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High contrast crystalline, dynamic, and excitation dependent room temperature phosphorescence by tuning acceptor structures

Weirao Ji^{a,1}, Yupeng Zhao^{b,1}, Yang Zhu^a, Lei Ma^{b,*}, Yongtao Wang^{a,**}

^a Guangxi Key Laboratory of Electrochemical and Magneto-chemical Function Materia, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin,

541004, China

^b Tianjin International Center for Nanoparticles and Nanosystem, Tianjin University, Tianjin, 300072, China

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ABSTRACT

Keywords: Room temperature phosphorescence Dynamic phosphorescence Host-guest doping Long-lived phosphorescence Organic phosphorescence Donor-acceptor (D-A) type luminogens play an important role in constructing efficient organic room temperature phosphorescent (RTP) materials, whose RTP properties heavily depend on various D or A units. To screen for an excellent acceptor (A) unit and explore the inherent RTP mechanism, three organic phosphorescence luminogens (MBBe, MBCN and MBXAn) were prepared by choosing morpholine and Ph-CHO/CN/CONH₂ units as D and A respectively. Three luminogens and their doped films showed different crystalline, dynamic, and excitation dependent RTP. Among of them, crystal MBXAn emitted bright green afterglow, with RTP lifetime of 404.84 ms and RTP quantum yield (Φ_p) of 0.377, indicating excellent RTP performance. Crystal analysis and theoretical calculations confirmed that $-CONH_2$ unit could not only enhance intermolecular interactions, but also change molecular conformations of excited states, improve intersystem crossing (ISC) and RTP radiation rates. The work provided an excellent RTP, and contributed to promoting a deeper understanding of RTP molecular design and intrinsic mechanisms.

obtaining efficient organic RTP luminogens.

thereby reducing the negative effects of non-radiative motion and triplet oxygen [21–28]. Even so, structure-RTP property relationships of the luminogens are still uncertain, while choosing different A units is very

beneficial for making clear structure-RTP property relationship and

namic and color-tunable afterglow replacing long afterglow and high

brightness have been new research hotspots, which can overcome the

shortcomings of single color RTP in the past and promote the rapid

development of high-level information encryption and anti-

counterfeiting [29-32]. The reported literature indicates that

non-traditional luminogens such as cellulose and sodium alginate easily

showed excitation and time dependent colorful RTP due to the forma-

tion of diverse RTP emissive species, but there was still a lack of effective

strategies to endow traditional conjugated aromatic compounds with

the aforementioned colorful RTP [33-35]. Some luminogens with

dual-band persistent thermally activated delayed fluorescence (TADF)

and RTP achieved time dependent afterglow because of different TADF

With the further development of pure organic RTP materials, dy-

1. Introduction

In recent years, room temperature phosphorescence (RTP) has attracted widespread attention due to unique excited state properties and long-lived delayed emission [1,2]. Compared with inorganic materials containing precious metals, pure organic RTP materials have potential application values in the fields of organic light-emitting diodes, oxygen sensing, biological imaging, and advanced data security because of their relatively lower cost and low toxicity, easy preparation, and high biocompatibility [3–12]. Promoting spin orbit coupling (SOC) between excited singlet and triplet states and suppressing non-radiative decay of triplet excitons are two important strategies to enhance RTP performance of organic materials, which mainly involves introducing heteroatoms, aromatic carbonyls, crystal engineering, copolymers, and host-guest doping systems [13-20]. Donor-acceptor D-A luminogens usually present small energy gap (ΔE_{ST}) between the lowest singlet (S₁) and lowest triplet excited (T1) states, which is beneficial for boosting the intersystem crossing rate (ISC) and generating more triplet excitons,

* Corresponding author.

** Corresponding author.

¹ Contributed equally.

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E-mail addresses: lei.ma@tju.edu.cn (L. Ma), wyt_shzu@163.com (Y. Wang).

and RTP radiation rates and lifetimes, but they often suffered from tuning ΔE_{ST} [36,37]. Besides, some host-guest doping systems show excitation wavelength dependent afterglow by unimolecular and excimer RTP [38,39]. Even so, dynamic and excitation dependent RTP are still scarce in traditional conjugated aromatic luminogens [40,44–47].

