylmethylpyridinium guest. Moreover, several phosphor-

escent complexes possessing different lifetimes are prepared and successfully applied in triple lifetime encoding for data encryption and anticounterfeiting.

 Zhou, W.-L.; Chen, Y.; Yu, Q.; Zhang, H.; Liu, Z.-X.; Dai, X.-Y.; Li, J.-J.; Liu, Y. Ultralong purely organic aqueous phosphorescence supramolecular polymer for targeted tumor cell imaging. *Nat. Commun.* 2020, 11, 4655.³ Owing to the stable 1:2 assembly by cucurbit[8]uril

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Scheme 1. Schematic Illustration of the Formation of Host-Guest Complexes and Supramolecular Co-assembly and the Applications of Supramolecular Co-assembly



and the multiple hydrogen bonds of hyaluronic acid, the supramolecular polymer has effective water-phase RTP (τ_{Phos} = 4.33 ms). Moreover, this supramolecular polymer is applied for cancer-cell-targeted phosphorescence mitochondrial imaging.

• Ma, X.-K.; Zhang, W.; Liu, Z.; Zhang, H.; Zhang, B.; Liu, Y. Supramolecular Pins with Ultralong Efficient Phosphorescence. Adv. Mater. **2021**, 33, 2007476.⁴ The supramolecular pins displayed robust phosphorescence with afterglow after incorporation into a rigid matrix ($\tau = 0.11$ s and $\Phi_{Phos} = 99.38\%$), which was credited to the effective intramolecular charge transfer induced from the "molecular folding" assembling formation.

1. INTRODUCTION

The development of purely organic room-temperature phosphorescence materials has received widespread attention owing to its potential applications in anticounterfeiting, biological imaging,^{6,7} and optoelectronic materials.⁸ Traditionally, organic molecules cannot emit phosphorescence at room temperature or in aqueous solution because of intrinsically weak spin-orbit coupling, which means that excitons could not effectively cross the single state and triplet state.⁹ That is, effective phosphorescence emission requires two conditions: one is fast and efficient intersystem crossing (ISC), which means that it facilitates singlet excitons to populate the triplet state, and the other one is slow k_{nr} , which means that it protects the energy of the triplet state from quenching.^{10,11} The progress of RTP enhancement is like water flowing through a pipe: if we want a large flow of water (strong and long-lived phosphorescence), we have to increase the width of the pipe (fast k_{isc}) and protect the water from being leaked (suppress the k_{nr}). Keeping these guidelines in mind, many brilliant organic RTP strategies have been developed, such as the polymer matrix,^{12–14} crystallization,¹⁵ H-aggregation,¹⁶ and noncovalent interactions.^{17,18} In the subsequent development, the "aggregation-induced emission" theory proposed by Tang et al. and the "assembly-induced emission" theory proposed by Tian et al. provided new perspectives for the mechanism and development of phosphorescence. However, most of the RTP materials are in the solid state, and disadvantages such as inefficient photoluminescence efficiency, poor water-solubility,

and so on exist, which restrict potential applications of RTP materials especially in a biological environment.

In this Account, we mainly summarize recent reports on supramolecular phosphorescence, utilizing the binding of the macrocyclic host and supramolecular multi-stage assembly to induce and enhance phosphorescence. We also summarize and propose the concept of "macrocycles enhance guest's phosphorescence" for developing RTP materials and its' application in biological imaging, data encryption, humidity sensors, and so on. We believe that this concept would offer illumination and help to exploit and construct supramolecular systems and emissive materials.

