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# Recent advances in dopant–matrix afterglow systems: high-performance organic afterglow materials and the critical role of organic matrices in materials fabrication

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Organic afterglow materials have garnered significant attention due to their long-lived excited states, demonstrating promising applications across diverse fields. Over the past few decades, these materials have experienced rapid development, particularly dopant–matrix systems. This review focuses on the progress made in dopant–matrix organic afterglow materials over the past three years, emphasizing two key aspects: high-performance organic afterglow materials and the critical role of organic matrices in materials fabrication. In the first section, we summarize strategies for enhancing afterglow performance through molecular design, focusing on representative luminescent systems such as benzophenone derivatives, polycyclic aromatic hydrocarbons, and difluoroboron  $\beta$ -diketonate compounds. The second section explores the pivotal functions of organic matrices, including protecting triplet excited states, facilitating intersystem crossing, sensitizing triplet states, and promoting charge separation, which collectively contribute to novel functionalities of afterglow materials. Beyond the molecular design of luminophores, the selection of organic matrices is equally crucial for achieving high-performance afterglow materials and expanding their functionality. This review provides a comprehensive compilation of chemical structures for various organic matrices, serving as a valuable reference for researchers. Given the intricate photophysical processes in organic afterglow systems, we also present experimental methods that support or refute specific mechanisms, providing critical insights for future studies. Overall, dopant–matrix organic afterglow materials represent a highly promising class of luminescent materials. We anticipate their large-scale adoption and high-value applications in real-world scenarios in the near future.

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## 1. Introduction

Luminescent materials play a vital role in applications such as displays, lighting, and analytical detection. Among these, room-temperature phosphorescent (RTP) materials and organic afterglow materials, with emission lifetimes exceeding milliseconds, have demonstrated exceptional performance in oxygen sensing, bioimaging, and anti-counterfeiting, witnessing rapid advancements over the past few decades.<sup>1–18</sup> Based on the number of components required for materials fabrication, organic RTP materials can be categorized into single-component, two-component,

and multi-component systems. Two-component and multi-component materials are typically prepared using doping methods, with dopant concentrations often below a few weight percent and organic matrices comprising over 90% of the total composition. Consequently, these systems are commonly referred to as dopant–matrix afterglow materials. Five years ago, single-component afterglow materials dominated the reported examples.<sup>19–23</sup> However, in the past five years, research into dopant–matrix afterglow materials has expanded significantly, with many research groups shifting their focus from single-component systems to dopant–matrix systems.<sup>24–26</sup> This transition has greatly enriched the diversity of dopant–matrix materials and led to the development of various functionalities, as documented in recent literature. Several comprehensive reviews have summarized the progress in dopant–matrix afterglow materials.<sup>24–26</sup> Additionally, reviews on polymer-based RTP materials,<sup>27–29</sup> supramolecular assembly systems,<sup>4,30–32</sup> stimuli-responsive RTP materials,<sup>33–35</sup> aqueous-phase RTP materials,<sup>36–38</sup> multicolor RTP systems,<sup>39,40</sup>

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functional afterglow materials,<sup>41–44</sup> and biomass-based RTP materials<sup>45</sup> have also briefly addressed advances in dopant–matrix afterglow systems. However, the examples covered in these reviews predominantly date back two to three years or earlier. Given the substantial progress in dopant–matrix afterglow materials in the past few years, we believe it is timely and essential to systematically organize and summarize these recent findings, thereby contributing to the further advancement of this field.

The dopant–matrix system presents several advantages in materials preparation, mechanistic studies, and functional applications (Fig. 1). Its components can be flexibly tailored by selecting or synthesizing various dopants and organic matrices, allowing researchers to obtain diverse samples with minimal synthetic effort, saving both time and costs. Moreover, the system facilitates systematic mechanistic investigations by enabling the modification of specific variables while keeping others constant, providing critical insights into the rational design of high-performance afterglow materials. Additionally, if dopants or organic matrices possess desirable properties—such as high-performance polymers or analytical detection capabilities—the resulting dopant–matrix materials can inherit these functionalities, enhancing their application potential. Furthermore, interactions between dopants and matrices that respond to external physical, chemical, or biological stimuli can result in tunable photophysical properties, enabling the development of intelligent sensing RTP materials with dynamic and responsive capabilities. These features collectively underscore the versatility and value of dopant–matrix systems in advancing room-temperature phosphorescent materials.

Owing to these advantages, the dopant–matrix system has, in recent years, yielded materials with extended luminescence lifetimes, enhanced efficiencies, or unique photophysical properties. Significant progress has been made in the rational design of luminophores and the selection of organic matrices,

with some dopant–matrix systems already successfully developed into functional afterglow materials. This review aims to summarize the advancements in dopant–matrix afterglow systems over the past three years. Given the existence of excellent recent reviews on supramolecular afterglow systems,<sup>4,30–32</sup> this work excludes discussions on supramolecular host–guest systems. This review focuses on two major aspects. The first is high-performance organic afterglow materials, introducing several representative luminophore systems, including benzophenone derivatives, coronene, triphenylene, pyrene, and difluoroboron  $\beta$ -diketonates. By emphasizing these systems, we aim to provide concrete examples of systematic strategies for controlling the excited-state properties of organic luminophores, with the hope of distilling universally applicable methodologies extendable to other luminescent systems. We also discuss emerging materials, such as TADF-type afterglow materials, organic long persistent luminescence (OLPL) systems, and narrowband afterglow emitters. The second aspect is the critical role of organic matrices in materials fabrication. Organic matrices typically provide crystalline or glassy rigid environments that suppress molecular motion of triplet excited states, thereby reducing nonradiative decay ( $k_{nr}$ ). Crystalline and some polar polymer matrices can inhibit oxygen diffusion, preventing quenching of triplet states by oxygen ( $k_q$ ). Additionally, the triplet energy levels ( $T_1$ ) of organic matrices can act as intermediaries to facilitate intersystem crossing (ISC) in luminophores. Certain matrices can reduce the singlet–triplet energy gap and enhance ISC or reverse ISC (RISC) *via* dipole–dipole interactions with singlet excited states of luminophores. Matrices that efficiently form triplet excited states upon excitation can sensitize dopants through energy transfer. In organic long persistent luminescence systems, the HOMO–LUMO alignment between matrices and dopants enables photo-induced intermolecular charge transfer and separation, with subsequent slow charge recombination leading to afterglow emissions lasting minutes to hours. In dopant–matrix OLPL systems based on two-photon ionization, organic luminophores absorb two photons to ionize, forming radical cations, while organic matrices capture free electrons as electron traps. Slow charge recombination in these systems generates OLPL emissions. This review integrates these recent findings to provide insights into the rational design and applications of dopant–matrix afterglow systems, fostering future advancements in this rapidly evolving field.

In dopant–matrix afterglow systems, the design of luminophores is essential for achieving high-performance materials, while the choice of organic matrices significantly influences afterglow properties, making their selection equally critical. This review not only highlights advancements in this field but also incorporates guidelines for selecting suitable organic matrices in relevant examples. Additionally, we provide a list of commonly used organic matrices, complete with their chemical structures and CAS numbers, to facilitate further research by potential investigators. Given the complexity of photophysical processes in organic afterglow systems, elucidating afterglow mechanisms constitutes a crucial aspect of research. To this

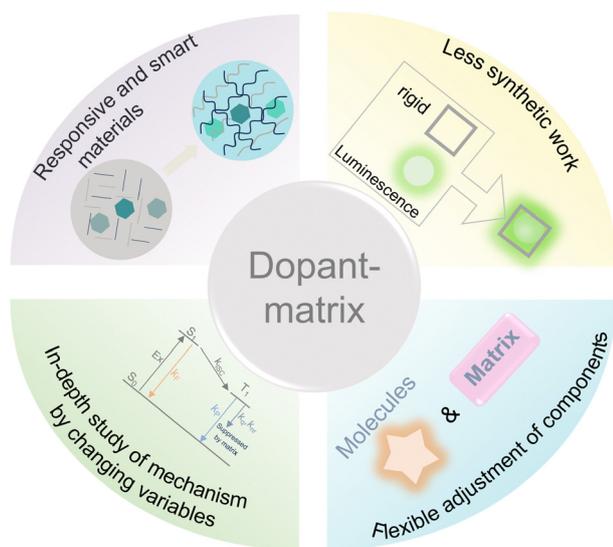


Fig. 1 Advantages of dopant–matrix design strategies for afterglow materials fabrication.



end, this review includes experimental approaches designed to exclude certain mechanisms and validate others, offering a comprehensive framework for understanding the underlying principles of various dopant–matrix afterglow materials.

As the dopant–matrix organic afterglow systems are undergoing rapid development, this review cannot comprehensively cover all advancements in this field over the past three years. Instead, we focus on two key aspects: high-performance afterglow materials and the critical role of organic matrices. The specific content is outlined as follows.

## 2. High-performance organic afterglow materials

### 2.1 Benzophenone-containing luminescent dopants

Benzophenone is a classic organic phosphorescent molecule, with its  $S_1$  state exhibiting  $n-\pi^*$  character, resulting in a relatively small fluorescence emission rate constant. The  $T_2$  excited state of benzophenone is very close in energy to the  $S_1$  state and exhibits  $\pi-\pi^*$  character.<sup>2,20</sup> According to the energy gap rule and the El-Sayed rule, the intersystem crossing (ISC) rate constant from  $S_1$  to  $T_2$  is significantly enhanced, resulting in an ISC efficiency approaching 100%. The resulting  $T_2$  excited state rapidly undergoes internal conversion to the  $T_1$  state, which has  $n-\pi^*$  character, and the phosphorescence emission rate constant in the  $T_1$  state is on the order of  $10^3 \text{ s}^{-1}$ .<sup>2</sup> In organic systems, this large phosphorescence rate constant aids in harvesting  $T_1$  excited state energy; however, it also implies that even when nonradiative decay and oxygen quenching are sufficiently suppressed, the phosphorescence lifetime is limited to the millisecond range. This presents a challenge for the development of long persistent afterglow materials.

To enhance the phosphorescence lifetime of the benzophenone system, one feasible approach is to introduce substituents, such as aromatic groups with significant  $\pi-\pi^*$  transition properties, into the benzophenone framework. This modification facilitates the mixing of  $^3\pi-\pi^*$  and  $^3n-\pi^*$  states, which weakens the  $n-\pi^*$  character of the  $T_1$  excited state and reduces the phosphorescence emission rate constant as reported by Tang and Shuai.<sup>46,47</sup> In a recent study, researchers introduced a series of common aromatic substituents at the *para* position of benzophenone.<sup>48</sup> The resulting luminescent molecules showed no room-temperature afterglow in their single-component powder or crystal state. However, when doped into a phenyl benzoate matrix, the dopant–matrix material exhibited phosphorescence lifetimes of several hundred milliseconds. Phenyl benzoate effectively protected the  $T_1$  excited state under ambient conditions. Notably, the naphthalene-substituted benzophenone molecule in phenyl benzoate exhibited a phosphorescence lifetime approaching one second (Fig. 2). After deuteration, where C–D vibrations are significantly weaker than C–H vibrations, the  $k_{nr}$  of the  $T_1$  excited state is further suppressed, resulting in a room-temperature phosphorescence lifetime of 1.8 seconds.<sup>48</sup> In TD-DFT calculations, the researchers found that the  $T_1$  excited state of naphthalene exhibits typical localized excitation characteristics and a lower  $T_1$  energy level. Therefore, the naphthalene group significantly contributes to the formation of the  $T_1$  excited state in the naphthalene-substituted benzophenone molecule, imparting typical localized excitation features. This results in a reduction of the phosphorescence emission rate constant by about three orders of magnitude, which explains the second-level phosphorescence lifetime of the system.

