

Targeting Compact and Ordered Emitters by Supramolecular Dynamic Interactions for High-performance Organic Ambient Phosphorescence

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Dedicated to the 20th anniversary of the Ningbo Institute of Materials Technology and Engineering

Purely organic room-temperature phosphorescence (RTP) materials have received intense attention due to their fascinating optical properties and advanced optoelectronic applications. The promotion of intersystem crossing (ISC) and minimalization of nonradiative dissipation under ambient conditions are key prerequisites for realizing high-performance organic RTP; However, the ISC process is generally inefficient for organic fluorogens and the populated triplet excitons are always too susceptible to be well stabilized by conventional means. Particularly, organizing organic fluorophores into compact and ordered entities by supramolecular dynamic interactions has proven to be a newly-emerged strategy to boost the ISC process greatly and suppress the non-radiative relaxations immensely, facilitating the population and stabilization of triplet excitons to access high-performance organic RTP. Consequently, well-defined organic emitters enable robust RTP emission even in the solution state, thus greatly extending the applications. Here, this review is focused on a timely and brief introduction to recent progress in tailoring ordered high-performance RTP emitters by supramolecular dynamic interactions. Their typical preparation strategies, optoelectronic properties, and applications are thoroughly summarized. In the summary section, key challenges and perspectives of this field are highlighted to suggest potential directions for future study.

afterglow lasts from several seconds to hours after photoexcitation under ambient conditions. The discovery of the afterglow miracle has a long history that can be traced back to 1602 when an Italian shoemaker observed the first “night-vision” substance, the Bologna stone.^[1] Since then, the afterglow materials have attracted considerable interest from scientists and laymen owing to their fascinating aesthetic value and promising applications. Initially, inorganic phosphors were prepared for practical utilities in afterglow displays, emergency signage, optoelectronic devices, and so on.^[2] Although these inorganic phosphors generally exhibit satisfactory afterglow in the dark, severe environmental pollution, high cost, harsh preparation conditions, and limited metal resources have been unavoidable and intractable problems.

In recent decades, organic RTP materials have received intense attention owing to their comparable mild reaction conditions, abundant chemical designs, superior biocompatibility, and variable properties. Briefly, organic RTP originates from a

tardily radiative transition of excitons from triplet excited state (T_1) to singlet ground state (S_0) (Figure 1), exhibiting attractive optical properties such as long luminescent lifetime, large Stokes shift, and sensitive stimuli-responsiveness. Therefore,

1. Introduction

Room-temperature phosphorescence (RTP) is a mysterious optoelectronic phenomenon in which self-sustained, night-visible

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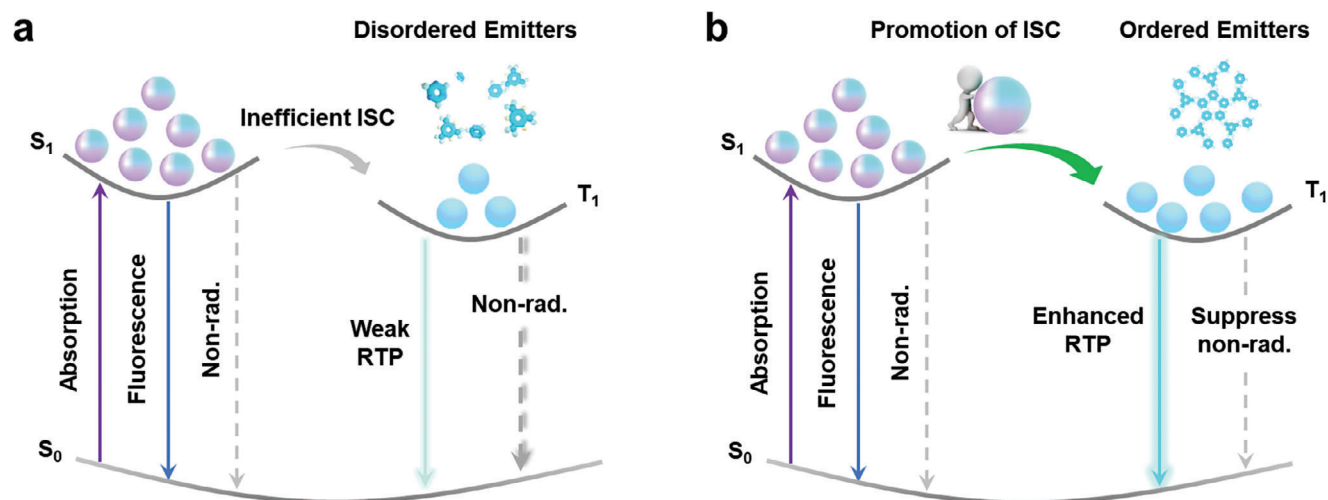


Figure 1. Schematic Jablonski diagram for a) disordered, b) compact and ordered organic RTP systems. The ordered and compact emitters generally display enhanced RTP performance compared with their disordered counterparts.

organic RTP materials provide a wide range of promising applications in organic light-emitting diodes (OLEDs), data encryption and anti-counterfeiting, bioimaging and diagnostics, chemical sensing, etc. The efficient population and effective stabilization of triplet excitons are two key prerequisites for achieving high-performance RTP; However, the forbidden transition of intersystem crossing (ISC) is generally unfavorable due to the low spin-orbit coupling (SOC) of organic fluorogens. In addition, the susceptible triplet excitons are easily quenched by molecular vibrations and external quenchers, especially for disordered and incompact systems (Figure 1a). As such, both the promotion of the ISC process and the suppression of nonradiative decay are highly essential for achieving high-performance organic RTP. To date, the following methods have been established to promote ISC by enhancing SOC including heavy-atom designs, the introduction of heteroatoms, and aromatic carbonyls, which are beneficial for populating more triplet excitons. For another, deuteration,^[3] organic crystallization,^[4] aggregation,^[5] matrix rigidification,^[6] construction of frameworks,^[7] and other strategies have been well explored to stabilize the susceptible triplet excitons for achieving long-lived RTP.

Among various strategies for achieving organic RTP, tailoring compact and ordered emitters by dynamic noncovalent interactions has proven to be an efficient method to access high-performance organic RTP in the crystalline, amorphous states, and even in solution phase (Figure 2).^[8] Driven by non-

covalent interactions such as hydrogen bonding, π - π stacking, electrostatic interaction, and van der Waal's forces, relatively compact and ordered organic emitters can be efficiently assembled, which is beneficial to promoting the ISC process and minimizing non-radiative relaxations for achieving high-performance RTP materials (Figure 1b). For one, the compact and ordered assembly and aggregation of fluorogens often result in more ISC channels and contribute to the minimization of singlet-triplet splitting energy (ΔE_{ST}) due to intermolecular/intramolecular charge transfer, electron distribution, and coupling, thus boosting the ISC process for populating more triplet excitons.^[8b,9] Also, significant SOC enhancement may be realized by the self-assembly of the organic fluorogens with the help of supramolecular dynamic interactions.^[9c,d] For another, the molecular motions such as vibrations and rotations of organic fluorogens, as well as intermolecular collisions are immensely inhibited by compact and crowded environments for stabilizing susceptible triplet excitons to greatly enhance RTP performance.^[8b,10] That is, unique and high-performance RTP materials can be effectively achieved even in solution and amorphous states by the strategy of tailoring fluorogens into ordered entities.

To date, a series of significant progress has been made in this field with rapid development in recent years. These impressive advancements motivated us to provide an in-depth and timely summary of achieving high-performance ordered RTP emitters by supramolecular dynamic interactions. Recent high-quality reviews mainly discussed supramolecular RTP materials with a focus on the summary of their photophysical properties, diverse applications, and unique strategies including host-guest encapsulation, nanoassembly, and macromolecule confinement.^[11] In this review, we aim to summarize the unique properties of order RTP emitters such as ultralong lifetime, high quantum yield and water-resistance, and disclose the underlying mechanism of the high-performance RTP emission. We begin with the status and development of preparation methods for achieving ordered organic RTP materials including the direct organization of organic small fluorogens and luminescent polymers by supramolecular

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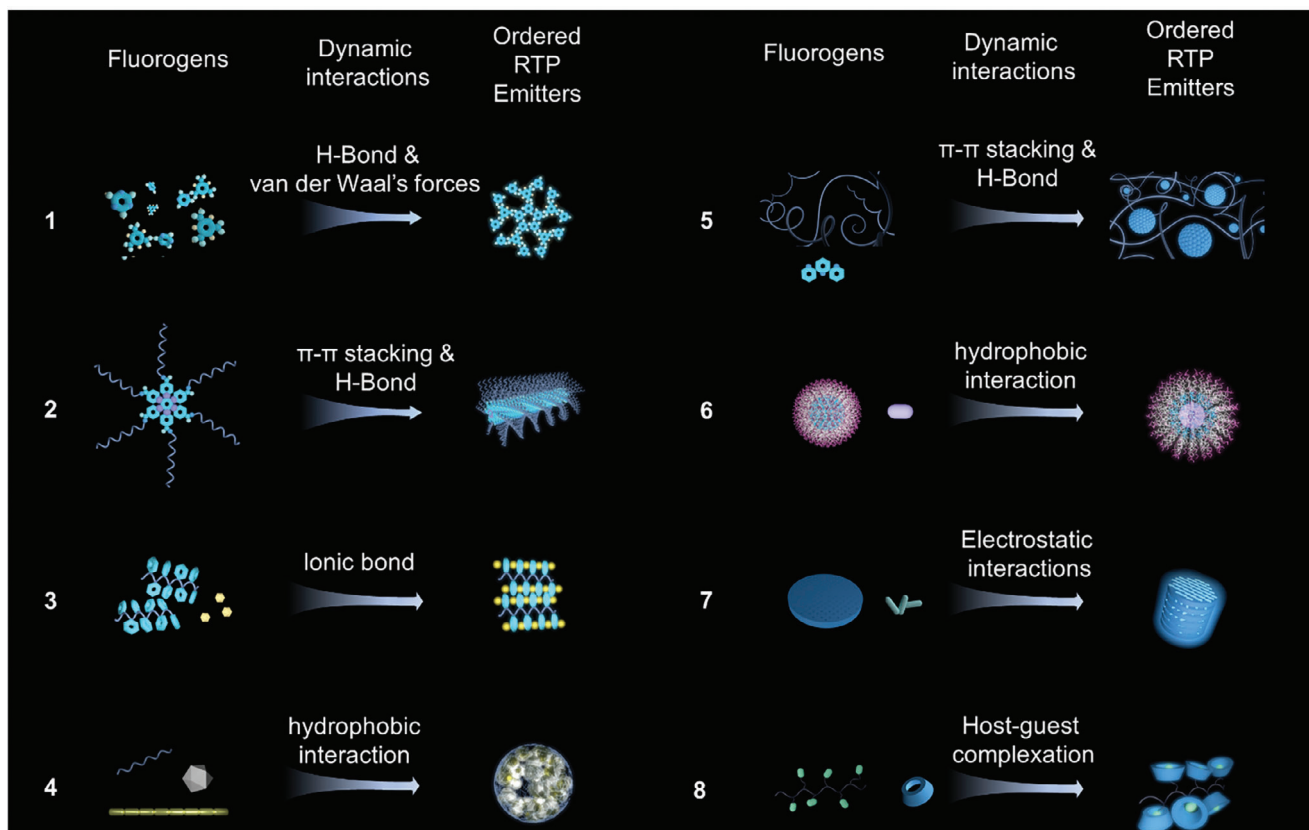


Figure 2. The strategies of preparing compact and ordered RTP emitters by dynamic non-covalent interactions. (1-2) The direct organization of small organic fluorogens to obtain ordered RTP emitters driven by multiple dynamic interactions. (3-4) The direct organization of emissive polymers to form relatively well-defined RTP emitters by leveraging dynamic interactions. (5-8) The assembly of fluorogens in the confined microenvironments (rigid polymeric matrices, supramolecular scaffolds, and macrocyclic hosts) to achieve high-performance RTP materials.

dynamic interactions, as well as assembly of fluorogens in confined environments (polymeric matrices, supramolecular scaffolds, and macrocyclic hosts); The tunable and abundant RTP properties and underlying luminescent mechanisms are also highlighted. Next, we summarize promising applications of related organic RTP materials spanning from bioimaging and afterglow display to information encryption and chemical sensing. In the final section, we present the current challenges and perspectives of this field for future development to motivate more research efforts and interests.

2. Preparation Strategies, Properties, and Mechanisms

Several approaches have been developed to achieve compact and ordered organic emitters with high-performance RTP emission by the organization of organic phosphors into well-defined phosphorescent emitters including the direct organization of organic small fluorogens and luminescent polymers, and assembly of fluorogens in confined microenvironments. (i) The organic small fluorogens can be organized into well-defined supramolecular architectures and nanostructures driven by dynamic interactions; (ii) Also, the emissive polymers are capable of forming relatively compact and ordered RTP entities by leveraging dynamic interactions; (iii) Especially, the fluorogens can be assembled into com-

compact and ordered RTP emitters in the confined microenvironments such as rigid polymeric matrices, supramolecular scaffolds, and macrocyclic hosts with the help of supramolecular interactions. It is worth noting that the ubiquitous supramolecular dynamic interactions endow the assembly process with excellent reversibility, promoting the formation of compact and ordered thermodynamically stable RTP emitters. In addition, the organic phosphors can be well immobilized in the ordered assemblies by supramolecular dynamic interactions. Thus, tailoring the fluorogens into compact and ordered emitters by supramolecular dynamic interactions generally exhibits a certain universality in preparing high-performance RTP materials. More importantly, the self-assembly process allows periodical and regular arrangement and stacking of organic phosphors, leading to the enhancement of SOC and minimization of ΔE_{ST} by providing more ISC channels and inter/intramolecular charge transfers. Furthermore, the compact and crowded environments that originated from the assembled architectures immensely inhibit non-radiative decay, facilitating the elongation of the RTP lifetime. More importantly, solution-state and robust RTP materials can be successfully achieved through tailoring fluorogens into ordered entities, which are challenging to be realized by conventional methods. In this section, we discuss the key advances in preparation methods, optical properties and fundamental mechanisms for compact and ordered organic RTP materials.