Here, the morpholine group as electron donor can promote $n-\pi^*$ transition, while CHO, CN, and CONH2 used as electron acceptors can change ΔE_{ST} , intermolecular interaction, stacking mode, and excited state molecular conformation [41,43]. Thereby, MBBe, MBCN, and MBXAn were synthesized (Scheme 1). The results indicated that crystals MBXAn emitted bright green afterglow, but not for crystals MBBe and MBCN. By host-guest doping, 1 % MBBe@PVA film showed dynamic afterglow from green to blue after 254 nm UV lamp radiation, but only with green afterglow after 365 nm UV lamp radiation, while 1 % MBXAn@PVA film invariably maintained blue afterglow after creasing 254 nm or 365 nm UV lamp radiation. 1 % MBCN@PVA displayed excitation dependent RTP, with blue and green afterglows respectively by 254 nm and 365 nm UV lamp radiation. Then, advanced encryptions were achieved based on the high-contrast RTP of MBBe, MBCN, and MBXAn. The relationships between RTP performance and electron acceptors were revealed by photophysical performance testing, crystal analysis, and theoretical calculations. The internal mechanism of dynamic and excitation dependent RTP was explored and revealed in detail, which would provide new ideas for developing new pure organic RTP materials and achieving color adjustable RTP [42].

2. Results and discussion

Owing to the push-pull electronic effect of morpholine and -CHO/ CN/CONH₂, absorption maxima of three dyes showed obvious red shifts overall with the increasing solvent polarity from n-hexane to DMSO (Fig. 1a-c), but abnormal shifts could also be found in THF and DCM for MBBe, ACN and DCM for MBCN, as well as ACN and Tol for MBXAn, which should be attributed to solvent effects. Different from a single fluorescence emission peak in n-hexane, MBBe gave two emission peaks in Tol, ACN, and DMSO, whose high and low energy level transitions corresponded to localized state (LS) and intramolecular charge transfer state emissions (ICT) respectively (Fig. 1d). Compared with MBBe, MBCN and MBXAn exhibited stronger ICT emission in DMSO, with a single ICT emission peak for MBCN, as well as higher intensity ratio between ICT and LS emissions for MBXAn (Fig. 1e-f). In n-hexane and toluene solution, MBCN and MBXAn displayed LS emission due to low solvent polarity. Furthermore, the relative fluorescence quantum yields (PLQYs) of three luminogens were investigated in solutions by using quinine sulfate as the reference (Table 1). The results indicated that the PLQY values of MBBe presented small fluctuations in three solvents due to weak ICT characteristic, but the PLQY values of MBCN and MBXAn showed significant enhancements from n-hexane, toluene to DMSO, which should be attributed to the enhanced ICT emission. Non-radiative transitions were difficult to suppress at room temperature in various solvents, without perceptible RTP for three luminogens. However, phosphorescence nature of three luminogens could be confirmed in DCM solution at 77 K, with phosphorescence maxima of 492 nm, 488 nm, and 500 nm for MBBe, MBCN, and MBXAn, respectively (Fig. S13). Powdered samples of MBBe, MBCN, and MBXAn had a single



Scheme 1. The synthetic route of MBBe, MBCN and MBXAn.

