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The luminescence mechanism of two pure organic room temperature phosphorescent isomers, mechanical force detection, 3D modeling, and dynamic data encryption

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ABSTRACT

Polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA) can provide a rigid and anaerobic microenvironment for pure organic room temperature phosphorescent (ORTP) luminogens, leading to significantly enhanced room temperature phosphorescence quantum yield (Φ_P) and extended lifetime. However, their brittleness and hydrophilicity limit further expansion of the application range of ORTP luminogens. Herein, two novel ORTP luminogens named as PM-BTDA and OM-BTDA were designed and synthesized based on isomerization and intramolecular charge transfer effects. Interestingly, PM-BTDA showed longer RTP and afterglow (667.19 ms and 10 s) lifetimes, as well as higher $\Phi_{\rm P}$ (0.26) than OM-BTDA (527.17 ms, 8 s, and 0.21) in PVA film, but with long-lived visible afterglow for OM-BTDA rather than PM-BTDA in PMMA and polyvinyl chloride (PVC) films. More importantly, OM-BTDA@PVC film demonstrated an outstanding flexibility and mechanical force responsive behaviors, with continuously decreasing room temperature phosphorescent (RTP) intensity and lifetime within the elongation ranges from 0 to 147.49 %. Based on Foerster resonant energy transfer (FRET) from RTP of OM-BTDA/PM-BTDA to Rhodamine B (RhB) in PVA matrix, light yellow and red afterglows were achieved, with emission maxima of 587–612 nm, energy transfer efficiency of 83 %, and Φ_P of 0.62. Based on different fluorescence and afterglow colors and lifetimes, as well as excellent flexibility of OM-BTDA@PVC film, complex dynamic digital encryption and various 3D models were successfully constructed. This work can be expected to provide more inspirations and possibilities for ORTP luminogens in molecular design and more application areas.

1. Introduction

As a substitute for traditional inorganic phosphorescent materials containing heavy metals, ORTP materials have the advantages of low cost, environmental friendliness, low toxicity, and easy structural regulation [1–4]. However, it is difficult to form a large number of triplet excitons through intersystem crossing (ISC) due to weak spin orbit coupling (SOC) between singlet and triplet excitons [5–8]. Meanwhile, slow phosphorescence radiation rate easily leads to triplet exciton quenching by molecular vibration and oxygen [9,10]. As a result, most of ORTP materials can't emit visible RTP. Currently, heavy atoms (Cl, Br, I) or heteroatoms with lone pair electrons (N, O, S, P) are introduced to enhance SOC [11–13]. Crystal engineering, H stacking, and

host–guest doping systems are used to provide a rigid environment for phosphorescent molecules, limiting molecular vibration and rotation while isolating non radiative transition pathways such as air or water from deactivation [14–16]. Thereby, ORTP materials have made significant progress in extending RTP lifetime and improving Φ_P . Even so, ORTP materials are mainly limited to the field of information encryption and data anti-counterfeiting [17,18].

The key factor affecting extensive application of phosphorescent chromophores is the suppression of molecular motions and oxygen diffusion, but which often leads to new problems [19,20]. For example, PVA used as the host material has long, entangled molecular chains and can form dense intramolecular and intermolecular hydrogen bonds, providing a rigid environment similar to crystals, reducing non radiative

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transition deactivation of phosphorescent chromophores, and inhibiting oxygen diffusion, thereby promoting the production of RTP [21-23]. However, owing to good water solubility, phosphorescence quenching and rapid decay often occur for host-guest doping systems containing PVA in aqueous environments [24,25]. PMMA is another commonly used host material, with excellent solubility in organic solvents [26]. Host-guest doping systems containing PMMA can maintain stable phosphorescence emission in aqueous environments, but poor flexibility and stretchability are not conducive to mechanical force detection and flexible three-dimensional modeling [27-29]. To make matters worse, most of ORTP luminogens prefer to present bright and persistent RTP in PVA or PMMA matrix [30,31], but with invisible afterglow in other stretchable polymer matrices [32], such as polyvinyl chloride (PVC). As we know that many organisms in nature show various defensive behaviors to hunt prey or deal with environmental threats, like mimosa, chameleon, morning glory, water lily, and seaweed. To simulate the above phenomenon, some fluorescent materials with mechanical stimulus response have attracted the attention of researchers and made significant progress [33,34], which show potential application value in the fields of pressure sensors [35], actuators [36], information encryption [37], repeatable erasable paper [38], while ORTP materials with mechanical stimulus response are still in the infancy stage.