In further studies, the phenyl-naphthalene group was covalently attached to different substitution positions on the benzophenone group.<sup>49</sup> Among the isomers obtained, the *ortho*-substituted

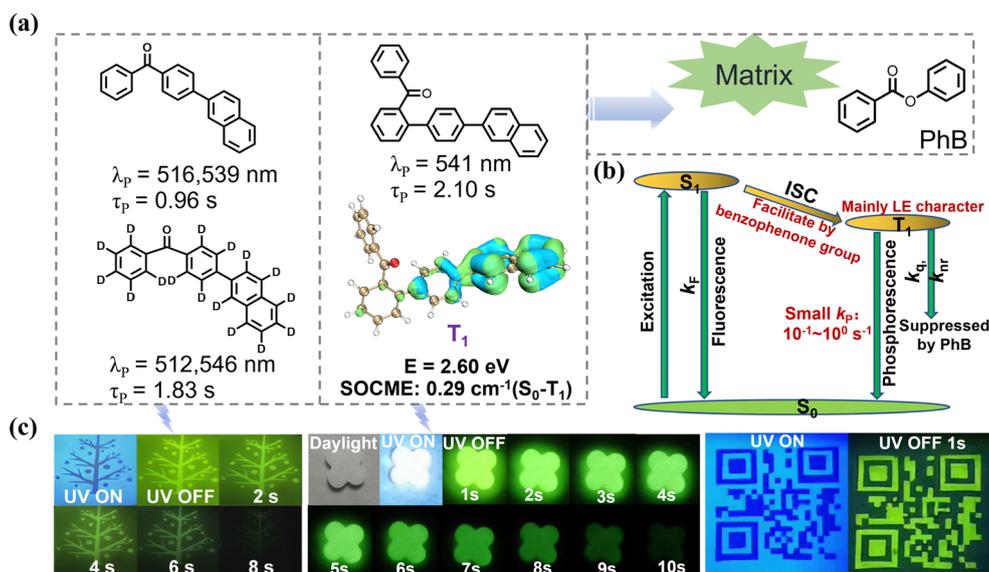


Fig. 2 (a) Chemical structures of benzophenone derivatives (dopants) and phenyl benzoate (PhB matrix). (b) Proposed room-temperature phosphorescence mechanism of doping systems of benzophenone derivatives. (c) Photographs of plant-shaped objects made by doping benzophenone derivatives into afterglow materials and a QR code representing "RTP" in a WeChat scanner.



molecule, when doped into phenyl benzoate, exhibited a remarkable room-temperature phosphorescence lifetime of 2 seconds (Fig. 2). TD-DFT calculations revealed that the  $T_1$  excited state of the *ortho*-substituted molecule is predominantly composed of the phenyl-naphthalene functional group. Additionally, the *ortho*-substitution-induced steric hindrance significantly increased the dihedral angle between the benzophenone backbone and the phenyl-naphthalene substituent. As a result, the  $n-\pi^*$  transition character of the  $T_1$  excited state in the *ortho*-substituted molecule was further weakened, leading to a reduction in the phosphorescence emission rate constant and thereby extending the phosphorescence lifetime of the system. In a very recent study conducted by Tang and coworkers,<sup>46b</sup> near-infrared phosphorescent materials have been obtained by balancing the  $n-\pi^*$  and  $\pi-\pi^*$  transitions in benzophenone derivative systems; the benzophenone matrix was used to enhance the RTP performance of the near-infrared materials.

In the benzophenone and its derivative systems, the presence of  $n-\pi^*$  transitions generally results in a relatively high spin-orbit coupling matrix element (SOCME), leading to efficient intersystem crossing. In some cases, the steady-state and delayed fluorescence spectra of dopant-matrix materials overlap, both exhibiting phosphorescence emission bands. To confirm that the long afterglow originates from the  $T_1$  excited state of the luminescent dopant, it is common to measure the delayed spectra of the dopant-matrix material at 77 K as well as the delayed spectra of the dopant at 77 K. If the two spectra show similar peak shapes and peak positions to the room-temperature delayed spectrum of the dopant-matrix material, it can be concluded that the room-temperature long afterglow originates from the  $T_1$  excited state of the luminescent dopant.

## 2.2 Polycyclic aromatic hydrocarbon luminescent dopants

Among polycyclic aromatic hydrocarbons, coronene is a particularly unique luminescent molecule due to its  $D_{6h}$  symmetry.

The symmetry of its  $S_1$  excited state is forbidden for fluorescence, resulting in a fluorescence emission rate constant of  $10^6-10^7 \text{ s}^{-1}$ .<sup>50-52</sup> In rigid environments, its fluorescence lifetime can extend to several hundred nanoseconds. The  $T_1-S_0$  transition of coronene is both spin-forbidden and symmetry-forbidden, with a phosphorescence emission rate constant in the  $10^{-2} \text{ s}^{-1}$  range, meaning that under conditions where non-radiative decay and oxygen quenching are effectively suppressed, the phosphorescence lifetime can reach tens of seconds.<sup>50-52</sup> PMMA (polymethyl methacrylate) can serve as the matrix for coronene, as its rigid glassy state helps suppress non-radiative decay of the  $T_1$  state. Under anoxic conditions, the quenching rate constant for the  $T_1$  state can also be reduced, allowing for phosphorescence lifetimes exceeding ten seconds at room temperature. Coronene and its derivatives have been doped into materials such as  $\beta$ -estradiol, 4-methoxybenzophenone, polyvinyl alcohol, polycarbonate, polyvinylpyridine, ABS (acrylonitrile-butadiene-styrene), and even SBS (styrene-butadiene-styrene), resulting in long afterglow emissions.<sup>53</sup> These coronene-based long-lived systems are used as afterglow donors, and when suitable fluorescent acceptors are incorporated, the system can achieve long-wavelength afterglow emission through excited state energy transfer. Coronene and its derivatives typically exhibit yellow-green phosphorescence, and to ensure efficient energy transfer, the fluorescent acceptor is often selected for good absorption in the yellow-green region. The efficiency of the energy transfer can be estimated by the shortening of the afterglow donor's phosphorescence lifetime.

Recently, researchers have synthesized several ester-substituted coronene derivatives through a multi-step synthesis route (Fig. 3).<sup>54</sup> These coronene derivatives exhibit enhanced solubility or dispersibility in organic solvents and polymer matrices. Additionally, the introduction of ester groups can enhance the intersystem crossing (ISC) process, altering the symmetry of the coronene system.

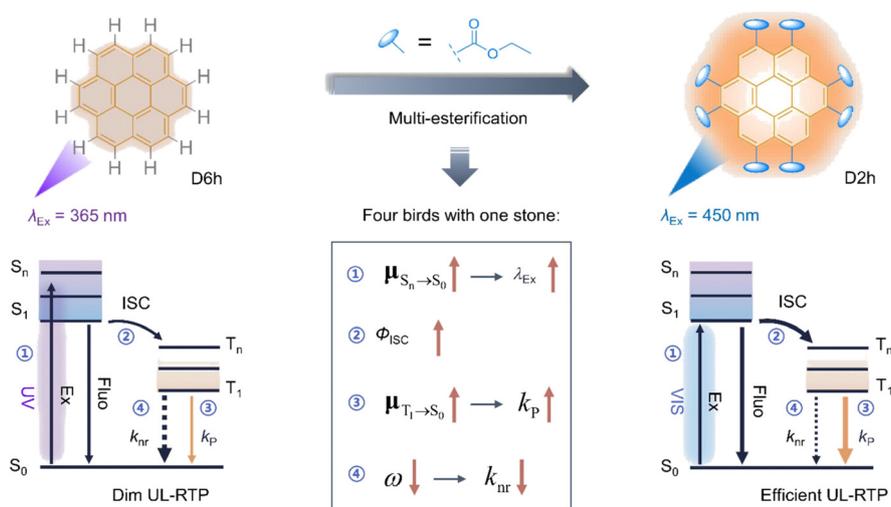


Fig. 3 A method is proposed to achieve efficient ultra-long room-temperature phosphorescence (RTP) under visible light through a multi-esterification approach. This strategy involves molecular esterification, resulting in several improvements, including a red-shifted excitation wavelength ( $\lambda_{\text{Ex}}$ ), enhanced intersystem crossing efficiency ( $\phi_{\text{ISC}}$ ), increased phosphorescence decay rate ( $k_{\text{P}}$ ), and reduced triplet nonradiative decay ( $k_{\text{nr}}$ ). In this context,  $\mu$  represents the transition dipole moment and  $\omega$  refers to the vibrational frequency of the phosphorescence site.



This change leads to a red shift in absorption and an increase in luminescence quantum yield. The esterification process does not affect the rigidity or large planar aromatic structure of coronene, allowing the derivatives to retain their second-level organic room-temperature phosphorescence properties. This multi-esterification strategy has successfully led to high-performance, visible-light-excited, ultra-long organic room-temperature phosphorescent materials in pure organic amorphous materials.

Some applications of organic afterglow materials are in aqueous or physiological systems, making the preparation of water-dispersible organic afterglow materials an important research topic. The typical approach is to first select a system with excellent afterglow properties in the solid state and then process the solid afterglow material into a water-dispersible afterglow system using mechanical grinding, strong ultrasound, or nanoprecipitation methods.<sup>36–38</sup> However, after these treatments, the rigid environment that originally protected the  $T_1$  excited state is often disrupted, leading to a significant reduction in room-temperature afterglow lifetime and efficiency. Leveraging the flexibility of the dopant–matrix system, researchers have proposed a method to prepare long-lifetime afterglow materials through emulsion polymerization.<sup>55</sup> In this process, coronene or deuterated coronene is dissolved in a monomer, and after deoxygenation, emulsion polymerization is carried out. Once the monomer polymerizes into a polymer, the coronene molecules dissolved in it become encapsulated in the polymer latex particles. Using methyl methacrylate (MMA) for

emulsion polymerization, the resulting PMMA latex particles provide a glassy environment that effectively suppresses non-radiative decay of the  $T_1$  state at room temperature. Moreover, as the emulsion polymerization occurs in an oxygen-free environment, the resulting water-dispersible solution exhibits a phosphorescence emission with a lifetime of up to 10 seconds at room temperature. This method avoids the disruption of the rigid environment commonly seen in traditional methods, effectively protecting the  $T_1$  excited state. Additionally, the latex particle size is controllable, ensuring long-term dispersion in water without precipitation.

Similar to the coronene system, the  $T_1$ – $S_0$  transition in the triphenylene system is spin-forbidden and symmetry-forbidden. Therefore, when the triphenylene system is well protected in the  $T_1$  state, it can exhibit second-level phosphorescence lifetimes. When triphenylene boronic acid (triphenylene-2-ylboronic acid) is doped into a polyvinyl alcohol (PVA) matrix (Fig. 4a), the resulting dopant–matrix sample displays a room-temperature phosphorescence lifetime of 3.29 seconds.<sup>56</sup> PVA is a transparent polymer that provides a rigid environment for the luminescent molecules, and it has a strong oxygen barrier capability. In a further study, Nile red and Cyanine 7 were doped into the triphenylene boronic acid–PVA system, achieving a two-step excitation energy transfer process that resulted in near-infrared (NIR) room-temperature afterglow materials, with an emission at 810 nm and a lifetime of 0.2 seconds.<sup>56</sup> Additionally, when triphenylene boronic acid was doped into a polyvinyl butyral (PVB) resin matrix (Fig. 4b), the researchers observed a

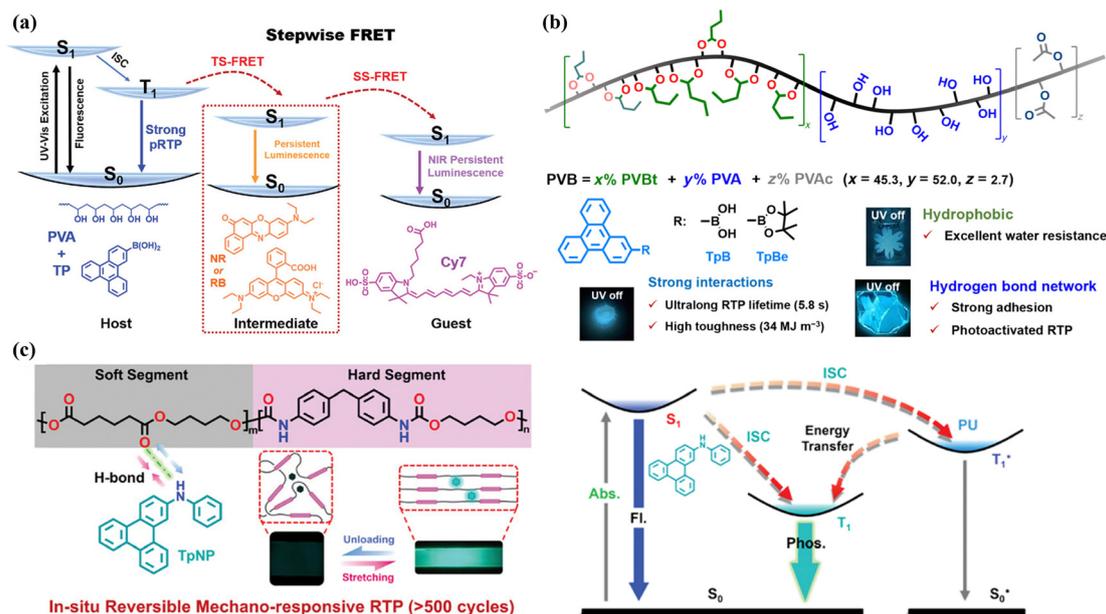


Fig. 4 (a) The system achieves near-infrared (NIR) persistent luminescence through stepwise energy transfer, using a robust RTP polymer matrix as the host, with TP@PVA as the intermediate guest and Cy7 as the final guest, incorporating various intermediates such as RB and NR. (b) PVB-based afterglow systems, with TP derivatives doped into the PVB matrix, display exceptional performance, offering ultralong RTP lifetimes, high mechanical toughness, strong adhesion, photoactivated RTP properties, and excellent water resistance, as shown by the schematic diagram of the PVB structure and phosphor chemical structures. (c) The reversible mechano-responsive TpNP@PU system, incorporating unique structural and functional properties, exhibits dynamic changes in phosphorescence as the PU chains stretch and unload. This behavior is driven by reversible hydrogen bonding interactions between TpNP and PU, supported by a proposed mechanism involving intersystem crossing transitions between the emitter and PU matrix.



