

## REVIEW

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# Room-temperature phosphorescence based on doping systems: material design, mechanisms, and applications

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Room-temperature phosphorescence (RTP) materials have received widespread attention in the fields of optoelectronics and biomedical sciences due to their extremely long phosphorescence lifetimes and unique time-resolved properties. This review systematically evaluated the intrinsic mechanisms of doping strategies in small molecule host–guest systems, polymer matrices, supramolecular self-assemblies, and nanoscale doping systems and deeply explored the structure–activity relationship between different doping structures and properties. A detailed analysis was conducted on the mechanism by which the host–guest doping system suppresses non-radiative decay through the rigid microenvironment of the matrix and promotes singlet–triplet intersystem crossing (ISC) through the regulation of guest molecules, thereby extending the lifetime of triplet excitons. Finally, the application scenarios of RTP materials were summarized. For example, researchers have developed organic phosphorescent nanoscintillators by introducing heavy atom effects, achieving low radiation doses and high-resolution X-ray imaging in deep tumor photodynamic therapy. This provides a new idea for using phosphorescent scintillators for optical deep tissue therapy. The future development direction of RTP materials was discussed, and performance evaluation standards and strategic design ideas for doped phosphorescent materials were proposed, providing theoretical support for continuous innovation in this field.

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## 1. Introduction

In the rapidly evolving field of luminescent materials, room-temperature phosphorescence (RTP) materials have garnered significant attention as a promising platform for diverse technological applications.<sup>1,2</sup> RTP refers to the emission of light from excited triplet states of molecules under ambient conditions, without the need for cryogenic cooling. It offers intrinsic advantages such as ease of integration into real-world devices and biological systems, enhanced stability against environmental fluctuations, and the ability to operate under ambient conditions. Despite these advantages, achieving efficient RTP remains challenging due to the inherently non-radiative decay processes that quench triplet states. Traditionally, RTP materials relied on rigid matrices and inert conditions, which limited their applications. The conceptual distinction between conventional RTP and ultralong RTP is fundamental: traditional RTP involves phosphorescence from the lowest triplet state ( $T_1$ ), typically enhanced *via* molecular rigidity and heavy-atom effects to promote intersystem crossing (ISC), while ultralong RTP often leverages host–guest interactions to generate or stabilize new, long-lived triplet states such as exciplexes. These mechanisms are markedly different, but both are crucial for advancing the field.

The conceptualization of RTP traces back to the last century, when researchers first postulated the theoretical feasibility of molecules exhibiting long-lived phosphorescence emission at room temperature. In 1944, Lewis *et al.* established key theoretical foundations by delineating triplet-state transition mechanisms underlying phosphorescence generation,<sup>3</sup> laying groundwork for subsequent exploration. However, early RTP research faced significant hurdles: molecules were inherently prone to non-radiative transitions that dissipate excited-state energy, while environmental factors like molecular collisions exacerbate quenching. As a result, early phosphorescent materials required harsh conditions (*e.g.*, cryogenic temperatures, rigid matrices, and inert gas protection) to exhibit phosphorescence, severely limiting their utility.

A breakthrough in overcoming these challenges was the emergence of doping strategies,<sup>4</sup> particularly host-guest doping,<sup>5,6</sup> which allows precise modulation of triplet states—either by suppressing non-radiative pathways or by promoting ISC—thereby producing efficient, stable RTP at room temperature. In 2017, the Adachi group demonstrated this paradigm by doping structurally tailored guest molecules into host matrices, achieving efficient,<sup>7</sup> stable room-temperature phosphorescence—pioneering work that validated doping as a powerful tool for RTP optimization and unlocked new application avenues.

Subsequent studies further highlighted doping's advantages in diversifying RTP systems. For instance, the Tian and Ma group utilized an ionic polymer matrix (PAB) as both a host and a regulator: bromide ions in PAB facilitated ISC *via* external heavy-atom effects to populate triplet states, while its rigid ionic network (formed by bromide anions and quaternary ammonium cations) inhibited non-radiative transitions.<sup>8</sup> This integrated design exemplifies doping's ability to synergistically modulate triplet-state generation and stabilization within a single system, with the amorphous nature of the doped materials adding processability—a critical feature for practical fabrication. Similarly, the Dang and Li group showcased doping's tunability by using polyvinylpyrrolidone (PVP) hosts with aromatic polycyclic aromatic hydrocarbon (PAH) guests of varying conjugation, achieving phosphorescence spanning green to near-infrared with lifetimes from 139 ms to 3850 ms—demonstrating how doping enables precise tailoring of emission properties for specific applications.<sup>9</sup>

The unique merits of RTP (ambient operation, long lifetimes, and environmental stability) combined with doping-induced advantages (enhanced efficiency, tunability, and processability)

have driven its expansion into diverse fields.<sup>10</sup> In bioimaging, long-lived RTP emission enables time-resolved detection to reduce background interference, facilitating prolonged dynamic tracking of biological processes.<sup>11</sup> In anti-counterfeiting, RTP's distinct temporal characteristics—amplified by doping-controlled lifetimes—create markers.<sup>12,13</sup> In sensing, doping systems like the boronic acid/ $\gamma$ -cyclodextrin platform developed by the Ma and Liu group exhibit multi-stimuli responsiveness (photoactivation and mechanical/thermal/humidity sensitivity), utilizing RTP's dynamic tunability for intelligent information storage and ultraviolet trajectory tracking.<sup>14</sup>

Against this backdrop, this review provides a comprehensive overview of the latest advances in doping-based RTP materials, focusing on material design, underlying mechanisms, and broad application prospects. It systematically discusses progress in host-guest doping strategies for organic small molecules, polymer matrices, supramolecular assemblies, and nanostructures, with an emphasis on how these innovations enable practical applications across optoelectronics, anti-counterfeiting, sensing, and bioimaging. By examining current challenges and future directions, this work aims to guide the rational design and facilitate the transition of doped RTP materials from laboratory research toward real-world technologies.

## 2. Material design and mechanisms of room-temperature phosphorescence based doping systems

### 2.1. The mechanisms of room-temperature phosphorescence based doping systems

The core of the luminescence mechanism of room-temperature phosphorescence (RTP) doped materials is the synergistic regulation of triplet exciton generation, stability, and radiative transitions by the matrix dopant, encompassing processes such as energy transfer, triplet population, and non-radiative suppression. The development strategies mainly include rigid matrices, exciton complexes, and energy transfer (Fig. 1). Most RTP-doped systems are made by doping organic chromophores into a rigid matrix. Choosing appropriate organic chromophore dopants and rigid matrices can establish strong intermolecular interactions between doped molecules, slow down non-radiative and radiative decay of triplet excitons, and achieve long-lived

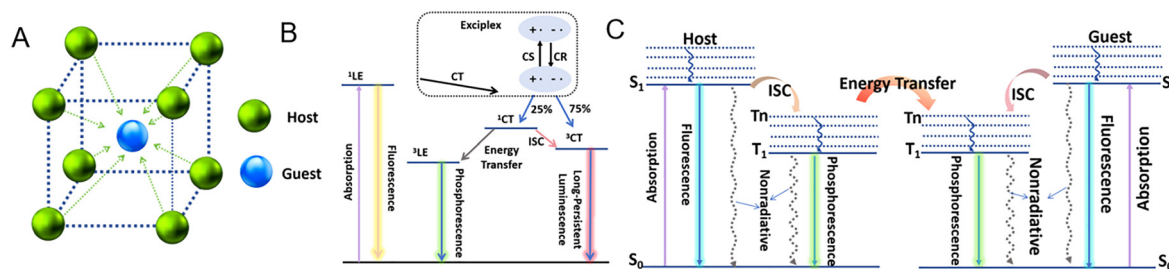


Fig. 1 The representative strategies for molecular doping RTP systems. (A) Rigidification strategy, (B) charge transfer strategy, (C) energy transfer strategy.

RTP emission. The matrix of doped RTP materials is often a rigid skeleton material (such as polymers, organic crystals, inorganic organic hybrid materials, MOFs, *etc.*), which serves (1) to provide a confined environment and suppress the vibration/rotational relaxation of dopant molecules; (2) as an “energy transfer medium”, and it absorbs photons and transfers energy to dopants; (3) by regulating the electronic energy levels and spin orbit coupling (SOC) strength of dopants through hydrogen bonding, coordination bonding, and other means. As a phosphorescent luminescent center, dopants need to possess two characteristics: (1) efficient ISC capability and (2) the triplet exciton has high efficiency in radiative transition to the ground state (*i.e.*, high phosphorescence quantum yields).

According to El-Sayed's rule, the ISC rate can be qualitatively estimated. If the singlet (S) and triplet (T) transitions involve changes in molecular orbital types, the ISC rate is relatively high. The ISC rate is mainly determined by  $\text{SOC}\langle S|\hat{H}_{\text{SOC}}|T\rangle$  and the energy difference  $\Delta E_{\text{ST}}$  between the S and T states, and the spin orbit coupling strength  $\lambda$  is proportional to the spin orbit coupling energy  $E_{\text{SO}}$  and inversely proportional to  $\Delta E_{\text{ST}}$ . To promote exciton ISC, it is necessary to either increase  $E_{\text{SO}}$  or decrease  $\Delta E_{\text{ST}}$ . Since  $E_{\text{SO}}$  is a function of atomic number and is related to electronic orbitals and spin magnetic moments, introducing atoms with higher atomic numbers into molecules can increase  $E_{\text{SO}}$ , enhance spin coupling between the singlet and triplet electronic orbitals, and make ISC more likely to occur. However, spin-orbit coupling weakens the transition barrier for triplet electrons to the ground state  $S_0$  and shortens the phosphorescence lifetime.

$$k_{\text{isc}} \propto |\langle S|\hat{H}_{\text{SOC}}|T\rangle|^2 \exp(-\Delta E_{\text{ST}}^2) \quad (1)$$

$$\lambda = E_{\text{SO}}/\Delta E_{\text{ST}} \quad (2)$$

In the equation,  $k_{\text{isc}}$  is the rate of intersystem crossing,  $\hat{H}$  is the Hamiltonian operator,  $\lambda$  is the spin-orbit coupling strength,  $\Delta E_{\text{ST}}$  represents the energy difference between the singlet and triplet states, and  $E_{\text{SO}}$  is the spin-orbit coupling energy.

In the exciton complex, matched donors and acceptors act as the guest and host matrix, respectively, exhibiting prominent RTP characteristics. In the exciton complex system, the selected electron donor and acceptor form a strong charge transfer (CT) state, promoting charge separation and transfer and generating free radical anions and cations under external excitation. Free radical anions migrate through charge hopping between receptor molecules, forming stable charge-separated states. The free radical anions and cations gradually recombine, producing long-lived radical complex RTP emission. In addition, doping fluorescent dyes (triplet energy acceptors) into the RTP host (triplet energy donor) can enhance the sensitized RTP emission of fluorescent dyes through triplet to singlet Förster resonance energy transfer (FRET) or the Dexter energy transfer process between triplet states, further obtaining doped RTP systems.

Based on the type of doping system, they can be classified into organic-organic, inorganic-organic, metal complexes, and inorganic doping systems. Organic-organic doping (*e.g.*, polymer/crystal with organic small molecules) relies on matrix rigid

confinement and the ISC (heavy atom/ICT effect) of the dopant, with energy transfer primarily *via* FRET. Inorganic-organic doping (*e.g.*, MOF/quantum dots with organic small molecules) achieves high Dexter transfer efficiency through channel confinement and heavy-atom effects at metal nodes (*e.g.*,  $\text{Zr}^{4+}$  and  $\text{Zn}^{2+}$ ). Inorganic doping (oxides with rare-earth ions) exhibits pronounced long afterglow characteristics due to f-f transitions of rare-earth ions and trap state regulation by the matrix. Representative doping systems are shown in Table 1.

## 2.2. Progress in the host-guest doping strategy of organic small molecules

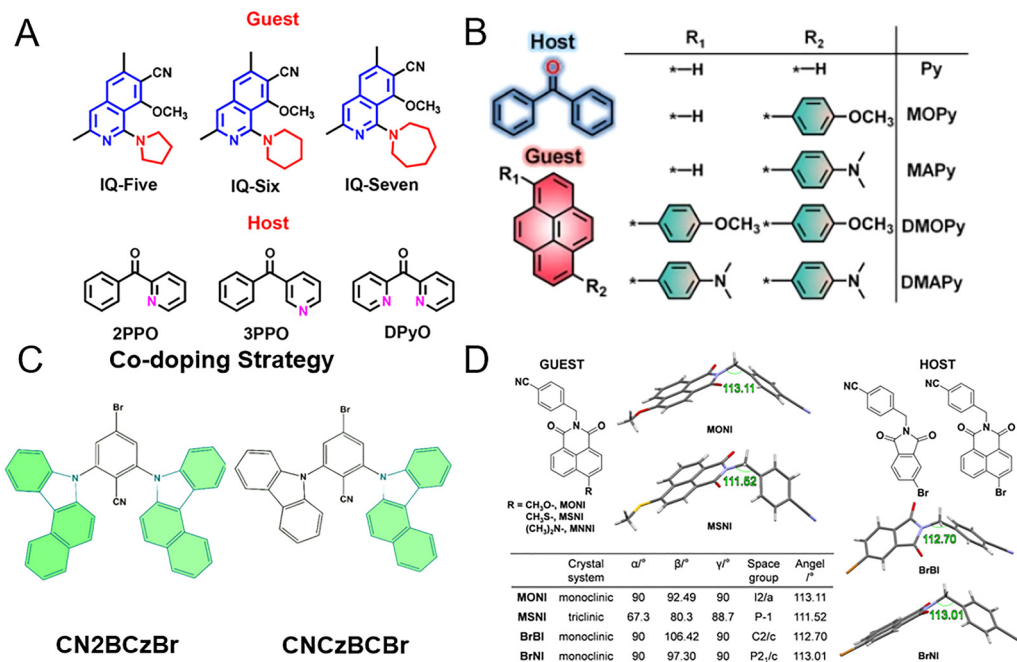
The host-guest doping strategy of organic small molecules exhibits unique advantages in suppressing non-radiative deactivation of guests and regulating luminescent properties by constructing host-guest systems. Small-molecule host materials can restrict the movement of guest molecules through rigid frameworks and promote ISC of guest excitons by adjusting the energy gap between the host and the guest. Xu *et al.* proposed that when the energy gap between the host and the guest satisfies  $\Delta E(\text{H}) > \Delta E(\text{H} \rightarrow \text{G} \text{ or } \text{G} \rightarrow \text{H}) > \Delta E(\text{G})$  [where  $\Delta E(\text{H})$  and  $\Delta E(\text{G})$  represent the (highest occupied molecular orbital - lowest unoccupied molecular orbital) HOMO-LUMO energy gaps of host and guest molecules, respectively;  $\Delta E(\text{H} \rightarrow \text{G})$  denotes the energy gap between the LUMO of the guest and the HOMO of the host;  $\Delta E(\text{G} \rightarrow \text{H})$  denotes the energy gap between the LUMO of the host and the HOMO of the guest], the doped materials exhibit RTP properties. Small-molecule hosts such as triphenylphosphine oxide and dibenzothiophene (DBT) have been confirmed to effectively enhance the luminescence performance of corresponding guest molecules.<sup>15</sup>

