Recent progress on pure organic room temperature phosphorescent polymers

Hao Gao  |  Xiang Ma

Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Shanghai, China

Correspondence
Xiang Ma, Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Shanghai 200237, China. Email: maxiang@ecust.edu.cn

Abstract
So far, pure organic room temperature phosphorescence (RTP) materials are developing rapidly and have become a research hotspot in the scientific community. They are regarded as valuable resources with great potential for development in many fields, such as biomedicine, information multi-level encryption, smart anti-counterfeiting, and so on. Among them, a series of pure organic RTP polymer systems emerged at the right moment based on the excellent properties of polymers such as easy processing, low cost, and good biocompatibility. Furthermore, the huge molecular weight, long-chain intertwined structure, and potential interactions with phosphors of polymers make them a focus for RTP emission. Herein, we describe the development history of this system in detail, explore the necessary factors for highly efficient emission from the phosphorescence emission process, and based on the dual effects of enhancing phosphorescence emission and shortening luminescence lifetime brought by heavy atoms, we summarize the internal mechanism and achievements of various researches from the perspective of heavy atom–containing and non-heavy atom systems.

KEYWORDS
heavy atom effect, room temperature phosphorescence, polymer

INTRODUCTION

Room temperature phosphorescence (RTP) materials have received widespread attention due to their excellent performance, including long emission lifetime and large Stokes shift. These unique advantages enable them to be applied in many fields such as organic light-emitting diodes (OLEDs) [1], biological imaging [2], information encryption [3–5], anti-counterfeiting [6–8], and so forth. According to the luminescence mechanism of phosphorescence emission, there are two key factors to construct high-efficiency RTP materials. One is to promote the intersystem crossing (ISC) from singlet to triplet state, which is a spin-forbidden process, and the other is to reduce the nonradiative inactivation of the triplet excitons and ensure that they can survive long enough to emit phosphorescence. Traditional RTP materials contain heavy metals [9,10], which can cause effective spin-orbit coupling (SOC), thereby enhancing the ISC process to populate triplet, but taking into account their toxicity, cost, and other defects, they are gradually being replaced by pure organic RTP materials that are inexpensive and easy to prepare. Therefore, the introduction of halogen heavy atoms into pure organic systems is currently a common strategy [11,12]. As early as 1949, the heavy atom effect was proposed by McClure [13] and later widely used to enhance phosphorescence emission. The existence of heavy atoms enables the spin-orbit interaction easy to occur, thus increasing the ISC rate. As for how to limit molecular motion and minimize nonradiative transitions, present reports have also proposed many feasible strategies. The core is to provide a rigid and protective environment for the phosphors, reducing molecular vibrations and intermolecular collisions, thereby avoiding energy dissipation as far as possible.

In 2010, the concept of crystallization-induced phosphorescence was proposed [14]. The molecular motion was limited by the crystal lattice and strong interactions between molecules, and the crystal lattice also simultaneously prevented the phosphors from contacting quenching sites such as oxygen and moisture, which greatly improved the luminescence efficiency. Therefore, in later years, crystal packing such a structural rigidification method was frequently used for obtaining highly efficient RTP materials [15–17]. However, the crystal preparation process is difficult to repeat and the operability is poor, so practical applications are tremendously limited. In addition, deuterium substitution to minimize the...
nonradiative deactivation of the luminophores is also a way to obtain metal-free and high-efficiency phosphors [18], but this requires an extremely complicated synthesis process. Meanwhile, because the polymer has a large molecular weight, a variety of interaction forces between the chains ensure a rigid environment, which can likewise inhibit the nonradiative transition of the phosphors. More than that, the long chains are intertwined, which can prevent triplet excitons from being quenched by oxygen. What is more worth mentioning is that the excellent properties of polymers make it another choice for the development of RTP materials [11,19-22].

This mini review summarizes the latest developments in pure organic room temperature phosphorescent polymer materials, focuses on how the interaction between the polymer matrix and phosphorescent groups influence luminescence behavior, and proposes the direction of future development in this field.

RTP POLYMERS BASED ON DIFFERENT INTERACTIONS

The interactions of RTP polymers mainly include covalent bond, hydrogen bond, halogen bond, host–guest interaction, π–π stacking, and so on. In simple terms, the heavy atom effect of halogen atoms can improve SOC, thus enhancing ISC; π–π stacking can stabilize triplet excitons, while the other two interactions make for a rigid environment and resistance of the nonradiative transition of emitters. These interactions can all facilitate the phosphorescent emission of the polymers.

On the one hand, halogen atoms could contribute to the ISC process and phosphorescence quantum yield, thereby efficiently enhancing phosphorescence emission; on the other hand, the introduction of halogen atoms will accelerate the nonradiative decay of triplet excitons and shorten the phosphorescence lifetime of the system [23]. Therefore, this mini review summarizes the progress in both the heavy atom–containing RTP polymer systems and the heavy atom–free RTP polymer systems, and discusses in depth the luminescence mechanism and property of the mentioned systems.

HEAVY ATOM–CONTAINING RTP POLYMERS

Doped polymer systems

The doped systems achieve effective RTP emission through physical mixtures of phosphor guests and polymer hosts. Phosphors can interact (such as hydrogen bonding) with the polymer through doping to enhance phosphorescence emission. Not only can small phosphorescent molecules act as doping guests, but also can phosphorescent polymers. The most commonly used doped polymer matrices are polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA).

