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Ultralong organic room-temperature phosphorescence, multiple stimulus responsiveness and high-level anti-counterfeiting based on multifunctional carbazolyl imidazolopyridine

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ABSTRACT

Ultralong organic room-temperature phosphorescence materials induced by host-guest doping and the underlying mechanism have become the current research focus. Furthermore, high-level anti-counterfeiting and information encryption require multifunctional luminescent materials. Here, CzIP and L-CzIP with push-pull electronic system are successfully constructed by imidazopyridine units and commercial/self-made carbazole. The comparison experiment results indicate that trace isomer doping not only shows slight influence on crystal stacking and molecular space conformation but also significantly changes fluorescence and phosphorescence spectra and phosphorescence lifetime by boosting intersystem spin-orbit coupling. Non-radiative relaxation of CzIP and L-CzIP can be effectively inhibited by polymethyl methacrylate (PMMA) doping but not for crystallize. PMMA doping further confirms intrinsic phosphorescent characteristic of L-CzIP, whose room-temperature phosphorescence lifetime (84.83 ms) is close to that of CzIP (100.14 ms). Concentration-dependent fluorescent and phosphorescent emission and dynamic phosphorescent emission are also observed for CzIP in PMMA film. More importantly, a new aminopyridine/CzIP-doped system gives room-temperature phosphorescence lifetimes of 657.56 ms and afterglow lifetimes of 4 s. Notably, CzIP also shows high-contrast mechanochromism, selective response and differentiation to HCl, CF3COOH, and CH3COOH, and excellent detection capability to picric acid in aqueous medium and solid state. Finally, various anti-counterfeiting and encryption patterns are successfully constructed based on multifunction of CzIP. This work not only provides a multifunctional luminous material but also more importantly provides a theoretical basis and experimental guidance for designing novel ultralong organic room-temperature phosphorescence materials and achieving high-level anti-counterfeiting and encryption.

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1. Introduction

Room-temperature phosphorescence (RTP) is a phenomenon of delayed photoluminescence at room temperature, which can be traced back to the night pearl in ancient China [1–4]. Traditional inorganic RTP materials often suffer from high biological toxicity, poor processability, and flexibility and are unsuitable for large-scale preparation [5,6]. Compared with traditional inorganic RTP materials, purely organic room-temperature phosphorescence materials

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(PORTPs) have good processability, excellent biocompatibility, and low biological toxicity and cost [7–10]. Owing to large Stokes shift, long phosphorescence life, and sensitivity to external environment such as temperature, oxygen, and humidity [11–14], PORTPs with long RTP lifetime (>100 ms) and high efficiency (>5%), defined as ultralong organic room-temperature phosphorescence (UOP) materials, have displayed widely promising applications in biological imaging, chemical sensing, data encryption, anti-counterfeiting, optical storage, and so on [15]. However, construction of UOP materials still faces great challenges because of weak spin–orbit coupling (SOC), ineffective intersystem crossing (ISC) between single (S_n) and triplet excitons (T_n), and rapid non-radiative transition of T_n [16,17].

Currently, enhancing the intersystem transition (IST) of S_n and T_n and inhibiting the non-radiative decay of T_n have become two







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important measures to obtain efficient UOP materials. On the one hand, heavy atoms (such as Br and I) [18], heteroatoms (such as N, P, S, B, etc.) [19], carbonyl groups, and charge-separated states [20,21] can enhance the intersystem SOC and produce more triplet excitons according to the EI-Sayed rule. On the other hand, host-guest doping can construct dense hydrogen bonds and a rigid external environment, which can effectively inhibit non-radiative transition and oxygen diffusion, thereby obviously enhancing RTP efficiency and prolong RTP lifetime [22,23]. Based on the above-mentioned molecular design strategies and non-radiative inhibition measures, a surging number of UOP materials have been reported during the recent years [24]. However, different explanations for the role of host and guest materials, together with sensitivity of UOP to the external environment, lead to lack of general strategy constructing host-guest-doped system and unclear internal mechanism. So far, the optimization of the host-guest-doped system still depends on luck and extensive screening of crystalline organic small molecules with low melting points [25].

As we all know, fluorescent luminogens can provide anticounterfeiting and information encryption with space resolution, while phosphorescent materials can be used as time-resolved anticounterfeiting and information encryption [26]. Taking advantage of fluorescent wavelength and phosphorescent lifetime at the same time, the level of anti-counterfeiting and information encryption can be significantly improved [27,28]. Furthermore, phosphorescent materials with diverse stimuli-responsive changes (light, stress, solvent vapor, heat, oxygen, acid/alkali, etc.) can provide more monitoring parameters, which is not only conducive to obtaining high-level anti-counterfeiting products but also conducive to expanding the application range of materials and reducing costs [29–32]. For example, scientists have found that the pH value of microenvironment around solid tumors is indeed lower than that of normal tissues and organs; thereby, some phosphorescent materials with pH response can selectively identify and kill tumor cells [33]. However, phosphorescent materials with various stimulus responses are still rare until now [34].