2. MACROCYCLES ENHANCE GUEST'S PHOSPHORESCENCE

2.1. Host-Guest Interaction and Co-assembly

Supramolecular chemistry has become a compelling area of chemistry owing to numerous achievements in intermolecular recognition, molecular assembly, the development of molecular machines, and so on. Host-guest interaction is the cornerstone of supramolecular chemistry, and the host-guest interaction mainly refers to the host compounds recognition of the guest compounds through reversible noncovalent interactions such as $\pi - \pi$ stacking interactions, hydrogen bonding, halogen bonding, electrostatic interactions, hydrophobic interactions, metal-ligand coordination, van der Waals forces, and so on.¹⁹ Host–guest interaction cannot be divorced from macrocyclic compounds. Cyclodextrins (CDs),²⁰ calixarenes (CAs),²¹ cucurbit[n]urils(CB[n]s),²² and pillar[n]arenes²³ are synthetic, well-designed macrocyclic compounds, and they possesses unique advantages such as a strong binding ability, simple synthesis, good water solubility, and ease of modification.²⁴ Macrocycles could specifically bind guest molecules via host-guest interaction, which would generate new properties and be applied in catalysts,²⁵ drug delivery,²¹ biomacromolecule recognition,²⁶ light-harvesting systems,²⁷ and RTP materials. Remarkably, the reports over the years about phosphorescent properties resulting from macrocyclic assembly arouse wide concern. Noticeably, this Account focuses on host-guest interaction via macrocyclic compounds. In addition, other remarkable host-guest strategies such as

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"polymer enhanced guest's phosphorescence" and "guestdoped host" and so on were reported in recent years.^{28,29} The formation of co-assembly and progress in multi-stage

assembly are further studied on the basis of the host-guest complexes (Scheme 1), which usually involve the formation of supramolecular nanoparticles via the second kind of macrocyclic compounds or polymer under hydrophobic or electrostatic interaction or host-guest interaction. Co-assembly provides capsule-like structure which protects the inside luminophore from water, oxygen molecules, or other outside impurities. Significantly, additional properties, such as biological targeting and bathochromic-shift emission, could be given from polymers assembled via multi-stage assembly. (These will be described in more detail later.)

2.2. Solid-State Phosphorescence

The macrocyclic compounds can bind the guest to the inside of the cavity and protect the internal luminophore from the outside quencher (Scheme 1). The macrocyclic cavity could suppress the molecular vibration and reduce the loss of energy from the triplet. Reports of macrocyclic compounds inducing phosphorescence have been reported in the 20th century, and most systems need a low temperature or external halogen anions conditions.³² However, there was still a lack of simple and effective methods for phosphorescent enhancement. In 2018, Tian's group first reported noncrystalline purely organic small compounds with RTP emission.³³ A series of β -CDs modified with different phosphors were designed, and the powder could display RTP owning to the strong intermolecular hydrogen bonding which could effectively suppress the nonradiative relaxation process (Figure 1). This report provides new ideas about the construction of RTP materials. Different from CDs, CBs are rigid macrocyclic compounds which are synthesized by the polymerization of glycoluril and formaldehyde. CBs are ideal host compounds for promoting phosphorescence owning to distinct advantages such as strong binding with positively charged guests and possessing many carbonyl groups which could form hydrogen bonds and halogen bonds. In 2019, we reported solid-state supramolecule phosphorescence enhanced by cucurbit [6] uril (CB[6]).¹ In Figure 2a, the PYCl (bromophenyl-methyl-pyridinium chloride) displayed high phosphorescence quantum yields from 2.6 to 81.2% after binding with CB[6]. Apart from the counterion affecting the luminous efficiency, the macrocycles would more sharply affect the phosphorescence emission. However, the significant enhancement for phosphorescence is particular for CB[6]. CBs with larger or smaller cavities display no such facilitation. Through the crystal structure of PYCl/CB[6], we found that CB[6] had a great deformation during the binding process (Figure 2b). This result is uncommon and uncovered that such a great improvement was attributed to the tight encapsulation of CB[6], which suppresses the nonradiative decay and promotes the ISC.