PMMA with a wide bandgap is a traditional inert polymer. It is often used as a host material for embedding phosphor groups to ensure efficient RTP because of its ability to form rigid glass. In 2013, Kim et al. embedded pure organic phosphor 2,5-dihexyloxy-4-bromobenzaldehyde (Br6A) (Scheme 1) in a glassy PMMA matrix, achieving bright RTP emission and a phosphorescent quantum yield of 7.5% [24]. Studies have shown that PMMA acted as a rigid matrix like a crystal, and its tacticity significantly influenced phosphorescence efficiency. The reduced beta (β)-relaxation of isotactic PMMA could suppress triplet nonradiative decay to the greatest extent. And this study also revealed that the key factor that promoted the full embedding of phosphor groups into the polymer matrix was the matching of their solubility parameters.

Later, Kim et al. explored a more versatile and feasible method of constructing high-efficiency amorphous RTP materials to suppress the vibrational dissipation of the luminophore and the diffusion of the matrix [25]. They purposefully introduced two types of strong noncovalent interactions between molecules into the system. One of them rooted in the halogen bonds between phosphors, which could not only promote the ISC process but also suppress the vibration of the phosphors; the other came from the strong hydrogen bonds interaction between the host matrix as well as the host and the phosphor groups to more effectively suppress the diffusion/vibration of the matrix and phosphors. Therefore, they successfully designed a new phosphor G1 with bromoaldehyde core and carboxylic acid side chains
shown in Scheme 1 and chose PVA as the host matrix due to its excellent hydrogen bonding ability. The phosphorescence quantum yield (ΦPh) of the final G1-PVA system was as high as 24%, as expected, far exceeding the previous Br6A-iPMMA system. It is worth mentioning that the RTP emission process, achieving the tunability of relative intensity of fluorescence and phosphorescence. Different molecular weights of BF2dbm(I)PLAs (Scheme 2) were designed to realize their versatility in the sensor field. The introduction of heavy atoms was believed to enhance the SOC, thereby increasing the ISC rate.

With the deepening of research, Fraser et al. found that the substitution position of heavy atoms could have a profound effect on the luminescence behavior of the system [30]. They designed a model of a mixture (BF2n(Br)bmPLA) of BF2-hdk dye and PLA shown in Scheme 2, and discovered that in this asymmetric system, the intramolecular charge transfer (CT) was dominant. When the bromine heavy atom was placed on the naphthalene ring with higher electron density, the heavy atom effect could be maximized and lead to a good separation of fluorescence and phosphorescence peak to realize the systematic adjustment of luminous intensity, lifetime, and oxygen sensitivity.

Taking into account the restriction of molecular motion caused by embedding the phosphor into a polymer matrix, Kim et al. proposed a method of Diels–Alder click chemistry to covalently cross-link the luminophores and polymer matrix, which was beneficial to improve the rigidity of the local environment, and as expected, the phosphorescence quantum yields in various polymer matrices were greatly improved [20]. As represented in Scheme 2, the product obtained by covalent cross-linking of a diene-reactive phosphor (DA1) and an ene-reactive polymer matrix displayed a phosphorescent quantum yield of 28%, which was two to five times higher than their blend system. However, the procedure of this method was complicated. It was exceedingly necessary to separately synthesize the polymer and modify Br6A, and the Diels–Alder click chemistry reaction between them was an indispensable step. What is more, there were certain restrictions on the solubility of these two substances, which damaged its applicability.

In 1982, Turro et al. first put forward that β-CD could induce RTP [31]. Macroyclic molecules gradually entered the researchers’ view [32], just as the polymer matrices provide a rigid environment, they can also limit the vibration of guest molecules and prevent them from being quenched by external oxygen and moisture. In 2014, our group reported the first case of supramolecular polymer hydrogel system with RTP emission [33], which opened up a new field for room temperature phosphorescent materials. Based on the host–guest recognition interaction between poly-BrNp (Scheme 2) obtained by radical binary copolymerization with acrylamide and poly-β-CD, along with the formation of a cross-linked network of hydrogen bonds between amide groups, a thermally responsive hydrogel system was obtained and could achieve rapid self-healing within 1 min in an ambient environment. The RTP signal was excited due to the inclusion effect caused by β-CD macrocyclic inclusion of α-BrNp moiety. When the aqueous solution of poly-Azo polymer was introduced into the system, the light-stimulated cis-trans isomerization of the azobenzene unit affected the competitive inclusion of β-CD and α-BrNp, resulting in the reversible adjustment of the signal intensity. In 2016, our group constructed a new poly-BrNpαγ-CD system based on the host and guest recognition of γ-CD macrocyclic molecules and luminous guest polymers [34], which could emit RTP in an aqueous solution. Like the previous research, its intensity was susceptible to change by the photo-isomerization of the Azo.

### Covalent polymer systems

Covalent polymers mean that the single-component systems themselves have characteristics of phosphorescence emission. There are several construction strategies as follows: (1) the potential phosphorescent groups are covalently connected with the polymer matrices to make the whole system emit RTP; (2) the polymers themselves have inherent RTP property; (3) the polymer matrices are covalently cross-linked to enhance RTP emission.