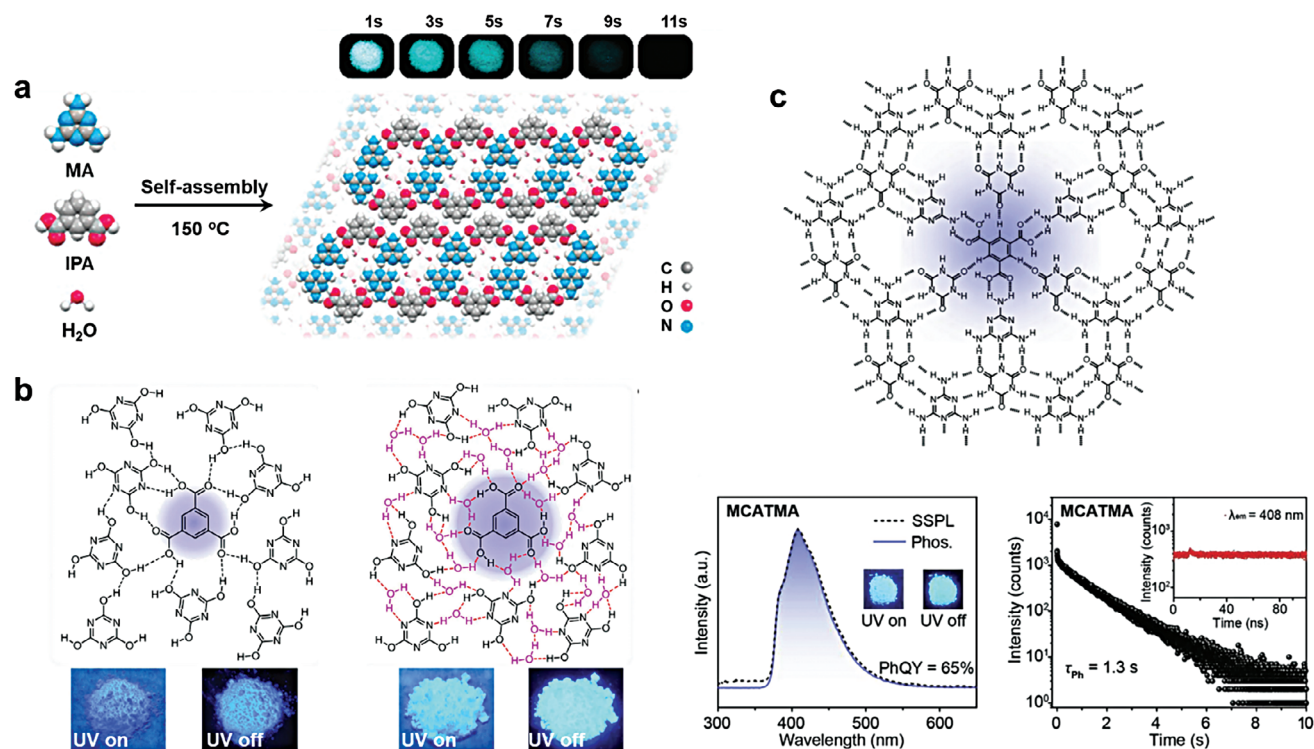


Figure 3. Self-assembly of organic small molecules to achieve highly ordered supramolecular networks with high-performance RTP emission. a) The self-assembly of aryl dicarboxylic acid (IPA) with melamine (MA) by strong hydrogen bonds and van der Waal's forces. Reproduced with permission.^[12] Copyright 2018, American Chemical Society. b) The assembled RTP materials by multiple hydrogen bonds between benzoic acid and cyanuric acid (CA) (left) and after water implementation (right). Reproduced with permission.^[13] Copyright 2020, The Author(s). c) Three-component assembly of MA, CA and trimesic acid (TMA) to provide 2D well-defined tricomponent supramolecular RTP network. Reproduced with permission.^[14] Copyright 2022 Wiley-VCH GmbH.

2.1. Direct Organization of Small Fluorogens

In general, the compact and ordered materials exhibit superior RTP performance compared with their disordered counterparts owing to lower molecular motion degrees of freedom and enhanced ISC process. The organization of small molecules into uniform and compact entities often render high-performance organic RTP, which can be driven by dynamic noncovalent interactions such as hydrogen bonds, π - π stacking interactions, hydrophilic and hydrophobic forces. In 2018, Huang and An et al. achieved a highly efficient ultralong organic RTP material (MA-IPA) through the self-assembly of aryl dicarboxylic acid (IPA) with melamine (MA) driven by multiple strong hydrogen bonds and van der Waal's forces (Figure 3a).^[12] By locking aromatic acids in such a rigid supramolecular network, the ISC process is greatly promoted by enhancing SOC, and nonradiative deactivation of triplet excitons is immensely inhibited, leading to bright bluish green RTP emission (488 nm) with a synchronously enhanced ultralong lifetime of up to 1.91 s and satisfactory phosphorescent quantum efficiency (PhQY) of 24.3%. As such, fascinating cyan afterglow lasting for ≈ 20 s can be observed by the naked eyes. Also by leveraging the coassembly of small fluorogen, Huang and Xing et al. achieved a new family of deep-blue RTP materials with high PhQYs and ultralong lifetimes up to 9.3% and 1.13 s, respectively (Figure 3b).^[13] It involves the introduction of benzoic acid derivatives (i.e., trimesic acid (TMA), isoph-

thalic acid (IPA), terephthalic acid (TPA), and phthalic acid (PA) as guest molecules into a rigid host matrix of cyanuric acid (CA). Owing to the assembly of benzoic acid derivatives with CA by multiple strong hydrogen bonds, efficient Dexter energy transfer from host to guest was realized to sensitize the population of triplet excitons of guest, and the nonradiative pathway of triplet excitons was immensely inhibited (Figure 3b, left). Moreover, the PhQY and lifetime were significantly enhanced up to 46.1% and 1.67 s, respectively, after implementing water to further rigidify the assembled matrix with more hydrogen bonding interactions (Figure 3b, right).

It is worth noting that achieving high-performance RTP with an ultralong lifetime and high PhQY at the same time is extremely challenging for conventional construction strategies. In 2021, Huang and Chen et al. reported highly stable deep-blue RTP composites with ultralong lifetime of up to 5.08 s and excellent PhQY of 16.1% by using CA as a rigid host to assemble and accommodate phosphor guest of 1,4-benzodiboronic acid (BDA).^[9d] Notably, the PhQY was considerably improved up to 37.6% after water implementation attributed to the enhanced hydrogen bonding for forming a more dense and rigid network to minimize triplet excitons quenching. In another attempt, they presented a three-component assembly of MA, CA and TMA to provide 2D tricomponent supramolecular RTP material (MCATMA) (Figure 3c).^[14] Outstandingly, the TMA phosphors were well settled and protected in the robust superlattices

by multiple hydrogen bonds, leading to significant suppression of non-radiative relaxation decays of triplet excitons, giving deep blue RTP with high PhQY (65%) and ultralong lifetime more than 1.3 s, simultaneously. Benefiting from the formation of a quenching barrier by the 2D superlattices, the resultant RTP material showed excellent stability of performance toward solvent, oxygen, pressure, mechanical grinding, light, and heat (up to 473 K), which is highly desirable for practical applications including information encryption and anti-counterfeiting. These impressive studies not only outlined the design and preparation principles for achieving compact and ordered supramolecular emitters with high-performance and robust RTP emission, but also expanded the scope of novel optical materials.

Recently, the formation of compact and ordered crystalline organic frameworks such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs) and hydrogen-bonded organic frameworks (HOFs) also has been proven to be an effective way to realize high-performance RTP materials.^[15] With the immobilization of fluorogens in these crystalline frameworks, the molecular vibrations and triplet–triplet annihilation are largely minimized, contributing to efficient RTP. In 2018, Wang and Feng et al. reported COF-based phosphorescence and disclosed that H-type aggregation and intermolecular distance played important roles in the properties of phosphorescence.^[16] Impressively, Perepichka and coworkers reported a family of COFs-based RTP materials by co-condensation of halogenated (Cl, Br) and unsubstituted phenyldiboronic acids.^[17] By regulating the halogen dopant, the optical properties including phosphorescence/fluorescence ratio, quantum yield (highest PhQY = 29.1%) and lifetime ($\tau_{\text{max}} = 259$ ms) could be finely modulated. Benefiting from the permanent porosity of COFs structure, the COFs-based RTP materials are highly desirable for oxygen sensing with an ultra-wide detection range. Strikingly, Wu and coauthors presented HOFs-based RTP materials with water resistance by in situ supramolecular assembly.^[18] It was found that the ordered and compact HOFs matrix immensely suppresses the vibrational relaxation and provides an excellent quencher barrier to isolate the populated triplet excitons, leading to aqueous phase RTP emission.

With no doubt, dynamic and stimuli-responsive RTP materials hold great promise for smart optical applications. Notably, Tang and Yu et al. presented photo-thermo-induced organizations of molecular rotors for achieving smart-responsive RTP materials (Figure 4a).^[19] The molecular rotors were designed and synthesized by introducing three bromobiphenyl units onto a triazine core (*o*-Br-TRZ, *m*-Br-TRZ, and *p*-Br-TRZ), which displayed superior photothermal effect by intramolecular rotation upon intense UV irradiation. Consequently, the photothermal effect allowed the molecular rearrangement of these rotors to create compact and ordered RTP entities, accompanied by an obvious increment of PhQY. In the same year, Chi and Tang reported guest-responsive dynamic RTP by assembling fluorogens into antiparallel molecular chains via intermolecular C–H \cdots O = S hydrogen-bonding and π - π interactions (Figure 4b).^[20] The assembled architecture had uniform small open cavities, and thus provided dish-like nanostructures to reversibly accommodate guest molecules such as DMF, THF, DMSO, and DCM. As a result, the RTP performance was improved significantly with PhQY increased up to 78.8% and a lifetime prolonged up

to 483.1 ms owing to effective suppression of nonradiative decay upon guest accommodation. Besides the aggregation of single components, Zhang and coauthors reported a bicomponent aggregation-induced phosphorescence (AIP) with PhQY up to 25.4% and a lifetime of 48 ms by blending a sp^3 -linked luminogen (BrBID) with a trace of its analog (X).^[21] Owing to the inhibition of compact packing by a sp^3 linker, the BrBID showed typical aggregation-induced emission (AIE) features with bright green–blue photoluminescence at solid state; However, long-lived RTP of BrBID was absent, unless the bicomponent host-guest system of BrBID and impurity X was implemented. By cocrystallization of BrBID and X, orbital interaction occurred between the σ^* (C–Br), π^* of BrBID and the non-bonding orbital (NME₂) of X, resulting in substantially prolonged RTP.

As one type of typical AIE luminophore, polysulphated benzene derivatives have attracted great interests in fabricating RTP materials.^[22] In 2014, Gingras and Ceroni et al. developed a novel paradigm for turning on RTP emission by dynamic coordination between terpyridine-functionalized hexathiobenzene and Mg²⁺.^[22b] Owing to the immense restriction of intramolecular motions by coordination with Mg²⁺, the assembled metal-organic coordination polymer displayed an intense RTP emission at 543 nm with a lifetime of 5.3 μ s in THF solution. In addition, the green RTP emission could be switched off upon the addition of fluoride ions due to the dissociation of metal-ligand coordination, thus enabling time-gated fluoride ion sensing. In the past few years, Zhu and coauthors employed hexathiobenzene derivatives as a fascinating prototype to systematically study the impact of their self-assembly and aggregation on RTP performance. In 2017, they presented self-assembly-induced RTP that revealed a switchable singlet-triplet emission by regulating helical supramolecular assembly and disassembly in both solution and solid state.^[23] It was found that the self-assembly of hexathiobenzene-based chiral phosphor had a great impact on the molecular energy level and ISC process so that phosphorescence-to-fluorescence conversion (from 550 to 428 nm) could be controllably realized in the solution state. On the contrary, the emission underwent an obvious red-shift in the solid state of such asterisk-shaped phosphor, displaying the merit of mechanoluminescence. In the same year, they reported tunable fluorescence-phosphorescence dual emission in the solution state based on molecular stacking variations.^[27] The organic phosphor was designed and synthesized by introducing six acetamide groups onto a hexathiobenzene core, which was prone to assemble into nanorods in DMF/H₂O mixtures with different water fractions. Owing to the compact molecular packing in relatively poor solution conditions, RTP emission at 550 nm with a lifetime of 16.43 μ s was activated, leading to multicolor luminescence from greenish to white and finally to yellow.