To construct multiple-stimulus-response UOP materials and explore the internal mechanism of host-guest-doped RTP system, two twisted donor-acceptor (D-A) luminogens with the same molecular structure, named as CzIP and L-CzIP, were constructed by choosing, respectively, commercial carbazole and self-made carbazole as raw materials (Scheme 1a). First, the short and twisted conjugation facilitates absorption spectra of CzIP and L-CzIP to be confined in the ultraviolet (UV) region so that anticounterfeiting pattern or information cannot be perceived in sunlight. Second, the nitrogen atom on imidazopyridine unit contains lone pair electron, which can bond with active proton and enhance intramolecular charge transfer effect, endowing CzIP with acidchromism, pH monitoring, and explosives detection ability. Third, conjugated heterocycles and twisted D-A molecular configuration in CzIP and L-CzIP are expected to boost the ISC and reduce energy gap (ΔE_{ST}) between S_n and T_n, thereby generating more triplet excitons. Fourth, polymethyl methacrylate (PMMA) and 2aminopyridine (AP) are used as host materials, suppressing the non-radiative transition and recombination of guest excitons. The results show that 1% CzIP@PMMA film (weight ratio of CzIP and PMMA = 1:100) has RTP lifetimes of 100.14 ms and afterglow lifetimes of about 1 s and simultaneously presents dynamic phosphorescent emission from blue to yellow green. More importantly, our newly developed AP/CzIP-doped system shows RTP lifetimes of 657.56 ms and afterglow lifetimes of 4 s, whose strong orange afterglow is visible to the naked eye in sunlight; moreover, the doped system can be excited by visible light of 420 nm. Comparative experiments indicate crystal CzIP and crystal L-CzIP have almost identical molecular conformation and stacking but significantly different fluorescence spectra and RTP lifetimes. Furthermore, 1% CzIP@PMMA film and 1% L-CzIP@PMMA film exhibit close RTP lifetimes. The results confirm that L-CzIP is an intrinsic phosphorescent material, but crystalline state cannot effectively inhibit molecular motion. Meanwhile, trace 1H-benzo[f] indole (Bd) derivative can boost ISC, leading to disappearance of the fluorescence emission band of charge transfer (CT) state. As expected, CzIP also shows excellent mechanochromism, selective acidchromism, and explosive detection performance. By photophysical property tests, crystal analysis, and theoretical calculation, the intrinsic mechanism of above results is further discussed in detail. Finally, high-level anti-counterfeiting and encryption patterns are constructed based on fluorescence, RTP, mechanochromism, and acidchromism of CzIP and L-CzIP.

2. Material and methods

CzIP and L-CzIP were prepared by facile synthetic reactions (Schemes S1–2, Supporting information) and characterized by ¹H and ¹³C nuclear magnetic resonance spectra, mass spectrometry, and X-ray single crystal diffraction. The PMMA-doped films were prepared by drop casting method, and the AP/CzIP-doped system was prepared by melt-casting method. The characterization methods were listed in the Supporting information.

3. Results and discussion

3.1. Solvatochromism and aggregation-induced enhanced emission

To investigate the luminescent characteristics of CzIP, ultraviolet visible (UV-vis) absorption spectra, the emission spectra, and fluorescence quantum yields (PLQYs) were first studied in various solvents. As shown in Fig. S1, absorption spectra of CzIP cover a broad UV region from 290 to 370 nm, and absorption maxima only show 2- to 3-nm shifts with increasing solvent polarity, illustrating tiny ground state dipole moment variation. Interestingly, three emission peaks can be observed in n-hexane under 338-nm excitation, including one main peak (375 nm) and two shoulder peaks (360 nm and 395 nm); furthermore, the excitation spectra show that the three different emission peaks come from the same transition energy level (Fig. S1c); thereby, multiple emission peaks may be due to different molecular vibration and rotation modes of excited states. With the increase of solvent polarity, two shoulder peaks gradually disappeared, accompanied by the increase of the full width at half maximum and the red shift of the main emission peak from 376 nm to 386 nm, which may be attributed to stabilization role of excited states by polar solvents and excited state gradual transition from the locally excited state to the weak intramolecular charge transfer state. With quinine sulfate as a reference, relative fluorescence quantum vields (PLOYs) of CzIP are 0.18 (nhexane), 0.48 (toluene), 0.64 (DCM), 0.32 (THF), and 0.15 (DMSO) under 355-nm excitation, respectively. Generally, CzIP exhibits excellent fluorescence emission in various solvents; compared with toluene, DCM, and THF, the lower PLQYs in n-hexane and DMSO may be due to different excited states and the significant increase of solvent polarity, respectively. By choosing THF and H₂O as benign and poor solvents, respectively, aggregation-induced enhanced emission (AIEE) properties of CzIP were investigated. Fig. S2 shows that the fluorescence intensity of CzIP reaches the maximum at water fraction of 30% and then continues to drop with water fraction from 30% to 90%; however, fluorescence emission maxima hardly shifted in the whole process, and thereby, we infer that the emission bands belong to local excited (LE) states. Besides, fluorescence intensities of CzIP in aqueous THF are always higher than that of THF, outlining AIEE activity.



Scheme 1. CzIP main performance diagram.