To obtain ORTP materials with excellent flexibility and mechanical stimulus responsiveness, it is crucial to conduct reasonable molecular design based on the research progress of ORTP materials at home and abroad. The lone pair electrons on the nitrogen atom of morpholine can form n- π^* transitions with the π system, effectively enhancing ISC ability of ORTP luminogens [39]. Meanwhile, oxygen atoms on morpholine can induce multiple supramolecular interactions, which are beneficial for increasing molecular rigidity in aggregated state and inhibiting non radiative transition process [40]. Besides, morpholine with a chair shaped non-planar spatial conformation can effectively avoid intermolecular π - π stacking and the resulting aggregation caused luminescence quenching [39,40]. Our research group had reported that dicyanoaniline derivatives showed long-lived RTP and thermally activated delayed fluorescence (TADF) [41,42]. Furthermore, the dicyanoaniline unit contains two strong electron withdrawing groups, which can be served as an electron acceptor. Thereby, morpholine and dicyanoaniline structural units are used as electron donor (D) and acceptor (A) respectively, and the triplet energy levels and ISC rates are expected to be tuned by changing the substitution position of morpholine. Of note, the distorted D- π -A type molecular configuration can reduce the energy gap (ΔE_{ST}) between the lowest excited singlet state (S₁) and triplet state (T₁), thereby increasing ISC rate and generating more triplet excitons, which can more effectively counteract the phosphorescence quenching caused by insufficient environmental rigidity and oxygen diffusion and reduce the selectivity of phosphorescent chromophores towards the polymer matrix [43–45]. Moreover, a small ΔE_{ST} easily leads to a shortened afterglow lifetime, which is a disadvantage for observation and application of RTP [46]. If ΔE_{ST} is adjusted to an appropriate value to achieve a good balance between polymer matrix selectivity and afterglow lifetime, ORTP materials with excellent flexibility and mechanical stimulus responsiveness are expected to be achieved. Here, two luminogens named as PM-BTDA and OM-BTDA were designed and synthesized, whose molecular structure and purity were confirmed. 1 % PM-BTDA@PVA film showed longer RTP and afterglow (667.19 ms and 10 s) lifetimes, as well as higher Φ_P (0.26) than 1 % OM-BTDA@PVA film (527.17 ms, 8 s, and 0.21). Furthermore, OM-BTDA could present RTP lifetimes of 170.16 ms and afterglow lifetimes of 3 s in PVC films, but with invisible afterglow for PM-BTDA in PVC films. Based on Foerster resonant energy transfer (FRET) from RTP of OM-BTDA/PM-BTDA to Rhodamine B (RhB) in PVA matrix, light yellow and red afterglows were achieved, with emission maxima of 587-612 nm and energy transfer efficiency of over 80 %. As the elongation increased, RTP intensity and lifetime of 1 % OM-BTDA@PVC film continued to decrease. Thus, 1 % OM-BTDA@PVC film will be expected to be used for

mechanical force detection. Using different fluorescence and multi-color afterglow, complex dynamic digital encryption was constructed by turning on/off a 365 nm UV lamp. Finally, the intrinsic luminescence mechanisms of two luminogens were discussed in detail by theoretical calculations. This work not only obtained new long-lived multi-color RTP host–guest doping systems, but also further expanded the application scope of ORTP materials, provided theoretical guidance and experimental support for further molecular designs.

2. Results and discussion

PM-BTDA and OM-BTDA were prepared via two-step reactions (Scheme 1), and characterized by ¹H NMR, ¹³C NMR, HR-MS, and highperformance liquid chromatography (HPLC) (Figs. S1-S8). In various diluted solvents, UV-Vis absorption maxima around 360 nm showed shifts of less than 15 nm, outlining small dipole moments for ground states of two luminogens. As the solvent polarity increased from nhexane to DMSO, fluorescence peaks presented significantly red shifts, especially for PM-BTDA, demonstrating bigger intramolecular charge transfer (ICT) effect for PM-BTDA than OM-BTDA. Of note, PM-BTDA showed a single fluorescence peak, while OM-BTDA had a main emission peak at high energy level and a shoulder emission peak at low energy level, corresponding to located state (LE) emission and ICT emission respectively (Fig. S9). Like the vast majority of reported literatures [47,48], PM-BTDA and OM-BTDA could not give visible afterglow at room temperature (RT) by switching on/off a 365 nm lamp. However, powder PM-BTDA and OM-BTDA emitted long visible afterglow at 77 K, lasting for 6 s and 4 s in turn (Fig. S18). Thereby, invisible afterglow of powder PM-BTDA and OM-BTDA at RT was attributed to non-radiative energy loss induced by molecular motions. In glassy DCM solution (10⁻⁵ M), PM-BTDA and OM-BTDA emitted bright green afterglow after switching off the 365 nm lamp, with phosphorescence maxima at 517 nm and 492 nm, confirming their phosphorescence nature (Fig. S11b). Possibly due to increasing ISC, PM-BTDA and OM-BTDA exhibited aggregation caused quenching (ACQ) activity in THF-H₂O solutions with water factor = 10 % (Fig. S10). As further evidence, RTP spectra of powder PM-BTDA and OM-BTDA could be measured, with RTP maxima at 458 nm and 492 nm respectively (Fig. S11a), but without visible afterglow.

In order to reduce triplet exciton quenching caused by molecular motions and triplet oxygen, PM-BTDA and OM-BTDA were doped into PVA matrix according to mass ratios of 0.1 %, 1 %, and 2 %, which were named as 0.1/1/2% PM-BTDA@PVA and 0.1/1/2% OM-BTDA@PVA films respectively. Furthermore, 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films sequentially emitted green and blue afterglow and presented strongest RTP intensity and longest afterglow lifetimes (Fig. 1a and Fig. S12), whose intrinsic mechanism lay in the formation of a small amount of triplet excitons at low doping concentrations, but excessive triplet excitons caused collision deactivation at high doping concentrations. By contrast, 1 % PM-BTDA@PVA film had longer RTP and afterglow lifetimes, as well as high Φ_P than 1 % OM-BTDA@PVA film, which were 667.19 ms, 10 s, 0.26, 527.17 ms, 8 s, and 0.21, outlining obvious isomer effects (Fig. 1d-e and Table S2). The internal mechanism was that the faster ISC process leads to faster triplet radiation deactivation, leading to shorter RTP lifetime for 1 % OM-BTDA@PVA film than 1 % PM-BTDA@PVA film. Of note, fluorescence emission peaks of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films were 453 nm and 501 nm respectively, while their RTP peaks red shifted sequentially to 512 nm and 515 nm (Fig. 1b-c), corresponding separately ΔE_{ST} of 0.32 eV and 0.07 eV. Considering the small ΔE_{ST} for 1 % OM-BTDA@PVA film, RTP or thermally delayed activated fluorescence (TADF) characteristics of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films were investigated by temperature-variable phosphorescence spectra (Fig. S13). As the temperature rose from 77 K to 298 K, emission intensity of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films sharply decreased, confirming their RTP rather than TADF characteristic.