fluorescence peak at 425 nm, 372 nm, and 418 nm, respectively (Fig. S14), but only powder MBXAn presented visible RTP, with RTP emission maxima at 510 nm (Fig. S15b), RTP lifetimes of 164.77 ms (Fig. S15c), and RTP quantum yield (Φ_P) of 0.239 (Table 2), demonstrating that high contrast RTP could be achieved by tuning acceptor structures. Furthermore, crystals MBXAn were obtained by slow solvent diffusion, whose RTP spectrum displayed fine vibration structure due to better non-radiative suppression, with two obvious emission peaks at 496 nm and 525 nm (Fig. S15b), corresponding to RTP lifetimes of 348.38 ms and 404.84 ms in turn (Fig. S15d), as well as Φ_P of 0.377 (Table 2). Switching on-off 365 nm UV lamp, powder and crystal MBXAn showed green afterglows, lasting separately 2 s and 3 s (Fig. S15a), with brighter emission for crystal MBXAn than powder MBXAn, which should be due to crystal MBXAn more effectively suppressing oxygen diffusion and non-radiative deactivation of triplet excitons. The main photophysical parameters further indicated that crystallization significantly increased the fluorescence radiation rate (K_{Fl}) and intersystem transition rate (KISC) of MBXAn and extremely reduced its phosphorescence non radiative rate (K_{Phnr}) (Table 3). It was worth noting that both MBBe and MBCN crystals exhibited an invisible afterglow at room temperature when exposed to a 365 nm UV lamp, but they emitted a bright green afterglow at 77 K (Fig. S29). Further confirmation of their phosphorescent properties was provided by temperature-dependent phosphorescence spectra, which showed that the emission intensity of these crystals rapidly decreased and eventually disappeared as the temperature rose from 77 K to 297 K (Fig. S29). Thus, the invisible afterglow of MBBe and MBCN crystals at room temperature can be attributed to the quenching of triplet excitons by molecular motions. The intrinsic mechanisms were further analyzed and discussed in detail by crystal analysis and theoretical calculations.

By dissolving MBBe/MBCN/MBXAn and PVA/PMMA in THF-H₂O solution at the mass doping ratios of 1:200, 1:100, and 1:20, different doping films were prepared and optimized. Taking 1 % MBBe@PVA as an example, the doping mass ratio between MBBe and PVA was 1:100. According to the naming rule of 1 % MBBe@PVA film, other doping films were defined. Fluorescence spectra indicated the MBBe@PVA and MBCN@PVA films presented dual-state fluorescence and phosphorescence emission, whose fluorescence lifetimes corresponded to the ns and ms scales in turn, while MBXAn@PVA films gave a single fluorescence peak (Fig. S16–S17). The absolute fluorescence quantum yields (Φ_{FI}) of 1 % MBBe@PVA, 1 % MBCN@PVA, and 1 % MBXAn@PVA films were 0.019, 0.012 and 0.023, respectively (Table 2), indicating the stronger fluorescence emission for 1 % MBXAn@PVA film than 1 % MBBe@PVA and 1 % MBCN@PVA films. Moreover, fluorescence emission maximum of the MBBe@PVA films displayed imperceptible shifts with increasing doping concentration, but with obvious red shifts for MBCN@PVA and MBXAn@PVA films, illustrating intermolecular interactions with stronger influences on fluorescence emission of MBCN and MBXAn. By contrast, 1 % MBBe@PVA, 1 % MBCN@PVA, and 1 % MBXAn@PVA films had the longest afterglow and the strongest RTP emission intensity in different doping concentrations (Figs. S18-S23), whose RTP lifetimes were 95.21 ms, 142.13 ms, 409 ms, 254.07 ms, 381.95 ms, and 172.76 ms respectively at 254 nm and 365 nm excitation (Fig. 2e-g). More interestingly, 1 % MBBe@PVA film presented dynamic afterglow from green to blue by the switching on-off of 254 nm UV lamp, but only with green afterglow after ceasing 365 nm UV lamp irradiation, accompanied by prolonged afterglow lifetimes from 1.5 s to 3 s (Fig. 2a). Different from 1 % MBBe@PVA film, the 1 % MBCN@PVA film showed longer blue afterglow after ceasing 254 nm UV lamp irradiation, lasting for 7 s, whose afterglow became green and was shortened to 4 s by the switching on-off of 365 nm UV lamp (Fig. 2b), while 1 % MBXAn@PVA film always maintained a blue afterglow after stopping 365 nm or 254 nm UV lamp irradiation (Fig. 2c), and with close afterglow lifetimes. Subsequently, the phosphorescence spectra at different excitation wavelengths were investigated. Fig. 3 indicated that RTP emission maximum (509 nm) of 1 % MBBe@PVA film maintained constant, which was inconsistent with



Fig. 1. UV-vis absorption spectra of (a) MBBe, (b) MBCN, (c) MBXAn and fluorescence emission spectra of (d) MBBe, (e) MBCN, (f) MBXAn in various solvents (10^{-5} M) .