### 2.2.1. Guest molecular design and performance regulation.

In terms of guest molecular design and performance regulation, researchers have continuously explored novel molecular structures to break through performance bottlenecks. In 2021, isoquinoline-based guests designed by Dong's team were dispersed in the host in the form of clusters.<sup>16</sup> The strong intermolecular interactions among guests stabilized triplet excitons, while the weak intermolecular interactions of the host enabled it to flexibly accommodate guest clusters, synergistically endowing the material with excellent RTP performance (Fig. 2A). In 2022, Ding's team extended the conjugation system of guests to lower the triplet energy level (Fig. 2B), combined with host-assisted exciton transfer, and successfully prepared near-infrared RTP materials with long wavelengths (600/657–681/732 nm) and long lifetimes (102–324 ms), breaking through the limitation of the energy gap law.<sup>17</sup> Subsequent studies have continued to deepen. Ma's team co-doped benzof[*j*]indole and carbazole derivatives, activated ultralong organic RTP (UORTP) through oxygen consumption in PMMA films (Fig. 2C), and achieved the photoactivated time-dependent color change *via* the lifetime difference of dual guests.<sup>18</sup> Zhang's team found that fluorescent naphthalimide derivatives can efficiently generate ultralong RTP (quantum yield  $\phi = 0.17$  and lifetime  $\tau = 243$  ms) in phthalimide hosts (Fig. 2D), further confirming the key role of strong host-guest interactions in exciton stabilization.<sup>19</sup>

**Table 1** The performance (lifetime, quantum yield, and stability) of different representative room-temperature phosphorescence doping systems

Type of RTP doping system	Representative doping components	Core mechanism	Performance data	Stability	Core advantages	Ref.
Organic small molecule host-guest doping system	(1) Host: triphenylphosphine oxide and dibenzothiophene (DBT); guest: isoquinoline derivatives	(1) Rigid host restricts guest motion; host-guest energy gap regulates ISC	(1) NIR RTP: emission 600/657–681/732 nm and $\tau = 102$ –324 ms	(1) O <sub>2</sub> -sensitive (e.g., benzo[ <i>f</i> ]indole/ carbazole in PMMA)	(1) Precisely tunable emission (green to NIR)	15–24
	(2) Host: phthalimide; guest: fluorescent naphthalimide derivatives	(2) Strong host-guest interaction stabilizes excitons; rigid host reduces guest vibration	(2) Ultralong RTP: $\Phi = 0.17$ , $\tau = 243$ ms	(2) Crystalline state (DBT-doped NT) > amorphous stability	(2) Clear host-guest interaction for mechanism study	
	(3) Host: PAB (ionic polymer); guest: bromide-containing compounds	(3) Bromide promotes ISC (heavy-atom effect); rigid ionic network inhibits non-radiative transitions	(3) Efficient stable RTP ( $\tau/\Phi$ unspecified)	(3) Amorphous materials: good processability	(3) Integrated design (PAB) for easy fabrication	
Polymer doping system	(1) Host: $\epsilon$ -polylysine ( $\epsilon$ -PL); guest: 9,10-diaminophenanthrene	(1) Rigid matrix restricts chromophores; chain entanglement inhibits quenching	(1) $\tau = 2504.7$ ms and afterglow = 15 s	(1) Humidity-sensitive (H-bond cleavage quenches triplets)	(1) Color-tunable (blue to red) for displays	38,39, 41,47
	(2) Host: pectin (PC)-melamine formaldehyde (MF) aerogel; guest: fluorescent molecules	(2) FRET tunes afterglow; non-covalent interaction builds a rigid network	(2) Afterglow 504 $\rightarrow$ 576/620 nm, $\tau = 1.99$ s, and modulus = 4.14 MPa	(2) Excellent mechanical stability; low friction coefficient	2. Balanced rigidity/lifetime for flexible devices	
	(3) Host: polyvinyl alcohol (PVA); guest: SDP, ODP, and 2,2-db	(3) Hydroxyl H-bonding inhibits non-radiative transitions	(3) UV-responsive ultralong RTP ( $\tau/\Phi$ unspecified)	(3) Stable in the dry/light-shielded environment	(3) Low-cost and simple fabrication	
	(4) Host: polyacrylic acid (PAA); guest: 1,10-phenanthroline (nitrogen-containing aromatics)	(4) Proton/charge transfer promotes ISC; spatial confinement reduces decay	(4) pRTP $\tau = 841$ ms	(4) Stable in high polarity; short-term humid use	(4) Heavy-atom-free, eco-friendly for sensing	
Supramolecular self-assembly system	(1) Host: cucurbituril (CB[6], CB[7], and CB[8]); guest: bromophenylmethylpyridine (PY) and benzopyridinium derivatives	(1) CB cavity encapsulates guest to promote ISC/ inhibit non-radiative decay	1. PYCl@CB[6]: $\Phi = 0.4\% \rightarrow 81.2\%$ ; guest@CB[6]: $\tau = 2.62$ s	(1) Solid: stable in ambient; aqueous: stable for hours	(1) Reversible interaction for dynamic regulation	51,52,54, 56,57
	(2) Host: $\beta$ -cyclodextrin; guest: 4,4'-biphenylboronic acid	(2) Host-guest inclusion restricts motion; H-bond stabilizes triplets	(2) Aqueous $\tau = 1.03$ s	(2) pH-tolerant (3–10)	(2) First aqueous ultralong RTP for bioapplications	
	(3) Host: pillar[5]arene derivative; guest: bromoethane (heavy atom source)	(3) Intracavity charge transfer (ILCT) enhances emission; heavy atom promotes ISC	(3) Alkyl halide-responsive RTP ( $\tau/\Phi$ unspecified)	(3) Solid stable; O <sub>2</sub> -sensitive (inert storage needed)	(3) Alkyl halide-responsive for chemical sensing	
Porous organic framework doping system	(1) Host: COF; guest: halogenated phenyldiboronic acid (covalent doping), coronene (Cor)/d-Cor (non-covalent doping)	1. Covalent/non-covalent doping tunes energy gaps; the rigid COF framework inhibits non-radiative decay	(1) Cor/d-Cor@COF-1: $\tau = 2830$ ms; halogen-doped COF: $\Phi \leq 29\%$	(1) COF: acid/base (pH 2–12)/solvent-resistant, and stable at < 400 °C	(1) COF: porous for gas sensing (O <sub>2</sub> ); customizable structure	60–63,66
	(2) Host: MOF-5; guest: phosphorescent molecules	(2) Water-induced MOF transformation (MOF-5 $\rightarrow$ ZnBDC·XH <sub>2</sub> O) activates RTP	(2) Water-activated RTP ( $\tau/\Phi$ unspecified)	(2) MOF: stable in humidity after activation; unstable at > 300 °C	(2) MOF: water-responsive for humidity sensing	
	(3) Host: HOF (melamine matrix); guest: cytosine (Ct), adenine (Ae), and thymine (Tm)	(3) Host-guest H-bonding stabilizes triplets; “1 + 1 > 2” sensitization for PL/phosphorescence	(3) PL = 94.55% and phosphorescence = 37.11% (sensitization effect)	(3) PL = ambient stability (solid state)	(3) HOF: high PL/phosphorescence efficiency for bioimaging	
Nanoscale doping system	(1) Host: 2D perovskite (B-EACC); guest: Mn <sup>2+</sup> and Mm ions	(1) Rigid inorganic layer inhibits non-radiative recombination; doping passivates traps	(1) Mn <sup>2+</sup> -doped: 610 nm red RTP, $\Phi = 44.11\%$ ; B-EACC: $\tau = 579$ ms, $\Phi = 14.86\%$	(1) Humidity/heat-sensitive (degrades at 85 °C/85% RH)	(1) Full-color emission (blue-green to red) for displays	69–72, 74–77
	(2) Host: carbon dots (CDs); guest: B/N/F heteroatoms, B <sub>2</sub> O <sub>3</sub> , and carboxymethylcellulose (CMC)	(2) CDs' (n, $\pi^*$ )/( $\pi,\pi^*$ ) promotes ISC; doping enhances spin-orbit coupling (SOC)	(2) B-CD@B <sub>2</sub> O <sub>3</sub> : afterglow = 5–12 s; Si-doped CDs: $\tau = 9.48$ –492.39 ms	2. Amorphous CDs: stable against light/solvents	(2) Gram-scale synthesis; biocompatible for bioimaging	



**Fig. 2** (A) Chemical structures of the guest and host molecules. Reprinted with permission from ref. 16. Copyright 2021 American Chemical Society. (B) Molecular structures of the guest and host molecules. Reprinted with permission from ref. 17. Copyright 2022 The Author(s). (C) Structures of **CNCzBCzBr** and **CN2BCzBr** compounds in the co-doping strategy. Reprinted with permission from ref. 18. Copyright 2023 The Royal Society of Chemistry. (D) Stick models showing  $sp^3$ -carbon-linked organic guest and host structures. Reprinted with permission from ref. 19. Copyright 2021 Wiley-VCH GmbH.

Huang's team designed DTPPAO and tBuDTPPAO, with a twisted donor-acceptor-acceptor (D-A-A') configuration.<sup>20</sup> By doping these molecules into different matrices, dual-emissive afterglow consisting of thermally activated delayed fluorescence (TADF) and RTP with tunable lifetimes (86.1–287.7 ms) is achieved. In 2021, the Huang team achieved a wide range of adjustable phosphorescence lifetimes from 3.9 ms to 376.9 ms by adjusting the triplet state energy levels of the host matrix, and its CIE chromaticity coordinate range was (0.39–0.42, 0.52–0.55).<sup>21</sup> The mechanism is that the host molecule provides a rigid environment to inhibit the motion of the guest molecule and the triplet quenching. Huang's team designed and synthesized host (H1, H2) and guest (G1–G3) molecules containing phosphine oxide groups, and constructed an amorphous host-guest ultra-long organic phosphorescence system.<sup>22</sup> By adjusting the ratio of host to guest, the saturation time of light activation can be adjusted in the range of 4 s to 6 s.

**2.2.2. Host material functionalization and energy transfer mechanism.** Significant progress has also been made in the functionalization of host materials. In 2022, Liu's team found that DBT hosts doped with 1 mol% nitrotoluene (NT) immediately induced orange phosphorescence.<sup>23</sup> Experiments on their derivatives, BrBDBT and BrBNT isomers, further indicated that host crystallinity and guest doping sites significantly regulate RTP performance (Fig. 3A). In the same year, Zhang's team deposited trace pyridine (Py) molecules on the surface of flexible needle-like triphenylethylene (TPhE) crystals, achieving high-brightness deep red RTP emission in centimeter-scale needle crystals *via* fluorescence resonance energy transfer (FRET) between the host and the

guest, which is rare in organic crystals.<sup>24</sup> The Ma team constructed a doped room temperature phosphorescence system based on exciton complexes. The host-guest materials were purified to eliminate impurity interference, and then the energy transfer process of charge transfer states in the exciton complexes was adjusted by introducing a third component.<sup>25</sup> This successfully achieved long afterglow luminescence with red delayed fluorescence and visible light excitation. Subsequently, a series of two-component long-lasting phosphorescent materials were constructed using polycyclic aromatic hydrocarbons as dopants and diphenylmethanone and its derivatives as the main materials.<sup>26</sup> By combining transient absorption spectroscopy with theoretical simulation, key metastable intermediates (triplet excited complexes) in the long afterglow generation process were observed, and a novel non-radiative energy transfer mechanism was proposed.

Beyond regulating RTP performance through guest doping or surface molecule deposition, adjusting the intrinsic structural properties of host materials also emerges as an effective strategy to manipulate triplet exciton behavior. Li's team realized the controllable transition of triplet excitons in the naphthalimide derivative NDOH by adjusting the conjugation length of host materials.<sup>27</sup> When the energy gap of the lowest triplet excited state between the host and the guest increased from 0.03 eV to 0.17 eV, the intensity ratio of TADF to RTP decreased by 200 times, leading to a significant red-shift of afterglow color (Fig. 3B). Mechanistic studies revealed that the short conjugation length of hosts increased the band gap, promoting efficient Dexter energy transfer while inhibiting Förster energy transfer.

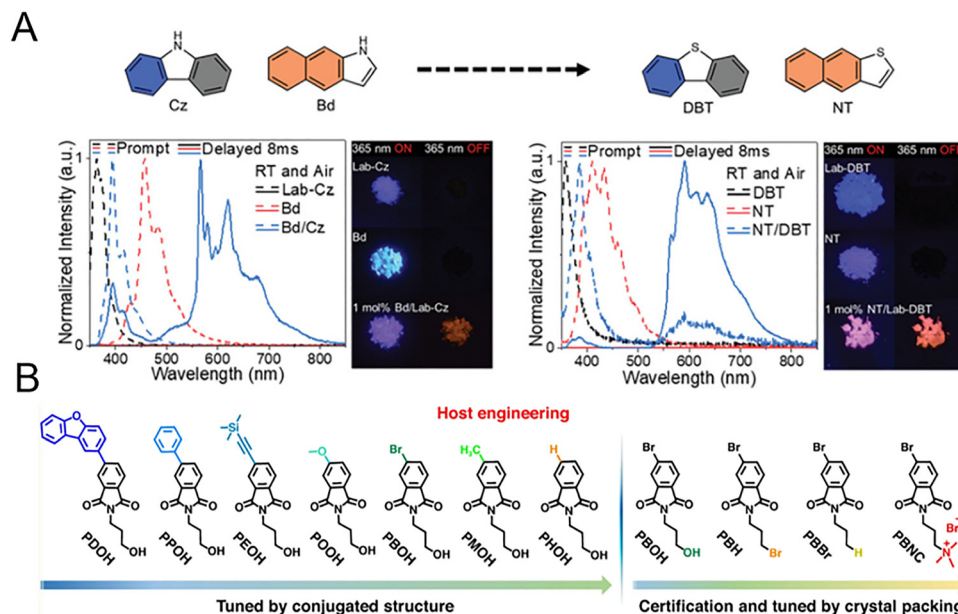


Fig. 3 (A) Chemical structures of Cz, Bd, DBT, and NT. Prompt and delayed (8 ms) photoluminescence (PL) spectra of crystalline powder components. Reprinted with permission from ref. 23. Copyright 2022 Wiley-VCH GmbH. (B) Chemical structures of the host molecules in host engineering. Reprinted with permission from ref. 27. Copyright 2024, The Author(s).

Li's team introduced methyl groups at the 1-position of the O-PTZ core or the ortho-position of the benzene substituent, and five derivatives with quasi-axial (ax) and quasi-equatorial (eq) conformations were prepared, realizing the precise regulation of molecular conformation; second, drawing on the research idea of the protein multi-level structure, a three-level structural model of "chemical structure – molecular conformation – molecular aggregation" for organic solids was proposed, which clarifies that low-level structures affect the formation of high-level structures, and molecular aggregation (tertiary structure) determines the final RTP performance.<sup>28</sup>

### 2.2.3. Application expansion of the host-guest doping strategy.

The host-guest doping strategy has also achieved fruitful results in multi-field applications. Tian's team realized multi-mode stimulus-responsive RTP by doping butterfly-shaped guest DPACs into small-molecule hosts (Fig. 4A).<sup>29</sup> Leveraging host crystallinity, the host-guest cocrystalline material developed by Yang's team not only exhibited a RTP lifetime of 0.82 s and a quantum yield of 12.3% (Fig. 4B), but also allowed afterglow color tuning by introducing fluorescent dyes.<sup>30</sup> Huang's team used polyacrylic acid (PAA) as the host to achieve high-temperature phosphorescence (HTP) with a lifetime of 208 ms at 373 K (Fig. 4C), demonstrating that strong host-guest interactions can effectively suppress non-radiative transitions at high temperatures.<sup>31</sup> The benzophenone derivative/carbazole guest system constructed by Ma's team achieved a RTP lifetime of 501.23 ms and a quantum yield of 31.19% (Fig. 4D), with its unique dual-band emission (550 nm/600 nm) originating from the synergistic effect of local triplet characteristics of guest monomers and the molecular structure of hosts.<sup>32</sup> In the development of characteristic materials, Dong's team doped naphthalenediimide guests into chiral tartaric acid hosts to prepare near-infrared circularly polarized RTP (CP RTP)

materials, realizing phosphorescence color tuning from green to red.<sup>33</sup>

Huang's team used the local rigid design strategy and host-guest coordination strategy to construct a  $\pi$ -conjugated system by introducing dibenzothiophene, so that the molecular absorption and excitation spectra were red-shifted to the visible light region.<sup>34</sup> And, they successfully synthesized three derivatives (Cphpz, 10-Cphpz, and 20-Cphpz) through a molecular locking strategy and sulfur atom oxidation regulation.<sup>35</sup> The benzothiazine skeleton is locked by a carbon single bond to enhance rigidity and reduce vibration coupling. At the same time, the oxidation of the sulfur atom (introduction of sulfone groups) and halogen substitution build a wealth of intermolecular interactions (such as C-H $\cdots$ O and C-H $\cdots$  $\pi$ ) to stabilize the triplet exciton. Zhao's team reduced the singlet-triplet energy gap ( $\Delta E_{st}$ ) by using the dipole-dipole interaction, thus realizing the high-efficiency afterglow of TADF.<sup>36</sup> Organic long afterglow is generated by charge separation (CS) and delayed charge recombination (CR), and the afterglow duration is extended to several hours. Aiming at the challenges of cumbersome crystal cultivation and poor performance in the powder state during the preparation of organic RTP materials, Yang's team achieved efficient RTP emission in the powder state by designing phosphors with benzophenone (BP) as the core.<sup>37</sup> The RTP lifetime of the powder state reached 64.12 ms, which was comparable to that of the crystalline state (64.48 ms), and the maximum quantum yield reached 4.33%.