Scheme 1. The synthetic route of PM-BTDA and OM-BTDA, as well as the chemical structure of RB.



Fig. 1. (a) Photographs of PM-BTDA@PVA and OM-BTDA@PVA films under 365 nm light irradiation at different doping concentrations. (b)–(c) The normalized fluorescence and phosphorescence emission spectra of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films. (d)–(e) The time-resolved RTP decay curves of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films.

Interestingly, OM-BTDA could exhibit persistent blue afterglow in PMMA and PVC at different doping mass ratios, but not for PM-BTDA. Compared to OM-BTDA, PM-BTDA had bigger bonding energy with PVC matrix (Fig. S21a). Thereby invisible afterglow of 1 % PM-BTDA@PVC film could not be attributed to weak intermolecular interactions between PM-BTDA and PVC matrix. Firstly, PMMA and PVC relative to PVA had weak intermolecular hydrogen bonds, which could not effectively suppress oxygen diffusion and molecular motions, easily leading to triplet excitons inactivation. Secondly, small ΔE_{ST} contributed to boosting the formation of more triplet excitons, thereby enhancing OM-BTDA's competitiveness of phosphorescent radiation relative to non-radiative deactivation of triplet excitons (Fig. 4c) [55–57]. Thirdly, PM-BTDA had a smaller steric hindrance than OM-BTDA, resulting in a faster radiation decay rate from triplet exciton to singlet exciton. These factors worked together to lead to shorter RTP lifetime for PM-BTDA than OM-BTDA in PMMA and PVC matrixes. Based on the optimization of different doping ratios, lifetimes of afterglow and RTP intensity, 1 % OM-BTDA@PMMA and 1 % OM-BTDA@PVC films were selected as the objects of investigation, with RTP and afterglow lifetimes of 167.29 ms, 3 s, 170.16 ms, and 3 s respectively, as well as RTP emission maxima of 489 nm and 504 nm, and Φ_P of 0.24 and 0.15 in sequence (Fig. S14). Although 1 % OM-BTDA@PMMA and 1 % OM-BTDA@PVC films showed shorter RTP and afterglow lifetimes compared with 1 % OM-BTDA@PVA film, excellent water resistance and flexibility were conducive to expanding application ranges of OM-BTDA. As shown in Fig. S15, placed in H₂O solution, 1 % OM-BTDA@PVA film presented invisible afterglow after turning off the 365 UV lamp, but afterglow lifetimes of 1 % OM-BTDA@PMMA and 1 % OM-BTDA@PVC films were almost unaffected. The former was attributed to water solubility of PVA matrix, resulting in

the loss of a rigid environment for OM-BTDA, while the latter was due to the excellent water resistance for OM-BTDA, PMMA and PVC matrixes. More importantly, flexible RTP film was suitable to be prepared as large area, long-lasting, and transparent three-dimensional entities by various stretching, folding, rolling, curling, and so on [49]. Moreover, flexible RTP film was expected to be used as a mechanical force detector, which was different from traditional mechanical force detection devices and could provide intuitive optical signals. Due to very poor flexibility for 1 % OM-BTDA@PVA and 1 % OM-BTDA@PMMA films (Fig. S19), only RTP performance of 1 % OM-BTDA@PVC film were tested after stretching. Fig. 2b indicated that 1 % OM-BTDA@PVC films could be stretched to 5.4 cm from 3 cm without breaking, whose afterglow lifetime and RTP emission maxima gave unobvious changes. However, RTP intensity and lifetime continued to decrease as the elongation increased (Fig. 2c-e). Subsequently, we investigated afterglow and RTP lifetimes of 1 % OM-BTDA@PVC film before and after stretching (elongation = 60 %) under an argon atmosphere. The results showed that 1 % OM-BTDA@PVC film had equivalent afterglow and RTP lifetimes before and after stretching (Fig. S24). Therefore, we believed that triplet excitons were more easily quenched after stretching due to the thinning OM-BTDA@PVC film. Comparing RTP intensity between 1 % OM-BTDA@PVC and 0.1 % OM-BTDA@PVC films (Fig. S14b), it could be seen that 1 % OM-BTDA@PVC film showed higher RTP intensity than 0.1 % OM-BTDA@PVC film. Therefore, the continuously decreasing RTP intensity and lifetime should be because continuously decreasing OM-BTDA content and easy quenching by triplet oxygen as the doping film became thinner. Furthermore, the influence of molecular conformation and intermolecular interactions should be stable owing to the stable RTP emission maxima.

To further investigate the mechanical properties of 1 % OM-BTDA@PVC films, uniaxial tensile experiments (Fig. 2a) were carried out (The films used for testing were prepared a standard dumbbell shape, the thickness was measured three times at different locations by using a millesima thickness gauge/AICE to take the average value). The

stress-strain curve indicated that tensile strength of 1 % OM-BTDA@PVC film significantly increased compared with the blank PVC film (Fig. 2a), and 1 % OM-BTDA@PVC film showed better elongation at break (129.87 %) than the blank PVC film (119.89 %) at the same tensile speed, which suggested that host-guest doping of OM-BTDA and PVC matrix could form more intermolecular interactions, leading to the enhanced mechanical properties. Comparing the FTIR spectra between 1 % OM-BTDA@PVC and blank PVC films, 1 % OM-BTDA@PVC film gave two new signals at 3441.04 and 3179.85 cm⁻¹, corresponding to NH2 and Ar-H of OM-BTDA (Fig. S20a). Furthermore, the glass transition temperature (64.39 °C) of 1 % OM-BTDA@PVC film was significantly higher than that (46.20 °C) of blank PVC film, confirming strong intermolecular interactions between OM-BTDA and PVC matrix (Fig. S20b). The visual interaction diagram of OM-BTDA and PVC matrix showed multiple intermolecular interactions between NH₂, CN, and O of OM-BTDA and Cl of PVC matrix (Fig. S21b). Of note, 1 % OM-BTDA@PVC film showed an outstanding tensile strength (19.39 MPa) and a big elongation at break (147.49%) at tensile speed of 10 min^{-1} . To investigate the variation of RTP emission wavelength during the stretching process, steady state and delayed RTP spectra of 1 % OM-BTDA@PVC films with elongation of 20 % and 60 % were tested and compared (Fig. S22). The results showed the two films had essentially identical steady-state (504 nm) and delayed RTP emission maxima. However, their RTP maxima continued to blue shift to 488/486 nm from 504 nm, 494/493 nm, and 490/491 nm with the extension of delay time, illustrating the existence of multiple RTP centers.