Table 1
Absorption and emission maxima, and the relative fluorescence quantum yields
of MBBe. MBCN and MBXAn in different solutions.

		n- Hexane	Toluene	DCM	THF	ACN	DMSO
MBBe	Abs. (nm)	312	323	238, 327	322	232, 326	332
	λ _F (nm)	417	390, 502	407	408	418, 523	418, 551
	Φ (%)	2.46	1.89	2.39	2.51	2.64	2.37
MBCN	Abs. (nm)	299	302	231, 291	304	220, 290	305
	λ _F (nm)	362	368	421	416	466	495
	Φ (%)	1.95	2.43	4.87	4.38	5.01	5.24
MBXAn	Abs.	212,	304	231,	301	218,	304
	(nm)	278		294		288	
	$\lambda_{\rm F}$	338,	366	380	374	390,	387,
	(nm)	365				453	457
	Φ (%)	3.06	7.36	7.57	7.44	9.23	9.54

the observed dynamic afterglow, while RTP emission maxima of 1 % MBCN@PVA (454-494 nm) and 1 % MBXAn@PVA (454-496 nm) films continued to redshift as the excitation wavelength increased (Fig. 3a-c), indicating the presence of multiple RTP emission centers. Based on the (CIE: Commission International de l'Eclairage) CIE coordinates, RTP of 1 % MBBe@PVA film was located in the green light region, but RTP of 1 % MBCN@PVA and 1 % MBXAn@PVA films covered blue and green light regions (Fig. 3d-f). To understand dynamic afterglow of 1 % MBBe@PVA film, we measured its delayed RTP spectra at different delay times (τ_d). When τ_d was 1 ms, 1 % MBBe@PVA film showed a strong emission peak at 520 nm and two weak emission peaks at 470 nm and 425 nm (Fig. S24a). The strong emission peak blue shifted to 512 nm, while the weak emission peaks at 470 nm and 425 nm disappeared and became a shoulder peak respectively when τ_d was 5 ms and 10 ms. As τ_d further increased to 30 ms, only the single strong emission peak with blue shifts of 3 nm remained. The delayed RTP spectra indicated that 1 % MBBe@PVA film also had multiple emission centers. Besides, the excitation spectra of 1 % MBBe@PVA film further confirmed the existence of multiple emission centers (Fig. S24b), displaying evident blue shifts and distinctions in excitation maxima and spectra. Obviously, the multiple emission centers should take responsible for dynamic afterglow of 1 % MBBe@PVA film. After being left at room temperature

Table 2

Emission maxima and quantum yields of three luminogens in doping films and solid states.

	λ_{em}			Φ		
	Fluo. (nm)	Phos. (nm) (λ _{ex} :254 nm)	Phos. (nm) (λ _{ex} :365 nm)	Fluo. (%)	Phos. (%) (λ _{ex} :254 nm)	Phos. (%) (λ _{ex} :365 nm)
1 % MBBe@PVA	411	509	498	1.85	3.95	4.32
1 % MBCN@PVA	366	454	494	1.24	3.21	3.39
1 % MBXAn@PVA Pristine	372	454	470	2.32	5.81	6.39
1 % MBXAn@PVA After a week	372		496	2.32		8.95
MBXAn Powder	418		510	3.52		23.89
MBXAn Crystal	369,		496,	6.77		37.65
	412		525			

Table 3

The main photophysical parameters of MBXAn Powder and Crystal.

	τ		k				
	Fluo. (ns)	Phos. (ms) (λ _{ex} :365 nm)	$k_{Fl} (s^{-1})$	$k_{ISC} (s^{-1})$	$k_{Ph} (s^{-1}) (\lambda_{ex}:365 \text{ nm})$	$k_{Phnr} (s^{-1}) (\lambda_{ex}:365 \text{ nm})$	
MBXAn Powder MBXAn Crystal	2.65 1.32	164.77 404.84	$\begin{array}{c} 1.33\times10^{7}\\ 5.13\times10^{7}\end{array}$	$\begin{array}{l} 3.64\times10^8\\ 7.06\times10^8\end{array}$	1.50 1.00	4.57 1.47	