3.2. Mechanochromism and RTP

By slow diffusion of n-hexane into DCM solution of CzIP, light brown block crystals were obtained, presenting two different colors under 365-nm UV irradiation (Fig. 1a). Crystals of two different colors give similar emission peaks but different intensity ratios among of 380 nm, 430 nm, 460 nm, and 570 nm, which are attributed to different morphologies rather than polymorphism (Fig. 1b). Before/after grinding, CzIP showed a high contrast mechanochromism. Under UV radiation, ground sample emitted bright blue fluorescence. Subsequently, reversibility of mechanochromism was investigated by DCM fuming and heating (Fig. 1c). Compared with crystals, the main emission peaks of the ground. heated, and fumigated samples hardly shift, but the emission intensity at 430 nm and 570 nm shows a clear downward trend. X-ray diffraction spectra show crystal CzIP has sharp and strong diffraction peaks (Fig. 1d), which are almost completely disappeared after hard grinding, suggesting that most lattice collapses, but there are still a few microcrystalline existed. After heating and DCM fuming, main diffraction peaks reappear, indicating regression of crystalline state. Moreover, stronger diffraction peaks can be observed for heating than DCM fuming, which is consistent with fluorescence emission spectra with better overlap between heated sample and initial crystals (Fig. 1c). Switching off the UV light, brown afterglow of crystals can be recorded using a digital camera, while ground sample suffers from afterglow attenuation due to more exposure to oxygen. Based on the above mentioned, a conclusion can be drawn that mechanochromism of CzIP is mainly attributed to phase transition from crystalline state to amorphous state, resulting in attenuation of triplet emission and subsequent significant changes of appearance color under natural light/UV light radiation.

To further study the intrinsic luminescence mechanism, temperature-variable delayed fluorescence spectra and corresponding steady state lifetimes of crystal CzIP were first provided. As shown in Fig. 2a, the emission intensity at 450 nm, 570 nm, and 615 nm decreases with the increase of temperature, showing typical RTP characteristic peaks. It is worth noting that the emission

intensity at 410 nm presents constant fluctuations when the temperature increased from 77 K to 317 K and reaches the maximum at 277 K, indicating TADF (Thermally Activated Delayed Fluorescence) nature (Fig. S3). The rise of temperature is conducive to the IST from triplet states to singlet state on the one hand, but it will lead to nonradiative intensification via molecular motions on the other hand. As a result, the synergistic effect of the positive contribution from IST and the negative role in non-radiative motion give fluctuating TADF emission. The delay lifetimes of emission peaks at 410 nm, 450 nm, 570 nm, and 615 nm are 2.78 µs, 6.90 µs, 6.61 ms, and 6.62 ms, respectively, in turn; thereby, RTP/TADF characteristic of the emission peaks are further confirmed (Fig. 2b). To gain a deeper insight, at the PBE0/6-311G(d) level, the lowest triplet excited state (T_1) structure of CzIP molecule constructed from the single crystal structure was optimized using time-dependent density functional theory (DFT), and then the intrinsic emission mechanism of CzIP was elucidated (Figs. 2e and S4). Fig. 2e displays that there are multiple ISC channels of $S_1 \rightarrow T_n$ (n = 1–4) below S_1 states, accompanied by the minimal energy gap and large SOC constant (ξ) for $S_1 \rightarrow T_4$ (0.01 eV and 0.26 cm⁻¹) and $S_1 \rightarrow T_3$ (0.18 eV and 0.17 cm^{-1}), which is conducive to the rapid generation of triplet excitons. Calculations indicated that T₁ (2.15 eV) and the second excited triplet states T₂ (2.76 eV) are corresponding to 577 nm and 449 nm, respectively, which keep good consistency with experiment results at 570 nm and 450 nm RTP peaks. Furthermore, it has become a recognized fact that commercial carbazole contains trace Bd [35]; according to the reported literature, Bd derivative's radical cation can generate three typical RTP emission peaks near 560 nm, 610 nm, and 660 nm [36]. From these, phosphorescence peaks of 610 nm and 560 nm should come from Bd derivative's radical cation, but possible contribution coming from T₁ state of CzIP also cannot be ruled out for RTP peak at 560 nm. Therefore, L-CzIP were prepared by self-made carbazole (Scheme S2), whose steady state delay spectral showed its intrinsic RTP peak was located at 575 nm with lifetime of 430 µs (Fig. 2c and S5), suggesting the RTP peak of CzIP at 570 nm may stem from combined contributions of Bd derivatives' radical cations and CzIP. Meanwhile, the inferior RTP



Fig. 1. (a) Comparison pictures of crystals before and after grinding. (b) Fluorescence spectra of different colored crystals ($\lambda_{ex} = 340 \text{ nm}$). (c) Fluorescence spectra and (d) corresponding X-ray diffraction patterns of CzIP in different states.

lifetime for crystal L-CzIP compared with crystal CzIP further confirms the important role of Bd derivative's radical cation in promoting RTP. By degassing experiments, RTP intensity of crystal CzIP has not been obviously enhanced (Fig. S6), but it can give longer afterglow after cryopreservation by liquid nitrogen. The results indicate crystallization itself can effectively inhibit oxygen diffusion rather than thermal deactivation, leading to shorter RTP lifetimes for crystal CzIP. More interesting, crystal CzIP and crystal L-CzIP exhibit obviously different fluorescence emission spectra (Figs. 1b and 2c). The fluorescent emission bands of the former are mainly located at 350–500 nm, which is consistent with the fluorescence spectra in solution, while the latter exhibits two emission bands located at 370-440 nm and 440-650 nm, respectively. For comparison, emission intensity of L-CzIP at 440-650 nm continuously enhanced from 1% L-CzIP@PMMA, 10% L-CzIP@PMMA to crystal L-CzIP (Fig. 2c), indicating that this emission band is closely related to the intermolecular interactions. Combined with fluorescent emission spectra of L-CzIP in PMMA and crystalline state, the weak emission band at 370-440 nm should come from LE state of L-CzIP, while the strong emission band at 440-650 nm originates from the intermolecular CT state of L-CzIP. To explore the internal mechanism of fluorescence discrepancy between crystal CzIP and crystal L-CzIP, single crystal of L-CzIP was also obtained by slow diffusion of n-hexane into DCM solution of L-CzIP. XRD analysis demonstrates that CzIP and L-CzIP present almost identical spatial molecular configuration and intermolecular arrangement and stacking mode, except for some tiny distinctions in dihedral angles among of ring A, B, and C, as well intermolecular weak interactions (Figs. 2d