ORTP materials with long-lived red and near-infrared (NIR) emission have aroused significant interest due to deep tissue permeability and shielding of background spontaneous fluorescence [50,51]. However, their construction faced a great challenge according to the energy gap law [52]. Currently, more and more red and NIR materials have been reported based on FRET [53,54]. Even so, the overlap degree between the emission spectra of phosphorescent donors and the absorption spectra of traditional dyes such as rhodamine B (RB) and fluorescein are



Fig. 2. (a) Stress–strain curves of blank PVC film and 1 % OM-BTDA@PVC film with a thickness of 0.112 mm and different tensile speeds (10, 20, and 50 mm/min). (b) Photographs of 1 % OM-BTDA@PVC stretching from original length 0 % (3 cm) to 80 % (5.4 cm) under 365 nm light irradiation. (c) Phosphorescence spectra of of 1 % OM-BTDA@PVC film stretching from original length 0 % (3 cm) to 80 % (5.4 cm). (d) The time-resolved RTP decay curves of 1 % OM-BTDA@PVC film stretching from original length 0 % (3 cm) to 80 % (5.4 cm). (d) The time-resolved RTP decay curves of 1 % OM-BTDA@PVC film stretching from original length 0 % (3 cm) to 80 % (5.4 cm). (d) The time-resolved RTP decay curves of 1 % OM-BTDA@PVC at different elongation.

still unsatisfactory. Fig. 3b and c indicated that absorption spectrum of 3 % RB@PVA almost completely covered RTP spectra of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films, implying good FRET efficiency for 3 % RB&PM-BTDA@PVA and 3 % RB&OM-BTDA@PVA films. To further investigate and optimize FRET efficiency, a series of doping films were constructed by fixing the doping mass ratio (1:100) between PM-BTDA/OM-BTDA and PVA and adjusting the doping mass ratios between RB and PVA from 0.2 %, 1 % to 3 %, which were named as m% RB&PM-BTDA@PVA and m% RB&OM-BTDA@PVA in turn according to doping mass ratios (m%) of RB (Fig. 3a). The fluorescence spectrum of 0.2 % RB&PM-BTDA@PVA film showed two emission peaks at 450 nm and 593 nm, corresponding to fluorescence emission maxima of PM-BTDA and RB respectively. As the doping concentration of RB increased, emission intensity at 450 nm continued to decline, accompanied by the continuous redshifts of the emission peak at 593 nm, which were attributed to FRET (Fig. S16a) from triplet excitons of PM-BTDA to singlet excitons of RB and enhanced intermolecular interactions between RB molecules. Similar to fluorescence emission spectra, the RTP spectrum of 0.2 % RB&PM-BTDA@PVA film also showed two emission peaks at 474 nm and 587 nm (Fig. S16c), corresponding to RTP emission maxima of PM-BTDA and fluorescence maxima of RB respectively. The increased RB concentration resulted in significantly improved FRET efficiency, reflecting in the continuous decrease of RTP intensity at 474 nm. Meanwhile, fluorescence maxima of RB red shifted to 612 nm from 596 nm and 587 nm due to enhanced intermolecular interactions, leading to the obvious transition of afterglow color from light yellow to red. To confirm that the maximum RTP emission wavelength (587-612 nm) of 0.2 %/1%/3% RB&PM-BTDA@PVA and 0.2 %/1%/3% RB&OM-BTDA@PVA films came from the fluorescence emission of RB, we investigated fluorescence emission spectra of 0.2 %/1%/3% RB@PVA films ($\lambda_{ex}\!\!:$ 517 nm), and RTP emission spectra of 0.2 %/1%/3% RB&PM-BTDA@PVA and 0.2 %/1%/3% RB&OM-BTDA@PVA films, which displayed good overlap in the long wavelength region (Fig. S23). Besides, 1 % PM-BTDA@PVA and 1 %

OM-BTDA@PVA films could not vield fluorescence emission under 517 nm excitation. Thereby, FRET from triplet excitons of PM-BTDA/OM-BTDA to singlet excitons of RB was confirmed. Based on the calculation results of spectral integration area, 96.52 %, 97.05 %, and 99.22 % of RTP emission spectra of 1 % PM-BTDA@PVA film were located within the absorption spectra of 0.2 % RB@PVA, 1 % RB@PVA, and 3 % RB@PVA films in turn, while corresponding values for 1 % OM-BTDA@PVA film were 87.65 %, 88.43 %, and 94.89 % respectively, indicating high FRET efficiency between PM-BTDA/OM-BTDA and RB. Unfortunately, afterglow lifetimes of 3 % RB&PM-BTDA@PVA film dropped down to 3 s from 7 s of 0.2 % RB&PM-BTDA@PVA film, whose main internal reason should lie in the increased FRET efficiency (Table S1), leading to an accelerated FRET rate. It was noteworthy that FRET efficiencies of 0.2 % RB&PM-BTDA@PVA, 1 % RB&PM-BTDA@PVA, and 3 % RB&PM-BTDA@PVA films were up to 38.13 %, 55.65 %, and 81.14 % respectively (Table S1), and with corresponding RTP lifetimes of 433.57 ms, 312.72 ms, and 138.87 ms, as well as Φ_P of 0.23, 0.62, and 0.60 in sequence (Fig. S17a-c and Table S2). By contrast, m% RB&OM-BTDA@PVA films showed higher FRET efficiency than m% RB&PM-BTDA@PVA films, but with smaller Φ_{P} , shorter afterglows and RTP lifetimes (Table S2). Notably, FRET efficiency and Φ_P of 3 % RB&OM-BTDA@PVA film were up to 0.83 and 0.53 respectively. Moreover, 0.2 % RB&OM-BTDA@PVC and 0.2 % RB&OM-BTDA@PMMA films could not emit visible afterglow in H₂O solution by turn on/off a 365 nm UV lamp, which was ascribed to water solubility of RB, causing intensified quenching of triplet excitons (Fig. S15).