Fig. 2. (a)–(c) Photographs of 1 % MBBe@PVA, 1 % MBCN@PVA and 1 % MBXAn@PVA films by turning on/off 254 nm and 365 nm UV light lamps. (d) Photographs of 1 % MBXAn@PVA film by turning on/off 365 nm UV light lamps. (e)–(g) The time-resolved RTP decay curves of 1 % MBBe@PVA, 1 % MBCN@PVA and 1 % MBXAn@PVA films at 254 nm and 365 nm excitation.

for one week, 1 % MBXAn@PVA film showed green afterglow rather than blue afterglow by the switching on-off of 365 nm UV lamp, along with shortened afterglow lifetime (2 s) (Fig. 2d). It is widely known that luminogens can migrate and gather in PVA film, resulting in the coexistence of monomers and different aggregates. Therefore, the green afterglow of 1 % MBXAn@PVA film should be due to the presence of aggregated MBXAn, while the blue afterglow come from unimolecular MBXAn. Furthermore, the excitation spectra of the 1 % MBBe@PVA, 1 % MBCN@PVA, and 1 % MBXAn@PVA films were measured under different RTP maxima (Fig. S30), which showed excitation maxima of 324 nm and 327 nm for the 1 % MBBe@PVA film, 307 nm and 337 nm for the 1 % MBCN@PVA film, as well as 335 nm and 348 nm for the 1 % MBXAn@PVA film. This phenomenon further confirmed that the above dynamic and excitation dependent afterglow derived from the multiple emission centers constructed by unimolecular and aggregated luminogens. In addition, 1 % MBXAn@PVA film gave the highest Φ_P (0.058), followed by 1 % MBBe@PVA (0.040) and 1 % MBCN@PVA (0.032) films under 254 nm excitation (Table 2). Under 365 nm excitation, the three doping films exhibited higher $\Phi_{\rm P}$, but maintained the same increasing order from 1 % MBCN@PVA film (0.034) to 1 % MBBe@PVA (0.043) and 1 % MBXAn@PVA (0.064) films. Of note, Φ_P of 1 % MBXAn@PVA film further increased to 0.090. Considering Φ_P of power (0.239) and crystal MBXAn (0.377) again, the lumnigons showed Φ_P enhanced by aggregation and crystallization.

3. Crystal structures and theoretical calculations

To explore the underlying phosphorescence mechanism, crystal structures of MBCN (CCDC 2444411) and MBXAn (CCDC 2444412) were determined based on single-crystal X-ray diffraction and divided into planes O (O₁, C₁ and C₂), A (C₁, C₂, C₃ and C₄), N (N, C₃ and C₄), and B (C₅, C₆, C₇, C₈, C₉ and C₁₀) (Fig. 4). Dihedral angles of plane O-A and N–B were 53.58° and 27.42° successively in crystal MBCN, while crystal MBXAn showed more twisted molecular conjugation, corresponding dihedral angles are 56.74° and 38.44°. Furthermore, MBCN and MBXAn adopted side-to-plane arrangement modes (Fig. S25), without intermolecular π - π stacking. As documented [41,43], the oxygen atom on the morpholine unit participates in stabilizing the molecular conformation through intermolecular interactions. More importantly, MBXAn relative to MBCN formed stronger and more intermolecular interactions by replacing CN with CONH₂ (Fig. S26), which should be responsible for bright RTP of crystals MBXAn.

To reveal the inherent luminescence behavior of MBBe, MBCN and MBXAn, the geometric configuration of three luminogens were optimized at the B3LYP/def2-TZVP level, whose the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) distributions, main energy levels and spin orbit coupling constants (ξ) were calculated (Fig. 5). The electron cloud density of HOMO and LUMO orbitals of three luminogens was mainly distributed on the



Fig. 3. (a)–(c) The normalized phosphorescence spectra of 1 % MBBe@PVA, 1 % MBCN@PVA, and 1 % MBXAn@PVA films at different excitation wavelengths. (d)–(f) CIE chromaticity coordinates of 1 % MBBe@PVA, 1 % MBCN@PVA and 1 % MBXAn@PVA films at different excitation wavelengths.