**2.2.4. Key scientific issues and development trends.** Despite significant breakthroughs in the host-guest doping strategy for organic small molecules, current research confronts two pivotal challenges: the synergistic enhancement of near-infrared RTP efficiency and lifetime, and the precise regulation of exciton dynamics in complex environments.

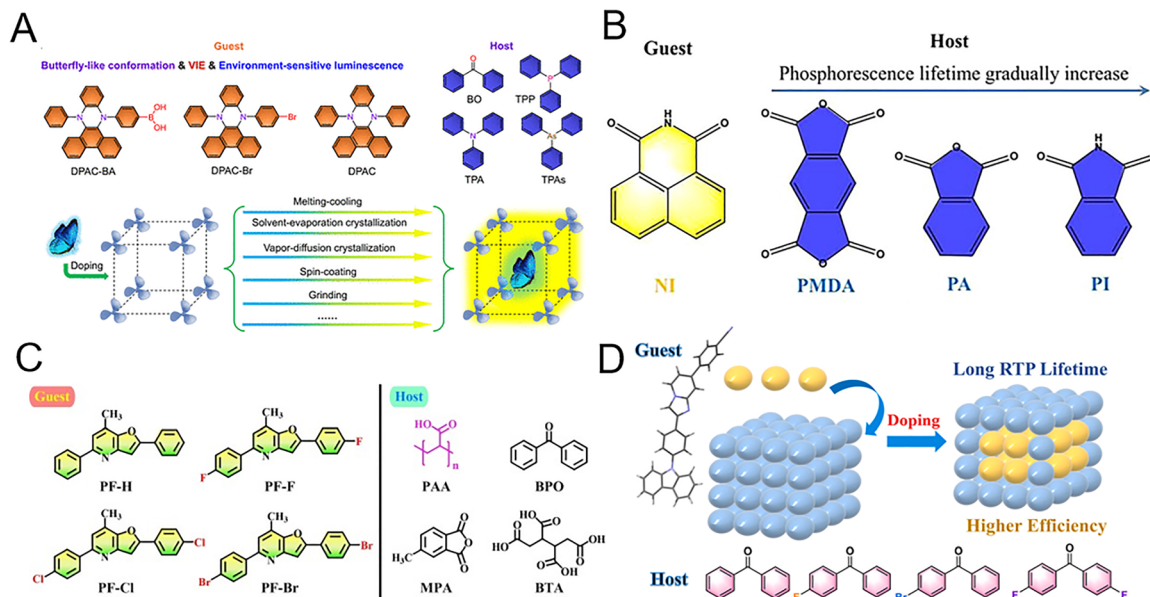


Fig. 4 (A) Components, fabrication, and the working mechanism of RTP systems. Reprinted with permission from ref. 29. Copyright 2024 The Authors. (B) Structure of host (PMDA/PA/PI) and guest (NI) molecules. Reprinted with permission from ref. 30. Copyright 2024 American Chemical Society. (C) Chemical structures of guest diarylfuro[3,2-*b*]pyridine derivatives and host molecules. Reprinted with permission from ref. 31. Copyright 2024 Elsevier B.V. All rights reserved. (D) Construction and fine-tuning of host-guest doping systems and the underlying mechanism of room temperature phosphorescence. Reprinted with permission from ref. 32. Copyright 2023 Elsevier Ltd. All rights reserved.

Organic small-molecule-doped RTP materials exhibit enormous application potential in diverse fields such as bioimaging, optical recording, information storage, and anti-counterfeiting, owing to their unique properties, including long lifetime, high brightness, and tunable emission colors. With ongoing research, optimizing matrix materials, developing novel host molecules, and designing intelligent responsive systems are expected to further expand their practical applications. However, critical issues remain, such as improving luminescence brightness and lifetime, as well as enhancing stability under high-temperature, aqueous, or oxygen-rich conditions. These necessitate in-depth investigations into the interaction mechanisms between small molecules and matrices, aiming to precisely tailor phosphorescence properties (*e.g.*, increasing quantum yields, extending phosphorescence lifetimes, and broadening emission wavelength ranges) through molecular design and material selection. Additionally, efforts should focus on developing simple, efficient, and cost-effective fabrication processes to enhance material stability and reproducibility.

Future research directions could focus on energy level engineering with D- $\sigma$ -A type hosts to precisely modulate the energy level matching between hosts and guests, thereby enabling broad-spectrum RTP emission; biomimetic multilevel structure design that leverages supramolecular interactions like hydrogen bonding and  $\pi$ - $\pi$  stacking to enhance exciton stability and suppress non-radiative transitions; and the development of intelligent responsive doping systems by integrating stimulus-responsive host materials such as temperature-sensitive or light-sensitive polymers, which can promote practical applications in dynamic encryption, bioimaging, and optoelectronic devices.

### 2.3. Polymer doping strategy for RTP

With the deepening research on organic RTP materials, RTP systems based on doped polymers have attracted extensive attention due to their environmental friendliness and easy modification. Host-guest doped organic RTP materials based on polymeric matrices exhibit broad application potential in biological, chemical, and optoelectronic fields, attributed to advantages such as simple preparation, flexible structural design, functional diversity, high phosphorescence efficiency, long lifetime, processability into flexible transparent films, low cost, and low toxicity. The persistent luminescence after ceasing external excitation significantly expands their application scenarios, primarily attributed to the unique advantages of polymeric materials over organic small molecules—excellent flexibility and ductility, good entanglement and rigidity, superior stability and processability, and unique electron mobility and thermal conductivity. Additionally, the low toxicity, low cost, and abundant resource reserves of polymers endow them with significant natural advantages in developing pure organic eco-friendly materials. The high molecular weight and long-chain structure of polymers lead to molecular chain entanglement and the formation of a highly rigid environment, which suppresses the vibration and rotation of phosphorescent chromophores through rich intermolecular interactions, reducing quenching by environmental oxygen and moisture. This allows triplet excitons to survive long enough at room temperature to exhibit phosphorescence. Recently, multiple strategies have been developed for preparing polymeric RTP materials, including doping, copolymerization, homopolymerization, and host-guest inclusion.

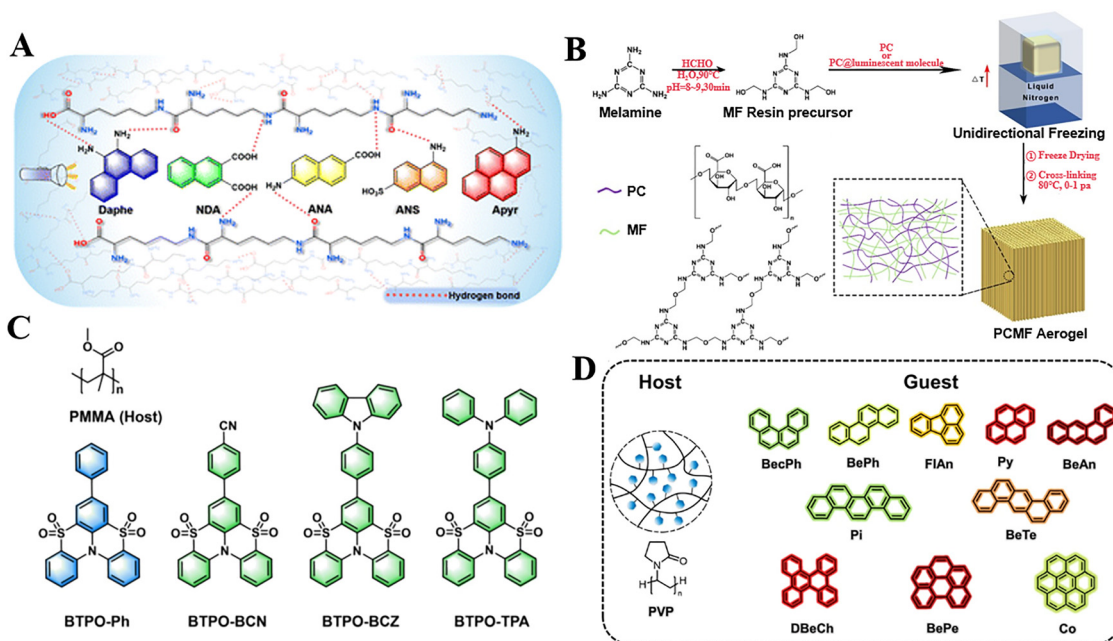
**2.3.1. Recent advances in polymer-doped RTP systems.** Following the strategy of constructing long-afterglow materials

via guest–host doping or polymer matrix regulation, researchers have also explored composite systems and novel molecular cores to further optimize RTP performance and expand functional applications. Wang and his research team successfully created a range of materials with adjustable colors (from blue to red) and long afterglow qualities by doping guest molecules into  $\epsilon$ -polylysine ( $\epsilon$ -PL).<sup>38</sup> Luminescent groups are given a stiff environment by the polymer matrix, which produces amorphous polymers with various long-term afterglow characteristics (Fig. 5A). Guo *et al.* recently prepared a composite aerogel by using the non-covalent interaction between pectin (PC) and melamine formaldehyde (MF) through resonance energy transfer (Fig. 5B).<sup>39</sup> The afterglow wavelength was found to shift from 504 nm to 576 nm and 620 nm, producing aerogel 30 with ultra-long yellow and red afterglow. The composite aerogel displays noteworthy stability and persistent phosphorescence, exhibiting a service life of 1.99 s and exceptional mechanical properties. Its compression modulus reaches 4.14 MPa, which is 490.8 times higher than that of the pure PC aerogel. Ma *et al.* proposed a novel phosphor based on a heteroarylsulfone-locked triphenylamine core (BTPO),<sup>40</sup> which exhibits excellent long afterglow properties in doped polymer matrices, with a lifetime of up to 818 ms and a quantum efficiency exceeding 20%. This performance is attributable to an efficient multi-channel ISC process driven by a narrow singlet–triplet energy gap and strong SOC between the lowest singlet state ( $S_1$ ) and higher triplet states (Fig. 5C). This mechanism is known to promote the generation of numerous triplet excitons, while the

relatively pure ( $\pi$ ,  $\pi^*$ ) configuration of the lowest triplet state ( $T_1$ ) ensures a low phosphorescence radiation rate ( $k_p$ ), thereby extending the lifetime.

Zhao's team selected eight kinds of organic phosphorescent materials, including SDP, ODP, and 2,2-db, and built an ultra-violet irradiation-responsive ultralong room-temperature phosphorescence system by doping them into polyvinyl alcohol (PVA).<sup>41</sup> The hydroxyl group in PVA can form a large number of hydrogen bonds with these phosphorescent materials, which will initially inhibit the non-radiative transition. Zhao and Huang's research team used acrylic acid (AA) as the main polymer chain, covalently grafted vinyl functionalized light-emitting units with different conjugation degrees onto the PAA chain through free radical cross-linking copolymerization, forming a dense hydrogen bond network, and constructing a rigid microenvironment.<sup>42</sup> This rigid microenvironment can not only limit the molecular vibration to reduce the non-radiative attenuation, but also isolate the triplet exciton in the oxygen-wet environment and suppress its quenching phenomenon. Chen's team utilized the self-assembly of terpyridine (Tpy) derivatives to form excimer complexes, which significantly reduces the singlet–triplet splitting energy ( $\Delta E_{ST}$ ) and thereby promotes the ISC process.<sup>43</sup> Meanwhile, the multiple hydrogen bonding confinement between PVA and Tpy, coupled with the compact aggregation of phosphors, collectively suppresses nonradiative transitions.

**2.3.2. Functional polymer matrices and mechanistic innovations.** This focus on optimizing RTP performance and functionality through the rational design of polymer matrices

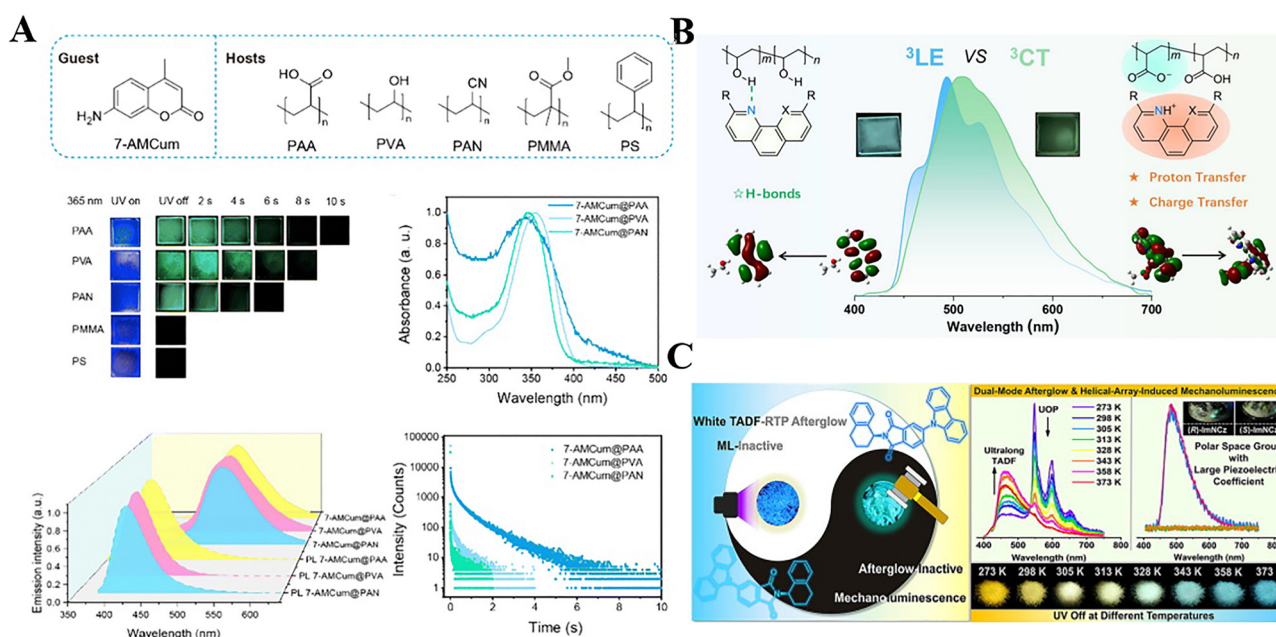


**Fig. 5** (A)  $\epsilon$ -Polylysine organic ultra-long room-temperature phosphorescent materials based on phosphorescent molecule doping. Reprinted with permission from ref. 38. Copyright 2024 The Royal Society of Chemistry. (B) Preparation process of the PCMF composite aerogel and the luminescent molecule doped PCMF composite aerogel. Reprinted with permission from ref. 39. Copyright 2025 Elsevier Inc. All rights are reserved, including those for text and data mining, AI training, and similar technologies. (C) Chemical structures of BTPO derivatives. Reprinted with permission from ref. 40. Copyright 2022 Elsevier B.V. All rights reserved. (D) Molecular structures of the host and guest molecules. Reprinted with permission from ref. 9. Copyright 2024, The Author(s).