In 2009, based on the previous work [28], Fraser et al. introduced heavy atom iodine into the dual-emission polymer system [29]. They systematically changed the length of the polyactic acid (PLA) chains during the polymerization process, achieving the tunability of relative intensity of emission without being quenched by water could also be effectively realized, especially white light emission. When it comes to heavy atom effects, it is generally achieved by covalently attaching halogen atoms to compounds or polymers, as mentioned before. The external heavy atom effect was rarely investigated. In 2019, Huang et al. synthesized a series of (4-(9H-carbazol-9-yl)butyl) triphenylyphosphonium (CBTP) (Scheme 1) with different halide anions(Cl−, Br−, I−) [26]. The compounds exhibited various emitted colors from blue to orange-yellow in the solid state. Experimental data showed that the external heavy atom effect could also enhance the SOC, thereby increasing the rate of ISC. The CBTP-Br, showing a strong blue emission, was doped into poly (ethylene glycol). When the counter ion I− in KI was introduced into the system according to different proportions, the different emission colors of the film could be effectively realized, especially white light emission. The quantum yields of this kind of film were in the range of 4.60%–7.83%.

It should be noted that high-efficiency phosphorescence emission without being quenched by water could also be achieved through the doping process. Zhang et al. developed an innovative co-assembly strategy for macro-molecules [27]. The luminescent molecule 9-acetyl-3,6-diiodocarbazole substituted with heavy atom iodine (RTP-9-CD) could induce RTP. Taking into account the restriction of molecular motion caused by embedding the phosphor into a polymer matrix, Kim et al. proposed a method of Diels–Alder click chemistry to covalently cross-link the luminophores and polymer matrix, which was beneficial to improve the rigidity of the local environment, and as expected, the phosphorescence quantum yields in various polymer matrices were greatly improved [20]. As represented in Scheme 2, the product obtained by covalent cross-linking of a diene-reactive phosphor (DA1) and an ene-reactive polymer matrix displayed a phosphorescent quantum yield of 28%, which was two to five times higher than their blend system. However, the procedure of this method was complicated. It was exceedingly necessary to separately synthesize the polymer and modify Br6A, and the Diels–Alder click chemistry reaction between them was an indispensable step. What is more, there were certain restrictions on the solubility of these two substances, which damaged its applicability.
unit of the poly-Azo in an aqueous solution. In addition to the macrocyclic molecule such as CD, cucurbituril can also bind well to numerous guests and is highly selective. What is more, CB[7] in this family has gotten tons of attention due to its good water solubility and the ability to encapsulate organic molecules of various sizes. Therefore, an inclusion complex of poly-BrNpA (Scheme 2) capsulated with CB[7] was formed \cite{35}, promoting the generation of phosphorescence due to the host–guest interaction.

It is not difficult to find that polyacrylamide plays an important role in the above several polymer systems. As a rigid matrix, it can not only effectively fix the emitters and isolate oxygen, but also assist in further enhancing RTP emission through hydrogen bond cross-linking between chains. Therefore, our group has tested its versatility \cite{4,36}. There were three types of phosphor groups used for binary copolymerization with acrylamide, and the amorphous powders of poly-BrBA, poly-BrNp, and poly-BrNpA (Scheme 2) were
finally obtained, which was different from the previous crystalline or film state. It has rarely been reported. Surprisingly, all three polymers exhibited excellent luminescence behavior with large Stokes shifts, which corresponded to the RTP emission property. The experimental results also showed their long lifetime and high quantum yield. Note that 1:50 was considered the most ideal polymerization ratio to prevent excessive phosphor concentration from weakening the protective effect of polyacrylamide. Furthermore, in order to prove the key role of the heavy atom effect, poly-NpA was synthesized, used for comparison with poly-BrNpA. There was no obvious phosphorescence emission under the same test conditions, which proved the necessity of heavy atom introduction. In this polymer system (Poly-BrCZ) (Scheme 2) of copolymerization of acrylamide and phosphors, we have also developed a new type of phosphor 2-bromocarbazole to achieve the high-efficiency blue-violet phosphorescent emission of this copolymer [21]. Experimental results have shown that different polymerization ratios could significantly affect the phosphorescence emission intensity, because an excessive amount of phosphor may weaken the rigidity of the polymer structure and the insulation effect on the quencher, while a small amount of phosphor would naturally reduce the emission intensity. What is more, the copolymer was found to be sensitive to water and expected to be used in the field of anti-counterfeiting.

As per the examples mentioned above, terminal modified polymer chains with chromophores tend to aggregate and thermally quench. Zhang et al. proposed a feasible solution to solve this thorny problem by introducing the emitter into the main chain [37]. They synthesized waterborne polyurethane (WPU) incorporated with naphthalimide derivatives (NIs) through polycondensation reaction, which became a one-component dual-emission optical material. Compared with polymers without heavy atom substitution (NI-PU3), NiBr-PU3 emitted RTP with ease because SOC was promoted.