room-temperature phosphorescence lifetime of 5.82 seconds, and this system could function as a binder for anti-counterfeiting labels.<sup>57</sup> Interestingly, when triphenylene-based aromatic secondary amines were doped into the polyurethane (PU) elastomer (Fig. 4c), the resulting dopant–matrix material exhibited mechano-responsive properties, with its phosphorescence brightness, quantum yield, and phosphorescence lifetime correlating well with the applied stress.<sup>58</sup>

Pyrene is also an excellent building block for constructing room-temperature phosphorescent materials. Dopant–matrix systems containing pyrene are characterized by a rich variety of afterglow colors, which can be tuned by controlling molecular aggregation and selecting excitation wavelengths, allowing for different afterglow colors, including red and even near-infrared phosphorescence.<sup>59–65</sup> Fig. 5 lists the chemical structures of these pyrene-containing luminescent molecules. Pyrene derivatives with polar functional groups or hydrogen-bonding donor/acceptor properties disperse well in polar matrices like polyvinyl alcohol (PVA), and the degree of molecular aggregation can be controlled by the doping concentration.<sup>59</sup> Hydrophobic pyrene derivatives can be dispersed in matrices like benzophenone (Fig. 5d),<sup>60</sup> and the resulting dopant–matrix afterglow materials can be ultrasonically processed using surfactants to achieve dispersion in water. Based on this approach, researchers have successfully developed near-infrared room-temperature phosphorescent materials dispersed in water, enabling deep-tissue biological imaging with minimal background interference.

### 2.3 Difluoroboron $\beta$ -diketonate luminescent dopants

Difluoroboron  $\beta$ -diketonate (BF<sub>2</sub>bdk) molecules are an interesting class of luminescent compounds, typically characterized by excited-state properties involving intramolecular charge transfer transitions.<sup>19,66–71</sup> These molecules often exhibit high molar absorption coefficients and high photoluminescence quantum yields. Fraser *et al.* were the first to report the room-temperature phosphorescence properties of difluoroboron  $\beta$ -diketonate–polymer systems.<sup>19</sup> In their work, the difluoroboron  $\beta$ -diketonate group was covalently bonded to the polymer, creating a single-component system that required multiple steps for materials synthesis. In recent years, there has been increasing research on small-molecule difluoroboron  $\beta$ -diketonate–matrix binary systems.<sup>66–71</sup> This progress can be attributed to the flexibility of the dopant–matrix approach, as well as the cascade reaction developed by Zhang *et al.* for the one-step synthesis of difluoroboron  $\beta$ -diketonate small molecules (Fig. 6a).<sup>67–69</sup> Essentially, a typical chemist can synthesize a difluoroboron  $\beta$ -diketonate molecule in one day using the cascade reaction and subsequently incorporate it into various commercial small-molecule matrices. This enables the preparation of multiple dopant–matrix materials and the observation of their afterglow properties within a day. This approach has significantly advanced the preparation of high-performance difluoroboron  $\beta$ -diketonate–matrix materials and the study of their photophysical mechanisms.

After synthesizing approximately 300 difluoroboron  $\beta$ -diketonate molecules and screening hundreds of organic matrices,

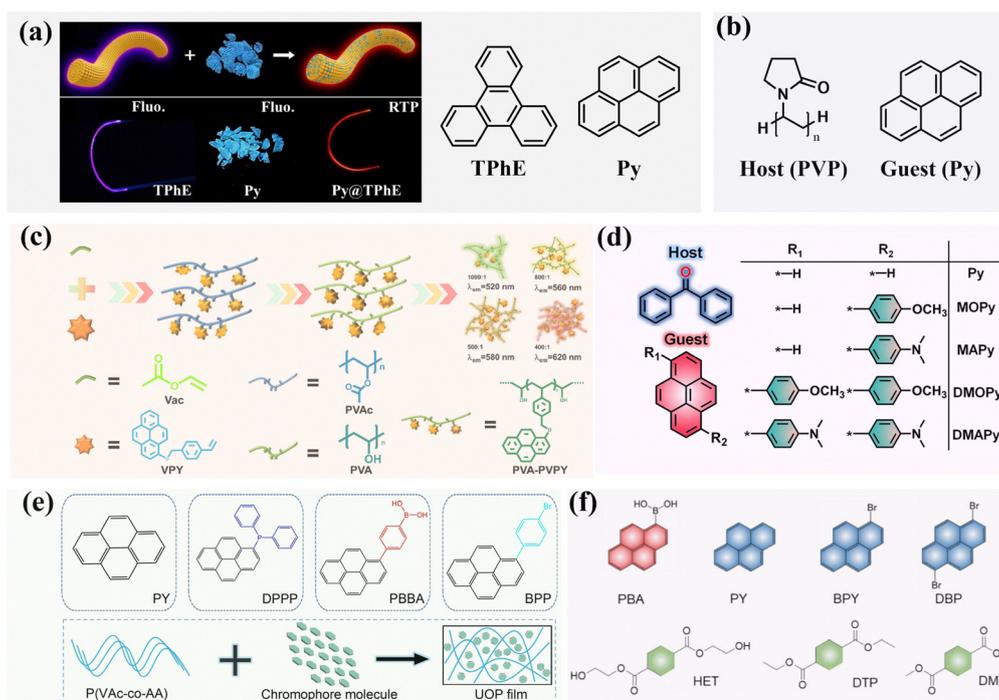


Fig. 5 (a) Photographs of Py and TPhE under 365 nm excitation and Py-coated crystals (Py@TPhE) from 1% Py/TPhE powder after removal of the 365 nm excitation. (b) Molecular structures of the PVP films and Py molecules. (c) Molecular structures of the guest and host molecules. (d) Design strategy of color-tunable polymeric RTP materials containing only a single phosphor. (e) Molecular structures of guests and schematic diagram for the preparation of RTP films. (f) Chemical structures of the emitter and matrix molecules used.



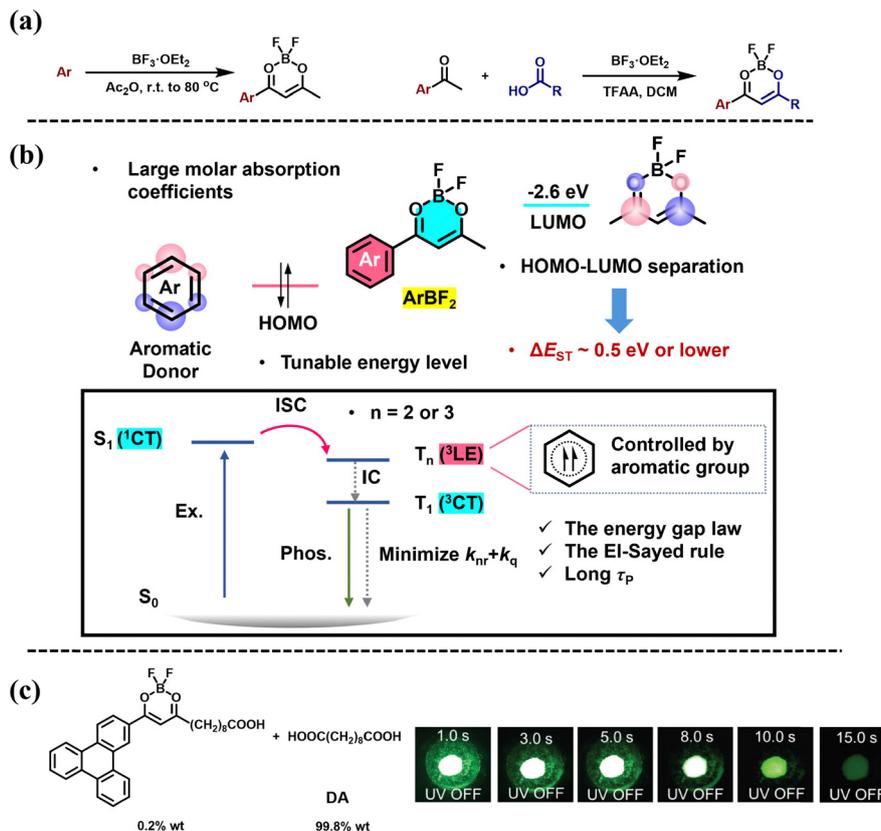


Fig. 6 (a) One-pot cascade synthesis of  $\text{BF}_2\text{bdk}$  compounds. (b) Basic photophysical properties of  $\text{BF}_2\text{bdk}$  systems and developing high-performance afterglow materials via manipulation of higher triplet excited states. (c)  $\text{BF}_2\text{bdk}$ -DA-0.2% sample composition (left) and photographs of  $\text{BF}_2\text{bdk}$ -DA-0.2% powders after turning off the UV lamp (right).

researchers have obtained several high-performance organic room-temperature afterglow materials. In some high-performance afterglow systems, the structure of the luminescent molecule is fixed, while the properties of the organic matrix are adjusted. It was found that the organic matrix not only protects the  $T_1$  excited state of difluoroboron  $\beta$ -diketonate but also promotes the formation of the  $T_1$  excited state through dipole effects (as discussed later).<sup>70</sup> Through the analysis and summarization of data on the afterglow systems of difluoroboron  $\beta$ -diketonate molecules, researchers have revealed their role in binary afterglow systems (Fig. 6b).<sup>69,71</sup> First, difluoroboron  $\beta$ -diketonate molecules have large molar absorption coefficients, which give them strong light absorption capabilities. Secondly, these molecules feature intramolecular charge transfer transitions, with a HOMO–LUMO separation and a  $\Delta E_{\text{ST}}$  of about 0.5 eV or less, which facilitates intersystem crossing.<sup>71</sup> The LUMO of difluoroboron  $\beta$ -diketonate molecules is primarily determined by the dioxaborine functional group, with an energy level of around  $-2.6$  eV, while the HOMO is mainly determined by the aromatic group. Common aromatic groups such as anisole, biphenyl, fluorenyl, and naphthyl have HOMO levels ranging from  $-6.4$  eV to  $-5.8$  eV. As a result, the  $S_1$  energy level of the difluoroboron  $\beta$ -diketonate molecule is around 3.0 eV, which coincides with the  ${}^3\text{LE}$  (LE represents localized excitation) energy levels of the aromatic groups. The  $T_n$  energy level formed by the aromatic group's  ${}^3\text{LE}$  in the difluoroboron

$\beta$ -diketonate molecule is close to  $S_1$ , with a significant difference in the type of excited state.<sup>69</sup> According to the energy gap rule and the El-Sayed rule, the intersystem crossing rate from  $S_1$  to  $T_n$  is significantly enhanced, promoting the formation of the  $T_1$  state. Based on this understanding, researchers can select the appropriate aromatic group based on its HOMO and  ${}^3\text{LE}$  energy levels to connect with the difluoroboron  $\beta$ -diketonate functional group. In the triphenylene-containing  $\text{BF}_2\text{bdk}$  molecule system, they achieved the brightest room-temperature  $\text{BF}_2\text{bdk}$  afterglow material to date, which continues to emit a white afterglow for up to 5 seconds after the excitation source is turned off (Fig. 6c).<sup>69</sup>

#### 2.4 TADF-type organic afterglow materials

In the dopant–matrix systems of difluoroboron  $\beta$ -diketonates and small-molecule matrices, researchers have designed difluoroboron  $\beta$ -diketonate molecules and utilized the organic matrix to modulate the excited-state properties of these molecules. This has led to the development of a new class of thermally activated delayed fluorescence (TADF) materials with room-temperature afterglow lifetimes of up to 300 milliseconds and afterglow quantum yields as high as 60–70% (Fig. 7).<sup>72</sup> It is important to note that neither of the two components exhibits room-temperature afterglow properties when used individually. By deuterating the luminescent molecules, molecular vibrations are reduced, which suppresses non-radiative decay of