and S7). Obviously, the absence or presence of trace Bd derivatives has a tiny influence on crystal arrangement and stacking, but what leads to remarkable fluorescence discrepancy between crystal CzIP and L-CzIP? Fluorescent and phosphorescent emission maxima of crystal L-CzIP are 515 nm and 576 nm, respectively; in this case, ΔE_{st} is reduced to 0.25 eV. Theoretically, such minor ΔE_{ST} can accelerate the IST between the singlet and triplet states and produce more triplet excitons; thereby, crystal L-CzIP should show better RTP than CzIP, but that is not the case. Based on the reported literature [37], the doping system containing trance Bd derivatives easily forms a charge-separated state after photo-radiation, which can enhance SOC between S_n state and T_n state. Therefore, for crystal CzIP, disappearance of the fluorescence peak at 515 nm should be ascribed to the enhanced SOC, leading to an energy transfer process from intermolecular CT state to T₁ state. Besides, the energy gap between T₂ and T₁ is up to 0.61 eV for CzIP, and such a large energy gap can make a slower relaxation rate between T_2 and T_1 than the radiative transition of $T_2 \rightarrow S_0$, which is helpful to facilitate $T_2 \rightarrow S_0$ radiative transition, thereby producing the RTP peak near 450 nm. However, crystal L-CzIP did not give the RTP peak; thereby, we are more inclined to speculation of Ma et al. [36], which is assigned to the intrinsic molecular phosphorescence of Bd derivatives.

To avoid harsh growth environment and poor repeatability of crystallization, doping films were prepared by doping CzIP/L-CzIP into PMMA with weight ratio 1.0% (1% CzIP@PMMA film and 1% L-CzIP@PMMA film) and 10% (10% CzIP@PMMA film and 10% L-CzIP@PMMA film), respectively. With the increase of doping ratio, fluorescence emission maxima shifted to 410 nm from 390 nm,



Fig. 2. (a) Temperature-variable phosphorescence spectra; (b) decay spectra at ambient condition of CzIP crystals. (c) Fluorescence and phosphorescence spectra of L-CzIP crystals and PMMA-doped films (delayed time = 1 ms, $\lambda_{ex} = 360$ nm). (d) Comparison of single crystal interaction forces of CzIP and L-CzIP, (e) CzIP single-molecule energy level diagram and SOC coefficient. PMMA, polymethyl methacrylate; SOC, spin-orbit coupling.

accompanied by a new shoulder peak at 500 nm (Fig. 3a). Under 365-nm radiation, 1% CzIP@PMMA film and 10% CzIP@PMMA film emit deep blue and light blue fluorescence, respectively (Fig. 3c). Obviously, CzIP presents doping concentration-dependent fluorescence emission. The situation is similar to fluorescence emission of 1% CzIP@PMMA film and 10% CzIP@PMMA film, which is attributed to fluorescence emission of LE state and intermolecular CT state, respectively. Furthermore, phosphorescence emission peaks of 1% CzIP@PMMA film and 10% CzIP@PMMA film red shift to 460 nm, 490 nm, and 560 nm, whose lifetimes are 225.17 µs (460 nm), 160.66 µs (490 nm), and 252.65 µs (560 nm) in turn (Fig. S8). Due to dilution and non-radiative suppression effect of PMMA, the absolute fluorescence quantum yields (Φ_F) and phosphorescence quantum yields (Φ_P) sharply increase from crystal to 1% CzIP@PMMA (Fig. S9). When the mass fraction of CzIP increased to 10% from 1%, PMMA matrix could not effectively suppress nonradiation, leading to significantly downward $\Phi_{\rm F}$ and $\Phi_{\rm P}$ from 29.19 and 4.93 to 6.27 and 1.52. Switching off UV light, the two doping films exhibit blue gray and pale brown afterglow, presenting doping concentration-dependent phosphorescence emission. Irradiating the two doping films with an ultraviolet lamp for 2 min to remove the oxygen inside films, and the afterglow of about 1 s can be observed, whose phosphorescence lifetimes increased to 100.14 ms (460 nm), 73.68 ms (490 nm), and 97.93 ms (560 nm) (Fig. 3b). By contrast, two phosphorescent emission peaks of 1% L-CzIP@PMMA and 10% L-CzIP@PMMA films are located at 490 nm and 510 nm, respectively, and corresponding lifetimes are 105.57 µs and 71.29 µs (Fig. S10). After UV radiation of 2 min, phosphorescent lifetimes of 1% L-CzIP@PMMA and 10% L-CzIP@PMMA increase to 84.83 ms and 79.41 ms (Fig. S11), approaching that of 1% CzIP@PMMA and 10% CzIP@PMMA films. The results indicated L-CzIP is intrinsically phosphorescent molecules, but PMMA film cannot effectively inhibit the diffusion of external oxygen.