In another attempt, Zhu and coauthors reported a photoexcitation-controlled self-recoverable AIP system (Figure 5a).^[24] The organic phosphor was designed and synthesized by introducing six carboxylate groups onto a hexathiobenzene core, exhibiting an interesting phenomenon that led to an aggregation in water upon light irradiation. Owing to molecular aggregation, the non-radiative pathway was profoundly suppressed, and thus activating green RTP (505 nm, 65.3 μ s) in aqueous media. In addition, such RTP emission was diminished immediately upon ceasing the irradiation light due

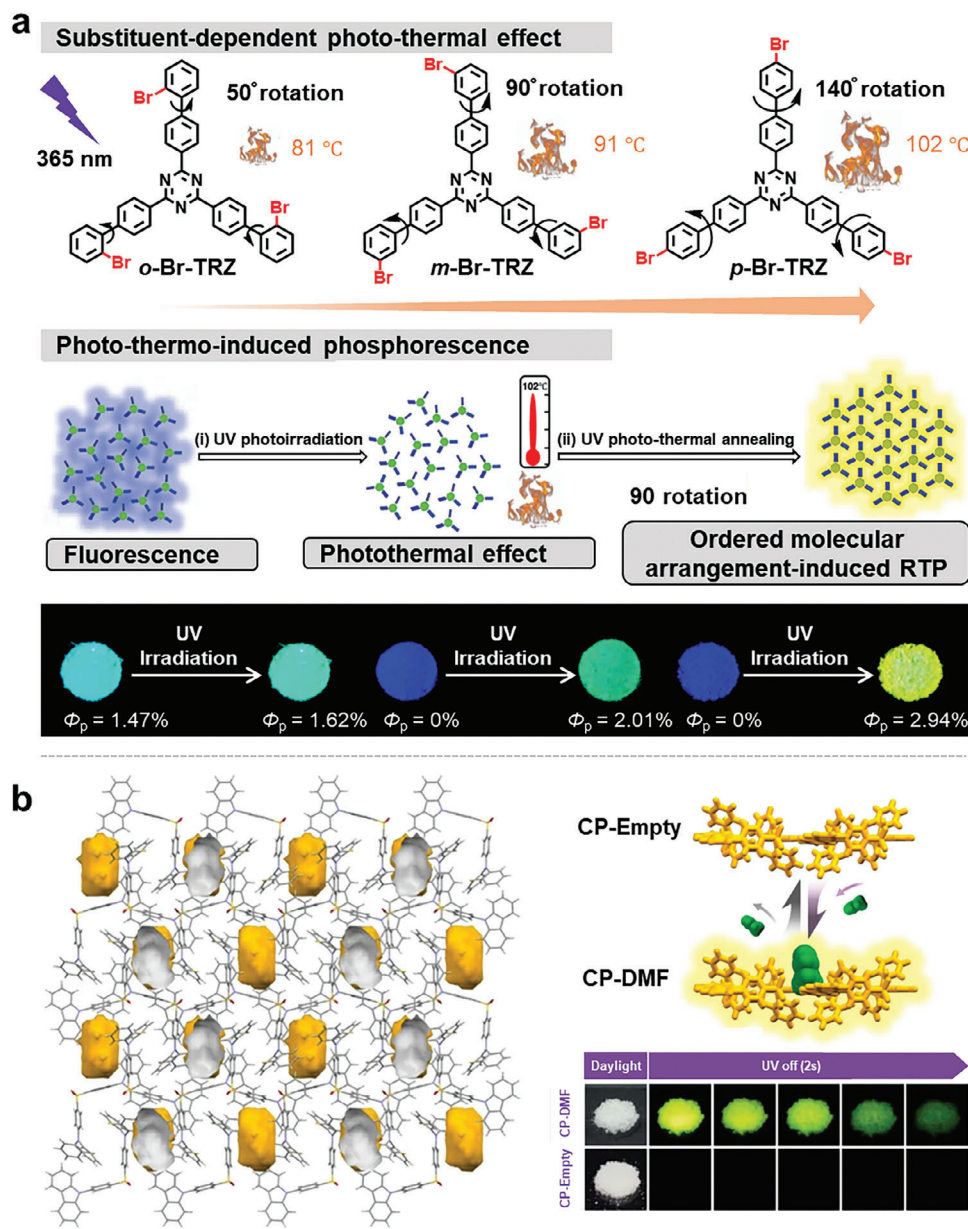


Figure 4. The dynamic assembly of fluorogens for accessing stimuli-responsive ordered RTP materials. a) The photo-thermo-induced organizations of molecular rotors for creating compact and ordered RTP entities. Reproduced with permission.^[19] Copyright 2022, The Author(s). b) The assembled dish-like architecture revealed the guest-responsive dynamic RTP phenomenon. Reproduced with permission.^[20] Copyright 2022, The Author(s).

to the dissociation of the assembly, showing self-recoverable and dynamic features. This photoexcitation-controlled self-recoverable RTP material holds great promise in dynamic flicker bioimaging under rhythmic irradiation. Later in 2020, the Zhu group developed a multi-stimuli responsive RTP system based on hexakis(pyridin-4-ylthio)-benzene (HPTB).^[28] This asterisk-shaped luminogen showed a blue luminescence (410 nm) in DMF solution due to its well-dispersion; However, such blue fluorescence could be converted into green (515 nm, 55.87 μ s), yellow (540 nm, 103.6 μ s) and orange (570 nm, 236.8 μ s) RTP emission upon the addition of CH_3OH , H^+ , and Ag^+ , which could be attributed to the self-assembly and aggregation of HPTB

into nanostructures. One year later, Zhu and Jia et al. developed a novel photoexcitation-controlled-aggregation-induced phosphorescence based on a phenyl group-modified hexathiobenzene derivative (Figure 5b).^[25] Upon irradiation with 365 nm light, the organic phosphors were prone to assemble into uniform nanoscale aggregates in organic solutions, inducing strong cyan RTP at 470 nm; However, the RTP emission at 470 nm disappeared under prolonged irradiation due to the formation of impurities from photo-oxidation. A similar phenomenon was also observed when this organic phosphor was doped with a poly(methyl methacrylate) (PMMA) gel, revealing a fascinating photoexcitation-controlled-AIP. Moreover, they presented a

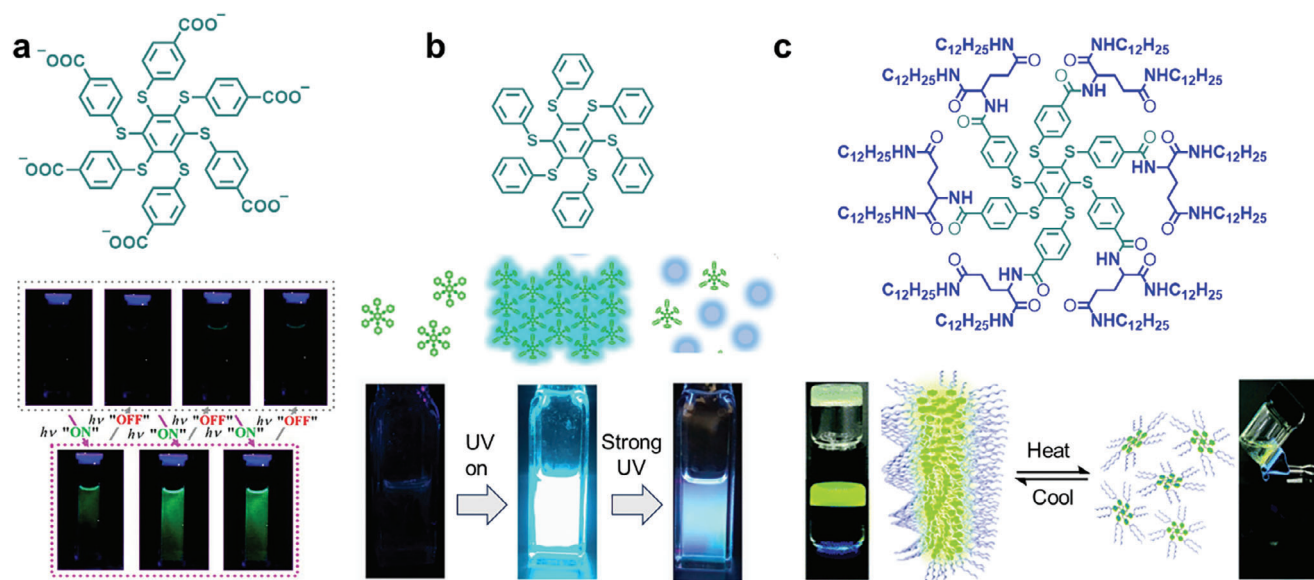


Figure 5. The assembly and photo-controllable aggregation of hexathiobenzene derivatives into compact and ordered entities to realize solution-state and gel RTP. a) The chemical structure of hexathiobenzene-based phosphor and its RTP activation by photoexcitation-controlled aggregation. Reproduced with permission.^[24] Copyright 2019, National Academy of Sciences. b) The photoexcitation-controlled-AIP based on a phenyl group-modified hexathiobenzene derivative. Reproduced with permission.^[25] Copyright 2021, American Chemical Society. c) A single-component RTP sol-gel system based on the self-assembly and disassembly of glutamic hexathiobenzene derivatives. Reproduced with permission.^[26] Copyright 2012, Royal Society of Chemistry.

single-component RTP sol-gel system with Circularly polarized luminescence (CPL) activity involving the self-assembly of glutamic hexathiobenzene derivatives (Figure 5c).^[26] The enantiomeric pair was able to act as a gelator to form a gel at room temperature, leading to green RTP emission at 530 nm. The resultant RTP emission exhibited a thermos-responsive behavior owing to the thermally induced disassembly of the gels. By tailoring polysulfated benzene derivatives into compact and ordered entities, solution-state RTP materials can be obtained successfully, which hold great promise in bioimaging and smart materials.

2.2. Direct Organization of Luminescent Polymers

Besides the formation of ordered emitters by direct organization of small fluorogens, the luminescent polymers can be also organized into compact and relatively ordered RTP emitters by leveraging dynamic interactions. In 2015, the Rao group presented one of the first examples of persistent near-infrared luminescent nanoparticles by the nano-precipitation of a fluorescent semiconducting polymer of MEH-PPV polymer with PS-PEG-COOH and a near-infrared dye of NIR775 (Figure 6a).^[29] Uniform persistent luminescent nanoparticles were facily achieved by co-aggregation of the MEH-PPV with a specific copolymer of PS-PEG-COOH, which was capable of being excited by white light. Taking advantage of efficient resonance energy transfer from the aggregated polymer system to the dopant of NIR775, a near-infrared persistent luminescence (780 nm) that lasted for ≈ 1 h was realized with a single excitation of white light. As such, it holds great promise as a novel biomaterial for bioimaging with a large, improved signal-to-noise ratio.

Alternatively, the luminescent polymers can be well rigidified and organized into compact and relatively ordered emitters by multiple dynamic interactions. In 2019, Huang and An et al. reported color-tunable RTP with a lifetime of up to 578.36 ms by ionization of poly(4-vinylpyridine) (PVP) with 1,4-butanedisulfone (Figure 6b).^[30] Since the chromophore motions could be effectively restricted by multiple directionless and non-saturating strong electrostatic interactions, the resulting ionic amorphous poly(4-vinylpyridine)butane-1-sulfonate (PVP-S) polymer revealed greatly enhanced RTP performance (524 nm, 578.36 ms) compared with PVP. Impressively, excitation-dependent multicolor RTP emission varying from 524 nm to 572 nm was observed due to multiple excited states derived from diverse chromophore aggregate states in the PVP-S. In more attempts, Huang and An et al. demonstrated that ultralong RTP could also be realized from other ionic polymers, such as poly(styrene sulfonic acid) (PSS) salts, PAANA, PMANA, and PSSNa-co-PMANA (Figure 6c).^[31] By riveting intermolecular subunits with strong ionic bonding interactions, the resulting ionically polymeric materials all showed long-lived RTP with a maximum lifetime of up to 2.1 s. These RTP materials also displayed excitation-dependent persistent emission with maximum peak shifting from 540 to 560 nm, which could be attributed to different aggregate domains of chromophores. These impressive studies proved that well organization of emissive polymers by supramolecular dynamic interactions played important roles in RTP performance.

In the past few years, cellulose-based RTP materials have attracted tremendous interest owing to their sustainability, natural abundance, environmental friendliness, and excellent processability.^[32] Recently, Zhang and coauthors reported aggregation-regulated RTP materials based on anionic phenyl

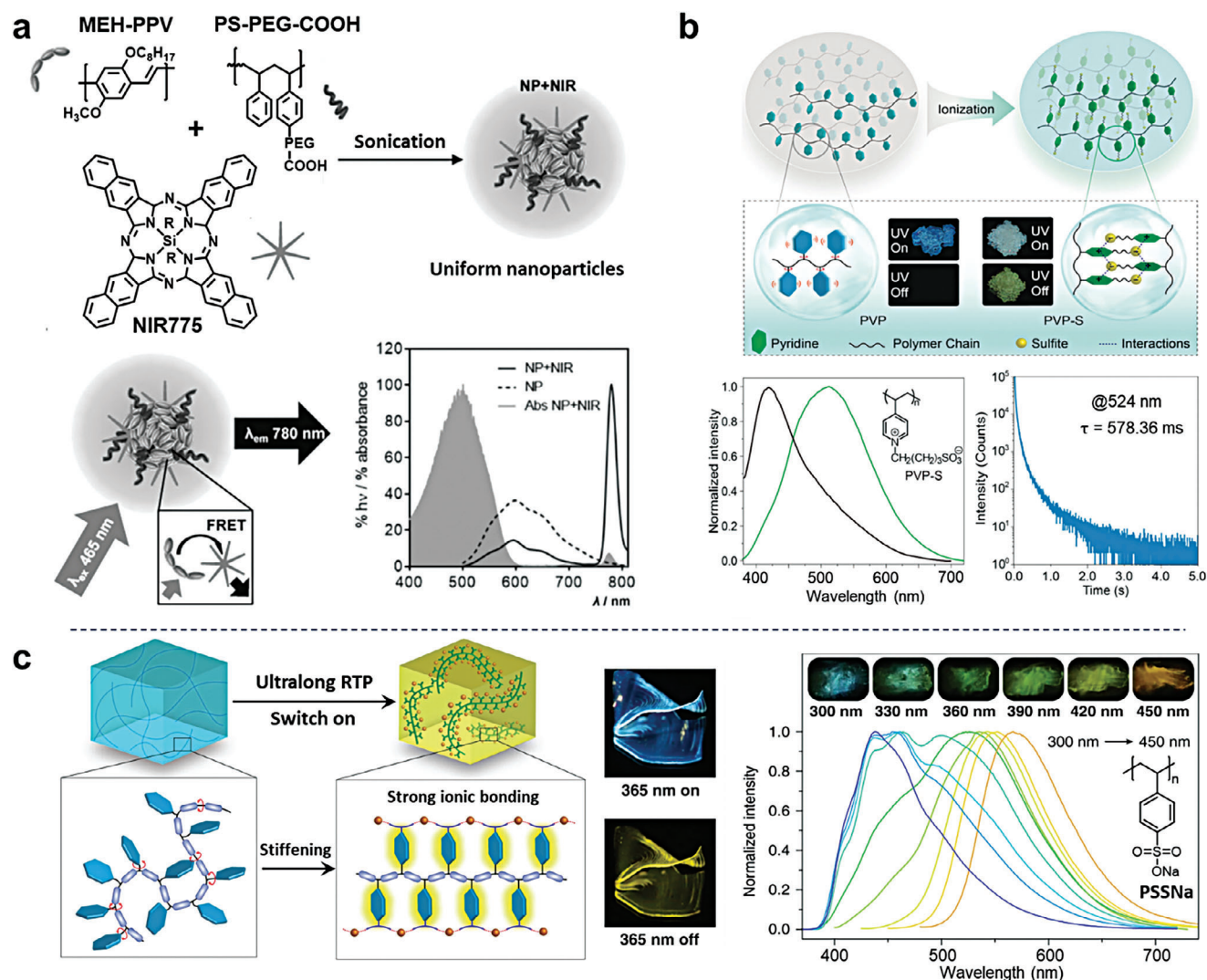


Figure 6. The organization of luminescent polymers into compact and relatively ordered RTP emitters. a) The nano-precipitation of a fluorescent semi-conducting polymer of MEH-PPV with PS-PEG-COOH and a near-infrared dye of NIR775 to render uniform persistent near-infrared luminescent nanoparticles. Reproduced with permission.^[29] Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) The ionization of poly(4-vinylpyridine) (PVP) with 1,4-butanedisulfone to obtain excitation-dependent multicolor RTP emission. Reproduced with permission.^[30] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. c) Riveting emissive subunits by strong ionic bonding interactions to achieve compact color-tunable RTP materials. Reproduced with permission.^[31] Copyright 2019, The Author(s).

carboxylate-functionalized cellulose (CBtCOONa).^[32b] By manipulating the aggregation of CBtCOONa via the formation of CaCO_3 in situ, multi-mode RTP emissions from blue (molecularly dispersed state) to green (aggregated state) were readily realized. In addition, the aggregated CBtCOONa was visible light-excitable to render a green or yellow RTP emission. Such multi-mode RTP materials with environmental friendliness hold great promise in anti-counterfeiting and intelligent labels.