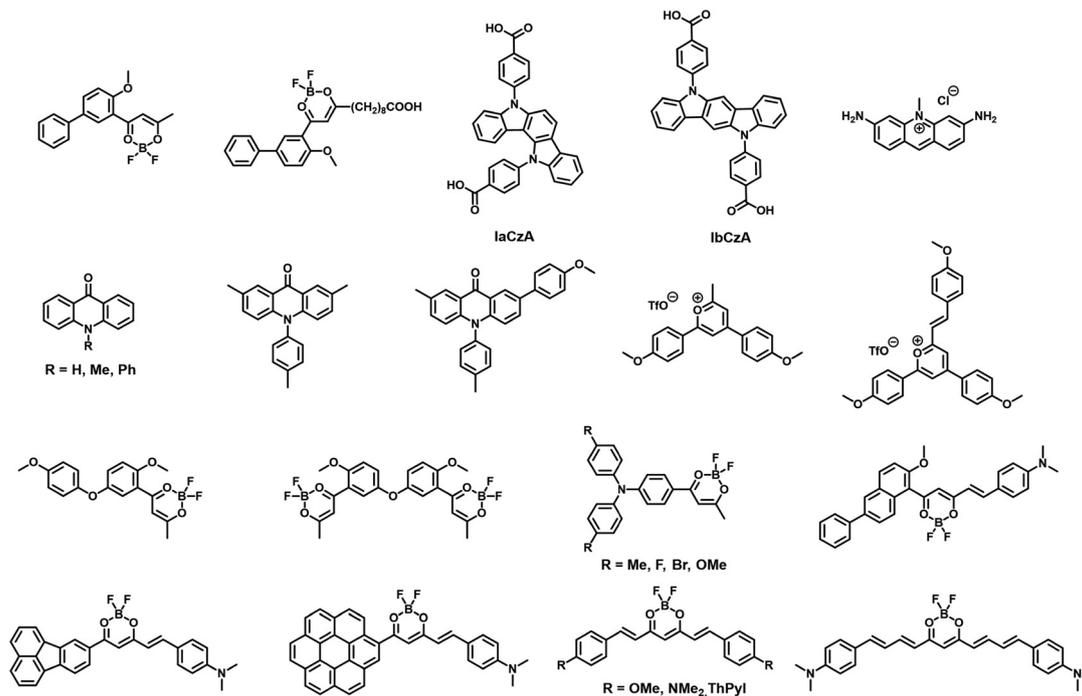


Fig. 7 Molecular structure of selected TADF-type afterglow dopants and molecules with TADF/RTP dual emission behaviors.

the excited state. In deuterated TADF-type afterglow material systems, the afterglow efficiency is further enhanced.<sup>73</sup> TADF-type organic afterglow systems are characterized by moderate reverse intersystem crossing rate constants ( $k_{\text{RISC}}$ ,  $10^0$ – $10^2$   $\text{s}^{-1}$ ), which significantly improve the utilization of triplet excited states while maintaining the room-temperature afterglow properties of organic materials. This provides a new pathway for constructing efficient organic room-temperature afterglow materials. The moderate RISC rate constant is a distinguishing feature of these systems, in contrast to the much higher RISC rate constants ( $10^3$ – $10^6$   $\text{s}^{-1}$ ) typically used in OLED-based TADF molecules.<sup>74</sup> In this system with a moderate RISC rate constant, other processes that deplete the triplet excited state must be suppressed. Crystalline organic matrices are ideal for protecting the triplet excited state, resulting in room-temperature long afterglow materials. In TADF-type afterglow systems, the reverse intersystem crossing rate is much larger than the phosphorescence rate at room temperature, showing TADF signals in the delayed emission spectra without significant RTP signals. If  $k_{\text{RISC}}$  and  $k_{\text{p}}$  are similar at room temperature, both TADF and RTP signals are prominent in the delayed spectra, indicating a TADF/RTP dual-emission afterglow material.<sup>75</sup>

In the literature, the majority of TADF molecules exhibit emission lifetimes ranging from microseconds to milliseconds, and even the emission behavior with lifetimes in the tens of milliseconds has often been used to rule out the TADF mechanism.<sup>76</sup> To address this discrepancy, researchers have further strengthened the characterization methods for TADF-type afterglow materials. Specifically, several approaches<sup>77</sup> have been employed to investigate the triplet-state behavior of TADF materials: temperature-dependent delay emission experiments,

which study the behavior of the triplet excited state, show that as the temperature increases, reverse intersystem crossing and delayed fluorescence are enhanced; TD-DFT theoretical calculations, which are used to study the singlet and triplet excited state energy levels, the nature of the excited states, and the intersystem crossing channels, providing insight into the mechanisms involved; oxygen-dependence experiments, which help explore the properties of the triplet excited state, as the presence of oxygen can quench triplet states and influence afterglow behavior; the linear dependence of delayed fluorescence intensity on excitation light intensity, which supports the TADF afterglow mechanism, as it demonstrates the expected relationship for a TADF process; temperature-dependent experiments, where the change in emission lifetimes with temperature, combined with the calculation of phosphorescence rate constants and reverse intersystem crossing rate constants, allows for the fitting of singlet–triplet splitting energies; and low-temperature studies, where when materials are excited under ultraviolet light at liquid nitrogen temperatures and then the excitation is turned off, materials with only triplet excited states are obtained. These materials emit green afterglow, and when placed in hot water, the afterglow color shifts to blue. The blue emission originates from the singlet excited state, providing a direct demonstration of the reverse intersystem crossing from triplet to singlet states as the temperature increases.<sup>73</sup> Additionally, in the short-wavelength region of the emission spectrum, where only the singlet excited state emission is present and there is no interference from triplet emission, lifetime measurements still show emission lifetimes exceeding 100 ms, further confirming the presence of TADF-type organic afterglow materials.<sup>77</sup> These comprehensive experiments offer a more robust validation of the TADF-type afterglow mechanism.



Regarding the design of TADF-type organic afterglow materials, the  $k_{\text{RISC}}$  of luminescent dopants at room temperature or higher should fall in the range of  $10^0$ – $10^2$   $\text{s}^{-1}$ , while this  $k_{\text{RISC}}$  should be much larger than  $k_{\text{p}}$  by around one order of magnitude or higher. Since such systems with moderate/modest  $k_{\text{RISC}}$  and small  $k_{\text{p}}$  of triplet excited states can be readily quenched, a protective environment provided by the organic matrix to reduce  $k_{\text{nr}}$  and  $k_{\text{q}}$  is required for TADF-type afterglow materials design.

Because  $k_{\text{RISC}}$  decreases with lower temperatures, while  $k_{\text{p}}$  remains temperature-insensitive, the afterglow colors or spectral properties of TADF afterglow materials or TADF/RTP dual-emission materials are sensitive to temperature changes. When IaCzA and IbCzA (Fig. 7) are doped into PVA, the delayed spectra reveal that the resulting material exhibits both TADF and RTP dual-emission at room temperature.<sup>75a</sup> The TADF emission band is in the 400–470 nm range, while the RTP emission band spans 480–600 nm. As the temperature increases, the proportion of TADF in the delayed spectra increases, the afterglow color changes significantly, and the afterglow lifetime decreases substantially. This material can thus be used as a temperature-sensitive anti-counterfeiting material. A very recent study showed that a coronene system in a melamine formaldehyde polymer matrix exhibited TADF/RTP dual emission and showed afterglow color change by temperature control. This system has a TADF lifetime of up to around 1 second above 100 °C.<sup>75b</sup>

In the field of organic afterglow, the vast majority of reported materials require UV light excitation, sometimes even higher energy UVB light. In contrast, in commercially available fluorescent dyes, there are many visible-light-excitable fluorescent molecules to choose from. Through screening, researchers discovered that doping commercial acriflavine into a PVA matrix resulted in a thin film exhibiting TADF afterglow properties.<sup>78</sup> Due to the absorption capacity of acriflavine in the visible light region, the TADF afterglow film can be excited by white light, making it suitable for use as an afterglow anti-counterfeiting label. Furthermore, researchers found that the TADF-type organic afterglow system can also be extended to pyrylium salts,<sup>79</sup> acridone,<sup>80</sup> and other compounds (Fig. 7).

To address the issue of low efficiency in long-wavelength room-temperature afterglow materials, researchers have applied charge transfer technology and introduced a phenyl linkage design along with the strong electron-donating triphenylamine functional group (Fig. 7).<sup>81</sup> The resulting difluoroboron  $\beta$ -diketonate, when doped into a 4-methoxybenzophenone matrix, exhibits yellow TADF-type afterglow with a quantum yield of 42.8% and an afterglow lifetime of 375 ms. Further enhancing the electron-donating ability of the triphenylamine functional group led to the development of a TADF-type afterglow material with an emission wavelength of 600 nm. By designing molecules with different electron-donating functional groups and increasing the conjugation of the donor groups, the doped difluoroboron  $\beta$ -diketonate molecules in the 4-methoxybenzophenone matrix resulted in an orange-red TADF afterglow material with a quantum efficiency of 56.3% and an afterglow lifetime of 313 ms.<sup>82</sup> Difluoroboron  $\beta$ -diketonate materials containing fluorene functional groups

exhibit room-temperature phosphorescence, while extending the conjugation length of the molecular structure causes spectral redshift and TADF afterglow with a fluorescence lifetime of 100 ms and a red TADF afterglow efficiency of 13%.<sup>83</sup> The introduction of the hemicurcuminoid structure into the boron difluoride system results in red TADF room-temperature afterglow materials.<sup>84</sup> Additionally, by using a curcuminoid-based BF<sub>2</sub>bdk molecule and increasing the conjugation of the donor functional groups, near-infrared emitting TADF afterglow materials with an emission wavelength of 723 nm can be achieved.<sup>85</sup>

## 2.5 Organic long persistent luminescent systems

Organic long persistent luminescence (OLPL) materials are characterized by their ability to emit light for extended periods, ranging from minutes to hours or even longer.<sup>86–101</sup> Early studies showed that a two-component system with *N,N,N',N'*-tetramethylbenzidine (TMB) doped into a PMMA matrix could exhibit hour-long OLPL afterglow at 20 K through a two-photon ionization mechanism.<sup>86</sup> When TMB was doped into a PPT (2,8-bis(diphenylphosphoryl)dibenzo[*b,d*] thiophene) acceptor in a two-component system, the material demonstrated OLPL at room temperature in an inert atmosphere.<sup>87</sup> Upon single-photon or normal excitation light, charge separation occurred, resulting in the formation of TMB cation free radicals and PPT anion free radicals. The subsequent slow charge recombination led to the emission of light with power law decay, lasting for hours. Further studies reported that CzPhAP molecules (a TADF molecule) doped into PPT, TPBi (2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole)), or PMMA, when irradiated with high-power light, could absorb two photons and undergo two-photon ionization.<sup>88</sup> The released electrons were captured by the surrounding matrix, forming charge-separated states. Later, CzPhAP molecules harvested energy from the recombination of charges, resulting in both singlet and triplet state emissions and exhibiting OLPL. These studies, along with other reported OLPL research studies, indicate that the charge separation and slow charge recombination processes are essential for the long-lasting photoluminescence observed in organic materials.