Fig. 4. (a) Molecular conformation and (b) the cell unit of crystals MBCN and MBXAn.

aromatic rings and N of morpholine unit, but obvious electron density migration could be observed from N of morpholine unit to the aromatic rings, indicating typical D-A type luminogens and intramolecular charge transfer (ICT) characteristics. Furthermore, the energy gaps between HOMO and LUMO were 4.336 eV, 4.699 eV, and 4.870 eV for MBBe, MBCN and MBXAn in turn, corresponding to the red shifted absorption maxima for MBBe than MBCN and MBXAn very well (Fig. 1a-c). The energy gap (ΔE_{S1T2}) of MBBe between S₁ and T₂ was 0.19 eV, with $\xi(S_1 \rightarrow T_2)$ of 0.354 cm⁻¹, effectively promoting ISC and generation of triplet excitons. Moreover, $\xi(T_1 \rightarrow S_0)$ related to phosphorescence radiation was 0.531 cm⁻¹. Similar to MBBe, MBCN also showed a main ISC channel from $S_1{\rightarrow}T_2,$ but with smaller $\xi(S_1{\rightarrow}T_2)$ (0.304 $\text{cm}^{-1})$ and $\xi(T_1 \rightarrow S_0)$ (0.363 cm⁻¹), as well as a significantly reduced ΔE_{S1T2} (0.06 eV). By contrast, $\xi(S_1 \rightarrow T_2)$ of MBBe and MBCN was equivalent, but the significantly reduced ΔE_{S1T2} and smaller $\xi(T_1 \rightarrow S_0)$ were respectively beneficial for promoting the rapid formation of triplet excitons and the slower phosphorescence radiation for MBCN than MBBe. As a result, 1 % MBBe@PVA film exhibited higher RTP quantum yield (Φ_P) and shorter RTP and afterglow lifetimes than 1 % MBCN@PVA film (Table 2 and Fig. 2). Different from MBBe and MBCN, the main ISC channel of MBXAn was $S_1 \rightarrow T_1$ rather than $S_1 \rightarrow T_2$, which could avoid the relaxation process of MBBe and MBCN from T₂ to T₁ and thereby reduce non-radiative energy loss. Meanwhile, Dihedral angles of plane N-B were 89.61° and 35.65° in S₁ and T₁ states in sequence, which contributed to endowing S_1 and T_1 states more $n-\pi^*$ and $\pi-\pi^*$ transition characteristics respectively based on the twisted S1 state and relatively flattened T1 state (Fig. S27), yielding big $\xi(S_1 \rightarrow T_1)$. MBXAn had bigger $\xi(S_1 \rightarrow T_1)$ (1.059 cm^{-1}) and $\xi(T_1 \rightarrow S_0)$ (2.927 cm⁻¹) than MBBe and MBCN, and with a tiny ΔE_{S1T1} (0.19 eV), which boosted the rapid formation and phosphorescence radiation of triplet excitons, corresponding to a significantly improved Φ_P for 1 % MBXAn@PVA film than 1 % MBCN@PVA and 1 % MBBe@PVA films (Table 2). Subsequently, natural transition orbitals (NTOs) analysis was performed for MBBe, MBCN, and MBXAn at the S₁, T₁, and T₂ states (Fig. S31). The results revealed that the introduction of different substituents had an obvious impact on the nature of the electronic transitions. The three luminogens exhibited S_1 states with predominantly 1 (n, $\pi)$ character. In contrast, MBBe showed T₁ and T₂ states with predominantly ${}^{3}(\pi, \pi)$ and ${}^{3}(n, \pi)$ characters, respectively, but T1 and T2 states of MBCN and MBXAn were characterized by predominant ${}^{3}(\pi, \pi)$ characters. These differences led to



Fig. 5. (a) HOMO and LUMO distributions of MBBe, MBCN and MBXAn. (b) Energy levels and spin orbit coupling constants (ξ) of MBBe, (c) MBCN and (d) MBXAn.

larger $\xi(S_1 \rightarrow T_1)$ for MBCN and MBXAn compared to MBBe (Fig. 5). Of note, the above-mentioned data illustrates that three luminogens possess phosphorescence nature, while invisible afterglow for crystals MBBe and

MBCN should be attributed to molecular motions and oxygen quenching. Overall, the fine-tuning of electron acceptors not only affected intermolecular interactions, but also changed molecular conformations



Fig. 6. Anti-counterfeiting application by using (a) 1 % MBBe@PMMA film, MBCN and MBXAn Powder, (b) the 1 % MBBe @PVA, 1 % MBCN @PVA and 1 % MBXAn @PVA doping systems.

of the ground state and excited states. Furthermore, the different twisted degrees between D and A units could tune n- π^* and π - π^* transition characteristics of excited states, leading to different ISC, phosphores-cence radiative rate (K_P) and K_{Phnr}. Among of three luminogens, crystal MBXAn showed the best RTP performance ($\Phi_P = 0.377$, $\tau = 404.84$ ms) due to the enhanced intermolecular interactions, ISC, and phosphores-cence radiation rates.

