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# Tuning triplet excitons and dynamic afterglow based on host-guest doping



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## HIGHLIGHTS

# G R A P H I C A L A B S T R A C T

- Host and guest materials were easily prepared on a large scale.
- The new doping system showed longlived TADF and RTP lifetimes.
- The persistent TADF, unimolecular and aggregated RTP were simultaneously found.
- The doping systems presents temperature responsive dynamic afterglow.
- High-level data encryption and dynamic anti-counterfeiting pattern were constructed.

### ARTICLE INFO

Keywords: Room temperature phosphorescence Thermally activated delayed fluorescence Host-guest doping Dynamic afterglow Dual-band emission



# ABSTRACT

Designing persistent dual-band afterglow materials with thermally activated delayed fluorescence (TADF) and room temperature phosphorescence (RTP) contributed to solving the problems of homogenization and singularity in long afterglow materials. Here, six aryl acetonitrile (CBM) and aryl dicyanoaniline (AMBT) derivatives, used as host and guest materials respectively, were successfully designed and synthesized based on the isomerization effect. Among of them, 0.1 % m-CBM/p-AMBT showed the longest dual-band TADF (540 ms) and RTP lifetimes (721 ms), as well as persistent afterglow over 8 s, whose fluorescence ( $\Phi_{FL}$ ), TADF ( $\Phi_T$ ) and RTP ( $\Phi_P$ ) quantum yields were 0.11, 0.06 and 0.22 in sequence. More interestingly, some doping systems constructed by CBM and AMBT series compounds showed persistent triple-band emissions composed of TADF, unimolecular and aggregated AMBT series compounds. What's more,  $\Phi_{FL}$ ,  $\Phi_T$  and  $\Phi_P$  of 1 % o-AMBT@PMMA film were up to 0.17, 0.17, 0.23 in turn, with TADF, RTP and afterglow lifetimes of 606 ms, 727 ms, and 10 s respectively. TADF and RTP emission of CBM/AMBT series doping systems was attributed to host sensitized guest emission. Besides, the comparison displayed AMBT series compounds had bigger intensity ratios between TADF and RTP emission in PMMA films compared to in CBM series compounds. Finally, a series of data encryption were successfully constructed based on different afterglow lifetimes of the doping systems, and a dynamic anti-counterfeiting pattern was prepared by using different temperature responses of TADF and RTP emissions.

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## 1. Introduction

In the luminescence process, if the energy gap ( $\Delta E_{ST}$ ) between the lowest singlet state (S<sub>1</sub>) and the lowest triplet state (T<sub>1</sub>) is small, the S<sub>1</sub> excitons easily undergo an intersystem crossing (ISC) to T<sub>1</sub> state, and then return to S<sub>1</sub> state by a fast reversible intersystem crossing (RISC), finally emitting fluorescence by the radiative transition from S<sub>1</sub> to the ground state (S<sub>0</sub>) [1–3], which is called thermally activated delayed fluorescence (TADF) [4,5]. Room temperature phosphorescence (RTP) is that T<sub>1</sub> excitons directly back to S<sub>0</sub> rather than S<sub>1</sub> state due to the big  $\Delta E_{ST}$  [6,7]. In theory, TADF and RTP belong to two competing processes [8–10]. TADF requires the assistance of small  $\Delta E_{ST}$  to boost RISC [11], while RTP requires appropriate  $\Delta E_{ST}$  to inhibit RISC. Therefore, it is very difficult to construct pure organic dual-band afterglow materials with TADF and RTP (TR), especially for long-lived TR materials [11–13].