(either *via* blending or selection of specific host polymers) has been further advanced by other research teams, who have explored diverse guest–host combinations and matrix types to expand material capabilities. The Dang team utilized highly conjugated PAH molecules as the guest and PVP as the host to construct an organic resonance energy transfer polymer based on tunable luminescent polymers.<sup>9</sup> These materials exhibit various phosphorescence wavelengths ranging from 550 nm to 757 nm and excellent photoactivation properties (Fig. 5D). Qiu *et al.* prepared RTP materials with tunable photophysical and mechanical properties *via* heterogeneous polymer matrices.<sup>44</sup> By doping difluoroboron  $\beta$ -diketonate derivatives into a blend of polystyrene (PS) and polybutadiene (PB), bright and persistent afterglow was achieved—neither pure PS nor PB alone exhibits RTP emission. Additionally, by adjusting the composition ratio of the polymer matrix, the Young's modulus of the prepared RTP materials can be conveniently regulated using the modulus difference between PS and PB. The Liang team achieved persistent RTP by doping polar coumarin derivatives with intramolecular charge transfer properties into a polymer matrix.<sup>45</sup> It was demonstrated that the polymers under investigation, PAA, were the most effective matrix in the present study. The results of the study also demonstrated that 7-AMCum@PAA and 7-DEAMCum@PAA were the most effective combinations (Fig. 6A). The phosphorescent film has a long lifetime of 711 ms and a high phosphorescence quantum yield of 31.29%. Qin's research team transformed the matrix from a pure hydrogen-bond network into a “hydrogen bond-covalent bond” composite cross-linked structure through boron-oxygen (B–O) covalent cross-linking between boric acid (BA) and

PVA.<sup>46</sup> This modification significantly enhances the rigidity of the matrix while suppressing the quenching of triplet excitons by oxygen and water vapor, breaking the traditional trade-off relationship between the two parameters.

To address the challenge posed by non-radiative transitions resulting from intermolecular interactions between small molecules and matrices in highly polar environments, Liu *et al.* combined continuous proton transfer with photoinduced charge transfer mechanisms to promote triplet charge transfer emission in highly polar polymer matrices.<sup>47</sup> The administration of nitrogen-containing aromatic guest compounds (for example, 1,10-phenanthroline and DM Phen, 7,8-benzoquinoline) into PAA has been demonstrated to result in excellent persistent room-temperature phosphorescence (pRTP) performance (Fig. 6B). Spectral studies and theoretical calculations indicate that performance enhancement is due to proton transfer and triplet charge transfer characteristics between the host and the guest. Furthermore, the spatial limitations imposed by PAA result in a maximum pRTP lifespan of 841 ms. Liang *et al.* pioneered the transformation of two classical aggregation-caused quenching (ACQ) compounds, namely sodium fluorescein (FluNa) and sodium calcein (CalNa), into color-tunable dual-mode organic afterglow materials excitable by ultraviolet (UV) light and white light through a host-guest doping strategy, with aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ) serving as the matrix.<sup>48</sup> At room temperature, these materials exhibit afterglow consisting of persistent thermally activated delayed fluorescence (pTADF) and ultralong organic phosphorescence (UOP), with an afterglow lifetime exceeding 600 ms.



**Fig. 6** (A) Chemical structures, photographs, and photophysical properties of 7-AMCum guests and polymer hosts. Reprinted with permission from ref. 45. Copyright 2024 Royal Society of Chemistry. (B) Proton transfer induced persistent triplet charge transfer phosphorescence in molecule-doped polymer systems. Reprinted with permission from ref. 47. Copyright 2021 Elsevier B.V. All rights reserved. (C) Colour-tunable dual-mode afterglows and helical-array-induced mechanoluminescence from AIE enantiomers. Reprinted with permission from ref. 48. Copyright 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

**2.3.3. Emerging materials and application frontiers.** Beyond optimizing molecular structures to regulate non-radiative decay and ISC efficiency, researchers have also explored diverse material systems—from modified polymer matrices to structural engineering of polymers themselves—to achieve high-performance ultra-long room-temperature phosphorescence. Zhang *et al.* prepared a series of organic materials, herein referred to as “ultra-long organic phosphorescent (UOP)” materials,<sup>49</sup> through a complex series of chemical reactions involving the doping of triphenylamine, 9-phenylcarbazole (PCz), and indolo [3,2,1-*jk*] carbazole (ICz) into an MF polymer matrix with a dense three-dimensional covalent network. It has been demonstrated through experimental and theoretical calculations that the restriction of intramolecular motion is of crucial importance in the suppression of non-radiative decay of triplet excitons. This is a prerequisite for achieving ultra-long room-temperature phosphorescence of organic molecules in polymer matrices. Recently, Yang’s team proposed a concise and efficient strategy to achieve ultralong phosphorescence lifetimes by inducing cyclization of polymer chains at room temperature.<sup>50</sup> Carboxyl and cyano groups undergo rearrangement and isomerization, forming imide rings at high temperatures. Compared to linear polymers, cyclized polymers show 17-fold (51.4–914.0 ms) and 9-fold (1.5–14.0%) enhancements in the phosphorescence lifetime and quantum yield, respectively. The mechanism involves significantly enhanced ISC channels due to polymer chain cyclization, coupled with increased system rigidity, enabling efficient phosphorescence at room temperature.

**2.3.4. Current challenges and future prospects.** Despite significant progress in polymer-based RTP materials, critical challenges persist, including non-radiative transitions in high-polarity environments, limited processability for complex functionalization, unclear interaction mechanisms between polymers and dopants, stability issues in harsh conditions, and the need for optimized large-scale fabrication processes to reduce costs. To address the existing challenges, future research should concentrate on designing polymer matrices with hierarchical rigid structures to inhibit exciton quenching in polar media, and simultaneously utilize advanced characterization techniques and theoretical calculations to understand the interaction mechanisms between dopants and polymers. Additionally, efforts should be made to develop smart, responsive RTP systems by incorporating stimuli-responsive polymers such as temperature or pH-sensitive chains, complemented by molecular modification and interfacial engineering to boost environmental stability. Furthermore, exploring copolymerization strategies to achieve the synergistic optimization of phosphorescence efficiency and mechanical properties, along with the creation of green and cost-effective fabrication technologies, will help promote the application of these materials in flexible optoelectronics, biological imaging, and anti-counterfeiting.

## 2.4. Supramolecular self-assembly for room-temperature phosphorescence

**2.4.1. Self-assembly of macrocyclic hosts and guests.** Supramolecular chemistry has emerged as a pivotal field in chemistry, with notable achievements in molecular recognition, assembly,

and machine development. The phenomenon of host–guest interaction pertains to the recognition of guest compounds through reversible non-covalent interactions, encompassing a variety of interactions such as  $\pi$ – $\pi$  stacking, hydrogen bonding, halogen bonding, electrostatic forces, and van der Waals forces. This interaction bears a close relationship with macrocyclic compounds, including cyclodextrin, calixarenes, and cucurbituril (CB), which offer distinct advantages, such as their ability to bind strongly, their ease of synthesis, their water solubility, and their capacity for straightforward modification. These materials have been shown to possess novel properties, including applications in catalysis, drug delivery, biomacromolecule recognition, light-harvesting systems, and RTP materials.

Among the macrocyclic compounds applied in supramolecular-regulated RTP, CBs have attracted significant attention due to their excellent encapsulation capability, and research teams have carried out a series of pioneering studies to validate their effectiveness. Liu’s team in 2019 proposed enhancing RTP through the supramolecular assembly of host–guest complexes.<sup>51</sup> Complexes formed by different counterions (PYX, X = Cl, Br, I, and PF<sub>6</sub>) with bromophenylmethylpyridine (PY) exhibited phosphorescence efficiencies from 0.4% to 24.1%, with PYI showing the highest efficiency (Fig. 7A). Notably, after complexing PYCl with cucurbituril, its phosphorescence efficiency under ambient conditions surged to 81.2%, attributed to CB’s strict encapsulation promoting ISC and inhibiting non-radiative transitions. They further demonstrated persistent RTP in solid-state supramolecules between CB[6] hosts and heavy-atom-free benzylpyridinium guests, where non-phosphorescent guests acquired an ultralong lifetime of 2.62 s upon CB[6] complexation, enabled by tight encapsulation that facilitated ISC, suppressed non-radiative relaxation, and shielded quenchers.

Building on the foundational work of using CBs to enhance RTP *via* host–guest encapsulation, subsequent studies have expanded the scope by exploring novel assembly modes and functional designs of CB-based supramolecular systems. Ma *et al.* reported the assembly of pure organic supramolecular pins composed of alkyl-bridged phenylpyridinium salts and cucurbit[8]uril (CB[8]) (Fig. 7B), which form *via* “one-host-one-guest” and “head-to-tail” interactions—distinct from conventional “one-host-two-guest” or “head-to-tail” binding modes—to overcome electrostatic repulsion and promote intramolecular charge transfer.<sup>52</sup> In the ensuing research, Liu’s team further refined an upgraded strategy for ultralong bright RTP (Fig. 7C),<sup>53</sup> entailing the polymerization of phosphor monomers with acrylamide and host–guest complexation with CB[6,7,8]. In contrast, non-phosphorescent monomers exhibited an ultralong lifetime of 2.46 s following copolymerization with acrylamide. This extended lifetime was attributed to the presence of abundant hydrogen bonds and carbonyl groups within the polymer. These groups were hypothesized to promote ISC, thereby suppressing non-radiative relaxation. The complexation of CB[6,7,8] with RTP resulted in a significant enhancement of the latter’s properties, primarily through the prevention of aggregation-induced quenching.

In 2022, a series of solid supramolecules based on acrylamide-phenylpyridinium copolymers with a range of substituents (P–R:

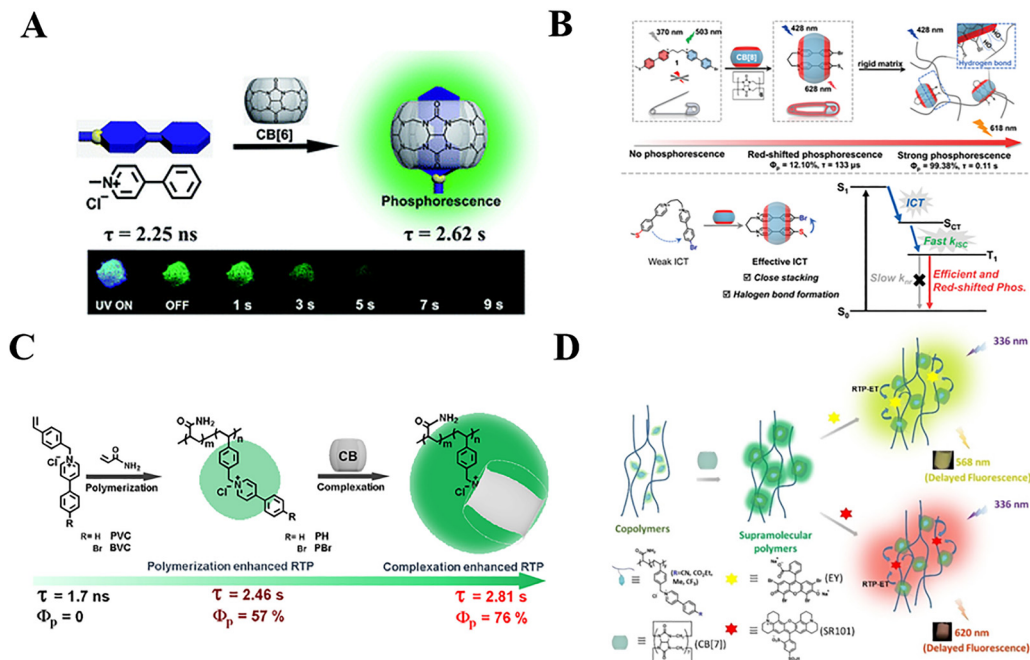


Fig. 7 (A) Ultralong room-temperature phosphorescence of a solid-state supramolecule between phenylmethylpyridinium and cucurbit[6]uril. Reprinted with permission from ref. 51. Copyright 2019 The Royal Society of Chemistry. (B) The formation and mechanism of supramolecular pin1/CB[8]. Reprinted with permission from ref. 52. Copyright 2021 Wiley-VCH GmbH. (C) A synergistic enhancement strategy for realizing ultralong and efficient RTP emission. Reprinted with permission from ref. 53. Copyright 2020 Wiley-VCH GmbH. (D) Supramolecular aggregate for cascaded purely organic RTP capturing with delayed NIR emission in aqueous solution. Reprinted with permission from ref. 54. Copyright 2021 Wiley-VCH GmbH.

R = -CN, -CO<sub>2</sub>Et, -Me, and -CF<sub>3</sub>) and CB[7] were shown to exhibit tunable RTP lifetimes (0.9–2.2 s) in amorphous states.<sup>54</sup> This is probably a consequence of the uncommon host-guest interactions between 4-phenylpyridine and -CF<sub>3</sub> with CB[7] *via* fluorophilic interactions. The RTP supramolecules in question (donors) have the capacity to form ternary systems with organic dyes (Fig. 7D). This enables the occurrence of ultralong phosphorescence energy transfer (PpET) and visible delayed fluorescence, a remarkable occurrence within the field. Liu's team prepared a poly(pseudorotaxane) dry gel by inserting a linear brominated aromatic aldehyde polymer into the cavity of  $\alpha$ -cyclodextrin.<sup>59</sup> It is evident that the network structure of phosphors is significantly restricted, which has a considerable impact on their vibration. In addition, non-radiative relaxation is inhibited, and white light is emitted at room temperature. Consequently, the dry gel displays RTP signals and exhibits dual fluorescence phosphor emission in the presence and absence of water. Furthermore, reversible photoluminescence switching between blue light and white light is realized.