As a kind of super engineering material, polyimides (PIs) are well known for their outstanding thermal and mechanical stability. Its carbonyl group, rigid structure, and strong intermolecular interaction provide the possibility for RTP emission. In 2016, Ando et al. jointly discovered a series of PIs containing 3Br-P1 and 3I-P1 (Scheme 2) with a large Stokes shift (approximately 10,000 cm⁻¹) and capable of emitting RTP [11]. Experiments showed that the pure PIs film only emitted fluorescence with a small Stokes shift, while the substitution of Br and I atoms in the diimide moiety could induce the generating of phosphorescence and a higher photoluminescence (PL) quantum yield due to heavy atom effect. Compared with these halogenated polymers in the air, the phosphorescence lifetime under vacuum was extended to 9.9 ms for 3Br-P1 and 3.3 ms for 3I-P1, so their oxygen sensitivity and large Stokes shift indicated that they would be widely used in oxygen sensors and spectral converters.

Apart from traditional conjugated light-emitting organic materials, nonconjugated luminous polymers are also quickly attracted attention due to their chain flexibility and structural tunability. They generally own electron-rich atoms, which enable them to have good hydrophilicity, environmental friendliness, biocompatibility, and so on. Consequently, our group designed a nonconjugated amphorous pure organic RTP polymer through copolymerization of different types of brominated olefins and acrylamide in different proportions [38]. Among them, poly-BrHexene (Scheme 2) displayed the most excellent blue-purple RTP emission. The aggregation of amino groups and carbonyl groups would lead to enhanced intermolecular interactions. The introduction of heavy atoms was conducive to the occurrence of ISC. Polyacrylamide could provide a rigid environment and the ability to isolate oxygen and other quenchers. It is believed that the three key factors together triggered unique RTP emission in this system.

Stimulus-responsive optical materials have always occupied a place in the field of photochromism. Our group has recently developed a multi-stimulus-responsive multicolor luminescent material [39]. Three color-switchable copolymers (P1, P2, and P3 shown in Scheme 2) through the relative copolymerization of benzaldehyde, 2,5-dihydroxy terphenylate, spiropropyran (SP), and acrylamide were designed. They could respond differently to light, temperature, and humidity. When alternately irradiated with UV light and visible light, they exhibited a variety of emission colors, especially white emission, benefiting from the photochromatic characteristics caused by the SP closing or opening ring. In addition, in this stimulus-responsive photochromic copolymer, the energy transfer process included not only the transfer of fluorescence energy but also the transfer of triplet energy.

Recently, through a reversible D-A reaction as illustrated in Scheme 2, three copolymers (Poly-Br-An, Poly-Br-An-Cp, Poly-Br-An-MA) fabricated by anthradiimide derivatives with acrylamide could produce RTP emission [40]. Moreover, Poly-Br-An even reached a high phosphorescence quantum yield of 12%. Similarly, the thermo-reversible dynamic covalent bonds brought the characteristics of external stimulus response to the copolymers, and the luminescence was tunable, showing a reversible blue–yellow–orange switch. This work provided valuable experience and ideas for multifunctional smart materials.

Due to the quenching effect of water on phosphorescence, the application of RTP materials in aqueous biosystems has been limited all through. Recently, Liu et al. skillfully introduced 4-(4-bromophenyl)-pyridine-1-ium (BrBP), a phosphor, into a polymer chain (hyaluronic acid) capable of targeting cancer cells, and co-assembled with cucurbit[8]uril (CB[8]) to form pseudorotaxane polymer [41]. It was surprisingly found that the phosphorescence emission lifetime of CB[8]/HA-BrBP system at 500 nm reached the millisecond level (4.33 ms) with a high quantum yield of 7.58% represented in Figure 1, which was very precious in aqueous systems. The interaction of π-π/Br-π, host–guest recognition, hydrogen bond, as well as heavy atom effect co-enhanced the efficient phosphorescence emission in this aqueous solution by inhibiting the vibration of phosphor groups.

HEAVY ATOM–FREE RTP POLYMERS

Doped polymer systems

It is apparent that the difference in the microenvironment brought by the host matrices and the interactions with the luminophore will have an unignorable influence on luminescence behavior. Therefore, Pant et al. chose PVA, PMMA, and cellulose acetate (CA) as three host matrices to study this [42]. Interestingly, it was found that the luminophore
1-naphthoic acid represented in Scheme 3 could only emit strong phosphorescence in a specific matrix. They used strong and weak hydrogen bond conformers and polymer heterogeneity to explain this phenomenon. That was to say, the reason why 1-naphthoic acid could emit strong phosphorescence in the PVA matrix was that strong hydrogen bonds could only be formed in this system, and PVA could form hydrogen bond interactions with water, inhibiting the quenching effect of water, thereby further enhancing phosphorescence emission.

In the same year, Reineke et al. designed a dual state emitter for dispersing single molecular aggregation of (BZP)PB (Scheme 3) in a PMMA matrix [43]. The nonradiative transition rate of the triplet state was minimized to $2.4 \times 10^6$ s$^{-1}$, phosphorescence lifetime reached 208 ms, and realized high-efficiency dual emission of fluorescence and phosphorescence.

Considering that the interaction of chromophores between polymer chains could prompt the rapid quenching of excitons, the photoluminescence quantum yield (PLQY) of the luminescent water-soluble conjugated polymer (WSCP) would be greatly lost in solid state, while a solid film was prepared by this WSCP and polymeric surfactants, such as PVA and polyvinyl pyrrolidone (PVP) [44], which could exhibit excellent RTP emission, and greatly improve PLQY. The surfactants used here were believed to destroy polymer aggregation, and could also form covalent bonds or cross-linked networks so that the polymer chains were confined to a rigid matrix and remained isolated.