A long lifetime is a non-negligible advantage for phosphorescence. However, the reports of long-lived RTP materials are still rare, especially ultralong phosphorescent materials which can still emit light after the light source is removed. An easy to prepare and extensive strategy for enhancing the phosphorescence lifetime is necessary. It is well known that the introduction of a heavy atom (e.g., Br or I) could enhance the spin coupling coefficient and speed up ISC, contributing to a high phosphorescence quantum yield, but this would lead to short-lived RTP. Our group explored the influence of



Figure 1. β -CD derivatives with RTP mission and mechanism of phosphorescence enhancement. Reproduced with permission from ref 33. Copyright 2018 American Chemical Society.

substituents on phosphorescence properties and synthesized phenyl-pyridine salts modified with different heavy atoms (F, Cl, Br, and I) and without heavy atom substitution (H) (Figure 2a).² By comparing the k_{isc} (intersystem crossing rate constant), the k_r (radiative decay rate constant of phosphorescence), and the k_{nr} (nonradiative decay rate constant of phosphorescence), we found that the encapsulation of CB[6]provided slow k_{nr} , which was necessary for resultful phosphorescence. And as the reduction of the heavy atom effect, $k_{\rm isc}$ and $k_{\rm r}$ were reduced and led to a significantly improved lifetime. Significantly, PBC/CB[6] powder exhibited an ultralong phosphorescence lifetime of 2.62 s and a decent efficiency of 9.7%. Taking advantage of the difference in phosphorescent lifetime, PBC/CB[6], PCC/CB[6], and PYCl/CB[6] were applied in time-dependent phosphorescent information encryption and information anticounterfeiting.

In addition to macrocycle-induced phosphorescence, polymerization is the other convenient approach to achieving longlived or high-efficiency RTP. And many brilliant works of enhancing RTP by polymers have been reported.^{35–37} For example, Kim et al. reported amorphous purely organic RTP polymer system.³⁷ By doping the phosphor possessing a bromoaldehyde core and carboxylic acid side chains into poly(vinyl alcohol), the film displayed bright phosphorescence (phosphorescence quantum yield is 24%) under ambient conditions. The efficient RTP results from intermolecular halogen bonds between phosphors and intermolecular hydrogen bonds between phosphors and polymers, and it should be noted that the polymer played a key role in restricting the vibration/diffusion motion of the phosphors. By combining the



Figure 2. (a) Schematic illustration of PYCl/CB[6], PCC/CB[6], and PBC/CB[6]. (b) Crystal structures of PYCl/CB[6] and CB[6], in which a great deformation of CB[6] resulting from tight binding could be found. Reproduced with permission from ref 1. Copyright 2018 Wiley-VCH VerlagGmbH&Co. KGaA. (c) Time-dependent phosphorescent information encryption and information anticounterfeiting of PYCl/CB[6], PBC/CB[6], and PCC/CB[6] powder. Reproduced with permission from ref 2. Copyright 2019 The Royal Society of Chemistry.

advantages of polymer and host-guest interaction, we developed a synergistic enhancement strategy to achieve effective RTP materials simply and efficiently, involving polymerization between phosphor monomers and acrylamide and host-guest complexation interaction between phosphors and CBs.³⁴ The polymerization between the guest (PH and PBr) and acrylamide offers a rigid network that is full of hydrogen bonds to lock phosphors, and then the molecular vibrations, rotations, and intercollision were suppressed (Figure 3a). The copolymer displayed decent phosphorescence with a 2.46 s lifetime and a 57% phosphorescent quantum yield. However, the increase in phosphors content would result in phosphorescence quenching, which is the aggregationcaused quenching (ACQ) effect (Figure 3b). To further restrain the effect from ACQ and suppress the nonradiative decay of phosphors, the CBs were added and then RTP was further activated, with a lifetime of 2.81 s (PH-0.1/CB[7]) and a phosphorescence efficiency of 76.0% (PBr-1/CB[6]) (Figure 3c). As comparison, the host-guest interaction alone would sharply weaken the RTP. By controlling the ratios and types of phosphors, RTP materials with different properties were achieved and applied for triple lifetime encoding for digit and character encryption.