Interestingly, 1% CzIP@PMMA film shows time-dependent phosphorescent emission from blue gray to yellow green, but 10% CzIP@PMMA film always maintains brownish yellow afterglow. To reveal the intrinsic mechanism of the time dependence RTP, the phosphorescence spectra of different delay times were tested for 1% PMMA@film (Fig. S12). The results show that the shoulder peak at 570 nm is continuously enhanced with the delay time, which constantly change the emission strength ratio between 460 nm and 570 nm, leading to time-dependent phosphorescence emission. The time-dependent phosphorescent emission endows the CzIPdoped films with the ability to dynamically monitor the encryption performance. As shown in Fig. 3c, 'Gui' and 'Lin' were written by using 1% CzIP@PMMA and 10% CzIP@PMMA, respectively. Under UV light irradiation, 'Guilin' showed blue fluorescence, and 0.1 s after UV light was extinguished, 1% PMMA@film still showed blue phosphorescence, but its phosphorescence changed from blue to pale green to green with time, while 10% PMMA@film showed persistent yellow phosphorescence. To illustrate the concentrationdependent RTP, T₁ structure of dimer CzIP constructed from the single crystal structure was also optimized using time-dependent DFT theory (Fig. 3d), which indicate the energy level of S_1 state fall by 0.03 eV for dimer CzIP than monomer CzIP, but its energy level of T₁ state remains constant, which is inconsistent with the RTP peaks of doping films. Furthermore, hole (red) and electron (green) distributions of T₁ excitations are also investigated by theory calculation. As shown in Fig. 3e, there is an obvious CT from nitrogen atom on carbazole to phenylimidazolopyridine, belonging to $n-\pi^*$ type transition; thereby, we speculate energy level of T_1 state can be adjusted by environmental polarity and space conformation, resulting in doping concentration-dependent RTP. For CzIP-doped films, RTP peaks at 460 nm and 490 nm may come from molecular phosphorescence of the Bd derivative based on a great difference between CzIP and L-CzIP at the same doping

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Fig. 3. (a) Fluorescence and phosphorescence spectra of CzIP@PMMA films at different doping concentrations (delayed time = 1 ms). (b) Time-resolved phosphorescence decay curves of CzIP@PMMA films excited at 360 nm. (c) Photograph of the corresponding films under UV light. (d) Energy level diagram and SOC coefficient of CzIP dimer. (e) The hole (red) and electron (green) distributions of T_1 and T_2 states. PMMA, polymethyl methacrylate; SOC, spin—orbit coupling; UV, ultraviolet. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

concentration, while the RTP peak at 560 nm is ascribed to its radical cation. Besides, if the Bd derivatives' radical cation wants to dominate the phosphorescent speetra, a certain doping concentration is required.

As host materials, LMOM have significantly improved RTP lifetime and intensity of guest materials. More importantly, the host-guest-doped system can quickly emit strong RTP without requiring a long time of UV radiation. By a series of screening experiments (triphenylamine, benzophenone, imidazole, 2-AP), the AP/CzIP-doped system was identified, and then, the doping concentration is optimized from 100:1 to 10,000:1(Fig. S13). When the molar ratio between AP and CzIP is 1000:1, the doped system shows the best RTP performance, whose delayed lifetime and afterglow rise to 657.56 ms and 4 s, respectively (Fig. 4b). Next, internal mechanisms of the AP/CzIP-doped system were analyzed and discussed by spectral measurement and theoretical calculation. UV-Vis absorption spectra indicate the doped system contains two absorption bands (Fig. 4c), located at 200-350 nm and 350-600 nm. Compared with AP and CzIP, no new absorption peaks were observed for the AP/CzIP-doped system, eliminating exciplex formation. It is worth noting that there is a big overlap at 310-400 nm between the emission spectra of AP and the absorption spectra of CzIP (Fig. S14), which may trigger a Föster resonance energy transfer (FRET) process affecting RTP properties of the doping system. Therefore, phosphorescence emission spectra of the AP/CzIP-doped system were measured under 290-nm, 340-nm, 360-nm, and 420-nm excitation (Fig. S15), which indicate the AP/ CzIP-doped system emits the strongest RTP at 360-nm excitation, followed by 420 nm, 340 nm, and 290 nm. Excitation wavelength at 420 nm is beyond the absorption range of CzIP in a single molecular state, but gives stronger phosphorescence emission than 290-nm and 340-nm excitation; thereby, the FRET process was ruled out

from CzIP to AP. As a control, the AP/L-CzIP-doped system was also constructed by a similar method, affording two phosphorescence emission peaks at 420 nm and 500 nm (Fig. S16). However, the corresponding phosphorescent lifetime at 500 nm is shortened to 10.59 ms, confirming the importance of Bd derivative' cations once again. To explore the internal mechanism of RTP behind AP/ L-CzIP and AP/CzIP-doped systems, theoretical calculations of host material AP were carried out (Fig. S17). There are two triplet excited states $(T_1 \text{ and } T_2)$ below the S_1 state, but it is difficult to promote the rapid generation of triplet excitons due to tiny ξ $(S_1 \rightarrow T_2 = 0.071 \text{ cm}^{-1})$ and large energy gap between S_1 and T_1 (1.85 eV). Moreover, the energy gap between T_1 of AP and S_1 of CzIP is up to 0.82 eV, which also denied the energy bridge role of AP between S₁ and T₁ of CzIP. It is worth noting that the T₁ state of AP is located between T_1 and T_2 of CzIP (Fig. 3d), and such a close triplet arrangement is supposed to effectively suppress the non-radiative deactivation of triplet excitons. However, the AP/L-CzIP-doped system fails to emit visible afterglow at the optimal doped concentration, which indicates close triplet arrangement is still not the key factor for the AP-CzIP-doped system with ultralong RTP. Therefore, we focused our attention on Bd derivatives' radical cations: Bd derivatives are dispersed homogeneously in AP matrix and easily generate radical cations by photo-irradiation due to a large energy difference between the neutral Bd derivatives and corresponding radical cations, which is further stabilized by AP matrix. Meanwhile, oxygen diffusion and molecular vibration are effectively inhibited; thereby, the doped system achieves ultralong phosphorescence. Importantly, AP is used as a starting material for the preparation of CzIP, which has a similar molecular structure to AP unit, as carbazole and its isomer Bd can enhance interaction between host and guest and generate beneficial defects to store excitation energy.