3. Theoretical calculation

The geometry optimizations of PM-BTDA and OM-BTDA were performed at the B3LYP/def2-TZVP level using D4 dispersion correction, and all single-point calculations were performed at B3LYP/def2-TZVP level. Then the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) distribution, energy



Fig. 3. (a) Photographs of RB&PM-BTDA@PVA and RB&OM-BTDA@PVA films under 365 nm light irradiation at different doping concentrations. (b)-(c) The phosphorescence emission spectra of 1 % PM-BTDA@PVA and 1 % OM-BTDA@PVA films after 365 nm excitation, and the absorption spectra of 0.2 %/1%/3% RB@PVA films.

levels, and spin orbit coupling constants (ξ) between singlet and triplet states were obtained. HOMO electron cloud density of two luminogens mainly located on the morpholine unit and benzene bridge, while their LUMO electron cloud density concentrated on dicyanoaniline, thereby strong ICT effect was confirmed based on the obvious electron cloud density migration. Compared with PM-BTDA, OM-BTDA had higher HOMO and LUMO energy levels, as well as smaller optical gap. Furthermore, OM-BTDA relative to PM-BTDA not only had a smaller ΔE_{ST} , but also larger $\xi(S_1 \rightarrow T_1)$ and $\xi(T_1 \rightarrow S_0)$, contributing to boosting the formation of more triplet excitons, accelerating phosphorescence radiation, but shortening RTP and afterglow lifetimes for OM-BTDA than PM-BTDA, which was consistent with the experimental results. Only comparing ΔE_{ST} (0.21 eV) and $\xi(S_1 \rightarrow T_1)$ (0.278 $cm^{-1})$ of OM-BTDA and ΔE_{S1T2} (0.25 eV) and $\xi(S_1 \rightarrow T_2)$ (0.258 cm⁻¹) of PM-BTDA, OM-BTDA also had a stronger ability to form triplet excitons compared to PM-BTDA.

4. Application

As shown in Fig. 5a, multiple geometric shapes including " \triangle ", " \pm ", " \Box ", and " \circ " were designed and fabricated by using 1 % PM-BTDA@PVA, 0.2 % RB&PM-BTDA@PVA, 3 % RB&PM-BTDA@PVA and 1 % OM-BTDA@PVA films. Based on different fluorescence and afterglow, numbers "1-9" were appointed, while their dark states were referred to as the number "0". These patterns were arranged in a "5x5" matrix, and then dynamic digital encryption was implemented by turning on/off 365 nm UV lamp. As time went on from 0 to 10 s, the above matrix presented eight times different alterations, thereby forming complex dynamic digital encryption. Then, various three-dimensional (3D) models were prepared (Fig. 5b–c) by utilizing the excellent flexibility of 1 % OM-BTDA@PVC film. Firstly, 3D airplane and windmill models were constructed by folding and curling 1 % OM-BTDA@PVC films. By turning on/off the 365 nm ultraviolet lamp, the two 3D models presented green afterglow, lasting for 3 s. More

importantly, 3D airplane and windmill models could be disassembled and assembled multiple times without any decay in afterglow lifetime. Finally, 1 % OM-BTDA@PVC film was stretched and woven into a bow, which was clearly visible when the 365 nm ultraviolet lamp was turned off.

5. Conclusion

In summary, isomerization and intramolecular charge transfer state strategy were adopted to construct two novel long-lived ORTP luminogens. Experimental tests indicated that RTP and afterglow lifetimes, as well as Φ_P of 1 % PM-BTDA@PVA film were up to 667.19 ms, 10 s, and 0.26. Systematic studies confirmed that the small ΔE_{ST} together with large $\xi(S_1 \rightarrow T_1)$ and $\xi(T_1 \rightarrow S_0)$ endowed OM-BTDA with long RTP and afterglow lifetimes, as well as high Φ_P in PVA (527.17 ms, 8 s, and 0.21), PMMA (167.29 ms, 3 s, and 0.24), and PVC (170.16 ms, 3 s, and 0.15) matrixes. The excellent flexibility and the enhanced intermolecular interactions of 1 % OM-BTDA@PVC film enabled mechanical force responses and 3D modeling behaviors. By FRET from RTP of OM-BTDA/ PM-BTDA to RhB in PVA matrix, light yellow and red afterglows with emission maxima of 587-612 nm were achieved, whose energy transfer efficiency and Φ_P were up to 83 % and 0.62 in turn. Complex dynamic digital encryption and various 3D models were successfully constructed via different fluorescence, multi-color afterglows, and flexible PVC doping films. This work not only obtained new long-lived multi-color ORTP materials, but also can be expected to provide more inspirations and possibilities for using ORTP materials in a more cutting-edge field, as well as theoretical guidance and experimental supports for further molecular designs.