While CBs and  $\alpha$ -cyclodextrin have shown great potential in regulating RTP through supramolecular assembly, other macrocyclic platforms—such as  $\beta$ -cyclodextrin and pillararenes—have also been actively explored to expand the design strategies and functional applications of RTP systems. Tian's team developed a series of amorphous organic small molecules that exhibit highly efficient RTPs through the modification of phosphorescent moieties into  $\beta$ -cyclodextrin.<sup>55</sup> The utilization of hydrogen bonds between cyclodextrin derivatives has been demonstrated to be an effective method of stabilizing phosphors, thereby suppressing

non-radiative relaxation processes and protecting against quenchers (Fig. 8A). This approach has been shown to facilitate efficient RTP, exhibiting satisfactory quantum yields. The research carried out by Li *et al.* revealed an ultralong RTP system in water that was found to have a lifetime of 1.03 s under ambient conditions in 2023 (Fig. 8B), dependent on host-guest inclusion and intermolecular hydrogen bonding. This system was found to be based on  $\beta$ -cyclodextrin hosts and 4,4'-biphenylboronic acid guests.<sup>56</sup> Zhu *et al.* described an alkyl halide-responsive RTP system using a *m*-formylphenyl-containing pillar[5]arene derivative.<sup>57</sup> The treatment of this system with bromoethane, a compound containing a heavy atom, resulted in enhanced emission *via* intraluminal charge transfer (ILCT) (Fig. 8C). Quantum chemical calculations, based on single-crystal X-ray diffraction, revealed the structural determinants of TSCT between the 1,4-dimethoxybenzene donor units and the formylphenyl group of pillar[5]arene. Liu's team assembled multivalent supramolecules  $G \supseteq CB[9]@SC4AD$  using CB[7] and sulfonated hetero[4]arene (SC4AD) modified with low-cycle dodecyl (Fig. 8D), where the spherical nanoparticles (80  $\mu$ m) showed a 40-fold enhanced phosphorescence intensity and a 52.4-fold prolonged lifetime (1.13 ms) compared to  $G \subset CB[7]$ , due to tight packing from co-assembly with amphiphilic SC4AD restricting non-radiative relaxation.<sup>58</sup>

**2.4.2. Room-temperature phosphorescence in porous organic frameworks.** Metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and hydrogen-bonded organic frameworks (HOFs) are star materials with structural diversity, tunability, and versatile applications. MOFs are constructed by metal-ligand coordination, COFs *via* dynamic covalent chemistry, and HOFs

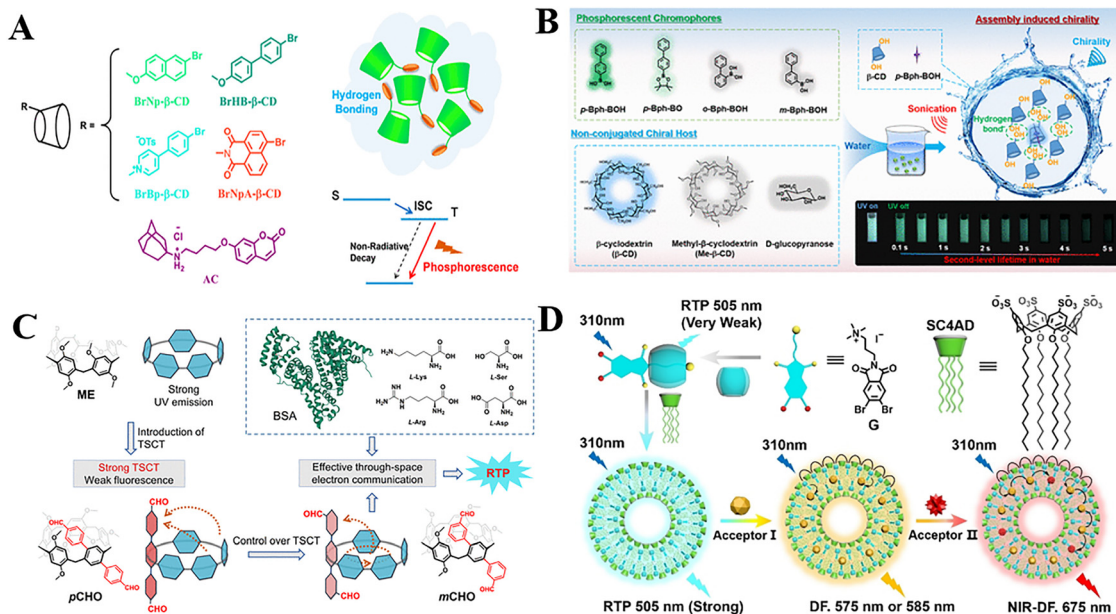


Fig. 8 (A) Molecular structures and the mechanism of RTP emissive cyclodextrin derivatives and the fluorescent guest molecule AC. Reprinted with permission from ref. 55. Copyright 2018 American Chemical Society. (B) The chemical structures of nonconjugated chiral hosts and phosphorescent guests, and the schematic illustration of the assembly process in water. Reprinted with permission from ref. 56. Copyright 2023 American Chemical Society. (C) The effects of structural modification on the intramolecular through-space charge transfer (TSCT) interactions within two isomeric functionalized pillar[5]arene frameworks. Reprinted with permission from ref. 57. Copyright 2023 American Chemical Society. (D) Ultrahigh supramolecular cascaded RTP capturing system. Reprinted with permission from ref. 58. Copyright 2021 Wiley-VCH GmbH.

through intermolecular interactions (*e.g.*, hydrogen bonding and  $\pi$ - $\pi$  stacking). Their unique and common features enable distinct development in luminescence: flexible tuning of luminescence properties (color, wavelength, bandgap, and stacking structure) *via* building block design, rigid frameworks suppressing non-radiative energy loss, highly porous structures with tunable pores for microenvironment control, and well-defined crystal structures facilitating mechanistic studies.

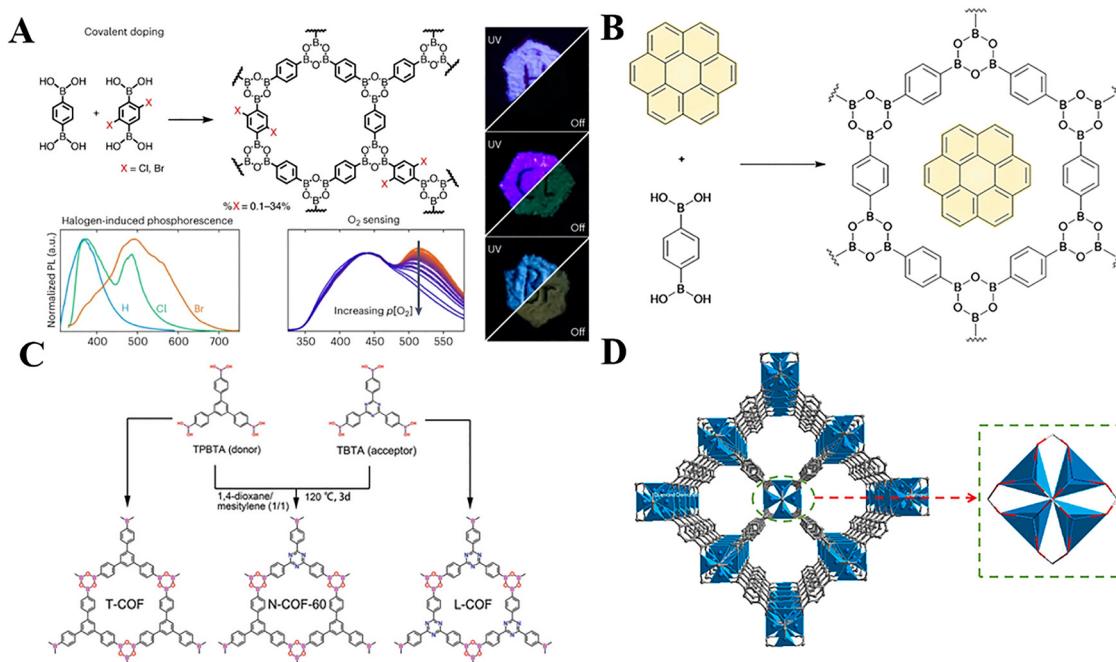
Perepichka's team reported the synthesis of covalently doped COFs, resulting from the copolymerization of halogenated and unsubstituted phenyldiboronic acids (Fig. 9A). This approach facilitates the random distribution of functional units, resulting in high phosphorescence (phos  $\leq$  29%) at room temperature.<sup>60</sup> The permanent porosity of COFs, when combined with singlet-triplet emission channels, has been demonstrated to enable the fabrication of oxygen sensors with ultra-wide dynamic ranges. In 2024, Zhang's team prepared RTP-COF materials with extended phosphorescence lifetimes *via* non-covalent doping and chemical modification.<sup>61</sup> The encapsulation of coronene (Cor) or deuterated coronene (d-Cor) in COF-1 during the synthesis process resulted in the formation of RTP-COFs with lifetimes that extended up to 2830 ms (Fig. 9B). Conversely, the chemical modification of these RTP-COFs with 2-phenylnaphthalene RTP groups yielded lifetimes of 1375 and 826 ms.

Beyond covalent doping and non-covalent encapsulation/chemical modification, researchers have further expanded the design paradigms for RTP-active COFs (and related porous frameworks like MOFs) by exploring energy transfer mechanisms and stimuli-responsive structure engineering. Cao's team in 2025

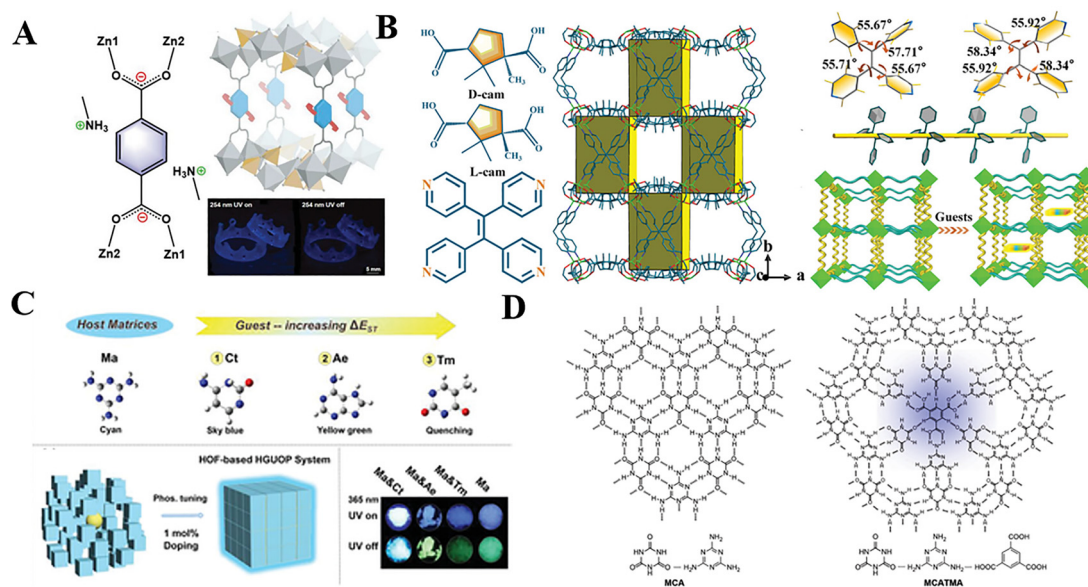
proposed a strategy to enhance RTP in heavy-atom-free COFs using donor-acceptor (D-A) systems, leveraging Förster resonance energy transfer (FRET) and Dexter energy transfer (DET).<sup>62</sup> The best-performing COF showed a phosphorescence lifetime of 4.35 ms at room temperature, with potential anti-counterfeiting applications (Fig. 9C). Duan's team in 2023 developed a hybrid strategy for preparing RTP composites *via* water-induced matrix structure transformation, where spraying water converted initial RTP-silent phosphor@MOF-5 composites into RTP-active phosphor@ZnBDC-XH<sub>2</sub>O (Fig. 9D), with enhanced quantum efficiency and water stability.<sup>63</sup>

Following the exploration of stimuli-responsive and composite strategies for MOF-based RTP, researchers have further advanced MOF design by focusing on ligand functionalization and chiral engineering—two approaches that endow MOFs with both high RTP performance and specialized functional attributes. Liu *et al.* reported a blue RTP MOF *via* ligand functionalization (Fig. 10A), featuring efficient blue RTP (quantum efficiency: 80.6% and lifetime: 169.7 ms) and applicability as MOF ink for 3D printing.<sup>64</sup> Gao *et al.* constructed luminescent chiral MOFs using enantiomeric camphoric acid and 1,1,2,2-tetrakis(pyridin-4-yl)ethylene (tpe) (Fig. 10B), where guest@MOF composites showed excitation wavelength-dependent RTP and dynamic circularly polarized luminescence, with pyrene@DCF-12 achieving a phosphorescence quantum yield of 75.39%.<sup>65</sup>

In a recent study, the Xue and Yan team prepared three HOF-based HGUOP cocrystals (Ma&Ct, Ma&Ae, and Ma&Tm) by doping 1 mol% cytosine (Ct) (Fig. 10C), adenine (Ae), and thymine (Tm) into melamine (Mel) matrices.<sup>66</sup> This method exhibited "1 + 1 > 2"



**Fig. 9** (A) Efficient room-temperature phosphorescence of covalent organic frameworks through covalent halogen doping. Reprinted with permission from ref. 60. Copyright 2022, The Author(s), under exclusive licence to Springer Nature Limited. (B) Schematic representation of synthesis methods for different RTP-COF materials: noncovalent doping. Reprinted with permission from ref. 61. Copyright 2024 American Chemical Society. (C) Synthesis diagram and structural features of N-COFs. Reprinted with permission from ref. 62. Copyright 2024 Wiley-VCH GmbH. (D) Structure of MOF-5 viewed along the *c*-direction. Reprinted with permission from ref. 63. Copyright 2022 Elsevier Ltd. All rights reserved.



**Fig. 10** (A) The ligand chromophores are monodispersed, realized by the designed co-ligands, and meanwhile, the molecular motions are strictly suppressed by coordination and host-guest interactions. Reprinted with permission from ref. 64. Copyright 2021 Wiley-VCH GmbH. (B) The structures and packaging methods of host frameworks and guest emitters. Reprinted with permission from ref. 65. Copyright 2023 Wiley-VCH GmbH. (C) Molecular structures of the host and three guests, and a schematic diagram of the HOF-based HGUOP system. Reprinted with permission from ref. 66. Copyright 2022 Wiley-VCH GmbH. (D) Chemical structures of the MCA-based 2D POA materials, and schematic and molecular structures. Reprinted with permission from ref. 67. Copyright 2022 Wiley-VCH GmbH.

sensitization effects for PL (94.55%) and phosphorescence (37.11%). Zhang *et al.* reported the synthesis of deep blue pure organic afterglow (POA) with high photoluminescence quantum

yield (65%), ultralong lifetime ( $> 1300$  ms), and excellent stability against oxygen, solvents, pressure, light, and heat (Fig. 10D). This was achieved by embedding phosphors in two-dimensional

hydrogen-bonded supralattices.<sup>67</sup> In a significant development, Yang's team has pioneered a method of creating tunable RTP materials *via in situ* self-assembly. This method involves the utilization of doped trimellitic acid (TMA) sensitized phosphors and hydrogen-bonded organic frameworks hardened phosphors, a breakthrough that facilitates intelligent RTP emission in water from coexisting phosphorescent HOF hosts and phosphor guests.<sup>68</sup>

**2.4.3. Challenges and future perspectives.** Despite significant advances in supramolecular self-assembly for RTP materials, the field confronts critical challenges: optimizing host-guest interaction efficiency, improving material processability, and extending applications to dynamic environments. Additionally, precise control over assembly processes, enhancement of structure–property reproducibility, environmental sensitivity of phosphorescence performance, and incomplete understanding of phosphorescence regulation mechanisms remain unaddressed. The insufficient stability and practicality in complex environments further necessitate innovative solutions.

Future research should focus on the rational design of macrocyclic hosts with tunable cavities for precise guest encapsulation, integrating theoretical calculations and advanced characterization to decode intermolecular interaction mechanisms and enable precise assembly control for improved reproducibility, alongside the development of stimuli-responsive supramolecular systems to achieve adaptive RTP, combined with molecular modification and interfacial engineering to mitigate environmental impacts (such as polarity and temperature) and enhance stability under harsh conditions. Additionally, efforts should be directed toward integrating supramolecular assemblies with porous frameworks to synergize rigidity and functionality, while exploring supramolecular chiral self-assembly for ultra-long RTP materials to broaden applications in 3D optical displays, optical data storage, and chiral optoelectronics, and self-healing functional designs can address stability challenges in complex environments.