The performance of OLPL materials is closely related to the various processes involved in their photophysical mechanisms. These processes include the degree of charge separation, where high-power excitation light sources are often needed to irradiate the sample for extended periods in two-photon ionization systems, promoting charge separation.<sup>88</sup> In donor–acceptor OLPL systems, careful selection of components can ensure that the excited state energy levels of the molecular charge transfer are lower than the T<sub>1</sub> levels of both the donor and acceptor, helping achieve a good degree of charge separation.<sup>89,90</sup> Another important factor is the stabilization or protection of radical intermediate species. In two- or three-component OLPL systems, at least two or three radical intermediates are involved, which are highly susceptible to deactivation. If these intermediates deactivate before charge recombination occurs, the OLPL properties will significantly deteriorate. Conversely, if the stability of the radical intermediates is higher, this is crucial for high-performance OLPL materials. It has been reported that inert atmospheres and

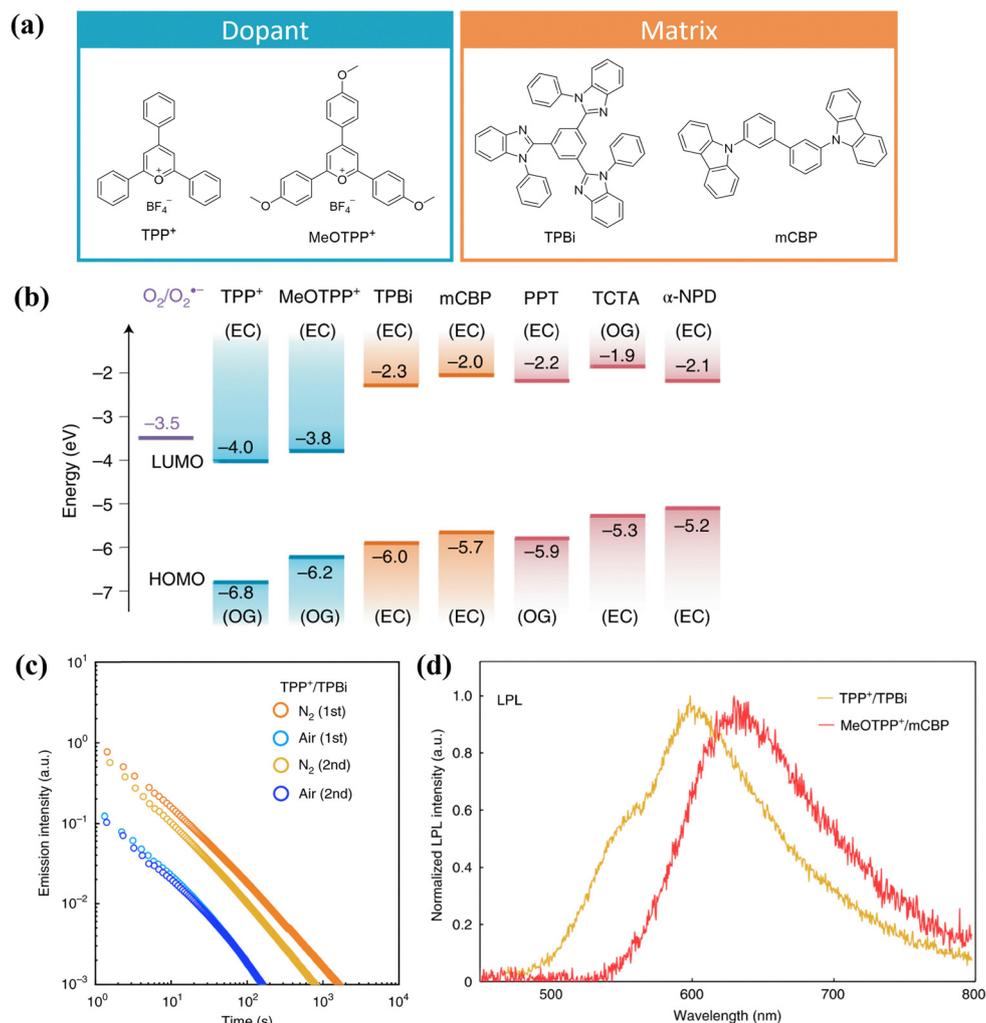


encapsulation can prevent quenching by oxygen and water vapor, protecting the reactive species in the intermediate state.<sup>87</sup> Crystalline matrices have also been shown to effectively protect these intermediates, enabling the development of high-performance OLPL materials, including those dispersed in water.<sup>91,92</sup> The kinetics of charge recombination also plays a key role. The addition of electron traps in n-type systems and hole traps in p-type systems can control the kinetics of charge recombination, significantly extending the OLPL duration.<sup>87,93,94</sup> Temperature and external fields have also been reported to influence the dynamics of charge recombination.<sup>95,96</sup> Finally, the photoluminescence quantum yield (PLQY) of luminescent molecules is crucial. Charge recombination produces singlet and triplet excitons, and the ability of luminescent molecules to harvest these states is key. The stronger the ability to harvest singlet and triplet excitons, the higher the brightness and longer the duration of the OLPL.<sup>88,96</sup> Therefore, enhancing the PLQY of the luminescent

molecules is a key factor in improving the performance of OLPL materials.

Currently, most OLPL systems reported in the literature are n-type systems, which are highly sensitive to oxygen. For example, the OLPL duration of the TMB-PPT system is on the order of hours in an inert atmosphere, but it significantly decreases when exposed to air.<sup>87</sup> To address this issue, researchers have developed p-type OLPL systems, utilizing commercial compounds such as pyrylium salts and TPBi or 3,3'-di(9*H*-carbazol-9-yl)biphenyl (mCBP) as matrices (Fig. 8).<sup>93</sup> The resulting dopant-matrix OLPL materials exhibit excellent OLPL properties under ambient conditions (Fig. 8c). Moreover, the emission wavelengths of these materials can extend into the red or near-infrared regions, making them promising for various practical applications (Fig. 8d).

In OLPL systems, the addition of fluorescent components can act as traps to prolong the OLPL duration. These components



**Fig. 8** (a) Chemical structures of dopant and matrix molecules. (b) HOMO and LUMO levels of materials and reduction potential of oxygen. HOMO and LUMO levels were obtained from electrochemical (EC) measurements. When the redox potential was out of the range of electrochemical measurement, the HOMO and LUMO levels were estimated from the optical gap (OG) that was calculated from the absorption edge. (c) OLPL duration under nitrogen and in air of TPP<sup>+</sup>/TPBi films excited at 365 nm. The optical properties were obtained under nitrogen and then after exposure to air for 24 h. The sample was evacuated again, and the second measurements were repeated. (d) The NIR LPL spectrum of TPP<sup>+</sup>/TPBi and MeOTPP<sup>+</sup>/mCBP films.



also serve as energy acceptors for charge recombination, enhancing the afterglow brightness and tuning the afterglow color.<sup>94</sup> In some systems, incorporating multi-resonant TADF dopants allows the absorption of visible light to sensitize donor–acceptor OLPL systems, giving them visible light excitation properties.<sup>97</sup> Some polymer-based systems, through doping and melt-processing, can also achieve OLPL materials with durations on the order of hours. Researchers synthesized a carbazole derivative (CBBU) doped into a polyethylene terephthalate (PET) matrix, yielding a transparent polymer film with an afterglow lifetime of up to 11 hours.<sup>98</sup> By attaching electron donor and acceptor functional groups to the main chain of the polymer molecules, they achieved uniform dispersion of the donor and acceptor, solving the issue of aggregation and phase separation typically found in p-type OLPL systems.<sup>99</sup> Specifically, using free radical polymerization, a copolymer was prepared with a small amount of electron-accepting 4-(4-(acryloyloxy)phenyl)-2,6-bis(4-methoxyphenyl)-pyrylium tetrafluoroborate (ATPP) monomer and a large amount of electron-donating 2-(9*H*-carbazol-9-yl)ethyl methacrylate (EMCz) monomer. Thin films were fabricated *via* a deposition method, and compared to simple molecular-doped films; the polymer films showed uniformity and excellent phase stability. This strategy led to higher-performance near-infrared LPL emission, which remained stable even under air exposure and at higher temperatures. The near-infrared emission property suggests potential applications in biological imaging.<sup>99</sup>

The methods for preparing OLPL materials mainly rely on melt casting, which requires high temperatures, and sometimes solution casting, which is time-consuming and involves large amounts of organic solvents. Mild and solvent-free methods for OLPL materials remain rarely reported. In a recent study, researchers used pyrylium salts as photocatalysts to induce the polymerization of vinyl carbazole, resulting in pyrylium salt-polyvinyl carbazole (PVK) materials that exhibited OLPL properties.<sup>100</sup> This preparation method does not require organic solvents or heating to temperatures of 200–300 °C, and the photopolymerization reaction occurs rapidly, with the material forming just a few seconds after light exposure. Furthermore, by selecting various compounds with HOMO energy levels higher than that of PVK (such as *N,N,N',N'*-tetrakis(4-methylphenyl)-benzidine), these compounds were used as hole traps and incorporated into the pyrylium salt–PVK system, leading to an improvement in the OLPL performance.

In the difluoroboron  $\beta$ -diketonate–phenyl benzoate system, in addition to the TADF-type organic afterglow, under strong excitation conditions, an organic long persistent photoluminescence phenomenon was observed (Fig. 9).<sup>73</sup> The emission originates from the singlet excited state, and the double logarithmic decay plot is linear, conforming to a power law decay, indicating a charge separation–slow recombination OLPL mechanism. In this system, upon excitation, difluoroboron  $\beta$ -diketonate molecules absorb two photons consecutively, resulting in ionization and the formation of free radical cations, with free electrons being captured by the matrix (Fig. 9c). In the solid-state medium, electrons and holes slowly recombine, producing

long-lasting emission lasting for tens of minutes. When the TMB dopant was further added to the difluoroboron  $\beta$ -diketonate–phenyl benzoate system, the resulting three-component material exhibited significant OLPL properties under normal or weak excitation light sources (Fig. 9d).<sup>101</sup> In the three-component system, after excitation, difluoroboron  $\beta$ -diketonate molecules form long-lived excited-state species. Their LUMO electrons have a certain probability of entering the LUMO orbitals of phenyl benzoate, and the HOMO electrons of TMB enter the HOMO orbitals of difluoroboron  $\beta$ -diketonate, promoting charge separation and the formation of phenyl benzoate radical anions and TMB radical cations. Charge recombination occurs on difluoroboron  $\beta$ -diketonate molecules, utilizing the TADF properties of difluoroboron  $\beta$ -diketonate to simultaneously harvest singlet and triplet excitons generated during recombination (Fig. 9d). This three-component system possesses both TADF-type afterglow and OLPL long-lasting luminescence mechanisms, with the two mechanisms coexisting in the same material, achieving the difficult task of efficiently preparing long-lifetime materials in this field.

In research on OLPL systems, some specific mechanisms are still not fully understood. The well-known and effective electron acceptors are PPT and TPBi. In recent work, a dopant–matrix material with TPBi as the matrix and TADF luminescent molecules as dopants was prepared, and the resulting material exhibited an OLPL lifetime of up to 24 hours (Fig. 10).<sup>96</sup> The researchers proposed that the trap depth in the system is determined by the energy difference between the LUMO levels of the dopant and the matrix. By adjusting the composition, the trap depth can be controlled, thus regulating the properties of the OLPL material. Additionally, some ester-based crystalline small molecules or polymers can also serve as electron acceptors. The electron donors are typically aromatic amines, some of which can also act as hole traps to enhance OLPL performance. In two-photon ionization or other mechanisms, TADF luminescent molecules are necessary. Studies have demonstrated the importance of long-lifetime luminescent molecules in these mechanisms. Firstly, in two-photon ionization mechanisms, long-lifetime luminescent molecules have a higher efficiency in absorbing two photons consecutively. Secondly, in other mechanisms, the charge separation process involves electron transfer, and long-lifetime luminescent molecules are essential as the starting point or bridge for electron transfer, leading to higher charge separation efficiency. Lastly, TADF luminescent molecules can simultaneously harvest singlet and triplet excitons generated during charge recombination, resulting in more efficient energy utilization.

## 2.6 Organic narrowband afterglow systems

Organic RTP and afterglow materials with narrowband emission hold great potential for applications such as multiplexed bio-imaging, where they reduce spectral interference among luminescent probes, and high-density information encryption, addressing the challenge of spectral congestion. Nevertheless, current research predominantly features RTP and afterglow systems with wide emission spectra, often exhibiting full-width at half-