Fig. 4. (a) Fluorescence and phosphorescence spectra of AP/CzIP at optimal doping concentration (delayed time = 1 ms, $\lambda_{ex} = 360$ nm). (b) Time-resolved decay curves of delayed fluorescence of AP/CzIP-doped material at a concentration of 1000:1 at room temperature (Inset: Photographs under 365-nm light irradiation and turning off the light irradiation). (c) UV absorption spectra of AP, CzIP, and AP/CzIP in solid states. (d) RTP mechanism diagram. AP, aminopyridine; RTP, room-temperature phosphorescence; UV, ultraviolet.

3.3. Acidchromism and pH monitoring

The imidazopyridine unit of CzIP can be used as a proton acceptor; in acidic environment, protonation of the nitrogen atom on imidazopyridine unit will enhance intramolecular push–pull electron effects and adjust intermolecular arrangement and stacking, leading to emission shifts or intensity change. To investigate acidchromism characteristics of CzIP, light yellow powder is fumigated upon exposure to acid vapor of volatile HCl, CF₃COOH, and CH₃COOH. As shown in Fig. 5a, the original emission band is completely quenched in the HCl environment, presenting a remarkably red-shifted emission band with emission maxima at 490 nm; under the irradiation of UV light, fumigated CzIP sample

emits green fluorescence. Interestingly, emission intensity of CzIP is significantly enhanced after TFA (Trifluoroacetic Acid) fumigation, accompanied by obvious color changes from light yellow to pink, but the emission wavelength and intensity remained basically unchanged in the CH₃COOH environment; consequently, CzIP shows acidchromism property and can recognize different volatile acids. As speculated, CH₃COOH and CzIP cannot form ionic salts due to weak acidity for CH₃COOH (pKa = 4.76), which leads to the absence of acidchromism. It is well known that fluorine is strongly electronegative and easily forms intermolecular hydrogen bonds, which can inhibit non-radiative energy loss; thereby, enhanced fluorescence emission is observed by CF₃COOH fumigation.



Fig. 5. (a) Fluorescence emission spectra of CzIP under different acid environments and corresponding photographs under UV light. (b) UV–Vis absorption spectra and (c) fluorescence emission spectra of CzIP at different pH conditions. UV, ultraviolet; UV-Vis, ultraviolet visible.

As an important intracellular substance, hydrogen ion (H⁺) in cells is related to multiple diseases. Therefore, construction of an excellent pH fluorescence probe is of great significance for accurate tracking and monitoring of intracellular pH concentration and its fluctuation. To investigate the pH monitoring property and explore the internal mechanism of acidchromism, the UV-Vis absorption and fluorescence emission spectra of CzIP are tested in detail at different pH values in DMSO/H₂O solutions (Fig. 5b-c). Under neutral conditions (pH = 7), two absorption bands can be observed at 285 nm and 340 nm; with the pH decreasing from 7.0 to 0.6, the absorption intensities at 285 and 340 nm gradually decrease after an increase but without wavelength shifts, which illustrates that various pH conditions basically do not affect molecular conjugation. When the pH of the solution decreases to 4.65, the absorption band at 340 nm becomes narrower; when the pH decreases to 2.88, a new absorption peak appears at 330 nm and reaches the maximum at 2.21, but does not shift with a further decrease of the pH value, which may be due to the formation of an imidazopyridine cation. The fluorescence emission spectra indicate that the emission maxima of CzIP are located at 410 nm at pH 7.0-4.65; when the pH of the solution decreases to 4.07, the long wavelength region at 475–600 nm begins to appear a level-off tail, corresponding to partial protonation of nitrogen atom on imidazopyridine, and then gives rise to a new emission peak at 510 nm with the further decrease of pH and reaches the maximum at pH 2.21 corresponding to completion of protonation, which is consistent with the absorption spectra. As shown in Fig. S18, pKa of CzIP are 4.15 at 380 nm and 4.21 at 410 nm ($R^2 = 0.9906$) by Sigmoidal fitting of the fluorescence emission intensity: therefore, CzIP can be used for pH monitoring in extreme acid environments, which also gives a reasonable explanation about the absence of acidchromism for CH₃COOH.