2.3. Phosphorescence in Aqueous Solution

Phosphorescence is common in metal-containing inorganic and organometallic complexes but suffers from poor watersolubility and biological toxicity. In addition, purely organic RTP materials tend to quench when dissolved in water because oxygen and water could consume energy from the triplet state easily. As a consequence, it is a challenging work to construct RTP materials with long lifetimes and considerable efficiency in aqueous solution. Solid dispersions or amphiphilic polymers are commonly used to improve the solubility of insoluble compounds. However, these treatment methods might not overcome the defects of poor water solubility and may result in serious performance reduction. And supramolecular assemblies, which are constructed from nanoparticle or assembled in water, even in biological environments, are a convenient and considerable strategy for protecting luminophores from disturbances in water. For example, our group constructed multi-stage co-assembly nanoparticles which are utilized to enhance NIR luminescence.³⁸ In Figure 4, the anthracene dye (ENDT) was synthesized with weak fluorescence emission at 625 nm. The multi-stage assembly process which resulted from CB[8] and amphiphilic sulfonatocalix[4]arene(SC4AD) greatly improved the luminescence and caused the emission to red shift. First-stage emission enhancement came from macrocyclic host CB[8], the "1:2" and "head-to-tail" binding forms contributed to the linear supramolecular polymer, and this slightly enhanced red-shifted (655 nm) fluorescence. In the second assembly stage, supramolecular polymer further interacted with SC4AD and formed supramolecular nanoparticles which showed even stronger fluorescence at 655 nm. Furthermore, the water-soluble supramolecular nanoparticles were used for NIR imaging. This report shows that multi-stage assembly is a convenient and considerable strategy for enhancing the photoluminescence efficiency in aqueous solution. On the strength of the development of solid-state phosphorescence, the water-soluble supramolecular assembly with biocompatibility was constructed by taking advantage of co-assembly and "macrocyclic host induces phosphorescence of guest".³ In Figure 5b, hyaluronic acid (HA) was modified with phosphor BrBp, and biaxial pseudorotaxane polymer was



Figure 3. (a) Synergistic enhancement (polymerization and complexation enhancement) strategy for ultralong and efficient room-temperature phosphorescence. τ represents the lifetime of PH-0.1 and PH-0.1/CB[6], and Φ_p is the phosphorescent efficiency of PBr-1 and PBr-1/CB[6]. Reproduced with permission from ref 34. Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA. (b) Time-resolved PL decay of copolymer with a different ratio of PH in the 490 nm state at room temperature in the solid. The results indicated that polymerization would significantly enhance phosphorescence but suffer from obvious ACQ effects. (c) Time-resolved PL decay of copolymer PH-1 with different CB[n]. The results indicated that the ACQ effect was significantly weakened by host–guest interaction.



Figure 4. Illustration of NIR fluorescent supramolecular assemblies and related supramolecular aggregates. Reproduced with permission from ref 38. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA.

formed after binding with CB[8]. Noticeably, this supramolecular polymer possessed an ultralong purely organic RTP lifetime in water of up to 4.33 ms with a quantum yield of 7.58%. The uncommon phosphorescence in water solution was owing to the stable 1:2 inclusion complex between CB[8] and BrBP and hydrogen-bond networks of the HA polymers: the





Figure 5. (a) Schematic illustration of the twin-axial pseudorotaxane. Reproduced with permission from ref 39. Copyright 2021 The Royal Society of Chemistry. (b) Construction and behavior of CB[8]/HA-BrBP supramolecular pseudorotaxane polymers in aqueous solution. Reproduced with permission from ref 3. Copyright 2021 Nature.