## 2.5. Nanoscale doping

**2.5.1. Metal halide materials.** Metal–organic halides, composed of inorganic metal halide frameworks and organic cations, exhibit unique advantages in optoelectronic devices due to their ordered assembly at the molecular level. Their ultra-long RTP properties originate from multiple mechanisms: appropriate organic units (such as those containing aromatic carbonyl groups or N/O heteroatoms) facilitate the ISC process between singlet and triplet states; the heavy atom effect introduced by transition metals or halogens enhances the ISC rate; and halogens as electron donors can generate radicals through photoinduction, enabling photochromism. The ordered arrangement of low-dimensional structures allows them to serve as optical waveguide microstructures, enhancing data encryption capabilities by integrating time-resolved RTP and color-resolved photochromism.

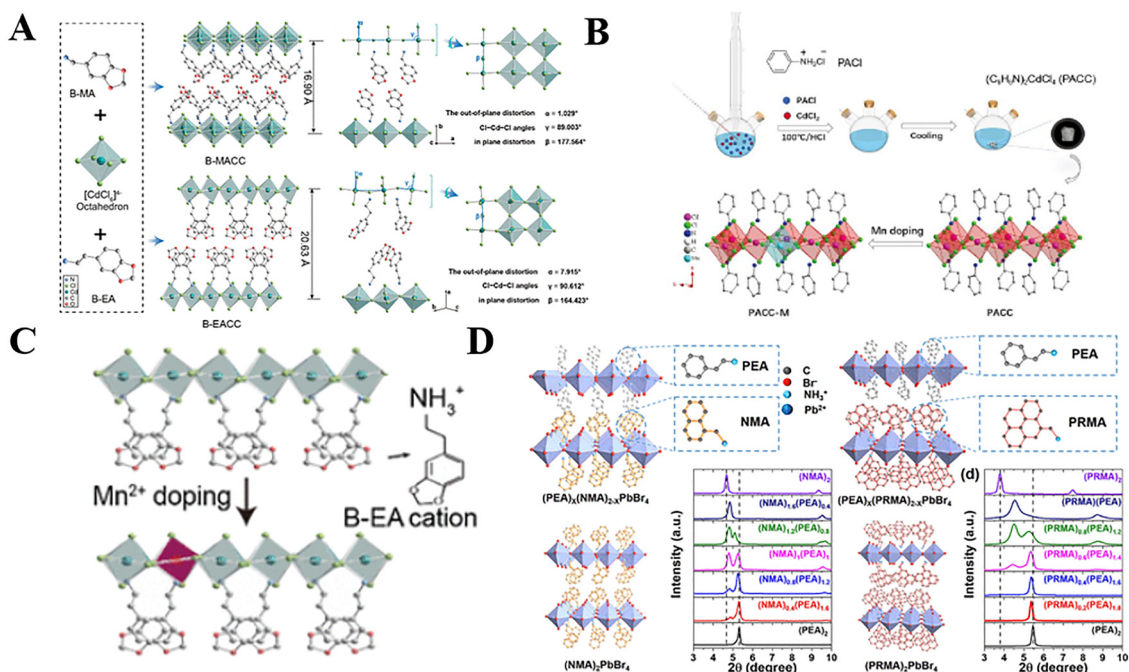
Two-dimensional (2D) perovskites, as layered self-assembled materials, combine the structural designability of inorganic components with the stability of organic components. The rigid inorganic layers suppress non-radiative recombination, enhancing luminous efficiency. The 2D structure forms quantum wells,

with an exciton diffusion distance of up to 100 nm, promoting energy transfer from inorganic layers to organic triplet excitons. The heavy atom effect further facilitates triplet state luminescence. Currently, high-efficiency RTP 2D perovskites predominantly emit in the blue-green region, with limited long-wavelength emission. However, structural regulation offers potential for expanding application scenarios.

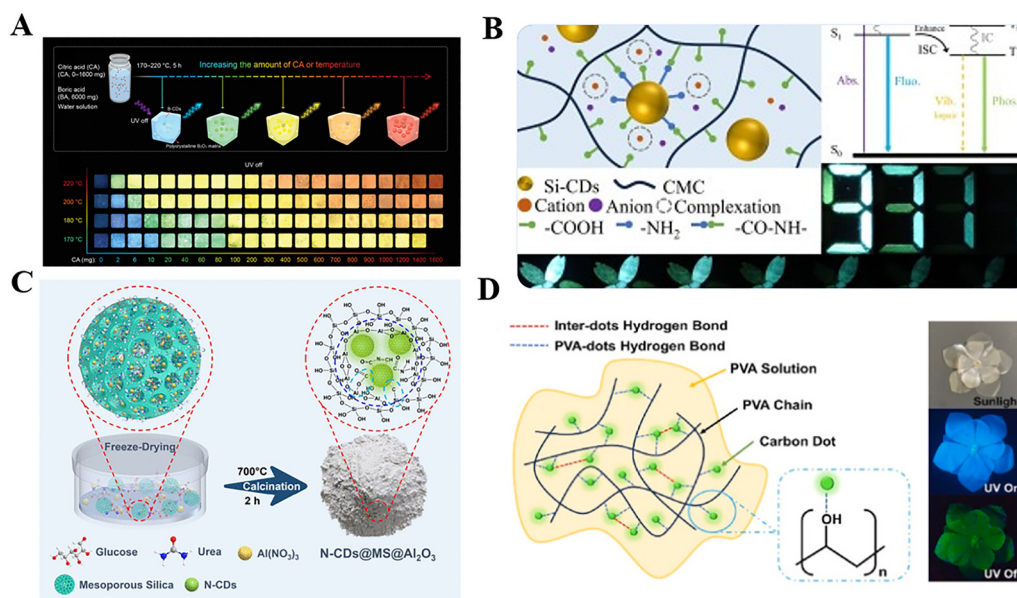
Recent studies have demonstrated significant progress. Chen *et al.* synthesized B-EACC by adjusting the alkyl chain length of organic cations.<sup>69</sup> The additional carbon atom in B-EA+ cations strengthened hydrogen bonding and  $\pi$ – $\pi$  stacking, achieving a phosphorescence lifetime of 579 ms and a quantum efficiency of 14.86% (Fig. 11A). Lin's team introduced Mm ions into 2D perovskites, enabling tunable RTP from blue to red by promoting exciton energy transfer between organic (Fig. 11B) and inorganic components and passivating deep trap states.<sup>70</sup> Chen's team achieved red RTP at 610 nm with a quantum yield of 44.11% and excellent stability (Fig. 11C) by doping Mn<sup>2+</sup> into cadmium-based 2D perovskites.<sup>71</sup> Tian's group realized white-light RTP and fabricated phosphorescent LEDs by replacing 2-phenylethylamine cations with naphthyl or pyrenyl organic cations (Fig. 11D), achieving a color rendering index (CRI) close to 90.<sup>72</sup> Huang's team enhanced phosphorescence performance by coordinating bipyridine derivative guests and metal halide salts (such as ZnCl<sub>2</sub>) within a benzophenone host matrix. The coordination interaction promoted ISC and restricted molecular motion, leading to substantial improvements.<sup>73</sup>

**2.5.2. Carbon dot materials.** Carbon dots (CDs), characterized by functional groups such as C=O and C–N, exhibit excellent RTP properties. The (n,  $\pi^*$ ) and ( $\pi$ ,  $\pi^*$ ) orbitals of these functional groups facilitate ISC, while intra- and intermolecular hydrogen bonds suppress triplet exciton quenching. Preparation methods primarily include the one-step method (simultaneous generation of CDs and the matrix) and the two-step method (preparing CDs first and then embedding them into the matrix). For instance, the one-step method involves microwave-assisted heating of ethanolamine and phosphoric acid aqueous solutions to rapidly produce gram-scale ultra-long RTP CDs, while the two-step method enhances RTP by confining polymer CDs within silica nanospheres through covalent and hydrogen bonding interactions.

Doping and composite systems have optimized the RTP performance of CDs. Qiu's team synthesized B-CD@B<sub>2</sub>O<sub>3</sub> composites *via* pyrolysis of citric acid and boric acid (Fig. 12A), achieving a tunable afterglow from 5 to 12 s and color-tunable RTP from blue to red.<sup>74</sup> Li's group adjusted the phosphorescence lifetime from 9.48 ms to 492.39 ms by doping silicon into CDs and combining them with carboxymethylcellulose hydrogels (Fig. 12B), facilitated by metal salts that enhance spin–orbit coupling.<sup>75</sup> Guo *et al.* promoted the transition from 1(n,  $\pi^*$ ) to 3( $\pi$ ,  $\pi^*$ ) states through nitrogen doping (Fig. 12C), strengthening spin–orbit coupling.<sup>76</sup> Ma's team extended the phosphorescence lifetime of fluorine-nitrogen co-doped CDs@PVA to 494 ms (Fig. 12D), attributed to the heavy atom effect of fluorine and the protective effect of C–F bonds.<sup>77</sup> Wang's group achieved blue, green, and orange RTP by pyrolyzing different conjugated



**Fig. 11** (A) Diagrams for  $[\text{CdCl}_6]^{4-}$  octahedra. Reprinted with permission from ref. 69. Copyright 2023 American Chemical Society. (B) Synthesis and structure of PACC and PACC-M. 70. Copyright 2023 Wiley-VCH GmbH. (C) Schematic representation of the structure evolution of B-EACC to B-EACC:  $\text{Mn}^{2+}$ . Reprinted with permission from ref. 71. Copyright 2023 American Chemical Society. (D) Schematic of the structures of 2D lead bromide perovskites. Reprinted with permission from ref. 72. Copyright 2025 American Chemical Society.



**Fig. 12** (A) Schematic illustration of the preparation process of B-CD composites featuring tunable full-color ultralong room-temperature phosphorescence (RTP) and optical photographs of B-CD composites synthesized from citric acid (CA) and boric acid (BA) under varied reaction parameters after the termination of excitation light under ambient conditions. Reprinted with permission from ref. 74. Copyright 2021 The Authors. Advanced Science published by Wiley-VCH GmbH. (B) Tailored fabrication of carbon dot composites with full-color ultralong room-temperature phosphorescence for multidimensional encryption. Reprinted with permission from ref. 75. Copyright 2024 Elsevier Inc. All rights are reserved, including those for the text and data mining, AI training, and similar technologies. (C) Schematic diagram of the *in situ* synthesis of  $\text{N-CDs@MS@Al}_2\text{O}_3$ . Reprinted with permission from ref. 76. Copyright 2024 Elsevier Ltd. All rights are reserved, including those for the text and data mining, AI training, and similar technologies. (D) Schematic diagram of the formation of hydrogen bonds of CDs in PVA solution. Reprinted with permission from ref. 77. Copyright 2024 Elsevier Ltd. All rights are reserved, including those for the text and data mining, AI training, and similar technologies.

precursors with urea or ammonium pentaborate.<sup>78</sup> Additionally, Lin's team synthesized zero-dimensional perovskites  $\text{PA}_6\text{InCl}_9$  and  $\text{PA}_4\text{InCl}_7$ , exhibiting blue RTP. The introduction of  $\text{Sb}^{3+}$  realized white and orange pure RTP with a CRI close to 90, expanding the cross-application of metal halides and CDs.<sup>79</sup>

**2.5.3. Challenges and future perspectives.** Despite their remarkable potential in optoelectronic devices and information storage through composition design, doping regulation, and structural optimization, metal halide- and carbon dot (CD)-based RTP materials face critical research limitations. Metal halide systems suffer from low long-wavelength emission efficiency, poor environmental stability (e.g., degradation under humid/high-temperature conditions), and unclear phosphorescence mechanisms, while CD-based materials are constrained by matrix-dependent luminescence, potential toxicity of doped elements, and insufficient understanding of excitonic dynamics. Additionally, both systems struggle with challenges in large-scale fabrication, thermal mismatch during device integration, and high production costs.

Future research on metal halides should prioritize structure-design engineering, such as surface passivation and hybrid framework construction, to enhance their environmental adaptability, while integrating *in situ* spectroscopic techniques and density functional theory (DFT) calculations to decode the mechanisms of phosphorescence generation. Additionally, efforts should be directed toward the development of low-cost synthesis methods, including solution processing and mechanochemical routes, to enable scalable production for applications in bioimaging and anti-counterfeiting. For CDs, key research directions involve defect engineering and heteroatom doping to optimize luminescence efficiency, complemented by self-healing functional designs to sustain RTP performance amid environmental fluctuations. Simultaneously, leveraging advanced characterization techniques like high-resolution electron microscopy and time-resolved spectroscopy, along with theoretical modeling, is crucial to clarify the structure–property relationships underlying phosphorescence regulation, while mitigating potential toxicity through strategic element substitution.

### 3. The applications of room-temperature phosphorescence based on doping systems

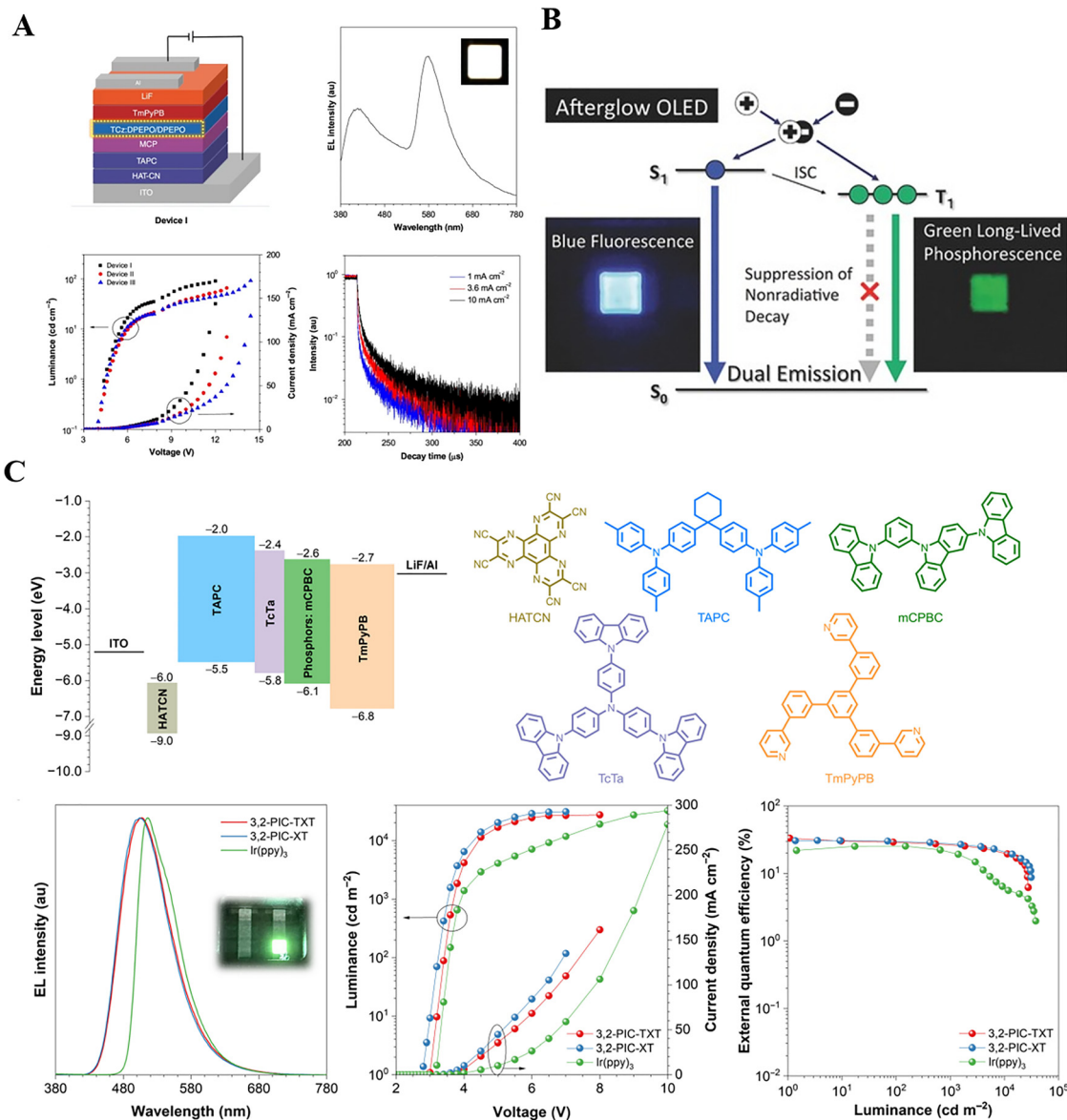
#### 3.1. Optoelectronic devices

Organic light-emitting diodes (OLEDs) are composed of luminescent organic semiconductors, which facilitate the conversion of electrical energy into light through a process known as electroluminescence (EL). The flexibility, low manufacturing cost, and lightweight nature of OLEDs are all factors that make them promising for next-generation full-color displays and energy-efficient solid-state lighting applications. In the context of fluorescent OLED systems, the spin state characteristics impede the internal quantum efficiency (IQE) to a maximum of 25%, a limitation that can be attained by only 25% of the singlet spin states. However, the introduction of heavy atoms

has been demonstrated to enhance the ISC process through strong SOC, thereby enabling the utilization of the remaining 75% of triplet spin states for light emission. This theoretical approach has the potential to achieve 100% IQE. However, the elevated expense, rarity of noble metals, and the comparatively fragile metal–ligand bonds that are concomitant with this method act as constraints on the widespread adoption of the process in OLEDs.<sup>80,81</sup>