4. Applications

Encryption is the process of converting plaintext information into ciphertext information, making it unreadable in the absence of special information and measures, which can effectively protect personal privacy, company and business secrets, and national security. Based on excitation dependent RTP and different RTP lifetimes of the dyes, a series of advanced encryption patterns were prepared. As shown in Fig. 6a, raindrops, cloud and sun were drawn respectively by MBCN Powder, 1 % MBBe@PMMA film (Fig. S28) and MBXAn Powder. Switching on-off 365 nm UV lamp, raindrops disappeared firstly, followed by cloud and sun, representing a weather transition process from rainy via cloudy to sunny day, Fig. 6b expressed the dynamic process of kicking and skateboarding from near to far. The person and ball were constructed by 1 % MBBe@PVA and 1 % MBXAn@PVA films in turn, in another picture, the person and skateboard were drawn by 1 % MBCN@PVA and 1 % MBXAn@PVA films respectively. By the switching on-off of 254 nm UV lamp, the person kicked the ball out in 1 s in a picture, which became 3 s after creasing 365 nm UV lamp radiation. In another picture, the blue clothed person became a green clothed person on a blue skateboard by different UV lamp radiation.

5. Conclusions

Based on NMR and HR-MS characterization, single-crystal X-ray diffraction, and HPLC analysis, molecular structures and purity of three D-A type luminogens were confirmed. By tuning electron acceptors, high contrast crystalline, dynamic, and excitation dependent RTP was achieved. Power and crystal MBXAn could present green afterglow, lasting for 2 s and 3 s in turn, whose RTP lifetimes and Φ_P were 164.77 ms, 0.239, 404.84 ms, and 0.377 in sequence, indicating crystal enhanced RTP, while MBBe and MBCN gave invisible RTP in power and crystalline state. Crystal analysis and theoretical calculations provided a detailed underlying mechanism analysis for the above high contrast RTP, which indicated that MBXAn had stronger intermolecular interactions, as well as bigger $\xi(S_1 \rightarrow T_1)$ and $\xi(T_1 \rightarrow S_0)$ compared with MBBe and MBCN, leading to bright afterglow and high Φ_P for crystal MBXAn, as well as longer unimolecular afterglow and high Φ_P for 1 % MBXAn@PVA film than 1 % MBBe@PVA and 1 % MBCN@PVA films. 1 % MBBe@PVA and 1 % MBCN@PVA film presented excitation wavelength dependent blue or green afterglows due to different RTP emission and lifetimes between unimolecular and aggregated luminogens, while the pristine 1 % MBXAn@PVA film maintained blue afterglow under different excitation wavelengths because of the absence of aggregated RTP. Migration and aggregation of MBXAn in PVA film leaded to green afterglow of aggregated MBXAn and shortened afterglow lifetime. This work not only obtained a long-lived and efficient crystal RTP luminogen, screened an excellent electron acceptor for RTP chromophore, simultaneously possessing the enhanced intermolecular interactions and ISC abilities, but also provided an excellent platform for building advanced encryption patterns by high contrast crystalline, dynamic, and excitation dependent RTP.

CRediT authorship contribution statement

Weirao Ji: Writing – original draft, Supervision, Methodology, Investigation, Data curation. Yupeng Zhao: Writing – original draft, Software, Data curation. Yang Zhu: Writing – original draft, Supervision, Methodology, Investigation, Data curation. Lei Ma: Writing – review & editing, Software, Methodology, Investigation. Yongtao Wang: Writing – review & editing, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Data availability

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

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

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Data availability

The authors do not have permission to share data.

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