3.4. Explosive detection

Based on fluorescence quenching mechanisms including photoinduced electron transfer (PET), FRET, and intermolecular CT, fluorescent probes have exhibited rapid response ability in the field of explosive detection [38]. Carbazole is a typical electron-donating unit, which can enhance the HOMO energy level of CzIP, while the nitro group is a typical electron-withdrawing unit, generally leading to electron-deficient property, a certain degree of acidity, and low LUMO energy level for nitroaromatic explosives. The abovementioned acidchromism and AIEE properties indicate that CzIP has proton-binding properties, and its fluorescence emission maxima can form good overlap with the absorption spectra of some explosives; thus, explosive detection is expected to be achieved by PET, FRET, or intermolecular proton transfer. As shown in Fig. 6a, the detection of explosives was performed by adding 10 equivalent nitroaromatic compounds including p-nitrotoluene(p-NT), 2,4,6trinitrotoluene (TNT), nitrophenol, p-nitrophenol (p-NP), o-nitrophenol, p-methyl phenol, 2,4-dinitrochlorobenzene (DNCB), 1,4benzenediol (p-DOM), and picric acid (PA) to THF/water (7:3, v/v) solution of CzIP. Obviously, CzIP exhibits high sensitivity toward PA and p-NP, especially for PA. For DNCB and TNT, fluorescence intensity decreased by 5% and 10%, respectively, but the quenching behaviors cannot be observed for other analytes. Then, competition experiments were completed by adding 10 equivalent PA and other nitro compounds to THF/water (7:3, v/v) solution of CzIP, as shown in Fig. 6b, and CzIP still exhibited a significant response to PA even in the presence of interferences, indicating highly selective sensing behavior, which suggests that CzIP can be a very promising chemosensory system for PA detection in real samples. More interestingly, p-NP with stronger quenching ability showed the minimal interference to fluorescence detection of PA in the above nitro



Fig. 6. (a) PL spectral responses of CzIP to different analytes (10 equiv.) in THF/water (v/v = 3:7) medium; (b) PL spectral responses of CzIP to the presence of interference from other nitro compounds in the same medium. (c) PL spectra of CzIP upon the addition of PA in the THF/H₂O (v/v = 3:7) mixture. Inset: photographs of CzIP under a UV lamp; (d) the linear relationship of CzIP between the fluorescence intensity and the PA concentration. (e) HOMO and LUMO energy-level diagrams of CzIP and PA. (f) Normalized UV–vis absorption spectra of PA and normalized fluorescence of CzIP. PA, picric acid; PL, photoluminescence; UV, ultraviolet; UV-vis, ultraviolet visible.

compounds, which should be attributed to stronger intermolecular hydrogen bond (N–H–O) for CzIP with PA than p-NP.

To further clarify the response characteristics of CzIP to PA, we performed fluorescence titration experiments. Fig. 6c showed that the fluorescence intensity of CzIP at 379 nm was gradually quenched by adding 1–10 equivalents of PA to the preparation solution of CzIP. The quenching effect can be assessed by the Stern–Volmer equation $I_0/I_1 = 1 + K_{SV}[M]$, where I_0 and I_1 are the fluorescence intensities before and after PA addition, respectively, [M] is the molar concentration of PA, and K_{SV} is the quenching effect coefficient. The titration experiment presented a hyperbola (Fig. S19), indicating the simultaneous existence of static quenching and dynamic quenching. The K_{SV} value of CzIP is determined to be $8.12 \times 10^5 \text{ M}^{-1}$ by fitting the linear part of the curve (Fig. 6d), and the lowest detection limit (LOD) of CzIP for PA is calculated using LOD = 3 σ/k , where σ is the standard deviation of the blank measurement and k is the slope of the fluorescence intensity vs. PA concentration curve. The results show that the LOD of PA is 3 nM, which is below minimum international drinking water standards (0.5 mg/L). Then, fluorescence detection of PA is investigated by actual contact experiments (Fig. S20). To the best of our knowledge, CzIP exhibits higher quenching efficiency and lower detection limit than the same class of imidazopyridine derivatives and some protonable derivatives based on anthracene and pyrazine [39–41]. In the experiment, concentrated THF solution of CzIP is dropped on the silica gel plate. Under the irradiation of a 365-nm UV lamp, CzIP shows strong earth-vellow fluorescence after the solvent evaporates naturally, and then 10 μ L of PA solutions of different concentrations $(10^{-8}-10^{-4} \text{ M})$ is dipped with a capillary tube for visual inspection. The results demonstrate that black circles of different degrees can be observed, meaning that CzIP can distinguish and respond directly to different concentrations of PA solution, even at low concentrations of 10^{-8} M, and thereby, CzIP is an excellent chemical sensor for the instantaneous visualization of trace amounts of PA in both aqueous solution and in the solid state.

To clarify the fluorescence quenching mechanism, DFT is used to calculate the HOMO and LUMO energy levels of CzIP and explosives at the PBE0/6-311G(d) level. Compared with other explosives, PA has the lowest LUMO energy, show that PA is readily available for electrons: meanwhile, its LUMO is just between the HOMO and LUMO of CzIP (Fig. 6e), so a certain PET occurs from the LUMO of PA to the HOMO of CzIP, resulting in partial fluorescence quenching. However, based on the calculated HOMO and LUMO (Fig. S21). there is no regularity to explain the above fluorescence quenching phenomenon only from the perspective of PET, especially for TNT and p-NP. TNT has a much lower LUMO relative to p-NP, but the latter shows a more significant fluorescence quenching effect than the former; thus, PET may not be the only fluorescence quenching mechanism for the explosives. To test the above conjecture, we investigate the absorption spectrum of PA and the emission spectrum of CzIP in the same solvent. Fig. 6f shows that the emission spectrum of CzIP overlaps with the UV absorption spectrum of PA very well in the range of 350 nm-450 nm, which means the FRET mechanism plays an important role in fluorescence detection of PA. Among the explosives, PA has the strongest acidity (pKa = 0.29), followed by p-NP (pKa = 7.15), while CzIP only can be used as pH monitoring in extreme acid environment; obviously, the factors are conducive to selective detection of PA. In addition, acidity also should be the reason why CzIP can respond to p-NP rather than TNT, m-NP, and o-NP, which can promote intermolecular interaction between p-NP and CzIP. Overall, selective detection of PA is the combination of PET. FRET mechanism. and acid-base intermolecular interaction.