As a self-luminous, thin, flexible, and energy-efficient technology for display and lighting, OLED devices based on multiple resonance TADF (MR-TADF) materials present an innovative solution. Incorporating phosphorescent materials as sensitizers enables the fabrication of hyperfluorescent OLEDs with high efficiency, narrow emission spectra, and extended operational lifetimes, thereby demonstrating significant potential in the ultra-high-definition display sector. Moreover, compared with traditional metal complex phosphorescent materials, pure RTP materials stand out for their cost-effectiveness, environmental friendliness, and compatibility with large-scale production processes, thus further expanding the material options available for OLED technological advancement.<sup>82,83</sup>

In 2015, the Adachi team first achieved electroluminescence in phosphorescent OLEDs by depositing the phosphorescent DMFLTPD onto the conductive host CzSte (Fig. 13A), which simultaneously served as both electron and hole transport materials.<sup>84</sup> Under an applied voltage, this OLED exhibited blue emission and green phosphorescence when the power was turned off. Tang and his team synthesized a series of commercially/laboratory-synthesized carbazole-based emitters (tcz-f, tcz-h, and TCZ oh) (Fig. 13B), and achieved molecular emission control from phosphorescence to fluorescence by gradually adjusting the substituents from fluorine to hydrogen and then to hydroxyl. Blue and white OLEDs were successfully fabricated using tcz-f-cm as the light-emitting layer.<sup>85</sup> The Wang group designed two twisted donor–acceptor–donor (D–A–D) organic emitters: the acronyms CzSe and TMCzSe are used to denote the two distinct entities.<sup>86</sup> Through precise modulation of the torsion angle between D and A units, it was possible to transition the lowest triplet excited state from a localized excited state, designated as  $^3\text{LE}$ , to a charge transfer state, termed  $^3\text{CT}$ . This adjustment facilitated the occurrence of both pure RTP emission and hybrid RTP/TADF emission. The fabrication of high-performance OLEDs based on CzSe and TMCzSe was successful, with the maximum external quantum efficiency (EQE) of pure organic RTP-based OLEDs reaching 8.9% and 25.5%, respectively. In 2025, Zhao's group designed and synthesized an efficient new RTP molecule, 3,2-PIC-TXT, based on the heavy atom effect of sulfur.<sup>87</sup> The enhancement of the spin–orbit coupling effect in the RTP molecule was achieved by the introduction of sulfur atoms, thereby promoting intersystem crossing and increasing the phosphorescent radiative transition rate (Fig. 13C). This, in turn, resulted in a reduction of the phosphorescence lifetime and, consequently, an improvement in the performance of electroluminescent devices. The doped OLED devices of 3,2-PIC-TXT exhibited a peak current efficiency (CE), a power efficiency (PE), and an EQE of  $92.2 \text{ cd A}^{-1}$ ,  $96.6 \text{ lm W}^{-1}$ , and 33.2%, respectively.



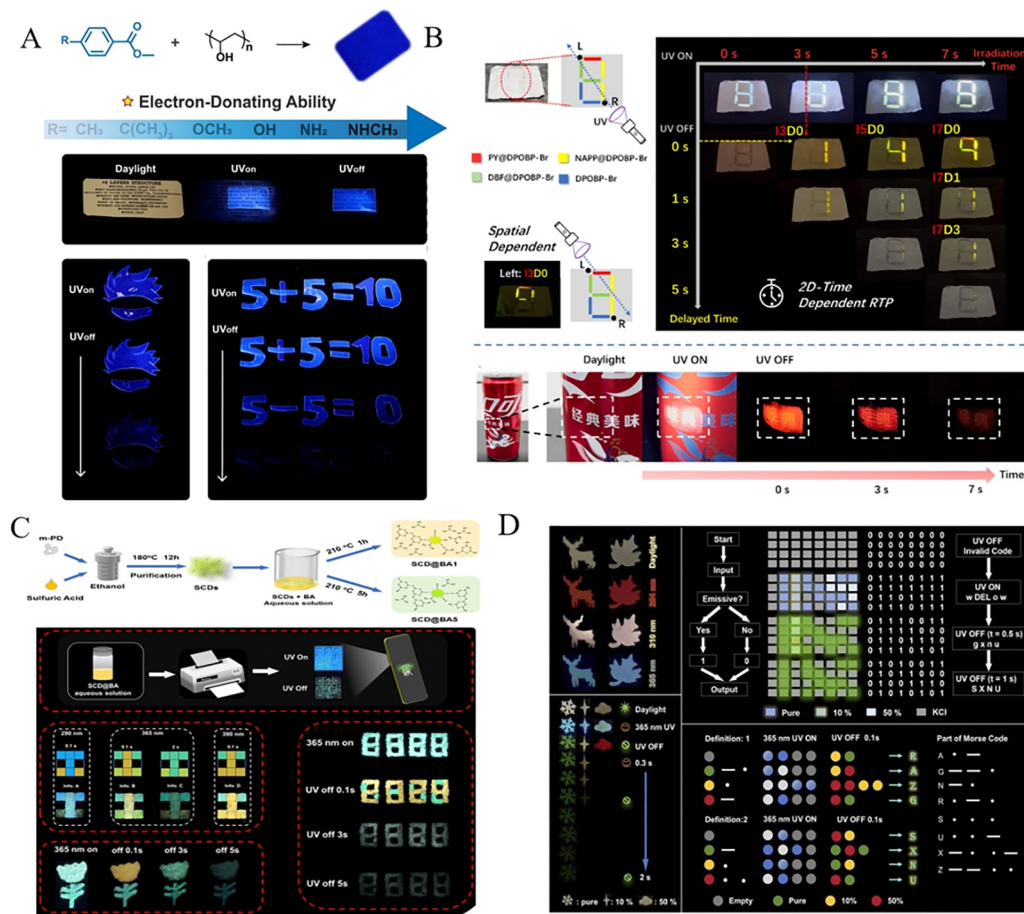
**Fig. 13** (A) Configuration of device I. b. The EL spectrum of device I at a current density of 3.6 mA cm<sup>-2</sup>. Reprinted with permission from ref. 83. Copyright © 2020, The Author(s). (B) An afterglow organic light-emitting diode (OLED) that displays electroluminescence with long transient decay after it is turned off is demonstrated. Reprinted with permission from ref. 84. Copyright © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (C) Energy map, device configuration, and chemical structures of functional materials, and electroluminescence performance of devices based on RTP emitter doped OLEDs. Reprinted with permission from ref. 87. Copyright © 2025, The American Association for the Advancement of Science.

### 3.2. Information anti-counterfeiting

Currently, information anti-counterfeiting technologies primarily rely on fluorescent materials, but their functions are relatively limited, offering limited information capacity. In contrast, RTP materials exhibit inherent long persistent luminescence, enabling not only ultraviolet (UV)-switchable anti-counterfeiting but also multi-level encryption strategies based on time-resolved or chemical-responsive properties. The emission lifetime differences of RTP materials provide possibilities for time-resolved multi-level encryption.<sup>30,88</sup> In the field of information anti-counterfeiting, significant progress has been made in RTP materials *via* host-guest doping strategies. Their

long-lifetime luminescence (millisecond to second scale), tunable multicolor emission, and stimulus-responsive characteristics offer a new research paradigm for high-security anti-counterfeiting technologies.<sup>89,90</sup>

The Ma group developed a simple strategy to achieve efficient dark blue RTP materials with an ultra-wide range of adjustable life (Fig. 14A). High-performance organic RTP materials with a phosphorescence lifetime of 796.8 ms and a phosphorescence quantum yield of 15.4% can be prepared by doping methyl p-hydroxybenzoate into PVA. The excellent phosphorescence properties of the material are used in light-emitting displays and optical anti-counterfeiting.<sup>91</sup> In 2024, the Chi and Yang



**Fig. 14** (A) The applications of the doped films are in luminescent displays and optical anti-counterfeiting. Reprinted with permission from ref. 91 Copyright © 2024 Wiley-VCH GmbH. (B) Schematic representation of the coating containing phosphorescence images of different dye@DPOBP-Br, irradiated from R to L with 360 nm UV light. Reprinted with permission from ref. 92. Copyright © 2023 Wiley-VCH GmbH. (C) Application of the SCD@BA1 composites with time-dependent and excitation-dependent RTP. Reprinted with permission from ref. 93 Copyright 2024 The Royal Society of Chemistry. (D) Anti-counterfeiting patterns and luminescence photographs with excitation-dependent properties designed using NBP-Cd:10% Mn<sup>2+</sup>. Reprinted with permission from ref. 94 Copyright 2025 The Royal Society of Chemistry.

group designed and synthesized a novel amorphous organic small-molecule host, DPOBP-Br, by combining 4-bromo-benzophenone and diphenylphosphine oxide.<sup>92</sup> The amorphous doped system enables dynamic luminescence color transformation controlled by the consumption and replenishment by the consumption and replenishment of ground-state oxygen, featuring self-recoverability (Fig. 14B). This new spatiotemporal resolution anti-counterfeiting method, enabled by the continuous thin films of amorphous systems, can be coated onto various curved surfaces, showing promising application prospects.

In 2024, the Yuan team designed sulfur-doped carbon dot composites (SCD@Ba1) (Fig. 14C), achieving a yellow-green dynamic afterglow color change within 2 s by tuning the bandgap *via* sulfur atoms.<sup>93</sup> The dual emission centers of surface states (yellow) and carbon core states (green), combined with different decay lifetimes, constructed a time-confined information encryption system. By controlling UV irradiation time, dynamic passwords that vanish over time can be written onto films. Zhang group's hybrid material ((NBP)Cd<sub>2</sub>Cl<sub>5</sub>·H<sub>2</sub>O) shows phosphorescence color transitioning from yellow-green (1% Mn<sup>2+</sup>) to red (50% Mn<sup>2+</sup>) with

simultaneous shortening of afterglow time in 2025 (Fig. 14D), suitable for multi-level encryption labels.<sup>94</sup> In 2025, Zhao's group developed MAPbBr<sub>3</sub>@Eu-MOF materials, realizing dual responses to excitation wavelength and time *via* quantum confinement effects.<sup>95</sup> Under 254 nm excitation, they exhibit green afterglow, while under 365 nm excitation, yellow afterglow is observed, enabling multi-dimensional anti-counterfeiting through spatial pattern design.

### 3.3. Intelligent sensing

Doped RTP materials exhibit long-lifetime luminescence ranging from ms to s, endowing them with broad application prospects in environmental monitoring, biosensing, food safety, and other fields. Additionally, RTP materials feature tunable multicolor emission, allowing color adjustment for specific application scenarios to meet detection requirements.<sup>96,97</sup> Their stimulus-responsive properties further enhance their value in intelligent sensing. By responding to external stimuli (*e.g.*, temperature, light, and chemical substances), RTP materials can alter their luminescence characteristics under specific

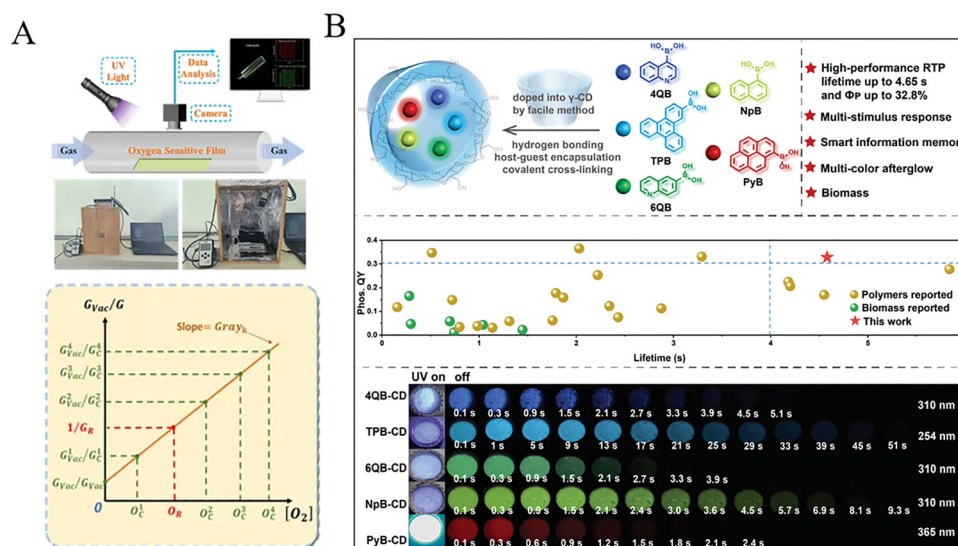
conditions, enabling highly sensitive detection of target analytes.<sup>98–100</sup> This feature allows RTP materials to (1) real-time monitor harmful gases or pollutants in environmental monitoring, (2) accurately track changes in biomarker concentrations in biosensing, and (3) rapidly identify hazardous substances or microbial contamination in food safety testing. Owing to their high sensitivity and low cost, RTP materials not only improve detection accuracy and efficiency but also reduce costs, enabling more application scenarios. They provide high-sensitivity, low-cost solutions for critical fields like environmental monitoring, biosensing, and food safety, significantly advancing intelligent sensing technologies.