In 2016, Lin et al. designed a single-component triple-mode emission (including PL, up-conversion PL, and phosphorescence) luminescent material [6] based on a composite of luminescent carbon dots (CDs) synthesized from m-phenylenediamine shown in Scheme 3 and PVA. Moreover, when the UV lamp (365 nm) was turned off, there was a green afterglow visible to the naked eye. This was the first report of a study on simultaneous triple-mode emission, and the achievement could be well applied to the advanced anti-counterfeiting field to achieve three modes of optical authentication.

Adachi et al. developed the first organic long-persistent luminescence (OLPL) polymer-based material, which was a dopant involved of the electron donor TMB and electron acceptor poly arylene ether phosphine oxide (PBPO) (Scheme 3) [45]. The system inherited the characteristics of the triplet emission of the donor and was simultaneously protected and restricted by the rigid environment of the acceptor polymer. After being excited by a low-power lamp at room temperature, the system emitted phosphorescence lasting for up to 10 s originated from the donor, and then the LPL was launched and continued for more than 7 min. This technology is simple and easy to implement and can be used to prepare various plastics and fiber products, but its long afterglow emitting time is much shorter than previously reported small molecule system [46], so further optimization may be needed.

In 2018, Zhao et al. presented a rational strategy to construct a stimulus-responsive ultra-long room temperature phosphorescent PVA film doped with a simple organic guest
molecule hexa-(4-carboxyl-phenoxy)-cyclotriphosphazene (G) represented in Scheme 3 \[3\]. They intended to introduce three strong interaction forces into the system. The hydrogen bonds formed between the guest molecules could effectively impede molecular motion and promote ISC. Another type of hydrogen bond incorporated between the guest and the matrix was beneficial to reduce the diffusion motion of the polymer chains. Covalent cross-linking between the polymer matrix generated by light excitation could further avoid vibration relaxation. Therefore, when the G-PVA film was irradiated with a 254 nm UV lamp for 65 min, its luminous intensity was significantly enhanced, the lifetime reached 0.71 s, and the quantum yield increased to 11.23%, which were 2.5 and 3.9 times than before excitation, respectively. Hence, an ultra-long room temperature phosphorescent polymer was obtained successfully.

Recently, Zhao et al. dedicated to developing a simpler way to implement UOP. The co-assembled film formed by the planar carbazolyl derivative (Scheme 3) and the PVA matrix was found to be able to emit long-lived RTP \[47\]. The planar structure was verified to be necessary to improve the emission lifetime because the planar molecules were dispersed in the PVA matrix, which could be strongly bound by the rigid matrix to reduce the dissipation of molecular vibration and could get rid of the phenomenon of light quenching caused by the accumulation of numerous molecules. However, it was formidable to restrict the vibrational motion of molecules in a twisted conformation, which easily caused nonradiative transitions of triplet excitons, thus greatly weakening the luminescence. In addition, this general method could also be used to fabricate multicomponent co-assembled films to achieve multicolor emitting, which showed the advantages of simple operation and high efficiency.

Zhao et al. also carried out a series of work to explain the excitation-dependent luminescence phenomenon, and constructed various color-tunable excitation-dependent ultralong luminescence polymer systems. Doping four pyrene derivatives named PYM, HPY, PCA, and PBA (Scheme 3), respectively, into the PVA matrix \[48\], the obtained films were capable of emitting from blue to red light by controlling the formation of aggregates and hydrogen bonds precisely, leading to the emission originated from different triplet states. Hence, they are expected to be used in multicolor interchangeable anti-counterfeiting signs. Similarly, in another report, they proposed that two new types of polyphosphazene derivatives (P2 and P4 shown in Scheme 3)
containing carbazole-based units were similarly doped into PVA films to achieve persistent luminescence [49]. The lifetime lasted for more than 1 s, along with excitation-dependent characteristics, and the luminous color extended from blue to green.

More recently, an ultralong RTP system constructed by Wang et al. through a dense 3D cross-linked network has brought fascinating results, including a super long phosphorescence lifetime of 2.28 s and a high quantum yield of 8.35% [50]. The system was obtained by simply doping tetramethylbenzidine (TMB) (Scheme 3) into the epoxy polymer. TMB acted as a chromophore because it contained $n$, $\pi$ electrons, which was beneficial to increase the rate of ISC. The epoxy polymer was competent to form a 3D network to tightly bind the emitter and suppress the nonradiative transition of triplet excitons. They also pointed out that the polymer could emit green phosphorescence for a few seconds yet under low-power excitation or sunlight, even at a high temperature of 60°C. In a manner of speaking, these brilliant performance parameters are record breaking, broadening the direction for the further development of optical materials.

However, most of the current work has only achieved phosphorescent emission excited in the UV range, showing noticeable application limitations. Recently, a breakthrough has been made in the research of pure organic ultralong RTP materials based on visible light excitation [51]. Louis et al. chose PMMA as a matrix to inhibit triplet nonradiative inactivation. As luminescent dyes, tetraphenylbenzidine (TPB) and four derivatives with bipyridine and phenanthroline cores shown in Scheme 3 were mixed with PMMA at a low concentration to form thin films. Both phenanthroline derivatives showed long-lived RTP emission that could be activated by visible light up to 420 nm and were expected to be used in the field of programmable tags and information encryption.