Figure 6. (a) Schematic illustration of pseudorotaxane whose binding form is 2:2 and head-to-head. Reproduced with permission from ref 42. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Photoluminescence emission spectra of phosphor with different ratios of CB[8]. And chromaticity coordinate of titration process to which phosphor was added with different ratios of CB[8]. Inset: photographs of TBP with equiv CB[8] in H_2O .

encapsulation of CB[8] could promote the guests' interaction such as $\pi - \pi$, Br $- \pi$, and halogen bonding; the multiple hydrogen bonding from HA could lock the BrBP units. Besides, the large supramolecular nanoparticles generated from co-assembly reduce the disturbance from the water environment. In other words, the multi-stage assembly restricted molecular motion and promoted ISC. Interestingly, the introduction of HA did not just greatly enhance phosphorescence but also allowed the targeting of the mitochondria of cancer cells. Furthermore, the addition of the up-conversion nanoparticles to the supramolecular polymer could achieve NIR-activated biological phosphorescence imaging. In addition to constructing nanoparticles, supramolecular assembly was utilized to enhance the intermolecular interaction between phosphors and then facilitate phosphorescence. Diethanolamine-modified phenylpyridine formed twin-axial pseudorotaxane after binding with CB[8].³⁹ Because of the "head-to-tail" binding form and hydrogen bond between diethanol amine and CB[8], the distance between Br and O=C was drawn close, and this promoted the formation of the halogen bond (Figure 5a). Furthermore, the cooperative effect of the host's rigid cavity and blocking of diethanol amine further protected the assembly from water. Benefitted by effective phosphorescence, the pseudorotaxanes were successfully used for the targeted mitochondria cell imaging of living cells with low biotoxicity.

Phosphorescence possesses unique merit when applied to biological imaging. Except for a long lifetime which could suppress interference from the cellular environment, a large Stokes shift is another advantage for phosphorescence imaging because it could penetrate more deeply into biotissues.^{40,41} Therefore, bathochromic-shift phosphorescent imaging be-



Figure 7. (a) Schematic illustration of supramolecular pins and the gradual enhancement of phosphorescence. Reproduced with permission from ref 4. Copyright Wiley-VCH GmbH. (b) Schematic illustration of the formation of a supramolecular nanoparticle with NIR emission. Reproduced with permission from ref 46. Copyright Wiley-VCH GmbH.

comes a potential research direction. Ma et al. reported a pseudorotaxane composed of a triazine-bridged guest and CB[8].⁴² The binding form of pseudorotaxane is 2:2 and headto-head, which would lead to bathochromic-shift photoluminescence emissions because of charge-transfer complexes (Figure 6a). Through adding different molar ratios of CB[8] to the guest solution, tunable emission which is from blue to white and yellow was achieved (Figure 6b). This approach, which utilizes a strong host-guest interaction to promote intermolecular interaction, provides design strategies for supramolecular RTP materials. It is well known that the ISC rate is closely related to spin-orbit coupling and the energy difference between S and T states (ΔE_{ST}), and reducing the $\Delta E_{\rm ST}$ can enhance the $k_{\rm isc}$.⁴³ Designing molecules with strong intramolecular charge transfer (ICT) is an effective strategy for minimizing ΔE_{ST} .⁴⁴ However, reports about regulating ICT by a macrocyclic host to facilitate phosphorescence are still rare. Recently, our group reported supramolecular assembly based on the molecular-folding binding form.⁴ Bridged phenylpyridinium salt fluorophores with donor-acceptor moieties formed a "supramolecular pins" assembly after binding with CB[8] (Figure 7a). Significantly, the fluorescence of assembly was completed quenched and effectively turned into phosphorescence, and the high quantum efficiency of ISC from S_1 to T_n states was attributed to the head-to-head form. Different from head-to-tail assembly, head-to-head assembly overcomes electrostatic repulsion and promotes intramolecular charge transfer so that the rate of ISC was effectively accelerated. Owning to the generation of the exciplex and Stokes shift of phosphorescence, the luminescence moves to the red area and could be distributed in the NIR region, and assembly was applied for biological imaging. In addition, the phosphorescence could be markedly improved after incorporation into a matrix rich in hydroxyl groups (phosphorescence quantum yields of up to 99.38%). Strong intramolecular charge transfer not only leads to the emission bathochromic shift but also might lead to the red-shift absorption.⁴⁵ Our group constructed a two-photon supramolecular ternary assembly with NIR fluorescence emission (Figure 7b).⁴⁶ Unbound guest (tetraphenylethene derivative) showed feeble fluorescence at 650 nm in aqueous solution. The emission was significantly strengthened and red-shifted to 680 nm after multi-stage assembly with CB[8] and HA-CD. Interestingly, such supramolecular nanoparticles with NIR emission having twophoton excitation were successfully applied for mitochondrial targeted cell imaging of A549 cancer cells. Photoluminescence excited by NIR light can avoid the absorption of proteins in cell culture. Molecules with two-photon absorption might provide a new gate for NIR RTP materials. Wu et al. reports difluoroboron derivatives possessing D-A structure, and the RTP could be excited by visible light and NIR owing to the intramolecular/intermolecular charge transfer and large two-photon absorption cross sections.⁴⁰ And the cellular imaging experiment was performed via dispersing the nanoparticles in water.