CRediT authorship contribution statement

Yang Zhu: Writing – original draft, Validation, Methodology, Data curation. Meiling Pan: Software, Data curation. Lei Ma: Writing –



Fig. 4. (a) HOMO and LUMO distributions of PM-BTDA and OM-BTDA. (b) Energy levels and spin orbit coupling constants (5) of PM-BTDA and OM-BTDA.



Fig. 5. (a) Anti-counterfeiting application by using the 1 % PM-BTDA@PVA, 0.2 % RB&PM-BTDA@PVA, 3 % RB&PM-BTDA@PVA and 1 % OM-BTDA@PVA doping systems. (b)-(c) Photographs of various large area, long-lasting and transparent art crafts prepared by stretching, folding, rolling, curling 1 % OM-BTDA@PVC film under ambient conditions.

original draft, Software. **Yongtao Wang:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.cej.2025.159245.

Data availability

The authors do not have permission to share data.

References

- [1] Y. Zhang, Q. Sun, L. Yue, Y. Wang, S. Cui, H. Zhang, S. Xue, W. Yang, Room temperature phosphorescent (RTP) thermoplastic elastomers with dual and variable RTP emission, photo-patterning memory effect, and dynamic deformation RTP response, Adv. Sci. 9 (2022) 2103402.
- [2] X. Yang, S. Wang, K. Sun, H. Liu, M. Ma, S.T. Zhang, B. Yang, A heavy-atom-free molecular motif based on symmetric bird-like structured tetraphenylenes with room-temperature phosphorescence (RTP) afterglow over 8 s, Angew. Chem. Int. Ed. 62 (2023) e202306475.
- [3] S. Sun, Y. Zhu, T. Li, G. Wang, F. Yin, F. Li, F. Tao, L. Wang, G. Li, Ultralong sodium alginate-based room temperature phosphorescence materials with advantages of color tunability, flexibility and facile large-area fabrication, Chem. Eng. J. 485 (2024) 149751.
- [4] J. Guo, Y. Zhao, L. Ma, Y. Wang, Ultra-long room temperature phosphorescence, intrinsic mechanisms and application based on host-guest doping systems, Chin. J. Struct. Chem. 43 (2024) 100335.

- [5] Z. Wu, J. Nitsch, T.B. Marder, Persistent room-temperature phosphorescence from purely organic molecules and multi-component systems, Adv. Opt. Mater. 9 (2021) 2100411.
- [6] C. Ren, Z. Wang, T. Wang, J. Guo, Y. Dai, H. Yuan, Y. Tan, Ultralong organic phosphorescence modulation of aromatic carbonyls and multi-component systems, Chin. J. Chem. 40 (2022) 1987–2000.
- [7] Y. Xiong, Z. Zhao, W. Zhao, H. Ma, Q. Peng, Z. He, X. Zhang, Y. Chen, X. He, J.W. Y. Lam, B.Z. Tang, Designing efficient and ultralong pure organic room-temperature phosphorescent materials by structural isomerism, Angew. Chem. Int. Ed. 57 (2018) 7997–8001.
- [8] S. Zhao, Z. Yang, X. Zhang, H. Liu, Y. Lv, S. Wang, Z. Yang, S.T. Zhang, B. Yang, A functional unit combination strategy for enhancing red room-temperature phosphorescence, Chem. Sci. 14 (2023) 9733–9743.
- [9] T. Ishi-i, R. Kichise, I.S. Park, T. Yasuda, T. Matsumoto, Room temperature phosphorescence in longer-wavelength red light region found in benzothiadiazolebased dyes, J. Mater. Chem. C 11 (2023) 3003–3009.
- [10] T. Wu, J. Huang, Y. Yan, From aggregation-induced emission to organic room temperature phosphorescence through suppression of molecular vibration, Cell Rep. Phys. Sci. 3 (2022) 100771.
- [11] G. Jiang, Q. Li, A. Lv, L. Liu, J. Gong, H. Ma, J. Wang, B.Z. Tang, Modulation of the intramolecular hydrogen bonding and push-pull electron effects toward realizing highly efficient organic room temperature phosphorescence, J. Mater. Chem. C 10 (2022) 13797–13804.
- [12] G. Pan, Z. Yang, H. Liu, Y. Wen, X. Zhang, Y. Shen, C. Zhou, S.T. Zhang, B. Yang, Folding-induced spin-orbit coupling enhancement for efficient pure organic roomtemperature phosphorescence, J. Phys. Chem. Lett. 13 (2022) 1563–1570.
- [13] X. Yang, G.I.N. Waterhouse, S. Lu, J. Yu, Recent advances in the design of afterglow materials: mechanisms, structural regulation strategies and applications, Chem. Soc. Rev. 52 (2023) 8005–8058.
- [14] X. Chen, W. Dai, X. Wu, H. Su, C. Chao, Y. Lei, J. Shi, B. Tong, Z. Cai, Y. Dong, Fluorene-based host-guest phosphorescence materials for information encryption, Chem. Eng. J. 426 (2021) 131607.
- [15] J. Li, R. Duan, Y. Zhu, M. Chen, X. Dai, G. Duan, Y. Ge, Triarylmethanol derivatives with ultralong organic room-temperature phosphorescence, Chem. Eur. J. (2024) e202403475.
- [16] Z. Lü, Q. Gao, M. Shi, Z. Su, G. Chen, H. Qi, B. Lü, F. Peng, Colorful roomtemperature phosphorescence including white afterglow from mechanical robust transparent wood for time delay lighting, Small Struct. 5 (2024) 2300567.
- [17] L. Shi, L. Ding, Y. Zhang, S. Lu, Application of room-temperature phosphorescent carbon dots in information encryption and anti-counterfeiting, Nano Today 55 (2024) 102200.
- [18] Y. Liu, W. Chen, L. Lu, B. Yang, Si-assisted n, p co-doped room temperature phosphorescent carbonized polymer dots: information encryption, graphic anticounterfeiting and biological imaging, J. Colloid Interface Sci. 609 (2022) 279–288.
- [19] B. Sk, S. Hirata, Symmetry-breaking triplet excited state enhances red afterglow enabling ubiquitous afterglow readout, Adv. Sci. 11 (2024) 2308897.
- [20] W. Gong, G. Huang, Y. Yuan, H. Zhang, Strong and multicolor-tunable pure organic circularly polarized room-temperature phosphorescence from cholesteric liquid crystal, Adv. Opt. Mater. 11 (2023) 2300745.