2.3. Tailoring Ordered RTP Emitters in Confined Environments

In theory, the uttermost promotion of spin-forbidden transition of the ISC process and stabilization of triplet excitons by the

suppression of molecular motions are two crucial prerequisites to achieving high-performance RTP materials.^[33] In the past few years, tailoring ordered and compact RTP emitters in confined environments such as rigid polymeric matrices, supramolecular scaffolds or macrocyclic hosts has been proven to be an effective and reliable approach to obtain high-performance RTP materials. By this way, flexible and solution-state RTP materials were efficiently achieved owing to the immense inhibition of molecular motions in confined environments. Moreover, the confined environments provided an excellent quenchers (oxygen, solvent, etc.) barrier for isolating organic phosphors. In this section, we mainly summarize the organization of fluorogens in confined environments to achieve ordered high-performance RTP emitters.

2.3.1. Assembly of Fluorogens in Polymeric Matrix

In comparison to other phosphorescent materials, polymer-based RTP materials possess the merits of lightweight, mechanical flexibility, excellent transparency, good stretchability, variable properties and modulable processability, thus becoming encouraging candidates for various optoelectronic applications.^[34] The polymers are capable of providing rigid amorphous environment to confine organic phosphors for stabilizing triplet excitons and suppressing non-radiative decay. Also, the polymer matrices isolated organic phosphors from the oxygen quencher, thus preventing the quenching of triplet excitons. Owing to their intrinsic strong inter- and intramolecular interactions, chemically and physically inert, and relatively wide bandgap, several classic polymers such as poly(vinyl alcohol) (PVA), PMMA, poly(lactic acid) (PLA), poly(styrene) (PS) were widely used as matrices to ideally embed organic phosphors for realizing high-performance RTP materials. Particularly, the organic small molecules can be organized into compact and ordered RTP emitters in the rigid polymeric matrices, resulting in immensely inhabiting molecular motions for the suppression of nonradiative deactivation.

In 2014, Kim et al. reported a bright RTP introduced *p*-bromobenzaldehyde derivative that was modified with carboxylic acid side chains into a PVA matrix (Figure 7a).^[35] Owing to multiple hydrogen bonds from the PVA matrix and strong intermolecular halogen bonding between the formyl group and the bromine atom, the vibrational dissipation was largely suppressed, leading to bright green RTP emission with a high PhQY of up to 24%. Chen's group also successfully realized a family of large-area RTP films by self-assembly and aggregation of terpyridine derivatives in the confined networks of PVA polymer (Figure 7b).^[36] The resultant RTP films exhibited a characteristic of excimer emission (485 nm) with a lifetime of up to 543.9 ms due to strong π - π stacking interactions between terpyridine chromophores. Owing to the synergistic effect of co-assembly, multiple hydrogen bonding and rigidification from polymeric matrices, the population of triplet excitons and suppression of nonradiative decay were greatly enhanced, thus leading to long-lived RTP. Following the doping strategy, Yue and Zhu et al. presented an autonomously photoswitchable RTP material in both solution and solid state by integrating hexacarboxylic sodium-modified hexathiobenzene derivative with a rigid and amorphous polymeric matrix of poly-(dimethyldiallylammonium)chloride (PDDA) via multiple electrostatic interactions.^[37] Due to the conformation change of hexathiobenzene core during photoexcitation, the solubility of phosphor correspondingly changed, thus enabling molecular aggregation and accordingly leading to AIP (500 nm) in the solution state. Differently, Only the Decrease of RTP Intensity Could be Observed in the Solid State upon 365 UV Irradiation.

Strikingly, Zhao and coworkers successfully achieved a series of high-performance polymer-based RTP films with advantages of large-area processability, excellent transparency and flexibility by co-assembly of planar heterocyclic aromatic compounds with PVA matrix (Figure 7c).^[38] The RTP films exhibited long-lived feature with a lifetime of up to 2044.86 ms and the longest afterglow duration of more than 20 s. Both detailed experimental results and theoretical calculations unveiled that the long-lived phosphorescence originated from the synergistic effect of the co-assembly of chromophores and abundant hydrogen bonding

from PVA chains. Compact nano aggregates were assembled in the PVA matrix via π - π stacking, and the molecular vibration and intermolecular collisions were largely inhibited. Besides, multiple hydrogen bonding between chromophores and PVA chains further suppressed the molecular motions, leading to the stabilization of triplet excitons to achieve RTP materials. In their contributions, the planar configuration of fluorophores was also proved to be a key factor for co-assembly-induced RTP.

2.3.2. Assembly of Fluorogens in Supramolecular Scaffolds

Although the direct organization of small organic fluorogens and emissive polymers has proven to be an effective strategy for achieving high-performance RTP materials, the limited selection of fluorogens and elaborated assembly process hinder the development of novel RTP materials to some extent. In addition to the co-assembly of fluorogens in rigid polymeric matrices, the supramolecular scaffolds can be well employed as assembly templates to activate RTP emission that usually reveals outstanding and unique phosphorescent properties, especially in the solution state. The confined space of supramolecular scaffolds dominates the self-assembly and aggregation of organic phosphors to tremendously suppress molecular motions, leading to great inhibition of non-radiative transitions for activating excellent RTP emission.

In 2016, Zhu and coworkers developed a co-micellar strategy to realize progressive RTP conversion (Figure 8a).^[39] An imidazolyl-modified diphenyl diacetylene (M) compound assembled with an amphiphilic block copolymer driven by hydrogen-bonding interactions to provide co-micellar entities. Interestingly, dimer (D) and trimer (T) species could be generated due to photocrosslinking under 254 nm UV irradiation in situ, leading to RTP emission conversion from pale green to white and ultimately to purplish blue. Such photoconversion of RTP may advance the development of smart luminescent devices. Impressively, Zhang and coworkers developed aqueous afterglow dispersions via emulsion polymerization of difluoroboron β -diketonate (spiroBF₂) dopants and methyl methacrylate (MMA) (Figure 8b).^[40] Due to the aggregation of phosphors in the confined environment, the as-prepared afterglow dispersions showed an outstanding ultralong RTP feature with delayed emission maxima at 521 nm and an average lifetime of 1.5 s. Moreover, the RTP performance could be enhanced by using deuterated spiroBF₂ (D-spiroBF₂), displaying an improved lifetime of 2.4 s and elongated afterglow duration of 20 s owing to the inhibition of molecular vibrations. Notably, aqueous afterglow dispersions demonstrated great promise in immunoassay by being decorated biotin.

The self-assembly of organic phosphors with charged laponite (LP) clay to form rigid and controllable entities was proved to be a feasible approach to achieve efficient RTP, especially for ambient solution-state phosphorescence. To be specific, the lamellar LP clay was employed as a rigid and periodic co-assembly template to limit the motions of organic phosphors and isolate oxygen to avoid quenching of triplet excitons, which was beneficial to RTP emission. In 2018, George group successfully achieved ambient aqueous and amorphous-state red RTP (615 nm, 347 μ s) via supramolecular hybrid co-assembly of cationic bromo-substituted naphthalene diimide derivatives

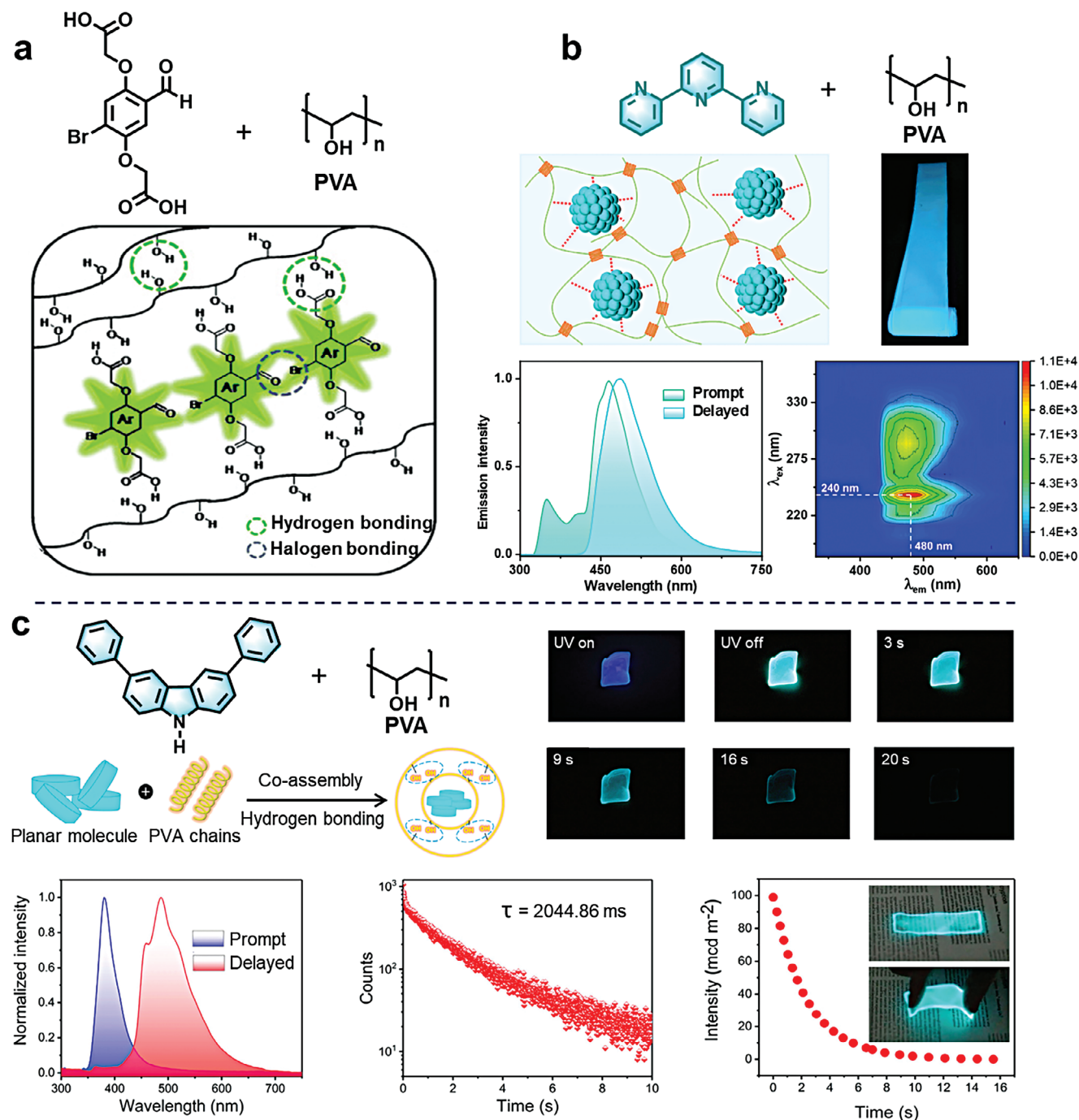


Figure 7. Organization of organic molecules in the polymeric matrix to render RTP materials. a) The introduction of *p*-bromobenzaldehyde derivative into PVA matrix for achieving bright green RTP. Reproduced with permission.^[35] Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) Self-assembly and aggregation of terpyridine and its derivatives in PVA matrix to form large-area RTP films. Reproduced with permission.^[36a] Copyright 2023, SCUT, AIEI, and John Wiley & Sons Australia, Ltd. c) Co-assembly of planar heterocyclic aromatic compounds with PVA matrix enables high-performance RTP films. Reproduced with permission.^[38] Copyright 2021, American Chemical Society.