2.4. Förster Resonance Energy Transfer Based on Supramolecular Assembly

Förster resonance energy transfer (FRET) means changes in the electronic interactions between a donor and an acceptor in close proximity. One of the advantages of FRET is a large Stokes shift. In 2017, we developed efficient artificial lightharvesting systems constructed from the noncovalent supramolecular assembly (Figure 8).²⁷ The OPV-I and SCD could generate supramolecular nanoparticle in aqueous solution via electrostatic interactions, and the fluorescence properties of OPV-I were greatly enhanced because the process of assembly promoted AIE. Notably, owing to hydrophobic space provided by co-assembly, Nile red dyes as acceptors could assemble with OPV-I/SCD, and then an ultraefficient fluorescence resonance energy transfer process with OPV-I could occur (Figure 8b). Most importantly, supramolecular multi-stage assembly brings about great benefits for fluorescence resonance energy transfer, and this supramolecular light-harvesting system displayed an ultrahigh antenna effect (up to 32.5) and donor/acceptor ratio (up to 125:1), which are better than for natural light-harvesting



Figure 8. (a) Construction of the light-harvesting system. Reproduced with permission from ref 27. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Fluorescence spectra of OPV-I/SCD in water with different concentrations of NiR.

systems. Different from fluorescence resonance energy transfer, phosphorescence resonance energy transfer (PRET) could achieve the transfer of phosphorescent properties or triplet-state energy transfer, which means that the acceptor could obtain the ability of a long-lived lifetime.⁴⁷ In aqueous solution, it is difficult to realize PRET because we need to control the distance between the donor and acceptor and maintain effective phosphorescence. Supramolecular co-assembly provides a convenient approach to achieving PRET. Our group reported a light-harvesting phosphorescence energy transfer base on a multi-stage supramolecular assembly (Figure 9).⁴⁸ 4- (4-Bromophenyl)-pyridine as a phosphorescence donor was modified β -cyclodextrin (CD-PY), and supramolecular assemble

bly CD-PY/CB[8] which possessed effective phosphorescence existed as nanoparticles. The further addition of a small amount of RhB could lead to highly efficient PRET with high energy transfer efficiency (84%) and exhibited an ultrahigh antenna effect (36.42). Multi-stage assembly occurred after adding adamantane-modified hyaluronic acid (HA-ADA), and the strong binding between CD and adamantane could further encapsulate the assembly and then enhance PRET. In addition, the nanoparticles could aggregate in the mitochondria of A549 cancer cells.



Figure 9. Construction of the supramolecular assembly for a purely organic light-harvesting PET system and related molecules. Reproduced with permission from ref 48. Copyright 2021 The Royal Society of Chemistry.



Figure 10. (a) RTP and reversible white-light emission switching based on the cyclodextrin polypseudorotaxane xerogel. Reproduced with permission from ref 49. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Photographs of (top) a hydrogel dropped into a glass before and after drying under 365 nm UV light and letters written by water before and after drying under 365 nm UV light and (bottom) a hydrogel coated into the surface of the diode before and after drying under 365 nm UV light.