In 2021, the Li group's host-guest doping system (OPPh<sub>3</sub>/BPPH) achieved multi-level stimulus responsiveness *via* grinding or acid-base treatment.<sup>101</sup> For example, grinding activated phosphorescence, while acid treatment shifted the phosphorescence color from blue to green, is suitable for variable information labels. In 2024, the Zhang group constructed a dual-module system integrating chromophores and chiral centers, enabling chiral recognition of natural amino acids within minutes *via* Dexter energy transfer.<sup>102</sup> This system covered 15 natural chiral amino acids and their non-natural enantiomers. The bromine atom further optimized phosphorescence enhancement, providing a new method for rapid biomolecule screening. In 2025, Yang's team developed pure organic RTP materials *via* a "folding-induced spin-orbit coupling enhancement" strategy, achieving thianthrene covalent trimerization.<sup>98</sup> These materials exhibited a 41.6% RTP efficiency and dual fluorescence-RTP emission, with RTP intensity sensitive to oxygen concentration changes. This enabled intrinsic ratiometric oxygen sensing without external references, with detection sensitivity improved by nearly 200-fold, suitable for low-cost real-time monitoring in industrial waste gas and deep-sea exploration (Fig. 15A). Moreover, the

Ma group's boronic acid/ $\gamma$ -CD system enables reversible phosphorescence intensity regulation under humidity changes and sets shelf life *via* UV activation time (Fig. 15B), applied as long-acting anti-counterfeiting labels for cold chain logistics.<sup>14</sup>

### 3.4. Bioimaging

RTP materials have made remarkable progress in bioimaging, leveraging their long-lifetime luminescence (ms to s) for various biological labeling applications. These materials feature tunable multicolor emission and environmental responsiveness, allowing the dynamic adjustment of luminescence colors and real-time bioinformation feedback in response to pH, temperature, or specific molecular changes.<sup>103,104</sup> In cell labeling, *in vivo* detection, and disease diagnosis, RTP materials exhibit high sensitivity and specificity, offering high-resolution, low-interference solutions.<sup>105,106</sup> They enable precise cell labeling without disrupting physiological functions, prolonged imaging for accurate data acquisition, and early-stage disease diagnosis and monitoring. In 2022, the He group developed an ultra-long aqueous phosphorescent probe with RTP emission lasting around 5 s and a lifetime of 743.7 ms (Fig. 16A). This probe achieved the specific targeting of live mouse cells and deep tumor tissues *via* immune phosphorescence imaging.<sup>107</sup> The probe showed signal-to-background ratios (SBRs) of  $\sim 69$  in *ex vivo* imaging and  $\sim 627$  in *in vivo* imaging, marking a 105-fold enhancement in the SBR for millisecond time-resolved *in vivo* bioimaging compared to fluorescence. In 2023, the Ma research group developed red/near-infrared (NIR) water-soluble RTP probes (cucurbit[8]uril/pyridinium salt system), which permitted two-photon imaging of lysosomal viscosity and millisecond time-resolved detection *via* synergistic aggregation-induced emission (AIE) and twisted intramolecular charge transfer (TICT) effects. In an inflammatory mouse model, this probe enhanced the phosphorescence imaging



**Fig. 15** (A) Thioanthracene covalent trimerization of a pure organic RTP material for highly sensitive detection of low concentration oxygen. Reprinted with permission from ref. 98. Copyright © 2025 Wiley-VCH GmbH. (B) Schematic diagram of the design strategy and structural composition of host-guest doping systems and comparison of room-temperature phosphorescence lifetimes and phosphorescence quantum yields between TPB-CD and other reported biomass- and polymer-based materials. Reprinted with permission from ref. 14. Copyright © 2024 Wiley-VCH GmbH.

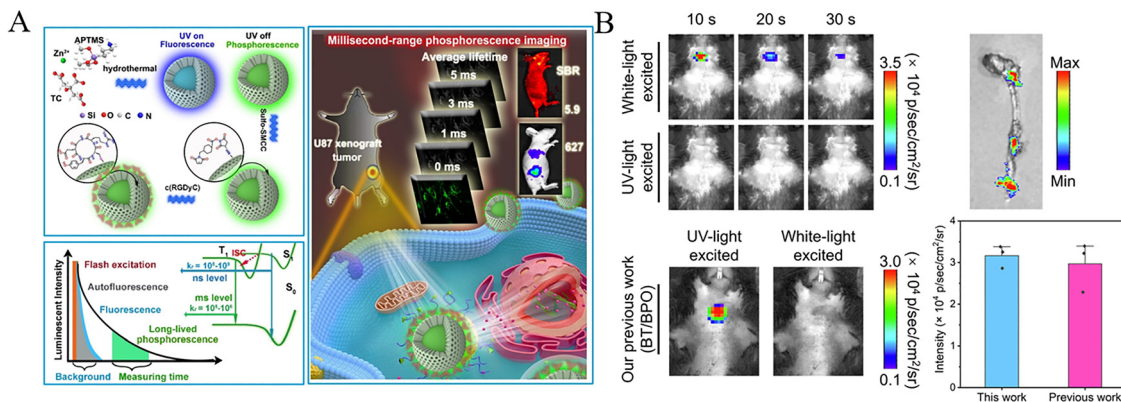


Fig. 16 (A) The design of phosphorescence probes, the principle of millisecond-range time-resolved phosphorescence imaging to suppress background, and the scheme for *in vitro* and *in vivo* millisecond-range time-resolved phosphorescence imaging with high SBR. Reprinted with permission from ref. 107. Copyright 2022 Wiley-VCH GmbH. (B) Time-dependent phosphorescence images of AS mice and their organs. Reprinted with permission from ref. 108 Copyright © 2025, The Author(s).

signal-to-noise ratio (SNR) by 2.3-fold in comparison to fluorescence, thereby facilitating dynamic monitoring through the adjustment of viscosity response thresholds.

The Ding group constructed a host-guest doping system using benzophenone (BPO) as the host and phosphorescent guests, exhibiting excellent white-light-excited organic RTP properties.<sup>108</sup> Such materials enhance imaging clarity and accuracy in bioimaging, enabling high-contrast visualization of complex biological structures in atherosclerotic plaque and intestinal disease imaging, and showing potential to improve surgical precision and reduce risks in orthotopic liver tumor surgical navigation (Fig. 16B). In 2024, the Liu group utilized cucurbituril (CB[8]) supramolecular confinement to combine hyaluronic acid-modified bromophenylpyridine (HAPY) with phenothiazine derivatives, achieving NIR phosphorescence emission (750 nm) and lysosome-targeted imaging—boosting the SNR in cancer cells by over 5-fold.<sup>109</sup> In 2025, Ma's team developed a novel red/NIR water-soluble organic RTP probe *via* induced luminescence and intramolecular charge transfer strategies, enabling two-photon imaging of lysosomal viscosity and high-time-resolution cell imaging.<sup>110</sup> The probe also monitored viscosity changes in inflamed mice with significantly superior SNR to fluorescence in *in vivo* phosphorescence imaging.

### 3.5. X-ray imaging

X-ray scintillators are capable of converting high-energy radiation into visible light, demonstrating significant application value in fields such as radiation detection, safety inspections, and biomedical imaging.<sup>111</sup> Taking the field of medical imaging as an example, high-resolution images can more accurately identify small lesions, providing important support for early diagnosis and treatment of diseases. Inorganic scintillators such as ceramics, glass, and metal halides (such as NaI (Tl) and CsI (Tl)) exhibit excellent scintillation performance due to their high absorption capacity for X-rays. However, its preparation process is limited by high-temperature synthesis conditions, making large-scale production difficult.<sup>112</sup> In addition, the preparation of inorganic luminescent materials requires

the introduction of heavy metal elements, with complex processes and strict conditions, resulting in high production costs. Compared with inorganic doped scintillators, organic doped scintillators have the advantages of wide raw material sources, low cost, easy processing and modification, and the ability to achieve large-scale preparation. Organic luminescent agents typically have lower processing temperature requirements, lower production costs, and shorter fluorescence decay times, which give them significant advantages in rapid detection and enable more efficient neutron/gamma ray analysis and identification. Through molecular design, the absorption and emission characteristics of light can be precisely controlled, thereby promoting the design and customization process of phosphors. In recent years, there has been a gradual increase in research reports on organic phosphor scintillators.<sup>113,114</sup> It is widely believed that introducing heavy atom effects can significantly improve the absorption efficiency of X-rays. The presence of heavy atoms not only enhances the absorption of X-rays but also promotes spin-orbit coupling, which is beneficial for conversion and luminescence processes. In addition, strong SOC increases the probability of intersystem crossing, enabling the collection of more triplet excitons and effectively enhancing the performance of scintillators.

In 2022, the Huang group developed organic phosphorescent nanoscintillators that exhibited dual functionality as both scintillators and photosensitizers.<sup>115</sup> A low dose of 0.4 Gy was administered, and no adverse reactions were observed, indicating the potential efficacy of these materials for deep tumor photodynamic therapy (Fig. 17A). This finding presents an alternative approach to optical deep-tissue therapy that utilizes pure organic scintillators. Subsequently, a host-guest dopant strategy was proposed, whereby X-ray absorption centers were designated as the hosts and emission centers were designated as the guests. When exposed to X-rays, these materials demonstrated intense and tunable emission, ranging from green (520 nm) to near-infrared (NIR, 682 nm). This observation revealed the relationship between X-ray absorption and the spatial arrangement of heavy atoms within the matrix (Fig. 17B). The potential of these

materials in the field of X-ray imaging was demonstrated through the utilization of wide-range color-tunable organic host-guest scintillators.<sup>116</sup>

In 2024, Gu's research group developed a temperature-adaptive organic scintillator capable of achieving efficient X-ray response across a temperature range of 77–400 kelvin *via* a combination of dual phosphorescence and TADF emission.<sup>117</sup> The scintillator has been shown to enable high-quality imaging in extreme environments, with a light yield of 78 229 MeV<sup>-1</sup>, a detection limit of 51 nGy s<sup>-1</sup>, and a spatial resolution of 21.7 lp mm<sup>-1</sup> (Fig. 17C). In the same year, the Gong group reported the discovery of sulfone-based organic molecules (C1–C7) with tunable molecular packing *via* different alkoxy chains (Fig. 17D). These molecules exhibited dual triplet trapping channels of TADF and RTP in the aggregated state, and unique radioluminescence under X-ray stimulation.<sup>118</sup> In 2025, the Zhu group designed ultra-high-temperature-stable organic ionic host-guest phosphors, suppressing triplet exciton thermal deactivation *via* spin-vibration coupling-assisted intersystem crossing and electrostatic confinement of rigid ionic hosts.<sup>119</sup> The material maintained efficient luminescence at 673 K, with an X-ray detection limit of 71.5 nGy s<sup>-1</sup> and a photoluminescence efficiency of 80.4% at 483 K, offering new solutions for high-temperature

industrial detection and medical imaging. Meanwhile, the Zhang group prepared transparent rare-earth hybrid glasses *via* low-temperature desolvation, maintaining structural stability through hydrogen bonds and achieving efficient luminescence *via* ligand-to-lanthanide energy transfer. With a spatial resolution of 20 lp mm<sup>-1</sup> and a quantum yield of >70%, this material provides new insights for flexible X-ray detectors.<sup>104</sup>

## 4. Conclusions and future prospects

In summary, RTP materials enabled by doping strategies have undergone significant advancements, propelled by breakthroughs in material design and mechanistic understanding. Doping approaches – including host-guest systems, polymeric matrices, supramolecular assemblies, and nanocomposites – have effectively mitigated early limitations of non-radiative decay by modulating ISC, stabilizing triplet excitons, and restricting molecular dynamics. These innovations have facilitated diverse applications in optoelectronic devices, anti-counterfeiting technologies, smart sensors, and biomedical imaging, underscoring their transformative potential for practical implementation.

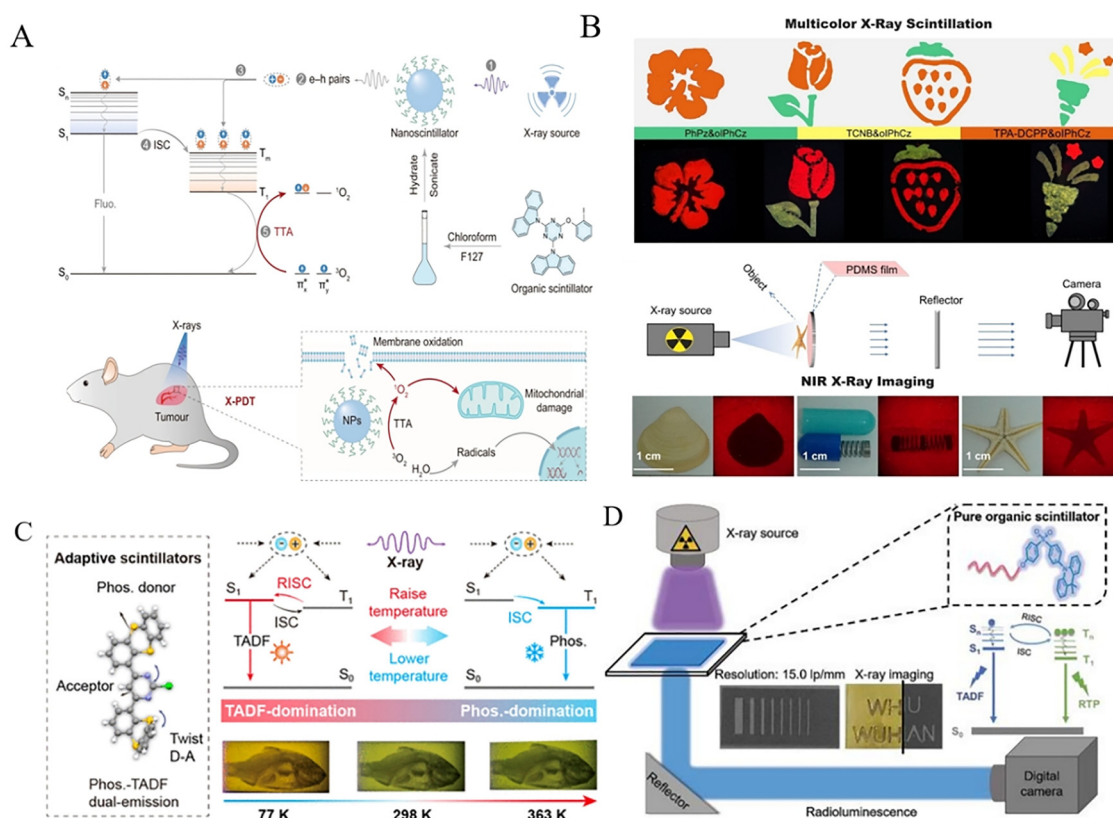


Fig. 17 (A) Process to prepare organic nanoparticles, subsequent <sup>1</sup>O<sub>2</sub> generation under X-ray irradiation, and illustration of the mechanism in the treatment of deep-seated tumors *in vivo*. Reprinted with permission from ref. 115. Copyright 2022, The Author(s). (B) Multicolor X-ray scintillation from three types of host-guest doping systems and a schematic diagram of X-ray imaging installation. Reprinted with permission from ref. 116. Copyright 2023 Wiley-VCH GmbH. (C) Temperature-adaptive organic scintillators for X-ray radiography. Reprinted with permission from ref. 117. Copyright 2024 American Chemical Society. (D) Organic molecules with dual triplet-harvesting channels enable efficient X-ray scintillation and imaging. Reprinted with permission from ref. 118. Copyright 2024 The Authors. Aggregate published by South China University of Technology, AIE Institute, and John Wiley & Sons Australia, Ltd.

Notwithstanding these achievements, several critical challenges remain. Precise tailoring of host–guest interactions to achieve predictable control over phosphorescent properties (e.g., lifetime, emission color, and quantum efficiency) remains an unmet scientific challenge. The absence of a unified theoretical framework for luminescence mechanisms hampers rational material design, while obstacles in large-scale synthesis and environmental stability continue to impede commercial translation. Future research should focus on (1) developing computational modeling approaches to engineer host–guest interfaces with atomic precision, (2) establishing standardized characterization protocols to resolve mechanistic ambiguities, (3) designing multifunctional doping systems with adaptive responses to complex environmental stimuli, and (4) integrating RTP materials into scalable manufacturing processes for device fabrication. Meanwhile, to strengthen the industry–university–research pathway, specific measures can be implemented: establishing joint research centers between universities, research institutes, and optoelectronic enterprises to focus on scalable synthesis technologies; launching pilot-scale transformation projects funded by cross-sectoral alliances to test RTP material applications in anti-counterfeiting or biomedical scenarios; and building a shared database of material performance and manufacturing parameters to align academic research with industrial production needs.

By addressing these bottlenecks, doping-based RTP materials are poised to unlock new frontiers in advanced optoelectronics, secure information processing, and precision diagnostics, heralding a promising trajectory toward broad-based commercialization.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

This is a review article and no new data were generated. All cited data are available in the referenced published literature.

## Acknowledgements

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