**Covalent polymer systems**

In 2007, Zhang et al. used boron difluoride dibenzoylmethane (BF$_2$dbm) to couple with PLA as shown in Scheme 4, and obtained a single-component, multi-emission material [28]. This method not only greatly improved the fluorescence quantum yield, but also produced oxygen-sensitive green RTP and temperature-sensitive delayed fluorescence. In this system, the thermal decay path of the triplet state was limited by the rigid structure of the matrix, making the phosphorescence lifetime of several seconds. As a polymer with good biocompatibility and degradability, PLA can be used to prepare luminescent materials by interacting with potential phosphorescent groups, which will further promote the development and application of multifunctional biomaterials for imaging and sensing.

Based on three determinant factors for improving RTP efficiency (enhancing ISC and the radiative transition of the triplet excitons and inhibiting their nonradiative decay), PLA was once again used as a rigid matrix to covalently connect with the donor-acceptor binary macromolecular phosphors, where carbazole moiety as a donor attached the acceptors...
through an N linkage [52]. Three biluminophoric systems (CZNI-PLA, CZBP-PLA, and CZAQ-PLA represented in Scheme 4) with different emission lifetimes and colors have been successfully constructed, and the absolute quantum yield was as high as 39.4%. Through the demonstration of experimental results and theoretical calculations, a semipirical rule for constructing dual phosphorescence emission was proposed: when a n→π* type lumophore and a π→π* one were introduced into the system at the same time, the chemical conjugation between them would lead to dual phosphorescence emission, and fluorescence-phosphorescence dual emission was usually caused by the conjugation between two π→π* molecules. This may inspire the exploitation and potential applications of multiemissive materials.

In 2015, Zhang et al. proposed for the first time to introduce dyes into the polymer backbone through a polycondensation reaction to more effectively prevent the aggregation and thermal quenching of the terminal phosphor groups, which has been mentioned above. They discovered a single-component dual-emission material (SDM) formed by covalently incorporation water-based polyurethane (WPU) with benzophenone substituted with amino groups [53], and the luminescence properties were adjustable under different chromophore concentrations. This was because as the concentration of the chromophore increased, the singlet-triplet energy gap would gradually narrow, thereby enhancing the communication between the two states, which in turn led to an upward tendency in ISC rate. It was revealed by the mechanism of polymer-enhanced intersystem crossing (PEX). According to the PEX mechanism, WPU was once again selected as the polymer matrix, and the delayed fluorescence and phosphorescence dual-emissive behavior of its copolymer as the polymer matrix, and the delayed fluorescence and phosphorescence dual emission was usually caused by the conjugation between two π→π* molecules. This may inspire the exploitation and potential applications of multiemissive materials.

In 2016, Zhang et al. reported on the luminescence phenomenon of nonconjugated polyacrylonitrile (PAN) (Scheme 4), and strongly demonstrated that its luminescence mechanism was clustering-triggered emission (CTE) [55]. The specific manifestation was that the dilute PAN solution has no significant photophysical phenomena, but when it was concentrated to nanosuspensions, or solid powders and thin films, the luminescence behavior became quite obvious, accompanied by a high quantum yield of 16.9%. This was because when molecules aggregated, various clusters were formed, and the structure became more rigid. The overlap of electrons also expanded the delocalization range, promoted the ISC process, and stimulated triplet emission, especially RTP.

Similarly, relying on the CTE mechanism, Yuan et al. subsequently explained the inherent luminescence behavior of the newly discovered nonconjugated nonaromatic poly(amino acids), and in-depth investigated their differentiated photophysical properties in different states [56]. The poly(amino acid) powder exhibited a quantum yield value of 7.9% and produced long-lived and durable phosphorescent emission. The key factor engendering RTP was the unconventional chromophores aggregated and induced electron overlap, which enhanced the rigid environment and the spatial communication of n and π electrons, in addition to the contribution of intra- and intermolecular interactions between polymer chains. A year later, they conducted an in-depth study of polyethylene terephthalate (PET) shown in Scheme 4 and revealed its concentration-enhanced emission and aggregation-induced emission (AIE) behaviors [57]. Different from weak luminescence in dilute solution, when it was in a solid powder state, fluorescence-phosphorescence dual emission characteristic was exhibited, which could also be explained by the above CTE mechanism. What is impressive was that a series of amorphous nonaromatic polymers with unique intrinsic emission and persistent RTP were also reported by them later, including poly(acrylic acid) (PAA), polyacrylamide (PAM), and poly(N-isopropylacrylamide) (PNIPAM) in Scheme 4 [58]. Furthermore, persistent RTP emission could be obtained from PAA and PAM solids under ambient conditions as well as PNIPAM under vacuum or nitrogen atmosphere.

Since the heavy atom effect can easily reduce the phosphorescence lifetime, our group was also committed to the development of heavy atom free pure organic ultra-long RTP systems. In 2018, a series of compounds (P1–P10) (Figure 2B) containing oxygen atoms were screened out for free radical copolymerization with acrylamide [19,59], where the oxygen atoms could facilitate the n→π* transition, thereby promoting ISC to populate the triplet excitons. Polyacrylamide, as we all know, is an ideal polymer matrix for fixing emitters with excellent performance. The interchain hydrogen bonds cross-linking network could further enhance this fixing effect. Ultimately, all polymers showed excellent RTP emission lifetime and quantum yield, especially P3 showed the longest phosphorescence lifetime (537 ms) as well as moderate quantum yield (15.39%), and as illustrated in Figure 2D, there was a blue afterglow visible to the naked eye lasting for several seconds.