Y. Zhu et al.

- [21] F. Zhao, T. Zhang, Q. Liu, C. Lü, Aphen-derived n-doped white-emitting carbon dots with room temperature phosphorescence for versatile applications, Sens. Actuators B 304 (2020) 127344.
- [22] W. Sun, B. Shi, Z. Xia, C. Lü, Visible-light-excited long-lived organic roomtemperature phosphorescence of phenanthroline derivatives in PVA matrix by Hbonding interaction for security applications, Mater. Today Chem. 27 (2023) 101297.
- [23] N. Li, X. Yang, B. Wang, P. Chen, Y. Ma, Q. Zhang, Y. Huang, Y. Zhang, S. Lu, Colortunable room-temperature phosphorescence from non-aromatic-polymer-involved charge transfer, Adv. Sci. 11 (2024) 2404698.
- [24] T. Li, Y. Zheng, C. Wu, C. Yan, C. Zhang, H. Gao, Q. Chen, K. Zhang, Crosslinkenhanced strategy to achieve multicolor long-lived room temperature phosphorescent films with excellent photostability, Chin. Chem. Lett. 33 (2022) 4238–4242.
- [25] B. Xu, Y. Jia, H. Ning, Q. Teng, C. Li, X. Fang, J. Li, H. Zhou, X. Meng, Z. Gao, X. Wang, Z. Wang, F. Yuan, Visible light-activated ultralong-lived triplet excitons of carbon dots for white-light manipulated anti-counterfeiting, Small 20 (2024) 2304958.
- [26] J. Jiang, J. Liu, C. Hu, Y. Wang, L. Ma, Construction and fine tuning of host-guest doping systems and the underlying mechanism of room temperature phosphorescence, Dyes Pigm. 222 (2024) 111931.
- [27] C. Wang, L. Qu, X. Chen, Q. Zhou, Y. Yang, Y. Zheng, X. Zheng, L. Gao, J. Hao, L. Zhu, B. Pi, C. Yang, Poly(arylene piperidine) quaternary qmmonium salts promoting stable long-lived room-temperature phosphorescence in aqueous environment, Adv. Mater. 34 (2022) 2204415.
- [28] J. Shi, W. Tao, Y. Zhou, P. Zhang, G. Liang, Air-stable and ultralong roomtemperature phosphorescence from doped poly(methyl methacrylate) for visual detection of volatile organic compounds, Chem. Eng. J. 498 (2024) 155737.
- [29] Z. Chen, J. Shi, Y. Zhou, P. Zhang, G. Liang, Polymer microparticles with ultralong room-temperature phosphorescence for visual and quantitative detection of oxygen through phosphorescence image and lifetime analysis, Chin. Chem. Lett. 110629 (2024).
- [30] J. Chen, S. Zhang, G. Liu, Y. Zhang, S. Xue, Q. Sun, W. Yang, Regulating organic dopant dispersion in polymer matrices for concentration-controlled color-tunable organic RTP emissions, Adv. Opt. Mater. 11 (2023) 2301163.
- [31] S. Xiong, Y. Xiong, D. Wang, Y. Pan, K. Chen, Z. Zhao, D. Wang, B.Z. Tang, Achieving tunable organic afterglow and UV-irradiation-responsive ultralong room-temperature phosphorescence from pyridine-substituted triphenylamine derivatives, Adv. Mater. 35 (2023) 2301874.
- [32] H. Chen, Z. Qian, H.-J. Qian, M. Dong, Y. Zhang, J. Shan, W. Huo, A. Lv, J. Guo, H. Ma, Z. An, W. Huang, L. Gu, Stretchable and flexible room-temperature phosphorescence copolymers based on microphase separation, Chem. Mater. 36 (2024) 5100–5109.
- [33] J. Guo, C. Hu, J. Liu, Y. Wang, L. Ma, Mechanochromism, tunable pure organic room temperature phosphorescence, single-molecule near-white emission, digital encryption, and anti-counterfeiting, Dyes Pigm. 221 (2024) 111760.
- [34] J. Jiang, C. Hu, J. Liu, L. Ma, Y. Wang, J. Guo, The dual-band emissions, multicolor continuous mechanochromisms, and application based on a single luminogen, J. Alloys Compd. 1008 (2024) 176594.
- [35] Y. Zhang, M. Gutierrez, A.K. Chaudhari, J.C. Tan, Dye-encapsulated zeolitic imidazolate framework (ZIF-71) for fluorochromic sensing of pressure, temperature, and volatile solvents, ACS Appl. Mater. Interfaces. 12 (2020) 37477–37488.
- [36] H. Shang, X. Le, M. Si, S. Wu, Y. Peng, F. Shan, S. Wu, T. Chen, Biomimetic organohydrogel actuator with high response speed and synergistic fluorescent variation, Chem. Eng. J. 429 (2022) 132290.
- [37] L. Hu, Y. Gao, Q. Cai, Y. Wei, J. Zhu, W. Wu, Y. Yang, Cholesterol-substituted spiropyran: photochromism, thermochromism, mechanochromism and its application in time-resolved information encryption, J. Colloid Interface Sci. 665 (2024) 545–553.
- [38] X. Li, H. Wang, J. Chen, Y. Tian, C. Xiang, W. Liu, Z. Zhou, J. Cui, X. Chen, Visiblelight-driven photoswitchable fluorescent polymers for photorewritable pattern, anti-counterfeiting, and information encryption, Adv. Funct. Mater. 33 (2023) 2303765.