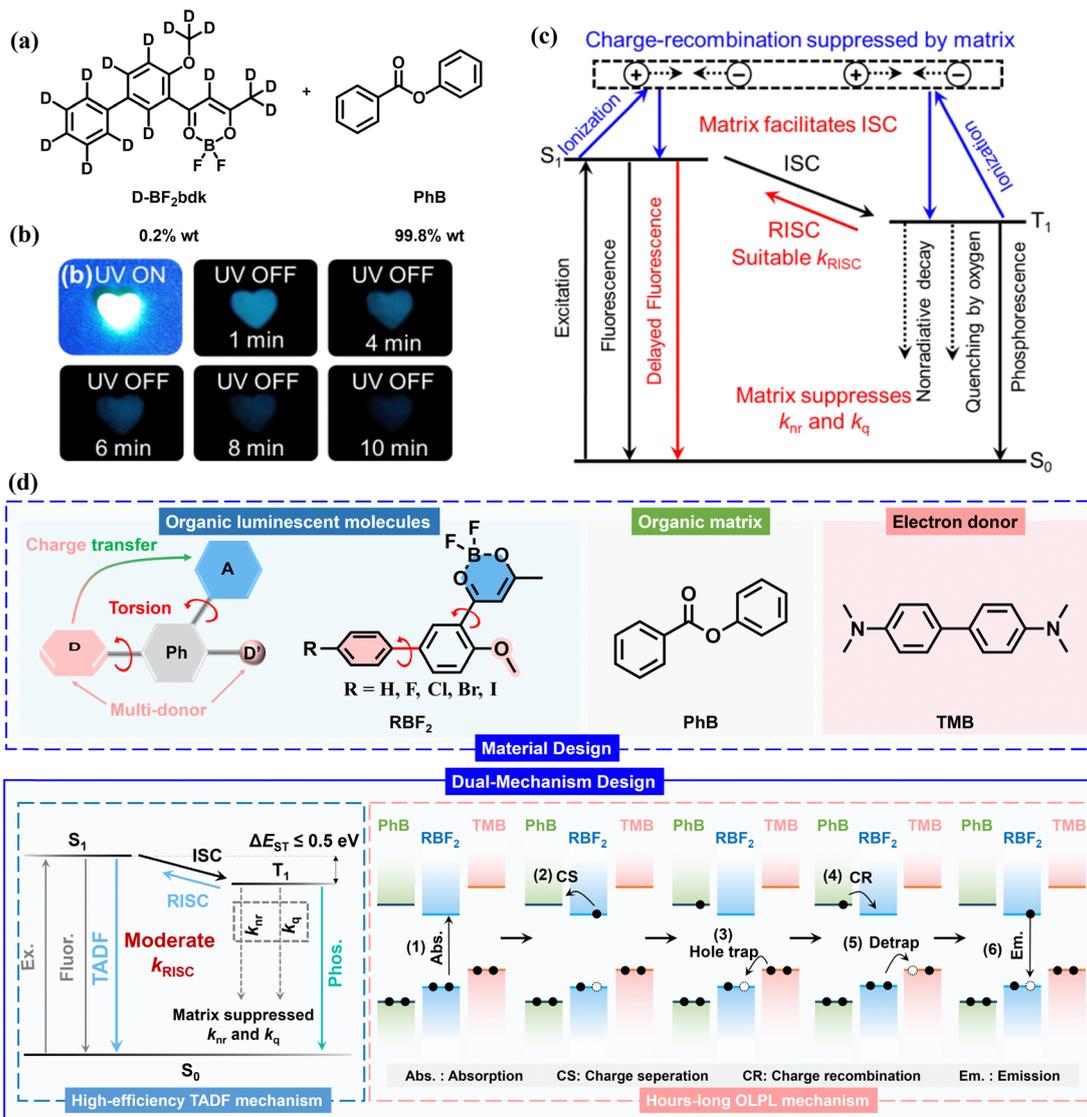


Fig. 9 (a) Illustration of D-BF<sub>2</sub>bdk-PhB afterglow materials. (b) Photographs of the heart-shaped BF<sub>2</sub>bdk-PhB-0.2% under a 365 nm UV lamp (75 W) and after removal of the UV lamp. (c) The proposed afterglow mechanism that merges TADF afterglow and two-photon ionization of the BF<sub>2</sub>bdk-PhB sample. (d) Material design and dual-mechanism of high-efficiency and long-lived organic afterglow materials of the BF<sub>2</sub>bdk-TMB-PhB sample.

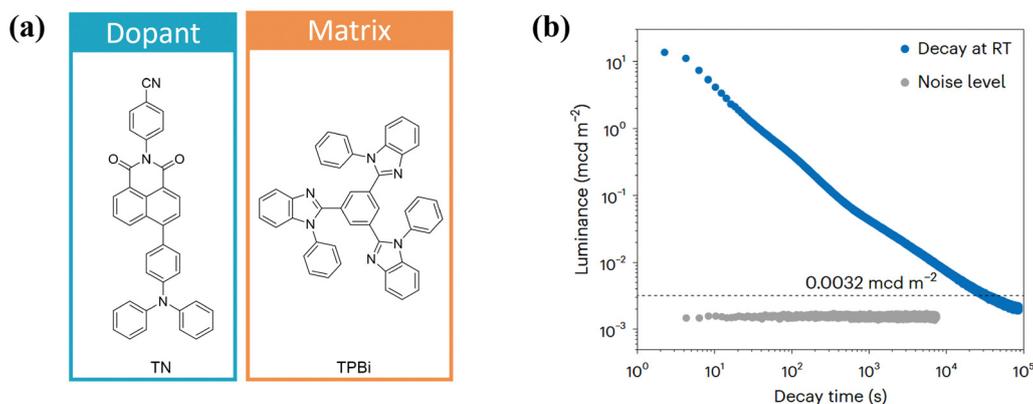


Fig. 10 (a) Chemical structures of dopant and matrix molecules. (b) OLPL decay curve of the TN@TPBi materials after excitation by a 365 nm UV lamp for 300 s at RT. Such emission can be detected by a photomultiplier tube (PMT) for 24 h.



maximum (FWHM) exceeding 50 nm, and in some cases approaching 100 nm.

BODIPYs are a class of narrowband fluorescence molecules with high absorption coefficients and PLQYs, and they are commercially available. The absorption and emission wavelengths of BODIPY molecules can be freely selected over a broad range. Researchers have incorporated BODIPY into organic room-temperature phosphorescent materials that are spectrally matched (Fig. 11a).<sup>102</sup> Through excited state energy transfer, they have achieved narrowband afterglow materials with a FWHM of 23 nm. The spectrum and lifetime of the system can be tuned by adjusting the BODIPY and the RTP donor. In another study, researchers selected benzophenone as a room-temperature phosphorescent donor and doped it with narrowband emitting molecules (Fig. 11b), resulting in a narrowband phosphorescent material with a FWHM of 30 nm at room temperature.<sup>103</sup> Furthermore, in polymer-based phosphorescent systems (Fig. 11c), the introduction of narrowband emitting molecules also enables the preparation of narrowband afterglow materials through excited-state energy transfer, with a lifetime of 1.64 s and a FWHM of 38 nm.<sup>104</sup>

The narrowband afterglow systems mentioned above are based on excited state energy transfer, while intrinsic narrowband organic afterglow is challenging to achieve. Analyzing the excited state properties of luminescent molecules, it is evident that the broadening of emission spectra in reported RTP/afterglow systems is mainly caused by two factors: (1) structural relaxation of excited states, particularly in luminescent systems with intramolecular charge transfer characteristics and (2) vibronic coupling between excited states and ground states. Recent studies on organic light-emitting diodes (OLEDs) have

shown that the multiple resonance effect in organic systems can result in localization of the HOMO and the LUMO on different atoms, suppressing vibronic coupling between excited states and ground states, thus yielding narrowband emission.<sup>105</sup> Based on the multiple resonance effect, a variety of multi-resonant TADF emitters were synthesized to display narrowband emission and high color purity, suitable for high-quality, energy-saving OLED devices. These multi-resonant TADF emitters exhibit a reverse intersystem crossing rate ( $k_{\text{RISC}}$ ) of  $10^3$ – $10^6$  s<sup>-1</sup>, which is necessary to prevent efficiency roll-off in OLED devices at high luminance. However, in the context of afterglow emitters, a large  $k_{\text{RISC}}$  of  $10^3$ – $10^6$  s<sup>-1</sup> corresponds to a short TADF lifetime ( $10^{-6}$  to  $10^{-3}$  s), which would be detrimental to afterglow materials designed for emission lifetimes longer than 100 ms. Therefore, a moderate or modest  $k_{\text{RISC}}$  ( $10^0$  to  $10^1$  s<sup>-1</sup>) in multi-resonant systems is proposed to be important to achieving narrowband multi-resonant TADF-type organic afterglow materials with an emission lifetime greater than 100 ms. The multiple resonance effect of acridone can weaken vibronic coupling, and the rigidity of its molecular skeleton can suppress excited-state relaxation. Based on these two structural characteristics, researchers have doped acridone into a phenyl benzoate matrix to obtain a dopant–matrix TADF room-temperature afterglow material with a FWHM of less than 40 nm (Fig. 11d).<sup>80,106</sup> Additionally, using emulsion polymerization and the dopant–matrix strategy, narrowband afterglow nanoparticles that are stably dispersed in water can also be achieved. Recently, researchers have synthesized a series of indolo[3,2,1-*k*]pheno-thiazine derivatives by molecular cyclization to suppress excited-state relaxation (Fig. 11e) and doped them into suitable

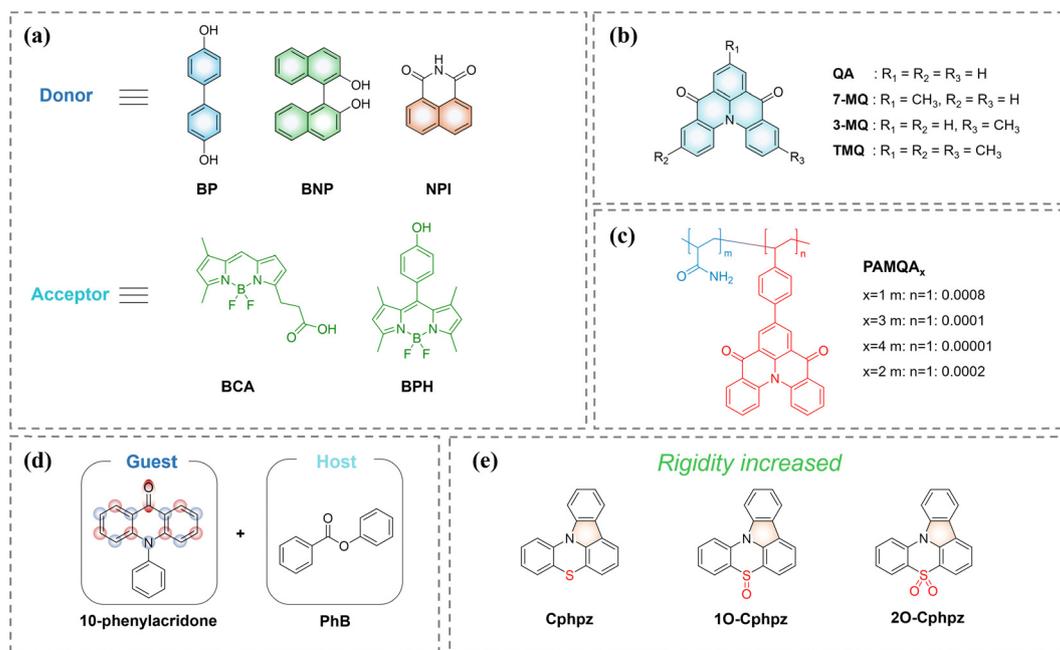


Fig. 11 (a) Chemical structures of donors and acceptors. (b) Chemical structures of the QA, 7-MQ, 3-MQ and TMQ phosphors. (c) Molecular structures of developed hyperafterglow polymers (PAMQA<sub>x</sub>). (d) Chemical structures of 10-phenylacridone and phenyl benzoate (PhB). (e) Chemical structures of Cphpz, 10-Cphpz, and 20-Cphpz.



polymer matrices, resulting in a dopant–matrix narrowband afterglow material with a FWHM of 36 nm.<sup>107</sup>

### 3. Critical role of organic matrices in materials fabrication

In addition to the design of luminescent molecules, the selection of organic matrices is crucial for the development of high-performance and functional afterglow materials. Fig. 12 and 13 illustrate the chemical structures and CAS numbers of commonly used organic matrices.

The basic role of organic matrices is to disperse luminescent molecular dopants. Several methods are commonly employed for this purpose. First, the matrix and luminescent molecules are dissolved together, and after the solvent evaporates, the dopant–matrix material is obtained. Second, the melt-casting method involves heating the matrix to its melting point, allowing it to dissolve or disperse the luminescent molecules more effectively. After cooling, the dopant–matrix material is formed. Third, the grinding method involves mechanically blending the matrix and luminescent molecules, allowing the latter to disperse within the matrix. During grinding, low-boiling solvents may be added to facilitate better dispersion of the luminescent molecules. Lastly, *in situ* formation involves using a liquid precursor of the organic matrix, which can dissolve the luminescent molecules. Through polymerization or other conversion processes, the matrix solidifies, encapsulating the luminescent molecules within.

Organic matrices are typically either crystalline or amorphous small molecules or polymers, and their rigid environments help suppress the intramolecular motion of dopant's triplet excited state, thereby reducing non-radiative deactivation at room temperature (Fig. 14a). For amorphous small molecules, such as PMMA, oxygen molecules are allowed to diffuse relatively freely within their structures. As a result, when these afterglow materials are prepared in an inert gas environment, they will immediately exhibit afterglow upon excitation. However, when prepared under ambient conditions, the materials typically require UV or visible light irradiation for a period of time to deplete the oxygen molecules, which are consumed by the triplet excited states formed, thus activating the materials to display their afterglow properties. In contrast, crystalline small-molecule matrices and certain polar polymers, such as PVA, effectively inhibit oxygen diffusion, preventing contact between the dopant's triplet excited states and oxygen molecules, thereby suppressing oxygen quenching. As a result, afterglow samples produced with these matrices either do not require activation or only need a brief activation (a few seconds) before exhibiting afterglow.

In RTP and TADF afterglow systems, the organic matrices typically possess structures with relatively low conjugation, which results in high  $T_1$  energy levels. This is essential because, upon excitation of dopant–matrix samples, the  $T_1$  excited state of the luminescent molecules may undergo energy transfer to the  $T_1$  state of the matrix, leading to afterglow quenching.