2.5. Humidity Sensor Mediated by Supramolecular Assembly

By controlling the supramolecular interaction, we could regulate the emission of phosphorescence. We report that a supramolecular xerogel possessing dual emission properties and photoluminescence could be reversible switched by controlled humidity.⁴⁹ In this work, a polymer with a bromobenzaldehyde core and PEG was synthesized (Figure 10a). After binding with α -CD, the linear polymer is threaded into α -CD cavities and a supramolecular polypseudorotaxane is constructed. Owning to the binding of cavities and the hydrogen-bonded network which originate among α -CDs, the xerogel displays fluorescence—phosphorescence dual emission. Interestingly, white light emission can be regulated by using water to destroy the hydrogen bond network. This feature is utilized for data encryption, the blue fluorescence emission of the characters which were written on the surface of the dry gel could be clearly observed under UV light, and the characters were erased after drying (Figure 10b). In addition, we constructed hybrid xerogel based on electrostatic interactions (Figure 11).⁵⁰ After incorporation into a cationic amino clay (AC), supramolecular assembly 7-[6-deoxy-6-(2-sulfonic)]- β -



Figure 11. (a) Construction of the AC/SCD⊃PYCl hybrid hydrogel and xerogel. Reproduced with permission from ref 50. Copyright 2020 Wiley-VCH GmbH. (b) Effect of humidity on the phosphorescence spectrum of the AC/SCD⊃PYCl gel (left) and phosphorescence spectra (at 503 nm) of the dry gel and the gel at 70% humidity (right). Inset: variation of the phosphorescence intensity with the number of drying/wetting cycles.

cyclodextrin (SCD) with the phosphor bromophenyl-methylpyridinium chloride (PYCl) could be coagulated in situ. Bound by electrostatic interactions, AC/SCD⊃PYCl could lead to fluorescence–phosphorescence dual emission. Notably, the intensity of the xerogel RTP varies with humidity and can be switched on and off repeatedly (Figure 11b).

CONCLUSIONS AND PERSPECTIVES

In this Account, we summarized recent advances in the supramolecular RTP systems involving the cooperative work of host-guest interaction, polymerization, and supramolecular multi-stage assembly, meanwhile, applications such as anticounterfeiting, data encryption, targeted imaging, and humidity sensor have also been preliminarily explored. The summary might be able to offer some possible hints and inspirations for developing purely organic RTP materials, and the organic combination of multiple strategies might be able to generate additional properties while improving RTP performance.

According to the recent progresses in supramolecular RTP materials, we would like to conclude and present the developing concept "macrocycles enhance guest's phosphorescence", and the core thought is that the "macrocyclic host limits the movement of guest and promotes multi-stage supramolecular assembly". Tang et al. proposed the significant concept "aggregation-induced emission, AIE", ³⁰ and they found that aggregation restricts the intramolecular movement by aggregation, which would overcome the weak luminescence in the solid state. In 2014, Tian et al. put forward a concept of "assembly-induced emission", which means "control molecular

motions, then control emission" via supramolecular assembly.³¹ With these concepts, "macrocycles enhance guest's phosphorescence" would further promote the development of RTP. This supramolecular strategy not only takes advantage of multiassembly to enhance luminosity but also incorporates extra components such as biocompatibility and then achieve the "1 + 1 > 2" effect.

Although there are still more challenges for purely organic RTP, which is to further improve biological compatibility and stability and enhance the performance of phosphorescence such as the long-lived lifetime in aqueous solution, NIR excitation and emission, and so on, the supramolecular assembly would be an enlightening solution for these difficulties: increasing the extent of conjugation or phosphorescence energy transfer provides feasible strategies for NIR RTP materials. AIE caused by supramolecular assembly provides potential strategies for more efficient RTP materials. In addition, other host-guest interaction systems such as "polymer enhanced guest's phosphorescence" and "guest doped host" would show extraordinary talents in supra-molecular phosphorescence.^{28,29,51} We believe the concept "macrocycles enhance guest's phosphorescence" would be bound to promote the development of RTP materials, biologically targeted systems, drug delivery systems, and so on.

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Notes

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