(BrNDI) with a water-soluble template of negatively charged LP clay based on multiple electrostatic interactions (Figure 8c).^[41] It was found that the rigid LP clay and BrNDI were alternatively packed to form hybrid assemblies to immensely suppress the non-radiative dissipation of triplet excitons and also pro-

vided supramolecular microenvironments as an oxygen barrier in both aqueous phase and film state. By using such a negatively charged template, Tian and Walther et al. presented a waterborne and bioinspired strategy by self-assembling RTP polymers with laminated nanoclay to obtain the first example

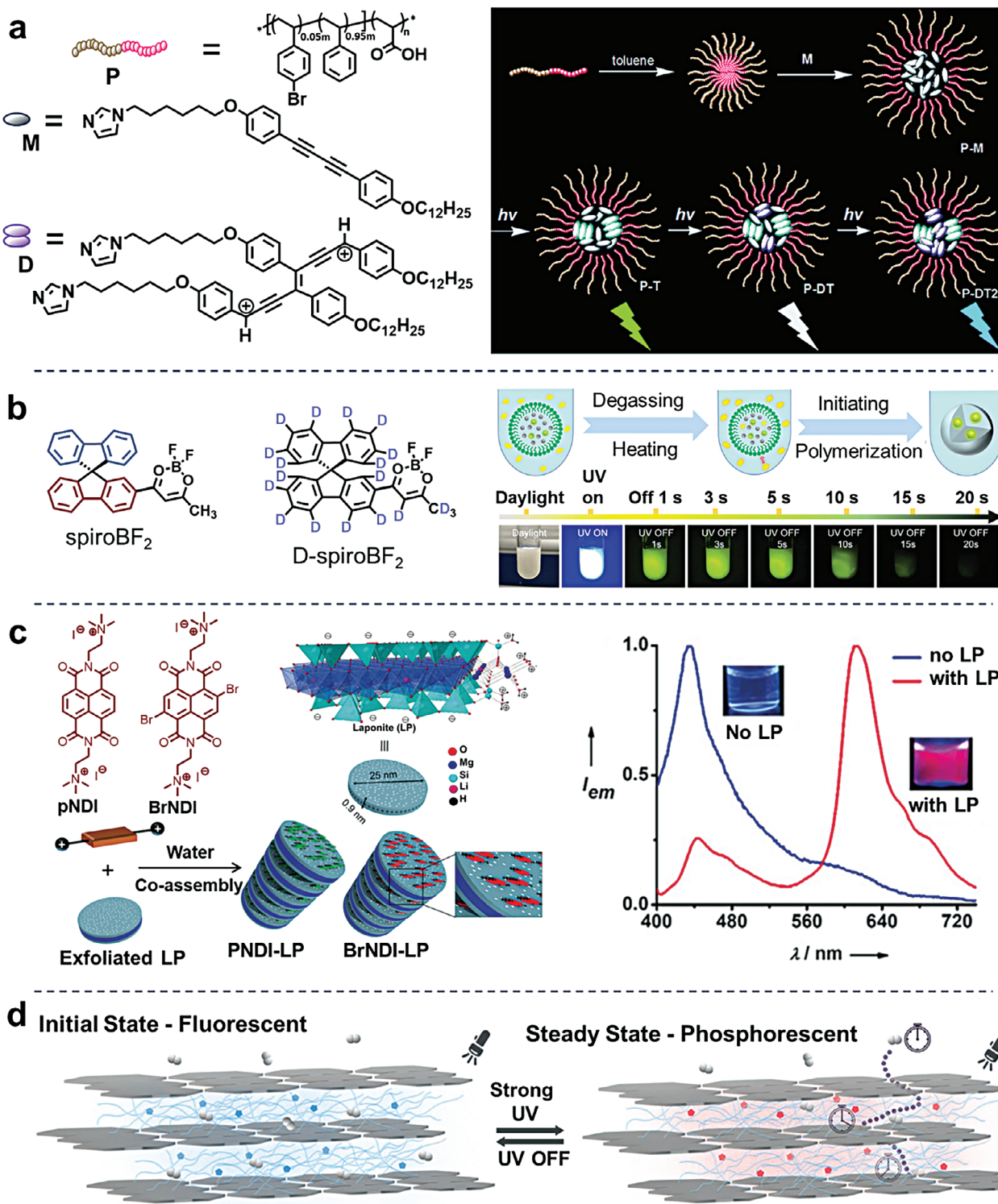


Figure 8. The coassembly of organic fluorogens with supramolecular scaffolds to access solution-state RTP emission. a) A co-micellar strategy that coassembly of imidazolyl modified diphenyldiacetylene with an amphiphilic block copolymer to realize progressive RTP conversion. Reproduced with permission.^[39] Copyright 2016, Royal Society of Chemistry. b) Emulsion polymerization of difluoroboron β -diketonate dopants and methyl methacrylate (MMA) to obtain aqueous afterglow dispersions. Reproduced with permission.^[40] Copyright 2022, WILEY-VCH GmbH. c) Supramolecular hybrid co-assembly of cationic bromo-substituted naphthalene diimide derivatives (BrNDI) with a water-soluble template of negatively charged laponite (LP) clay to achieve ambient aqueous and amorphous-state red RTP. Reproduced with permission.^[41] Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) Self-assembly of RTP polymers with laminated nanoclay to obtain the nacre-mimetic RTP films. Reproduced with permission.^[42] Copyright 2020, WILEY-VCH GmbH.

of nacre-mimetic RTP films (Figure 8d).^[42] The 4-bromo-1,8-naphthalic anhydride derivative (BrNpA) as an organic phosphor was copolymerized with *N,N*-dimethylacrylamide (DMA) and 2-[2-(2-methoxy ethoxy)ethoxy]ethyl acrylate (mTEGA) to afford RTP copolymers with variable T_g . Thereafter, the RTP copolymers were self-assembled with laminated nanoclay to prepare nanocomposites RTP films. It was found that higher T_g facilitated the suppression of non-radiative decay (K_{nr}) to provide brighter RTP emission. More importantly, the well-ordered laminated mesostructure provided an excellent oxygen barrier to activate RTP emission by preventing oxygen diffusion and permeability, leading to elongated RTP retention time. As a result, such RTP nacre-mimetic nanocomposites emerged as good candidates for transient photolithographic information storage and anti-counterfeiting materials based on photo-activable and self-erasable RTP emission. Besides, Liu et al. recently reported aqueous ultralong RTP relied on multivalent supramolecular assembly.^[43] The 4-(4-bromophenyl)pyridine-1-ium grafted HA (HABr) assembled with cucurbituril CB[8] to form a supramolecular cross-linked polymer HABr/CB[8] and then further interacted with LP to result in lamellar aggregates. As such, the organic phosphor was well stabilized by host-guest encapsulation and electrostatic interactions from LP, resulting in a long water-phase RTP lifetime of up to 4.79 ms. Moreover, the organic dyes including rhodamine B (RhB) and sulfonated rhodamine 101 (SR101) were introduced into such ternary RTP system to afford multicolor emissions with high phosphorescence energy transfer efficiency (73-80%). These impressive works demonstrated that the assembly of fluorogens within supramolecular scaffolds was a reliable and feasible strategy for obtaining solution-state RTP materials.

2.3.3. Host-Guest Recognition Systems

In contrast to the assembly strategies mentioned above, the accommodation of organic phosphors within the rigid macrocyclic hosts to form host-guest complexes is a more accurate and controllable strategy to realize high-performance RTP emission. The encapsulation of phosphor guests in rigid hosts to form compact and ordered emissive units leads to unique RTP emission even in dynamic media such as aqueous and gel states. Generally, the molecular vibration of the phosphor guest is largely restricted and the nonradiative relaxation is well suppressed by immobilizing organic phosphor within the hydrophobic host cavity. In addition, the rigid host molecule offers an effective barrier for phosphor guests so that the excited triplet states of phosphor can be well shielded from the collision with quenchers such as triplet oxygen and other molecules. Thus, the RTP materials induced or enhanced by host-guest interactions generally exhibit outstanding performance, including high PhQY, and ultralong lifetime even in the aqueous and gel states.

To date, rigid macrocyclic hosts including cyclodextrin (CD) and cucurbituril (CB) have been broadly applied to bind organic phosphors within their hydrophobic cavities to access high-performance RTP materials. The first example of CD-based RTP can be traced back to 1982 by Turro et al.^[44] Ever since then, plenty of RTP materials have been fabricated by assembling inclusion complexes. Impressively, Tian and Ma reported a myriad of excel-

lent RTP materials based on the host-guest recognition of organic phosphors and CDs. In 2014, Tian and Ma et al. reported the first example of RTP hydrogel with a lifetime of 0.56 ms by integrating β -CD host polymer (poly- β -CD) and α -bromonaphthalene (α -BrNp) polymer (poly-BrNp) (Figure 9a).^[45] Although the dynamic and aquiferous nature of hydrogel materials, the host-guest recognition interactions between BrNp and β -CD enabled a highly cross-linked supramolecular network for the immobilization of the BrNp phosphors to enhance RTP performance. Moreover, poly-azobenzene (Azo) was introduced into the hydrogel material to reversibly regulate the RTP performance based on cis-trans isomerization of the Azo units under alternative irradiation at 365 nm and 254 nm. In more attempts, the same group reported aqueous-state RTP by assembling 4-bromo-1,8-naphthalic anhydride (BrNpA) polymer (poly-BrNpA) with γ -cyclodextrin (γ -CD) (Figure 9b).^[46] The as-prepared poly-BrNpA/ γ -CD system displayed aqueous-phase RTP emission at 580 nm with a lifetime of 0.32 ms owing to host-guest inclusion between γ -CD and the BrNpA moiety. Moreover, the RTP properties could be reversibly regulated by introducing a competitive binding unit of Azo unit based on the cis-trans isomerism process.

Except for larger size CDs, the smallest rigid CD with six repeated units (α -CD) is widely used for turning on excellent RTP emission. Liu group reported a polypseudorotaxane xerogel displaying fluorescence-phosphorescence dual emission based on the host-guest interaction between PEG-modified bromobenzaldehyde derivatives and α -CD (Figure 9c).^[47] By threading the organic phosphor polymer G into the cavity of α -CD to form a polypseudorotaxane network, the vibration dissipation and nonradioactive decay of organic phosphors were immensely suppressed, leading to an appealing fluorescence (445 nm)-phosphorescence (550 nm) dual emission properties. In addition, the same group developed a strategy that combined polymerization, assembly and photoswitches to afford switchable RTP emission in the solid state.^[49] First, a naphthylpyridinium derivative monomer was polymerized with acrylamide to render fluorescence (425 nm)-phosphorescence (550 nm) dual emission with ultrastrong white light photoluminescence. Thereafter, the resultant copolymer was further complexed with sulfobutylether- β -cyclodextrin (SBE- β -CD), leading to an enhanced PhQY of up to 71.3%. More importantly, diarylethene monomers as photoswitches were introduced into such binary supramolecular systems to controllably and reversibly regulate RTP emission based on the effect of phosphorescence resonance energy transfer.

Recently, the group of Ma presented emission-tunable RTP polymer materials based on host-guest mediated reversible photocyclodimerization of anthracene.^[50] The anthracene-grafted monomer was copolymerized with acrylamide to yield RTP polymer (Poly-AC). Then, the RTP performance was further enhanced by the introduction of γ -CD as host molecules to stabilize the triplet excitons. Notably, the RTP emission could be controllably and reversibly tuned from cyan color ($\lambda_{max} = 486$ nm) to blue color (broad band from 400 to 600 nm) by 360 nm irradiation owing to dynamic supramolecular-mediated photocrosslinking of anthracene. Upon photodimerization of anthracene, the conjugation of organic phosphor was reversibly changed, leading to adjustable RTP emission between cyan and blue. Most recently, Li and colleagues reported aqueous-phase RTP by taking advantage of host-guest inclusion and intermolecular hydrogen

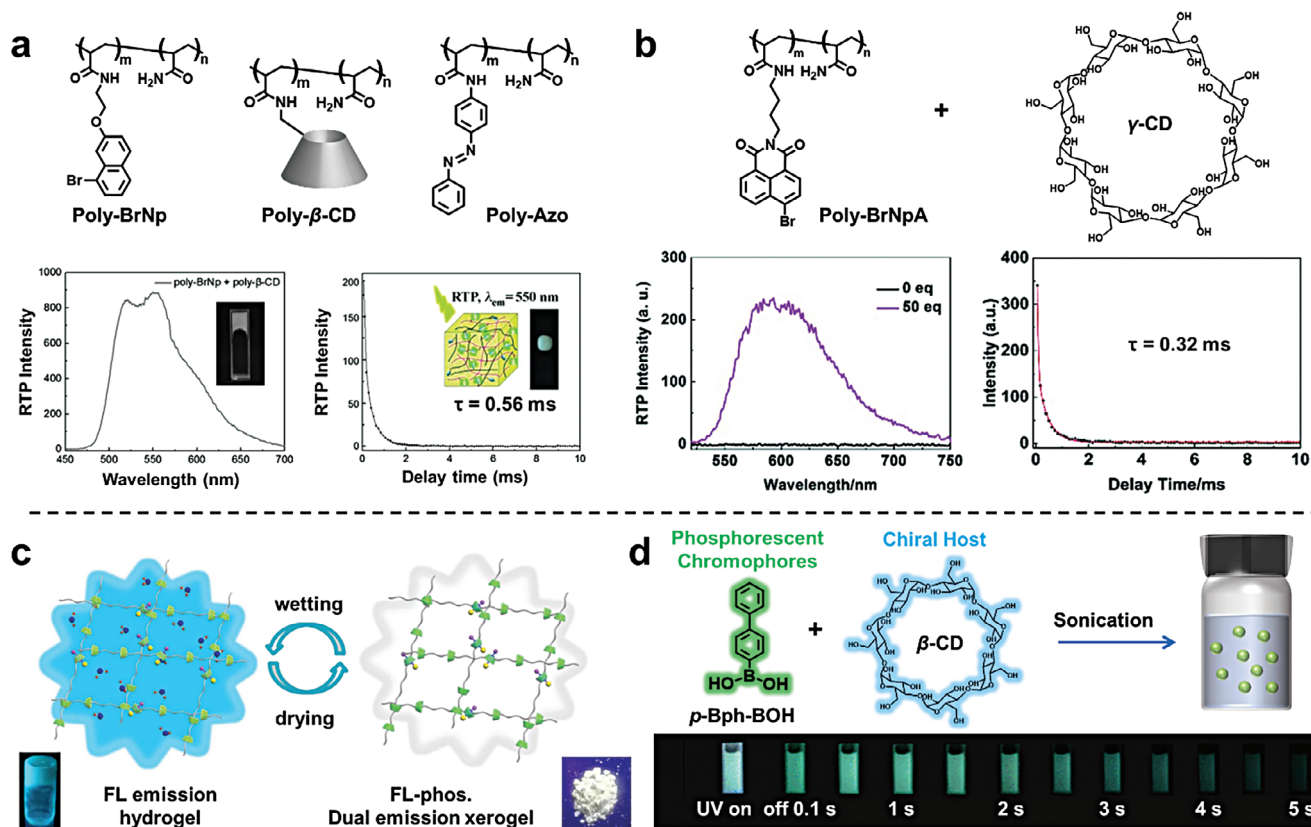


Figure 9. The inclusion of organic phosphors within CD hosts by host-guest interactions to activate RTP emission. a) The complexation of β -CD host polymer (poly- β -CD) and α -bromonaphthalene (α -BrNp) polymer (poly-BrNp) to prepare the first example of RTP hydrogel. Reproduced with permission.^[45] Copyright 2014, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) The assembly of 4-bromo-1,8-naphthalic anhydride (BrNpA) polymer (poly-BrNpA) and γ -CD to render aqueous-state RTP. Reproduced with permission.^[46] Copyright 2016, Royal Society of Chemistry. c) The fabrication of fluorescence-phosphorescence dual emissive polypseudorotaxane xerogel based on the host-guest interaction between PEG-modified bromobenzaldehyde derivatives and α -CD. Reproduced with permission.^[47] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) The preparation of aqueous-phase RTP by host-guest inclusion and intermolecular hydrogen bonding between *p*-biphenylboronic acid (*p*-Bph-BOH) and β -CD. Reproduced with permission.^[48] Copyright 2023, American Chemical Society.