3.5. Applications of stimuli-responsive materials

Based on multifunctional characteristics of CzIP, a series of encryption and anti-counterfeiting patterns were designed. First, a piece of filter paper was soaked in molten AP and cooled, and then CzIP and L-CzIP were dissolved in DCM at a concentration of



Fig. 7. (a–b) Anti-counterfeiting application using the outline of the AP/CzIP doping system. (c) Photographed with a badminton racket on a filter paper with CzIP powder dispersion in daylight and in UV light. (d) Motifs designed using CzIP multiple-stimuli responsiveness. AP, aminopyridine; UV, ultraviolet.

 1×10^{-4} M. Subsequently, a teddy bear face was outlined by DCM solution of CzIP and L-CzIP. After drying, no trace could be observed in sunlight, which was due to absorption spectra of AP, CzIP, and L-CzIP mainly located on the UV region below 400 nm (Fig. 7a). Under a 365-nm UV lamp, the teddy bear face with deep blue color clearly appeared due to a similar fluorescence emission between AP/CzIPand AP/L-CzIP-doped systems. Turning off the UV lamp, only a part of the bear's facial features could be observed, showing an obvious color change from deep blue to orange yellow, which were attributed to different phosphorescence lifetimes between two doped systems. Notably, orange yellow emission can last more than 2 s. From the imperceptibility in the sunlight, to the bear face containing false information, and finally to the real facial features of the bear, advanced encryption and anti-counterfeiting patterns are successfully constructed. When a drop of hydrochloric acid was dropped on the bear's nose, its fluorescent color did not change under 365-nm irradiation, but the corresponding phosphorescent emission disappeared, leaving a black spot on the bear's nose. Strong RTP of AP/CzIP-doped systems also provided a chance to direct writing. On a piece of filter paper soaked with molten AP and then dried, 'CzIP and RTP' were written by adopting DCM solution of CzIP. Switching on/off the UV lamp, bright blue and yellow written words can be clearly presented even in sunlight (Fig. 7b). Recently, mechanochromic materials have been used to prepare rewritable paper, which is conducive to reducing tree cutting and protecting the ecological environment. By immersing the porous filter paper into CzIP solution, after drying, a badminton racket and a shuttlecock were drawn by a hard tool, which show an obvious contrast between the filter paper and patterns under 365-nm irradiation (Fig. 7c). Finally, the clover, pentagram, and heart were constructed, respectively, by crystal, hydrochloric acid fumigated, and ground CzIP (Fig. 7d), and the different patterns show bright pale yellow, green, and blue fluorescence in turn under UV lamp radiation. After the UV light was turned off, the clover and hearts emitted pale brown phosphorescence, while the green pentagram disappeared. To emphasize, multifunctional CzIP has great potential for enhancing anti-counterfeiting and encryption. If PA and triethylamine fumigation are combined with the above-mentioned, more encryption modes will be achieved.

4. Conclusions

In conclusion, CzIP and L-CzIP were successfully prepared by choosing commercial and self-made carbazole. Trace Bd derivatives only show slight influence on the intermolecular arrangement, stacking, and molecular space conformation of the crystalline state, but they can significantly change the fluorescence spectra, phosphorescence spectra, and phosphorescence lifetime of crystals by boosting intersystem SOC. Generally, crystals CzIP and L-CzIP cannot effectively inhibit non-radiative energy loss like the PMMA film, while the PMMA film cannot effectively inhibit the diffusion of external oxygen. RTP lifetimes of CzIP and L-CzIP are up to 100.14 ms and 84.83 ms, respectively, in PMMA-doped films after UV radiation of 2 min, indicating L-CzIP is intrinsically phosphorescent. More interestingly, CzIP displays concentration-dependent fluorescent emission and phosphorescent emission in PMMA, and 1% CzIP@PMMA film also shows dynamic phosphorescent emission, whose color transition from blue gray to yellow green can be clearly observed within afterglow time of 1 s. More importantly, our newly developed AP/CzIP-doped system has RTP lifetimes of 657.56 ms and afterglow lifetimes of 4 s, whose strong orange afterglow is visible to the naked eye; moreover, the doped system can be excited by visible light of 420 nm. The ultralong RTP involves generation of Bd derivatives' radical cations, well dispersion of CzIP in AP, and non-radiation suppression. By grinding-fuming/heating process, CzIP can present reversible and high-contrast mechanochromism due to phase transition and the resulting enhancement or attenuation of RTP. By selective protonation and variation of intermolecular arrangement and stacking, CzIP responds selectively and distinguishes HCl, CF₃COOH, and CH₃COOH. Especially, CzIP shows excellent detection capability to PA in both aqueous medium ($K_{SV} = 8.12 \times 105 \text{ M}^{-1}$ and LOD = 3 nM) and solid state. Based on RTP, mechanochromism and acidichromism of multifunctional CzIP, repeatable writing paper, various anticounterfeiting and encryption patterns are successfully constructed. This work not only provides an alternative high-efficiency material for the selective detection of PA, simple recognition of volatile HCl, CF₃COOH, and CH₃COOH, and high-contrast mechanosensors but also more importantly provides a theoretical basis and experimental guidance for designing novel UOP materials and achieving multiple anti-counterfeiting and encryption.

Author contribution statement

Jianfeng Jiang and Kai Wang contributed equally to this work. This paper is completed under the guidance of Professor Yongtao Wang, and theoretical calculations are provided by Professor Lei Ma.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

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