- [39] D. Jiang, C. Du, Z. Yan, S. Ge, Z. Feng, L. Wan, P. Lu, Modulating room temperature phosphorescence through intermolecular halogen bonding, J. Mater. Chem. c. 11 (2023) 4203–4209.
- [40] D. Jiang, T. Lu, C. Du, F. Liu, Z. Yan, D. Hu, A. Shang, L. Gao, P. Lu, Y. Ma, Utilizing morpholine for purely organic room temperature phosphors, Sci. China Chem. 66 (2023) 1132–1138.
- [41] L. Shi, J. Liu, L. Ma, Y. Wang, The dual-band emission with long-lived thermally activated delayed fluorescence and room temperature phosphorescence by trace ingredient incorporation, Chem. Eng. J. 493 (2024) 152492.
- [42] Y. Hong, Y. Zhao, L. Ma, Y. Wang, Tuning triplet excitons and dynamic afterglow based on host-guest doping, Spectrochim. Acta. A Mol. Biomol. Spectrosc. 324 (2025) 124955.
- [43] J. Chen, J. Sun, Y. Zhan, X. Lian, S. Lu, D-π-A type dicyanoethylene derivatives modified by tetraphenylethylene exhibiting aggregation-induced emission and high-contrast mechanofluorochromism, J. Mol. Struct. 1309 (2024) 138204.
- [44] J.-P. Malval, S. Achelle, L. Bodiou, A. Spangenberg, L.C. Gomez, O. Soppera, F.-R.-L. Guen, Two-photon absorption in a conformationally twisted D-π-A oligomer: a synergic photosensitizing approach for multiphoton lithography, J. Mater. Chem. C 2 (2014) 7869–7880.
- [45] M. Du, Y. Shi, Q. Zhou, Z. Yin, L. Chen, Y. Shu, G.Y. Sun, G. Zhang, Q. Peng, D. Zhang, White emissions containing room temperature phosphorescence from different excited states of a D-II-A molecule depending on the aggregate states, Adv. Sci. 9 (2022) 2104539.
- [46] L. Ai, W. Xiang, J. Xiao, H. Liu, J. Yu, L. Zhang, X. Wu, X. Qu, S. Lu, Tailored fabrication of full-color ultrastable room-temperature phosphorescence carbon dots composites with unexpected thermally activated delayed fluorescence, Adv. Mater. 36 (2024) 2401220.
- [47] J. Jiang, C. Hu, Y. Wang, L. Ma, J. Guo, Ultralong organic room-temperature phosphorescence, multiple stimulus responsiveness and high-level anticounterfeiting based on multifunctional carbazolyl imidazolopyridine, Mater. Today Chem. 30 (2023) 101548.
- [48] Z. Wu, J.C. Roldao, F. Rauch, A. Friedrich, M. Ferger, F. Wurthner, J. Gierschner, T. B. Marder, Pure boric acid does not show room-temperature phosphorescence (RTP), Angew. Chem. Int. Ed. 61 (2022) e202200599.
- [49] F. Guo, Y. Chen, C. Li, X. Wang, Q. Li, M. He, H. Hou, C. Yang, Visualization detection of ultralow temperature based on flexible cross-linked polymer systems, Adv. Funct. Mater. (2024) 2416465.
- [50] C. Wang, X.K. Ma, P. Guo, C. Jiang, Y.H. Liu, G. Liu, X. Xu, Y. Liu, Highly reversible supramolecular light switch for NIR phosphorescence resonance energy transfer, Adv. Sci. 9 (2022) 2103041.
- [51] Z.A. Yan, C. Yin, H. Tian, X. Ma, Near-infrared room-temperature phosphorescence from monocyclic luminophores, Angew. Chem. Int. Ed. (2024) e202417397.
- [52] C. Long, Y. Guan, C. Ren, J. Lu, C. Jin, P. Wang, P. Wang, H.-L. Xie, Near-Infrared room temperature phosphorescence from single polymers containing benzoselenadiazole groups, ACS Appl. Polym. Mater. 6 (2024) 4896–4903.
- [53] F. Lin, H. Wang, Y. Cao, R. Yu, G. Liang, H. Huang, Y. Mu, Z. Yang, Z. Chi, Stepwise energy transfer: near-infrared persistent luminescence from doped polymeric systems, Adv. Mater. 34 (2022) 2108333.
- [54] L. Kong, Y. Zhu, S. Sun, H. Li, S. Dong, F. Li, F. Tao, L. Wang, G. Li, Tunable ultralong multicolor and near-infrared emission from polyacrylic acid-based room temperature phosphorescence materials by FRET, Chem. Eng. J. 469 (2023) 143931.
- [55] K. Narushima, Y. Kiyota, T. Mori, S. Hirata, M. Vacha, Suppressed triplet exciton diffusion due to small orbital overlap as a key design factor for ultralong-lived room-temperature phosphorescence in molecular crystals, Adv. Mater. 31 (2019) 1807268.
- [56] Y. Xu, K. Zhang, M. Hu, X. Gao, J. Leng, J. Fan, Triplet exciton dynamics of pure organics with halogen substitution boosted two photon absorption and room temperature phosphorescence: a theoretical perspective, Spectrochim. Acta. a. Mol. Biomol. Spectrosc. 270 (2022) 120786.
- [57] L. Gao, J. Huang, L. Qu, X. Chen, Y. Zhu, C. Li, Q. Tian, Y. Zhao, C. Yang, Stepwise taming of triplet excitons via multiple confinements in intrinsic polymers for longlived room-temperature phosphorescence, Nat. Commun. 14 (2023) 7252.