Based on the ability of hydrogen bond network enhancing luminescence, Ogoshi and his co-workers have studied the luminescence behavior of another simple polymer poly(styrene sulfonic acid) (PSS) shown in Scheme 4 [60]. By adjusting the ratio of the introduced sulfonic acid groups and molecular weight, the green phosphorescence lifetime could exceed 1 s. Revealingly, increasing the proportion of sulfonic acid groups could promote the formation of a complete tight hydrogen bond network, thus inhibiting molecular vibration to obtain a stable and highly active excited state, which was consistent with the effect of increasing molecular weight. In addition, the quenching effect of water on phosphorescence was reversible, and the dried PSS has a phosphorescence lifetime of 1.22 s in the air. This adjustable feature of lifetime makes PSS earn a place in advanced data security intelligence technology.

As the above successful cases show, long-lived RTP is generally achieved by constructing a tight hydrogen bonding network. However, compared to hydrogen bonds, ionic bonds reveal more appealing characteristics such as stronger interaction, nondirectionality, unsaturation, and so on. As a result, whether the cross-linking of ionic bonds could replace the cross-linking network of hydrogen bonds to inhibit the nonradiative transition of chromophores has become a question taken into account by Huang et al. [61]. In poly(styrene sulfonic acid) sodium (PSSNa) shown in Scheme 4, the aro-
matic phenyl group was considered to be a chromophore, and the sodium sulfonate substituent provided ionic bonds to lock the chromophore tightly so that it could be firmly connected to the vinyl skeleton through covalent bonds. The polymer emitted bright blue fluorescence under the irradiation of 365 nm UV lamp and showed super long yellow phosphorescent afterglow when the lamp was turned off. Amazingly, its phosphorescence lifetime reached a value of 2.1 s. In addition, the system could emit multicolor long-lived RTP by adjusting the excitation wavelength. At the same time, their group applied this ionic bond interlocking mode into nonaromatic polymers, proving the universality of this method.

Based on the strong interaction of ionic bonds, Huang et al. designed a new system named PVP-S (Scheme 4) that could emit greenish ultra-long RTP through PVP matrix [62]. The pyridine ring was considered as a candidate for forming ionic bonds because of the basicity and strong coordination ability of the pyridyl nitrogen. The products ionized by different organic acids not only exhibited ultra-long organic phosphorescence (578.36 ms), with a phosphorescence efficiency of 6.4% but also could emit multi-color RTP under different excitations. The multiple isolated and aggregated states of the polymer formed disparate excited states, thereby generating multicolor luminescence that could cover the entire visible area.

In addition to the three cross-linking network strategies constructed by hydrogen bonds or ionic bonds or covalent bonds mentioned above to fix chromophores, Wu et al. developed a new facile approach to obtain effective RTP materials by building boron-based coordination polymers [63]. Therefore, copolymer (p-BAA) shown in Scheme 4 was prepared through radical binary copolymerization of 4-vinyl phenylboronic acid (4VPBA) and acrylamide (AA), exhibiting phosphorescent emission (λ_{max} = 477 nm) under 360 nm excitation in ambient condition, the emission lifetime reached up to 351 ms. Moreover, a green afterglow lasting over 4 s was visible to the naked eye after removing the excitation. The B atom and the N, O atoms were connected to each other through coordination bonds, which became a bridge for CT to fill the triplet state, as well played a crucial part in suppressing the vibration of the emitters. It is worth noting that these dynamic coordination bonds, together with the hydrogen bonds in the system, endowed the polymer self-healing ability, providing new available resources for some anti-counterfeiting technologies.

Regarding the issue of CDs emitting RTP, it is still in the exploratory stage, and there are very few reports of systematic and in-depth research on its luminescence mechanism or regular emission. Currently, a high-yield N-doped polymer CD capable of emitting tunable RTP was developed [64], based on a one-step hydrothermal addition and carbonization reaction, in which acrylamide was used as a starting material. The degree of carbonization could be precisely controlled by the hydrothermal temperature, leading to the adjustable emission lifetime and emission wavelength within a certain range. The main factor that caused RTP tunability was that as the degree of carbonization increased, the degree of graphitization enhanced, which was conducive to the formation of sp^2 carbon domain, resulting in a greater extent of conjugation, and ultimately narrowing the RTP central emission bandgap. This tunable multicolor luminous material is suitable for multilevel anti-counterfeiting and encryption technology.

What is impressive was that, just recently, Liu et al. proposed a synergistic effect of polymerizing phosphorescent group 4-phenyl-1-(4-vinylbenzyl)pyridinium chloride with acrylamide and then complexing with cucurbit[6,7,8]urils

![Diagram](https://example.com/diagram.png)
(CB[6,7,8]) to achieve ultra-long phosphorescent emission of this system [65]. Significantly, when the monomer phosphor molecular was recognized and complexed with cucurbituril, such high-performance phosphorescent emission would not be produced. While after the phosphorescent group was copolymerized with acrylamide, the presence of carbonyl groups was able to enhance the intersystem crossing. At the same time, the abundant hydrogen bond network and the rigid matrix could inhibit and block the phosphorescent group vibration and the external quenchers, which induced this copolymer (PH) shown in Scheme 4 to emit phosphorescence with a long lifetime, and then, with the decrease of the monomer ratio, the phosphorescence lifetime of the copolymer could be further improved to a certain extent. Amazingly, when the polymer was combined with cucurbituril, the phosphorescence lifetime of PH-0.1/CB[7] could reach the maximum value (2.81 s). It is the participation of cucurbituril that can further inhibit nonradiation relaxation and reduce aggregation-caused quenching (ACQ). Undoubtedly, this synergistic effect involving polymerization and host–guest inclusion has profound significance for the construction of phosphorescent materials with excellent properties.