bonds to immensely inhibit nonradiative relaxation and avoid contacting quenchers (Figure 9d).^[48] The organic phosphor of *p*-biphenylboronic acid (*p*-Bph-BOH) assembled with β -CD to form aggregate driven by host-guest encapsulation and hydrogen bonding interactions with the assistance of sonication, rendering high-performance green RTP emission (500 nm) with a lifetime of up to 1.03 s in water. For the corresponding powder state, the lifetime was further elongated to 2.23 s along with 18 s afterglow which could be observed by the naked eyes. In addition, the emission could be finely tuned to pink (600 nm) by introducing fluorescent dye, Rhodamine B, through radiative energy transfer.

In addition to CDs, the rigid host CBs were also broadly employed to construct outstanding RTP materials. In 2007, Zhu and colleagues first employed CB[n] ($n = 7$ or 8) to bind quinine and its derivatives to obtain solution-phase RTP emission.^[51] Notably, Ma and Tian et al. developed a new assembly-induced RTP system in 2020 that is based on a quaternary host-guest structure (Figure 10a).^[52] The organic phosphor (TBP) was designed and synthesized by modifying the triazine core with 4-(4-bromophenyl)pyridine, which was assembled with CB[8] to form a structure-restricted D, resulting in RTP emission at 565 nm,

with a long lifetime of 0.19 ms in water. The optical properties were further regulated by varying the amounts of CB[8] and introducing a competitive guest. Importantly, the absorption was bathochromic-shifted to the visible-light region due to the assembled charge-transfer effect, enabling visible-light excitation. In addition, multicolor hydrogels were facily obtained by dispersing a 2:2 host-guest complex in the matrix of agarose. In the same year, Liu and coauthors constructed aqueous RTP pseudorotaxane polymers (CB[7]/HA-BrBP and CB[8]/HA-BrBP) by leveraging host-guest interaction between CBs and pyridinium-grafted hyaluronic acid (HA-BrBP) (Figure 10b).^[53] Interestingly, CB[7]/HA-BrBP and CB[8]/HA-BrBP were prone to assemble into nanofibers and large spherical nanoparticles, respectively. The host-guest encapsulation protected the triplet excitons from collision with quenching species (triplet oxygen and solvents, etc.) and was beneficial to the restriction of molecular motions. Moreover, the multiple hydrogen bonding, halogen bonding and aggregation of phosphors synergistically promoted the inhibition of non-radiation decay of organic phosphors, resulting in long-lived RTP (500 nm) emission with a lifetime of up to 4.33 ms in the aqueous phase.

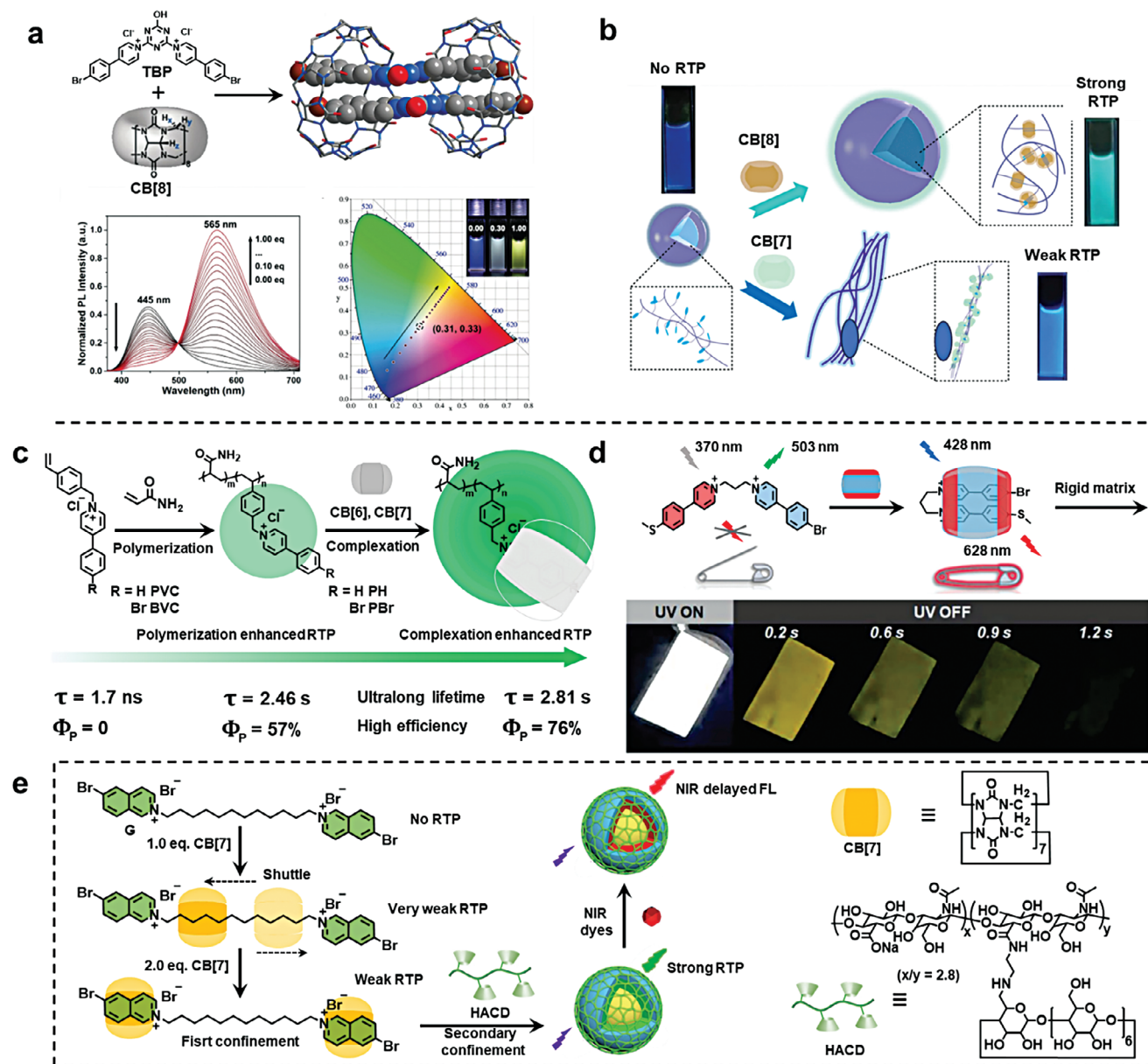


Figure 10. The host-guest interactions involve the complexation of CBs with organic phosphors to activate RTP emission. a) Self-assembly of TBP and CB[8] to form a quaternary host-guest structure that displayed tunable aqueous RTP emission. Reproduced with permission.^[52] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) The assembly of RTP pseudorotaxane polymers by host-guest interaction between CBs and Pyridinium-grafted hyaluronic acid (HA-BrBP). Reproduced with permission.^[53] Copyright 2020, The Author(s). c) A synergistic strategy of polymerization and host-guest complexation enhances the RTP performance. Reproduced with permission.^[54] Copyright 2020, WILEY-VCH GmbH. d) The preparation of supramolecular RTP pins by encapsulating alkyl-bridged phenylpyridinium salts within cucurbit[8]uril (CB[8]). Reproduced with permission.^[55] Copyright 2021, WILEY-VCH GmbH. e) Cascaded assembly of organic phosphor and CB[7], and then β -cyclodextrin-grafted hyaluronic acid (HACD) to afford an aqueous supramolecular RTP. Reproduced with permission.^[56] Copyright 2022, WILEY-VCH GmbH.

Moreover, the Liu group used a synergistic strategy of polymerization and host-guest complexation to enhance the RTP performance (Figure 10c).^[54] An excellent RTP copolymer was prepared by polymerization of organic phosphor monomer with acrylamide. It exhibited excellent high-performance cyan RTP (490 nm) emission with a lifetime of up to 2.46 s and phosphorescence QY 57% owing to multiple hydrogen bonds and a protective environment provided by the polymer ma-

trix. Moreover, the RTP performance was further enhanced by host-guest complexation. Upon the addition of host molecules (CB[6,7,8]), the lifetime was increased up to 2.81 s along with QY of more than 76% by blocking the ACQ effect and immobilization of organic phosphor. In more attempts, the same group presented purely organic supramolecular pins involving the encapsulation of alkyl-bridged phenylpyridinium salts within cucurbit[8]uril (CB[8]) (Figure 10d).^[55] Owing to the suppression

of nonradiative decay by strict host-guest encapsulation and the promotion of ISC by intramolecular charge transfer (ICT) from “head-to-head” folded phosphor, the as-prepared supramolecular pins exhibit strong RTP (618 nm) emission with highest PhQY of up to 99.38% after integration with filter paper. Recently, they reported an aqueous supramolecular RTP by cascaded assembly of dodecyl-chain-bridged 6-bromoisquinoline derivative (G) and CB[7], and then β -cyclodextrin-grafted hyaluronic acid (HACD) (Figure 10e).^[56] In the forefront step, the G was assembled with CB[7] to form a dumbbell-shaped structure, promoting the ISC process and accommodation of phosphor to suppress molecular motions. Next, the as-formed host-guest complex further assembled with HACD by multivalent interactions, leading to a prolonged lifetime from 59.0 μ s to 0.581 ms. Taking advantage of the delayed sensitization effect, long-lived NIR-emission was successfully realized by doing NIR dyes in the supramolecular RTP system, which contributed to targeted imaging of cancer cells. Undoubtedly, the host-guest complexation strategy provides an elaborate and efficient way to form compact and ordered emissive units for realizing high-performance RTP emission, especially in an aqueous state.

3. Potential Applications

Benefiting from their abundant and unique optical properties, organic RTP materials have found wide applications such as bioimaging, optoelectronic display, encryption and anti-counterfeiting, and chemical sensing. It is worth noting that the RTP materials have significant advantages over fluorescent materials for the above-mentioned applications owing to their long-lived afterglow emission, large Stokes shift and sensitive stimuli-responsiveness. Especially, the compact and ordered RTP emitters often display superior RTP performance compared with their disordered counterparts, thus largely extending their practical applications. For example, the compact and ordered RTP emitters generally possess the merits of a long lifetime, excellent PhQY and robust performance, offering more opportunities for applications in bioimaging, afterglow display, information encryption, chemical sensing, etc. In this section, we mainly summarize the promising applications of ordered RTP emitters.

3.1. Bioimaging

Owing to their inherent merits of ultralong lifetime, large Stokes shifts and good biocompatibility, RTP materials exhibit superior performance on bioimaging in comparison to the traditional fluorescence imaging. Particularly, the time-resolved phosphorescence imaging offers distinct advantages of high resolution and contrast, and improved signal-to-noise ratio (SNR) owing to the long-lived afterglow could be well distinguished from tissue autofluorescence and excited light. For instance, Rao et al. demonstrated the outstanding ability of NIR775-doped MEH-PPV polymer nanoparticles for *in vivo* imaging (Figure 11a).^[29] Benefiting from the long persistent luminescence (LPL) feature and re-excitable for several days, the nanoparticles were excited by irradiation of white light before being injected into a living mouse. Within 24 h, the nanoparticles in the mouse body could be ex-

cited repeatedly by a white light source. Thereby, the tissue autofluorescence background and photobleaching were significantly reduced compared with the existing fluorescence imaging.

To overcome the disadvantage of the existing traditional imaging materials with poor performance in aqueous media, phototoxicity and low cell penetrability of UV excitation, Wu and coworkers reported the first example of bright RTP that was capable of being activated by visible and NIR light in aqueous solution (Figure 11b).^[57] Such water-dispersible RTP nanoparticles were fabricated by the self-assembly of carbazole-modified difluoroboron β -diketonate derivatives via the nanoprecipitation method. These nanoparticles exhibited similar red RTP with a lifetime of more than 17 μ s upon excitation by visible light at 470 nm in an aqueous solution. In addition, these water-dispersible nanoparticles also showed RTP under NIR irradiation at 820 nm due to the two-photon absorption feature of the difluoroboron β -diketonate unit, which greatly facilitated cellular imaging. Based on systematic experimental results and theoretical calculations, the RTP of nanoparticles could be attributed to the compact antiparallel dimeric packing of organic phosphors. Owing to multiple interactions and intermolecular charge transfer, the ISC process was largely promoted and the molecular vibrations and nonradiative transition were immensely inhibited, leading to efficient RTP of these nanoparticles.