Studies have reported that if the  $T_1$  energy level of the organic matrix is sufficiently high, it can prevent this energy transfer, thus contributing to the development of high-performance organic afterglow materials.<sup>108–111</sup>

In addition to the aforementioned scenario, the  $T_1$  energy level of the organic matrix plays a crucial role in afterglow performance through other mechanisms. In some luminescent molecular systems where the energy gap between the  $S_1$  and  $T_1$  states is large, researchers have proposed that introducing an organic matrix with a  $T_1$  energy level located between the  $S_1$  and  $T_1$  of the luminescent molecule can facilitate matrix-mediated intersystem crossing, thereby enabling the creation of dopant–matrix afterglow materials (Fig. 14b).<sup>112</sup> It has been observed that by adjusting the  $T_1$  energy level of the organic matrix, the afterglow lifetime of the dopant–matrix system can be controlled, leading to the development of lifetime-encoded afterglow anti-counterfeiting materials.<sup>113</sup> A very recent study further discussed the role of the matrix's  $T_1$  state in the afterglow system.<sup>114</sup>

In luminescent molecular systems of intramolecular charge transfer (ICT) character, researchers have found that upon excitation, the  $S_1$  state of the luminescent molecule exhibits a significant dipole moment. By selecting an organic matrix with a pronounced ground-state dipole moment, a dipole–dipole interaction between the  $S_1$  state of the luminescent molecule and the organic matrix can be established. This interaction effectively lowers the  $S_1$  energy level while having minimal impact on the  $T_1$  energy level, thereby reducing the  $\Delta E_{ST}$  (Fig. 14c).<sup>67,70,72</sup> This facilitates both intersystem crossing (ISC) and reverse intersystem crossing (RISC), which are advantageous for the preparation of high-performance afterglow materials. According to estimates, a 0.1 eV reduction in  $\Delta E_{ST}$  can increase the ISC/RISC rate by approximately 100 times.<sup>115</sup> This dipole effect on enhancing ISC has also been supported by the literature.<sup>116</sup> In practice, researchers have accumulated experience in selecting matrices for ICT-based afterglow systems. When the  $T_1$  energy level of the luminescent molecule is high, matrices with a high  $T_1$  energy level, such as phenyl benzoate, are preferred, as they promote ISC while preventing energy transfer from the luminescent molecule's  $T_1$  state to the matrix's  $T_1$  state, which could lead to afterglow quenching. On the other hand, if the  $T_1$  energy level of the luminescent molecule is lower, matrices like benzophenone or 4-methoxybenzophenone are more suitable, as these matrices have a stronger dipole moment than phenyl benzoate enhancing the ISC/RISC process. Moreover, they are effective at dispersing ICT luminescent molecules, enabling higher doping concentrations and resulting in dopant–matrix materials with higher afterglow brightness. In systems where benzophenone and its derivatives are used as matrices, excited state energy transfer from the matrix to the dopant may lead to afterglow. To test whether there is energy transfer, experimentally, a longer excitation wavelength is chosen to selectively excite luminescent dopants, avoiding the absorption region of the matrix. If there is still significant afterglow by long-wavelength excitation, one can confirm that the luminescent molecules' own ISC and phosphorescence decay processes are sufficient to produce



## Small molecule matrix

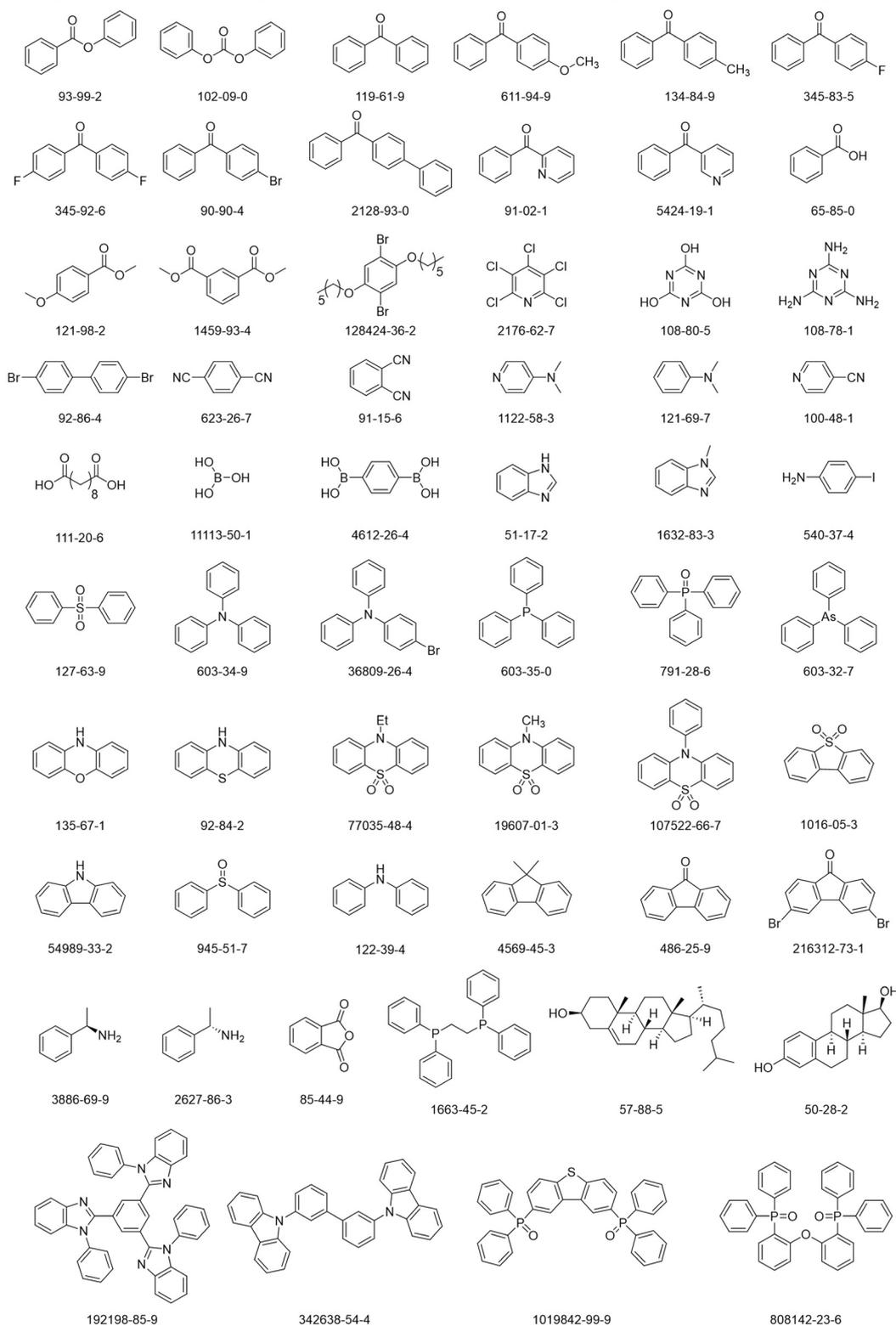


Fig. 12 Chemical structures and CAS numbers of commonly used small molecule matrices.

afterglow, without relying on energy transfer from the matrix to the luminescent molecules.

Excited state energy transfer is an effective method for preparing dopant–matrix afterglow materials (Fig. 14d).<sup>117–120</sup>



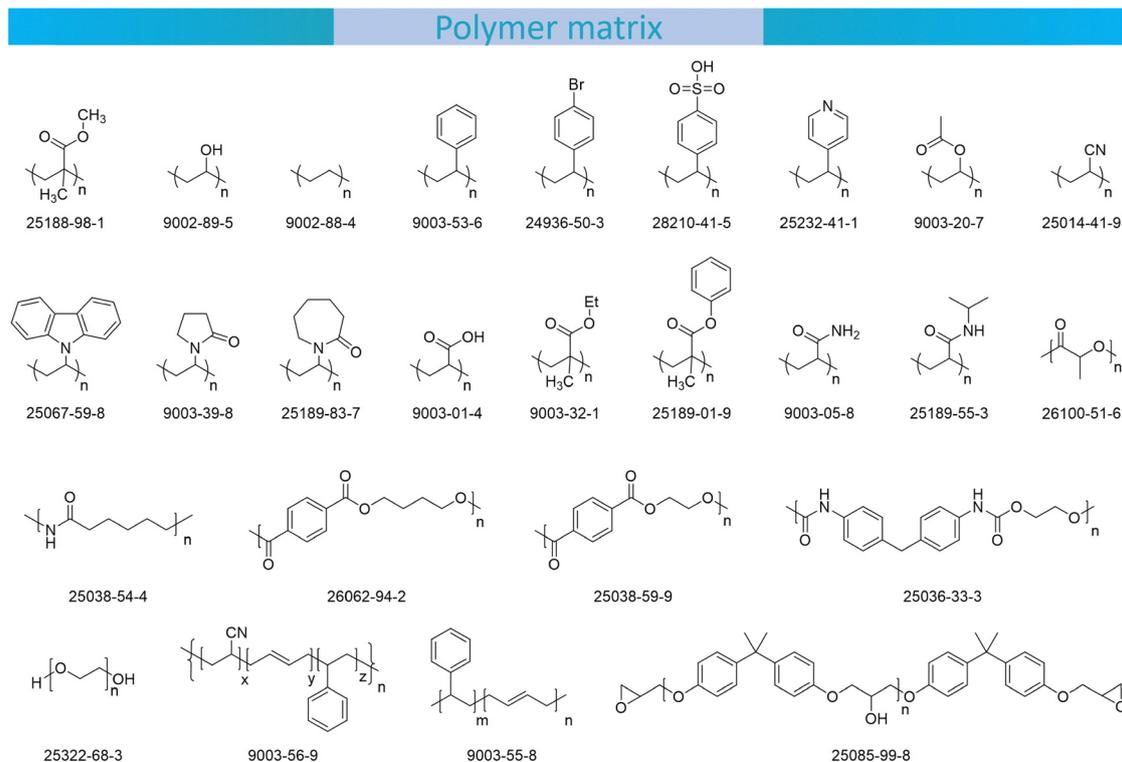


Fig. 13 Chemical structures and CAS numbers of commonly used polymer matrices.

By selecting an efficient ISC organic matrix in combination with an organic luminescent dopant that effectively accepts  $T_1$  energy from the matrix—particularly those with small  $k_p$  values—the resulting dopant–matrix materials exhibit efficient and long-lived afterglow properties.<sup>117</sup> Additionally, excited state energy transfer serves as a strategy for preparing long-wavelength afterglow materials.<sup>118</sup> By selecting spectrally matched long afterglow donor materials and long-wavelength luminescent acceptors, doping the luminescent acceptors into the long afterglow donor materials enables the fabrication of afterglow materials in the red to near-infrared regions, which are typically difficult to achieve using direct methods.<sup>56,120</sup>

In OLPL systems based on the donor–acceptor mechanism, the organic matrix not only plays a role in matching the HOMO/LUMO levels with the dopants but can also function as an electron trap or hole trap. In fact, there are numerous donor–acceptor pairs, and what kind of specific pair that leads to effective performance is still under investigation. Currently, it is known that PPT and TPBi are promising matrices,<sup>87</sup> and some long-lived OLPL materials have been successfully developed using these matrices. Furthermore, if certain components can form relatively stable radical intermediates during charge separation, this significantly impacts the performance of OLPL materials. For instance, the TMB component can form a stable TMB radical cation.<sup>87</sup> Some ester-based small molecule or polymer matrices,<sup>86,98,101</sup> when combined with suitable luminescent molecules, can also yield OLPL materials, possibly through the two-photon ionization mechanism or other undefined mechanisms. However, the exact role of the organic

matrix in these OLPL systems is not yet fully understood. Further systematic research is required to elucidate the matrix's contribution in OLPL systems, which is crucial for the development of high-performance materials.