At present, as mentioned above, the polymer matrices commonly used, including PVA, PMMA, PLA and so forth, are all insulators. As a consequence, such polymer-based phosphorescent materials are difficult to be endowed with charge transport capabilities and applications for light-emitting diodes, which greatly limits the development of the field of electrophosphorescent devices. In response to this problem, Wang et al. are committed to constructing electroactive RTP polymer to make it suitable for the fabrication of high-efficiency polymer light-emitting diodes. By adopting the geometric configuration of D-O-A, they designed the polymer P-(DMPAc-O-TPTrz) (Scheme 4) [66]. Compared to the oxygen atom-free D-A system, the introduction of oxygen atoms has been shown to contribute to reducing hole-electron orbital overlap so that CT fluorescence could be suppressed, and enhanced spin-orbit coupling to promote efficient phosphorescence emission. The result was that the polymer could emit electrophosphorescence after light excitation, and its external quantum yield has reached an astonishing value of 9.7%, which was a record achievement.

SUMMARY AND OUTLOOK

Generally speaking, covalent bonds are stronger than other weak noncovalent interactions. Hence, compared with doped polymer systems, covalent polymer systems can more effectively suppress molecular vibration, featuring better luminescence performance. In addition, the strategy of covalent cross-linking can further increase the rigidity of the matrix and inhibit the nonradiative transition of triplet excitons, and the emission efficiency will be greatly improved accordingly. Moreover, the problem of phase separation can also be successfully avoided. However, commonly used polymerization methods such as free radical copolymerization, ring-opening polymerization, covalent cross-linking, often require stringent environment, noble metal catalysis, and other high-cost reaction conditions, which is unfavorable to the development of this system. In fact, many efforts have been made to deal with the time-consuming and low efficiency of covalent polymerization. For example, a feasible one-step B-O click chemistry was put forward to construct high-efficiency RTP polymers, hopefully realizing large-scale production of luminescent materials [67]. On the contrary, the doped polymer system is exactly simple in operation, which is regarded as a more versatile and highly successful method. However, in terms of the choice of polymer hosts, their compatibility with the phosphor guests needs to be considered to avoid phase separation.

In summary, polymers have been widely applied in the development of various pure organic RTP materials due to their superior properties of simple synthesis, low cost, and good biocompatibility. Scientists are also constantly exploring polymer matrices with better performance. In addition to traditional aromatic conjugated luminescent materials, the inherent luminescence phenomena of some nonconjugated polymers have also been discovered. The potential phosphorescent groups are mixed with the polymer matrix in different forms, and finally, single-component or multicomponent polymers are obtained. They often appear in different states, such as amorphous powders, films, self-healing gels, and even nanocrystals to meet the requirements of various application fields. In addition, the methods of constructing a rigid environment to suppress the nonradiative transition of triplet excitons are gradually expanding, from the commonly used hydrogen bond cross-linking, host–guest interaction, halogen bond bonding to fix the emitters to the later development of ionic bond interlocking, dynamic covalent bonds, boron-based coordination bonds, etc. For the sake of putting into market applications with better luminescence performance, stimulus-response, multi-stimulus response, and multi-color luminescent materials have also been designed. In response to the adverse effects of the quenching effect of water, scientists have also developed several materials that emit RTP stably and efficiently in the water phase. All in all, pure organic RTP polymer systems are booming.

It can be inferred that the development direction of RTP polymer systems lies in the following aspects: (1) In case of in-depth research on the internal mechanism of polymer luminescence behavior, most of the current reports are limited to explaining the benefits of rigid environment, but for the exact structure of polymers as well as the inherent and authentic energy transfer process also requires the joint efforts of polymer physical chemists and optical researchers; (2) more attempts to expand the commonly used polymer matrix; (3) the pursuit of more excellent performance and overcoming the current thorny problems to obtain RTP materials with good water dispersibility, near-infrared light emission, adjustable, and long lifetime; and (4) expansion of application areas and making progress in developing resources that are easy to process, meet market demand, and can be mass-produced. It is believed that pure organic RTP polymers will be developed by leaps and bounds in the future.

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Xiang Ma obtained his BS from Tianjin University in 2003 and PhD from ECUST in 2008 under the supervision of Prof. He Tian. Prof. Ma has been a Professor of Chemistry and Fine Chemical Engineering at ECUST since 2016. His research interest mainly focuses on organic electronic and optical functional dyes, supramolecular machines and switches, and polymer materials. Prof Ma is a Fellow of RSC and now serves as Executive Editor of Dyes Pigm. and on the Colour Index Pigment and Solvent Dyes Technical Board of The Society of Dyers and Colourist (SDC).