Importantly, Pu and coworkers employed a top-down strategy to realize water-soluble ultralong organic RTP nanoparticles for *in vivo* imaging (Figure 11c).^[58] Solid dyes were directly transformed into water-soluble nanoparticles instead of the nanoprecipitation method (bottom-up), which showed a similar packing mode of dye molecules for facilitating the stabilization of triplet excitons. Notably, these RTP nanoparticles were insensitive to oxygen and water, leading to the outstanding ability of long-term *in vivo* imaging without tissue autofluorescence. Also by using a top-down method, Li and coworkers presented a near-infrared organic RTP nanoprobe (Figure 11d).^[59] The crystals of phosphor (*N,N*-bis(4-methoxyphenyl)-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (mTPA) were doped with a fluorescent luminogen of 3-naphthalocyanine bis(trihexylsilyloxy) (NCBS) in the presence of an amphiphilic copolymer (F127) to form compact and uniform nanoparticles, which exhibited NIR afterglow at \approx 780 nm on the basis of energy transfer from triplet state of mTPA to NCBS. Benefiting from deep tissue penetration, the resultant NIR RTP nanoparticles enabled the mapping of lymph nodes in living mice with high NSR. By using the same strategy, Tang and Li et al. developed new RTP materials with long-live lifetime and PhQY in aqueous media, which revealed excellent application in high-contrast labelling *in vivo*.^[60] Besides, Liu et al. demonstrated that the pseudorotaxane polymer CB[8]/HA-BrBP possessed a tumor-cell-targeting ability for specific imaging of mitochondria in tumor cells.^[53] The cancer cells (A549, HeLa, KYSE-150) incubated with CB[8]/HA-BrBP showed strong green RTP in the region with mitochondria while no visible RTP was observed for normal cells (293T). Interestingly, Zhu and coauthors presented dynamic flicker bioimaging based on a photoexcitation-controlled self-recoverable AIP system by incubating HeLa cells with aqueous solutions of hexathiobenzene-based phosphor.^[24] By rhythmic irradiation, dynamic flicker emission could be observed for the cells, providing a unique visualization method in bioimaging.

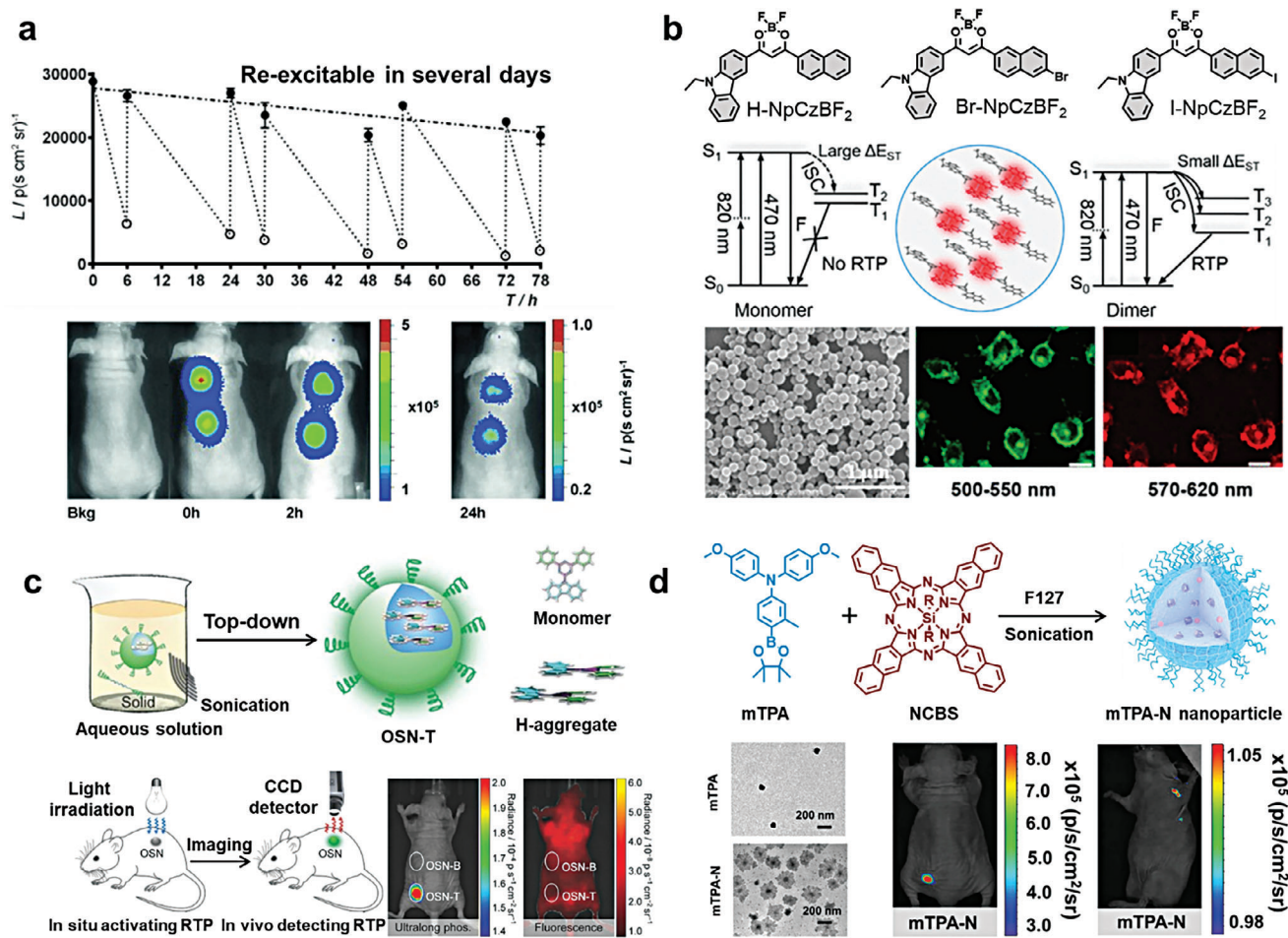


Figure 11. The compact and ordered RTP nanoparticles used for bioimaging. a) NIR775-doped MEH-PPV polymer nanoparticles for in vivo imaging. Reproduced with permission.^[29] Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) Visible and NIR light-excitable RTP nanoparticles for cellular imaging. Reproduced with permission.^[57] Copyright 2019, American Chemical Society. c) Top-down strategy for fabricating water-soluble ultralong organic RTP nanoparticles for in vivo imaging. Reproduced with permission.^[58] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. d) The preparation of near-infrared organic RTP nanoprobe by using a top-down method. Reproduced with permission.^[59] Copyright 2020, Wiley-VCH GmbH.

3.2. Afterglow Display

In most OLEDs, most excited species belong to a populated nonradiative triplet state (75%) in addition to 25% of the singlet state upon electric excitation.^[61] Thus, the development of OLEDs based on phosphorescent materials is widely considered as an important alternative way to improve emission efficiency. In 2019, Zhang and coworkers designed and synthesized a series of 4,4'-biscarbazole (BCZ) derivatives that revealed both AIE and AIP features (Figure 12a).^[62] The RTP quantum yield of BCZ derivatives was up to 64% in the solid state, which could be attributed to the biscarbazole structural design to greatly inhibit the nonradiative decay pathways by reducing the possibility of intermolecular π - π stacking. Notably, the nondoped OLEDs fabricated by these AIP-active chromophores showed maximum external quantum efficiency (η_{ext}) up to 5.8%, which was significantly superior to the fluorescence counterpart. Interestingly, Zhao and coworkers presented multichannel afterglow LED arrays by directly coating RTP precursor onto commercial LED

chips (Figure 12b).^[38] Stable blue fluorescence and long-lived green afterglow were visible when the applied voltage turned on and off, respectively. In addition, emissive 3D objects were fabricated on the basis of the flexibility and tailorability of polymer-based RTP films. Most recently, Chen and coworkers also presented an interesting afterglow display by coating transparent RTP materials on a glass tower (Figure 12c).^[36a] The cyan afterglow emission lasted for ≈ 2.5 s in the dark after ceasing UV light. In addition, they demonstrated intelligent afterglow display through the photomask method based on large-area polymer-based RTP film.

3.3. Information Encryption

Information leakage has already become a worldwide issue. Nowadays, most of the optical materials that are used for information encryption primarily rely on displaying different colors under different conditions.^[63] These conventional

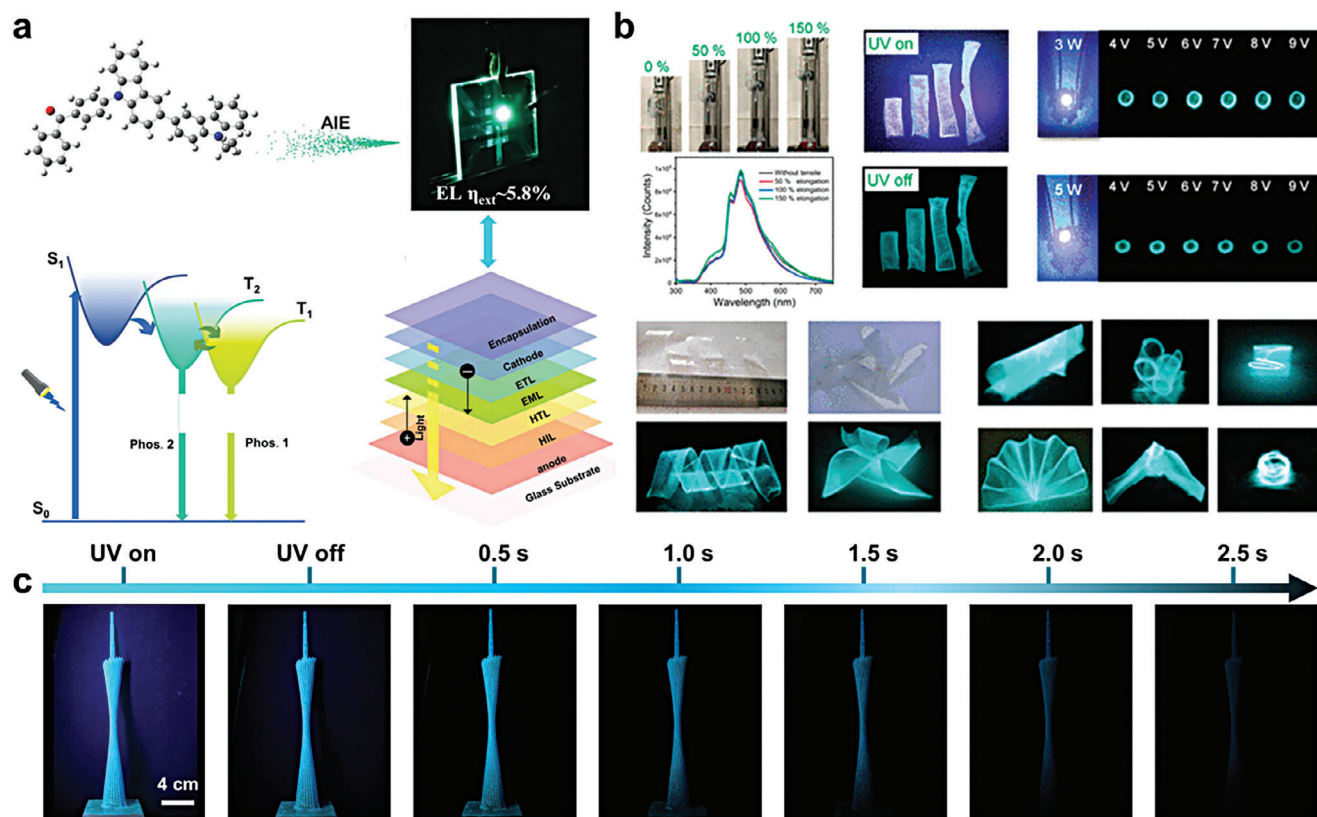


Figure 12. The compact and ordered RTP materials for afterglow display. a) Aggregation-induced phosphorescence material was applied in the nondoped OLEDs. Reproduced with permission.^[62] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. b) The fabrication of multichannel afterglow LED arrays and flexible 3D afterglow objects by using polymer-based RTP materials. Reproduced with permission.^[38] Copyright 2021, American Chemical Society. c) RTP material as a luminescent coating on a glass tower model for afterglow display. Reproduced with permission.^[36a] Copyright 2023, SCUT, AIEI, and John Wiley & Sons Australia, Ltd.

spatial-resolved optical technologies suffer a high risk of being duplicated or decrypted. Particularly, RTP materials possess a higher security level for information encryption by adding an additional time dimension, revealing spatial-time-resolved cryptographic advantage. Impressively, Tang and Yu et al. demonstrated a high-level encryption system based on sequential photo-thermo-phosphorescence conversions of three isomeric molecular rotors (Figure 13a).^[19] Target information could be written with such photo-thermo-activatable RTP materials on black paper using imprint lithography. The letters “R” and “P” written by *p*-Br-TRZ and *o*-Br-TRZ, respectively, were distinguishable with different colors from the other blue letters under the irradiation of weaker 365 nm light (216 mW cm^{-2}). Thereafter, the letter “T” displaying a cyan color could be observed under stronger 365 nm light 516 mW cm^{-2} . Finally, the target information “RTP” was decrypted by such sequential conversions, revealing multilevel information encryption. Also, by leveraging a dynamic RTP system, Chi and Tang et al. further presented time-resolved and temperature-dependent encryption and decryption systems (Figure 13b).^[20] The Chinese character consists of five different crystals (growth from different solvents) that showed spatial-temporal variations after creasing UV light. Moreover, the information could be changed by controlling the temperature based on the release of guest molecules.