The organic matrix has a significant influence on afterglow properties. In certain systems, the change in the type of organic matrix can result in alterations in the color of room-temperature phosphorescence.<sup>121–123</sup> In a difluoroboron  $\beta$ -diketonate system containing a triphenyl group, researchers observed different phosphorescent colors depending on the matrix used.<sup>121</sup> According to Kasha's exciton model, the  $T_1$  excited state in organic systems exhibits minimal dipole moment in its transition to the ground state, making the  $T_1$  energy level (NOT phosphorescence intensity) insensitive to the microenvironment. Once the molecular structure is determined, the  $T_1$  energy level is essentially fixed. The triphenyl group-containing difluoroboron  $\beta$ -diketonate molecule, which is linked by multiple single bonds, exhibits flexibility and adopts different conformations in various matrices. These conformational changes lead to variations in its  $T_1$  energy level, resulting in different phosphorescent colors in different polymer matrices, making it a potential probe for label-free polymer phase separation in afterglow applications.<sup>121</sup>

Small structural changes in the organic matrix can lead to significant alterations in the afterglow mechanism of dopant–matrix materials.<sup>122,123</sup> In a recent study, researchers doped a luminescent molecule containing triphenylamine and triphenyl groups into a benzophenone matrix, achieving dopant–matrix afterglow materials with the RTP afterglow mechanism.<sup>123</sup>



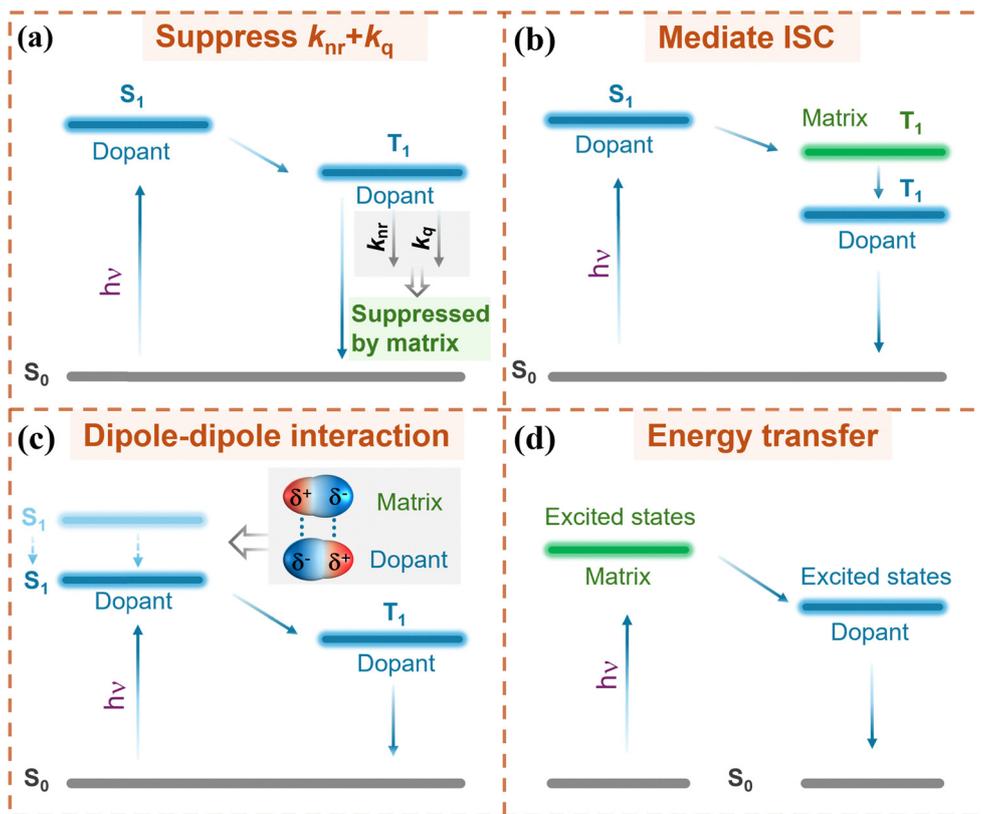


Fig. 14 The role of matrix: (a) the matrix can provide a rigid microenvironment for the dopant, suppressing its  $k_{nr}$  and  $k_q$ . (b) The triplet states of the matrix can mediate the ISC process of the dopant. (c) The dipole–dipole interaction between the dopant and the matrix can decrease the energy level of the dopant's  $S_1$  state, leading to a smaller  $\Delta E_{ST}$ . (d) The energy transfer from the matrix to the dopant occurs when the matrix is excited.

Interestingly, when a fluorinated benzophenone matrix was used, intermolecular charge transfer occurred between the dopant and the matrix, leading to the formation of a TADF-type organic afterglow material.

The responsiveness of organic afterglow materials to external mechanical stimuli has been reported in the literature, primarily in single-component systems.<sup>33–35</sup> Recent studies have demonstrated the response of afterglow in dopant–matrix materials to ultrasound.<sup>124</sup> Afterglow materials based on fluorinated benzophenone, prepared *via* the melt-drop emulsification method, were found to form dispersions in water. Researchers discovered that after subjecting these dispersions to ultrasonic treatment, the afterglow properties were significantly weakened. This was attributed to the ultrasound disrupting the fluorinated benzophenone microcrystals, which in turn compromised the protection of the dopant's  $T_1$  state. This ultrasound-responsive behavior was also extended to long-wavelength TADF afterglow materials in water-dispersible systems, highlighting their potential as smart, responsive afterglow materials.<sup>124</sup>

When the organic matrix is a polymer, the resulting polymer-based room-temperature afterglow material exhibits excellent processing, dispersion, and mechanical properties.<sup>27–29</sup> Conventional methods for preparing polymer-based afterglow materials include solution casting and melt molding. Solution casting requires a large amount of solvent and slow evaporation, while

melt molding necessitates high temperatures that may damage certain luminescent molecules. In contrast, some researchers have opted for solvent-free, mild photo-initiated bulk polymerization.<sup>125–127</sup> In this method, a small amount of phosphorescent molecules is dissolved in the liquid monomer, and after exposure to light, the material is cured to form polymer-based room-temperature afterglow materials with excellent processability and flexibility.<sup>125</sup> The residual monomer is less than 0.2% after polymerization, and the presence of photoinitiator residues does not affect the afterglow performance.

In previous reports, polymers with a glass transition temperature ( $T_g$ ) higher than room temperature have often been used as matrices because they can suppress molecular motion. Researchers developed flexible RTP materials by doping 4-biphenylboronic acid into polyvinylidene fluoride (PVDF) with a  $T_g$  of  $-27.1$  °C, achieving for the first time RTP emission with a long lifetime of 1275.7 ms in a low- $T_g$  polymer (Fig. 15a).<sup>128</sup> The RTP performance can be further tuned by adjusting the crystallinity and various polymorphs ( $\alpha$ ,  $\beta$ , and  $\gamma$  phases). The low  $T_g$  of the PVDF matrix allows segmental motion of the polymer under microwave radiation. Upon exposure to 2.45 GHz microwave radiation, the crystallinity of the polymer decreases, and the fraction of the  $\alpha$  phase increases, resulting in an RTP material with microwave-stimulated responsiveness (Fig. 15b).



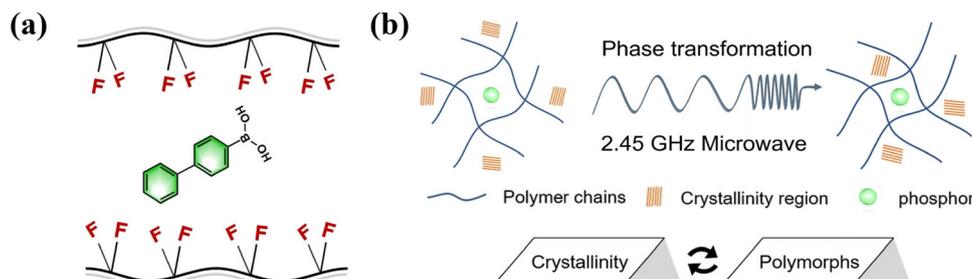


Fig. 15 (a) Illustration of BPBA in PVDF. (b) The crystalline modifications and phase transformation of BPBA/PVDF films with crystalline regions and different polymorph microenvironments.

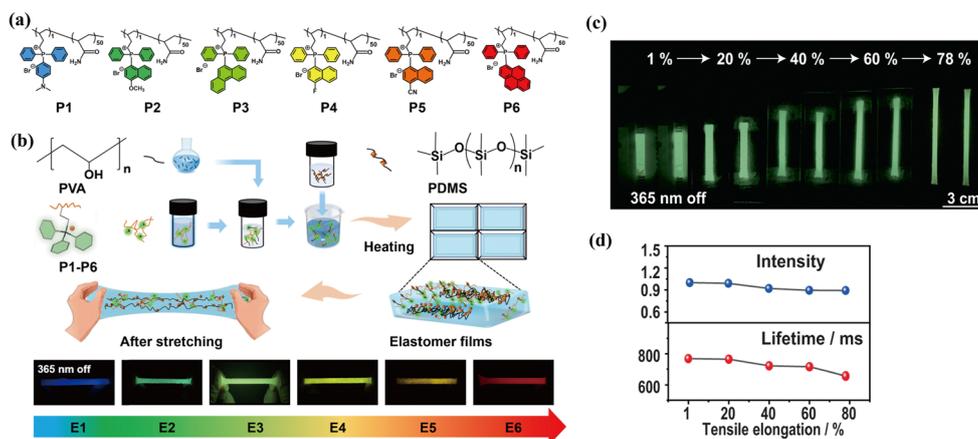


Fig. 16 (a) The preparation of persistent RTP elastomers involves both molecular design and synthesis strategies. The chemical structures of amorphous RTP copolymers, P1 to P6, are specifically designed to achieve tunable phosphorescence properties. (b) A schematic representation illustrates the step-by-step procedure for creating full-color persistent room-temperature phosphorescent elastomers, highlighting their customizable optical characteristics and structural versatility. (c and d) For E3, the RTP afterglow emission under strain demonstrates significant optical alterations, with measurable variations in phosphorescence intensity and emission lifetime.

Through emulsion polymerization and the dopant–matrix strategy, a small amount of luminescent molecules is dissolved in monomer droplets, and after polymerization, the monomers are transformed into a glassy polymer matrix.<sup>129–131</sup> This rigid microenvironment protects the  $T_1$  state, resulting in afterglow emulsions with lifetimes comparable to bulk materials. The emulsions are stable, with high solid content, uniform size, and adjustable properties. By copolymerizing in emulsions and performing specific ligand surface modification, afterglow microspheres were obtained with the capability to specifically recognize proteins in aqueous dispersion.<sup>129</sup> Utilizing the stability of luminescent molecules of all aryl structures, afterglow emulsions were developed, which are resistant to acids and bases and are biocompatible, demonstrating functionality for microenvironmental oxygen detection.<sup>130</sup> TADF-type afterglow emulsions with dual responses to temperature and oxygen were also constructed.<sup>131</sup> In these emulsion systems, as long as the luminescent molecules are in a nanometer-scale glassy microenvironment,  $k_{nr}$  can be effectively suppressed. This concept challenges the conventional belief that afterglow can only be observed in bulk, powder, or film samples. Extending this idea, it can be envisioned that in certain multicomponent polymer

systems, if one component can protect the  $T_1$  state of the organic luminescent molecules and induce afterglow, the selection of other components becomes relatively flexible, which is beneficial for the development of functional afterglow materials. Researchers have blended phosphorescent polymers into a polydimethylsiloxane (PDMS) matrix to create a range of room-temperature phosphorescent elastomers (Fig. 16).<sup>132</sup> After repeated stretching of the elastomer, it was found that its phosphorescence intensity and lifetime only decreased slightly, indicating excellent resistance to mechanical deformation. This property promotes the practical application of RTP materials in wearable optoelectronic devices, flexible displays, and advanced anti-counterfeiting technologies.

## 4. Concluding remarks and outlook

This review summarizes the recent advancements in the field of dopant–matrix organic phosphorescence over the past three years, from the perspective of high-performance materials and the role of the matrix. With the increasing number of research publications and the deepening of studies, strategies for



designing luminescent molecules have gradually been mastered. From the  $n-\pi^*$  systems represented by benzophenone to the  $\pi-\pi^*$  systems of polycyclic aromatic hydrocarbons, and then to the intramolecular charge transfer systems exemplified by difluoroboron  $\beta$ -diketonate compounds, various methods for achieving high-performance afterglow materials have been identified. Research over the years has also increasingly highlighted the crucial role organic matrices play in the manipulation of excited states, such as protecting the  $T_1$  state, promoting ISC/RISC, and forming donor-acceptor OLPL systems. The dopant-matrix system consists of many slow processes, and because organic matrices can suppress  $k_{nr}$  and  $k_q$  in the  $T_1$  state of luminescent molecules to very low values, some traditionally overlooked slow processes in conventional photophysics may emerge or even dominate in afterglow systems at room temperature. This could lead to unprecedented photophysical phenomena, which are of significant importance for the development of photophysics and photochemistry, as well as for the development and application of new photofunctional materials. Given that inorganic afterglow materials have already found large-scale applications, organic afterglow materials outperform their inorganic counterparts in flexibility, processability, sustainability, and transparency. Therefore, the successful enhancement of organic materials' performance and large-scale production will represent a key milestone in the real-world applications of organic afterglow materials. Achieving these future prospects will require intense effort from researchers and close collaboration with industry, but it is believed that they will be realized in the near future.

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

The authors declare no competing financial interest.

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