Creatively, Chen and Huang et al. prepared water-jet rewritable paper by coating a water-enhanced RTP composite on filter paper for time-resolved anticounterfeiting application.^[9d] No visible information could be observed for water-jet printed patterns under daylight and UV light, while high-resolution anti-counterfeiting patterns were easily captured by naked eyes and cameras after the removal of the UV excitation source. In addition, the water-jet printed patterns could be easily erased by fuming with DMSO vapor and reused for several cycles. Besides, Tian and Walther et al. demonstrated self-erasable transient information storage and photolithographic encryption based on nacre-mimetic nanocomposite RTP films.^[42] By irradiating nanocomposite RTP films with a customized photo-mask, repeated information imprinting was successfully realized with anti-interception functionality. Recently, Ma and Tian et al. developed a new thermal encryption system by taking advantage of the multilevel thermal responsiveness of RTP emission (Figure 13c).^[64] The information can be camouflaged under sunlight when printed with RTP material on the blue cardboard. The target pattern only appeared under the irradiation of 365 nm UV light. Moreover, the emission of the designed pattern can be changed from blue to yellow-green under thermal annealing at $70 \text{ }^\circ\text{C}$, and then recovered by heating at $50 \text{ }^\circ\text{C}$, revealing multicolor encryption and smart regulation. A spatial-time-resolved anti-counterfeiting

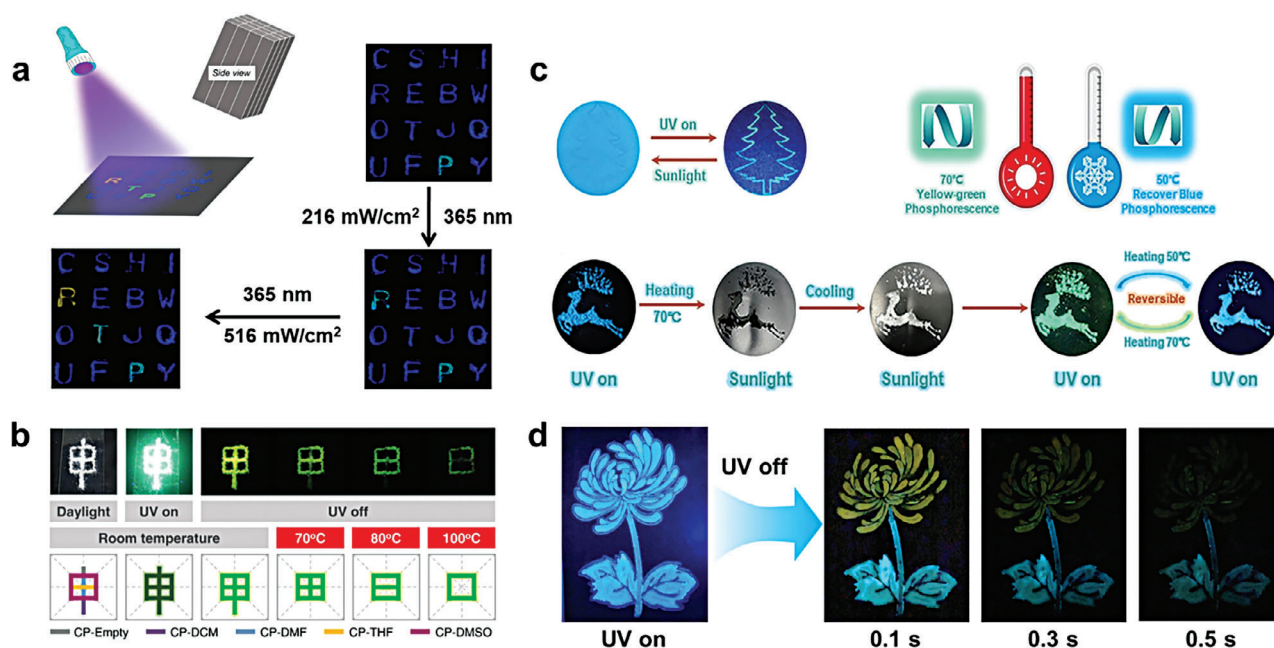


Figure 13. The assembly and aggregation-activated RTP materials for encryption and anti-counterfeiting. a) Sequential photo-thermo-phosphorescence conversions for multilevel information encryption. Reproduced with permission.^[19] Copyright 2022, The Author(s). b) Time-resolved and temperature-dependent encryption and decryption systems based on five kinds of dynamic RTP materials. Reproduced with permission.^[20] Copyright 2022, The Author(s). c) The thermal encryption system based on multilevel thermal-responsiveness of RTP emission. Reproduced with permission.^[64] Copyright 2022, Wiley-VCH GmbH. d) The spatial-time-resolved anti-counterfeiting pattern painted by RTP materials. Reproduced with permission.^[36a] Copyright 2023, SCUT, AIEI, and John Wiley & Sons Australia, Ltd.

pattern painted with two RTP materials was designed by Chen's group, exhibiting largely improved security to verify the authenticity (Figure 13d).^[36a] The chrysanthemum pattern displayed strong cyan emission under UV light, while a vivid chrysanthemum pattern with spatial-time-resolved evolution appeared after the removal of UV irradiation. Benefiting from their abundant and variable properties, these RTP materials demonstrated great promising applications in the information encryption and anticounterfeiting.

3.4. Chemical Sensing

Due to the susceptibility of triplet excitons toward external the environment (temperature, oxygen, solvents, etc.), RTP materials generally display excellent stimuli-responsive properties, which can be well employed for chemical sensing.^[65] In 2009, Fraser and coworkers developed the fluorescence-phosphorescence dual-emissive nanoparticles by nanoprecipitation of iodide-substituted difluoroboron dibenzoylmethanepoly(lactic acid) (BF₂dbm(I)PLA) (Figure 14a).^[66] Since high oxygen sensitivity and dual emission features, the resulting boron nanoparticles enabled the application for quantifying tumor hypoxia. Strikingly, Kim and colleagues developed a sensitive sensor for detecting dissolved oxygen (DO) based on the phosphorescent core-shell nanoparticles that self-assembled from crosslinked amphiphilic block copolymers (Figure 14b).^[67] Impressively, they utilized phosphor with two double bonds as crosslinkers to rivet together the hydrophilic polymethyloxazoline shells and oxygen-permeable polystyrene cores. As a result

of the restriction of molecular motions by the covalent polymeric network and resulting confined nanostructures, the nonradiative transition was largely inhibited, and thus leading to improved RTP properties. Thereby, the resultant water-soluble nanoparticles revealed excellent oxygen sensitivity for DO with a limit of detection (LOD) of 60 nM.

Based on oxygen-sensitive nature, Wu and coworkers developed an organic ratiometric hypoxia sensor based on a single chromophore (Figure 14c).^[68] The supramolecular oxygen nanoprobe was assembled by quadruple-hydrogen bonds of BrNpA-UPy and Ph-bisUPy in a miniemulsion, which exhibited dual emission of fluorescence and phosphorescence simultaneously. Notably, the supramolecular polymer showed stable fluorescent emission upon changing the concentration of oxygen, which could serve as an internal standard. Meanwhile, the organic ratiometric hypoxia nanoprobe displayed efficient long-live RTP with a lifetime of 3.2 ms and phosphorescent quantum yield of 7.7% in aqueous solution, which was highly sensitive to oxygen concentration and thus could be used as an oxygen indicator. In comparison to previous hypoxia indicators, it revealed various advantages of improved accuracy, stability, water solubility, and dispersibility. Therefore, such an organic sensor based on monochromophore was well applied for ratiometric hypoxia detection and imaging in living cells.

4. Summary and Perspectives

In the present review, we highlighted the recent advances in compact and ordered RTP materials. We discussed the impressive design and preparation methods, unique optical properties,

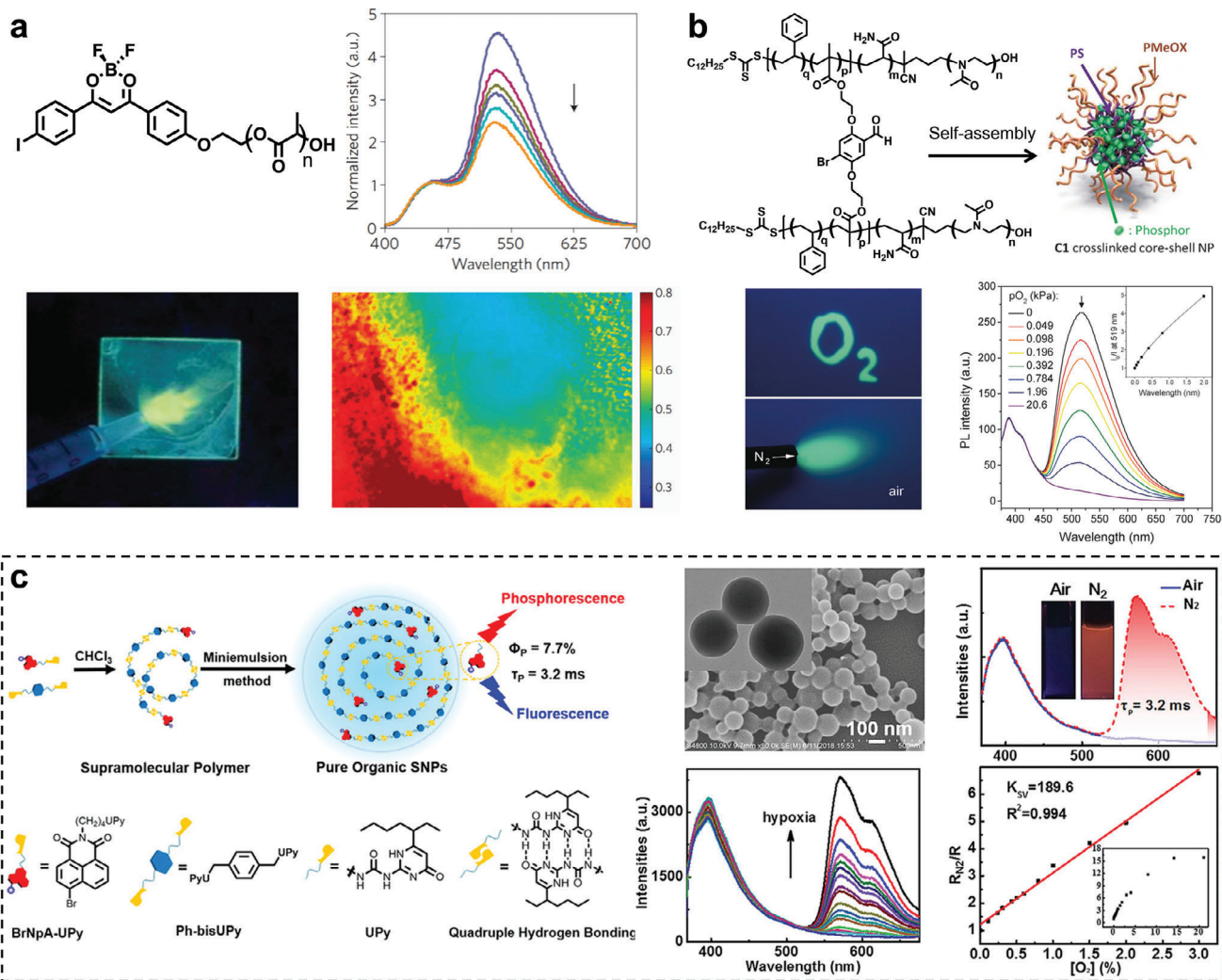


Figure 14. The assembly and aggregation-activated RTP materials for chemical sensing. a) The fluorescence-phosphorescence dual-emissive nanoparticles for sensing oxygen and quantifying tumor hypoxia. Reproduced with permission.^[66] Copyright 2009, Springer Nature Limited. b) The core-shell nanoparticles as a sensitive sensor for detecting dissolved oxygen. Reproduced with permission.^[67] Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. c) The supramolecular RTP polymer as oxygen nanoprobe for ratiometric hypoxia detection. Reproduced with permission.^[68] Copyright 2020, Wiley-VCH GmbH.

underlying luminescent mechanisms, and advanced optoelectronic applications. Briefly, high-performance RTP materials can be efficiently achieved by the direct organization of small organic fluorophores and luminescent polymers into relatively compact and ordered RTP emitters with the help of multiple supramolecular dynamic interactions. The organic molecules and polymers are prone to assemble into compact and ordered entities driven by dynamic noncovalent interactions such as multiple hydrogen bonds, π - π stacking interactions, electrostatic interaction, hydrophilic and hydrophobic interactions. Alternatively, organic phosphors can be assembled into compact RTP emitters in confined spaces including rigid polymeric matrices, supramolecular scaffolds and macrocyclic hosts, providing unique optical properties. Benefiting from these reliable and effective strategies, the spin-forbidden ISC process is greatly promoted by enhancing SOC and the molecular motions of

organic phosphors are immensely suppressed, facilitating the population and stabilization of susceptible triplet excitons to access high-performance RTP. Notably, outstanding RTP materials even in solution state are realized successfully, which is extremely difficult to achieve by traditional methods. As a result, the compact and ordered RTP materials offer more opportunities for optoelectronic applications in bioimaging, afterglow display, information encryption, chemical sensing, and so forth.

Despite the past decade having witnessed significant and impressive progress in ordered RTP materials, the universality and application of the method need to be further expanded, and the corresponding underlying luminescent mechanisms require to be well elucidated. Because the fluorogens should be well designed to have suitable molecular structures and intermolecular interactions for forming ordered RTP emitters, the universality of material construction is limited to a few specific molecules with

abundant bonding donors and acceptors. Therefore, the development of new assembly methods, such as the use of confined space-mediated self-assembly, is urgently needed to expand the universality for meeting more practical applications. In addition, the underlying luminescent mechanisms require to be well explained. For example, how do electron distribution and coupling from ordered molecular assembly enhance SOC for boosting ISC? A deep understanding of the impact of molecular arrangement on RTP properties is essential for the rational design of next-generation optical materials. Last but not least, the organic RTP performance needs to be further improved to match their inorganic counterparts. As a burgeoning research field, great breakthroughs and crucial progress are surely forthcoming, provoking the development of new generations of optical materials in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

optoelectronic applications, ordered emitters, room-temperature phosphorescence, supramolecular dynamic interactions

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