Designing TR materials, and further adjusting the two different luminescent modes will enrich the long afterglow materials [14-16], thereby helping to solve the problems of homogenization and singularity in long afterglow materials [17]. Wang et al. [18] found that crystal carbazole derivatives exhibited dynamic afterglow from blue to orange, with afterglow lifetimes exceeding 1 s. Further research showed that the above dynamic afterglow came from TR emission and different TADF and RTP decay rates. Sun et al. [19] found that the doping system composed of 4-methoxy benzophenone (MeOBP) and spirofluorene boron complex exhibited TR emission, with RTP and TADF lifetimes of 1.1 s and 1.0 s, respectively. Yang et al. [20] obtained TR materials by host-guest doping, showing linearly tunable afterglow with the changes of temperature, whose TADF and RTP lifetimes were up to 1.81 s and 1.76 s, respectively. Zhang et al. [21] constructed a host-guest doping system with TR emission by using MeOBP and organic boron complexes. The theoretical calculation results showed that the spin orbit coupling constant ( $\xi$ ) of S<sub>1</sub>  $\rightarrow$  T<sub>3</sub> of boron complexes was 0.31 cm<sup>-1</sup>, promoting ISC and RISC. Chen et al. [22] adjusted the ISC and RISC efficiency of guest excitons by selecting different host materials. When the T<sub>1</sub> state energy level of host materials sandwiched the S1 and T1 states of the guest, and  $\Delta E_{ST}$  between the T<sub>1</sub> state of the host and the S<sub>1</sub> state of the guest was small, the doping system mainly exhibited TADF emission from the guest. Han et al. [23] designed two twisted donor-acceptordonor (D-A-D) organic luminescent materials. By changing the twist angle between the D and A units, T1 state of luminescent materials could be modulated to a triplet charge transfer state (<sup>3</sup>CT) from a locally excited triplet state (<sup>3</sup>LE), thereby achieving TR emission. Diboroanthracene derivatives were doped into methyl polyacrylate (PMMA) to achieve long-lived TR emission, with RTP and afterglow lifetimes of 3.2 s and 25 s respectively [24]. 9-acridone and its derivatives were doped into polyacrylamide (PAM) and polyvinyl alcohol (PVA), respectively [25,26], achieving time, temperature, humidity, and excitation dependent persistent luminescence, and giving long TADF (548 ms) and RTP lifetimes (1152 ms). Li et al. [27] introduced sulfur atoms with strong electron donating ability into three isomers of polyaromatic frameworks, exhibiting TADF, RTP, and TR emissions, respectively. Wang et al. [28] obtained an exciplex by using phenothiazine and its oxides as electron donors and acceptors, respectively, which exhibited efficient TADF with the quantum yield of up to 61 % and RTP afterglow lasting for more than 3 min. Levofloxacin, sodium fluorescein, and sodium calcein were embedded into the inorganic matrix, exhibiting high brightness TR emission characteristics [29,30]. Deng et al. [31] designed and synthesized a "triplet exciton pump" endowing Rhodamine TR emission by host-guest doping. Wang et al. [32] tuned intensity ratios between TADF and RTP by modifying the structure of hosts. Even so, there were only a few molecular skeletons and doping systems with TR emission, and the construction of TR systems still had many contingencies and uncertainty [33]. Moreover, there were multiple intrinsic mechanisms behind TR emission. Therefore, the molecular design and structure-function relationships of TR systems cannot be achieved overnight [34].

To obtain long-lived TR materials and explore the underlying mechanism, o-CBM, m-CBM, and P-CBM, as well as o-AMBT, m-AMBT, and p-AMBT were designed and synthesized based on molecular isomerism and host-guest doping [34,35], and had the following advantages: short synthesis steps, mild reaction conditions (RT), and high yield (>80 %) [36]. Then a series of host-guest doping systems were constructed and optimized by using CBM and AMBT series compounds as host and guest materials separately, as well as tuning the doping mass ratio between host and guest materials [37,38]. Meanwhile, RTP and RT performance of CBM and AMBT series compounds were investigated in crystalline state and polymethyl methacrylate (PMMA)/polyvinyl alcohol (PVA) films. Further research indicated that crystal m-CBM presented bright green persistent RTP, with RTP and afterglow lifetimes of 212 ms and 3 s in turn, but the other host and guest materials presented invisible afterglow in crystalline state and solid state. Phosphorescent nature of CBM and AMBT series compounds were confirmed in DCM solution at 77 K, and TR characteristic of AMBT series compounds were revealed in PMMA and PVA films. More amazingly, the doping systems constructed by CBM and AMBT series compounds not only showed TR attributes, but also provided significantly prolonged RTP and TADF lifetimes. Of note, m-CBM/o-AMBT showed long TADF (540 ms) and RTP lifetimes (721 ms) at the mass ratio of 1:1000, as well as persistent afterglows lasting over 8 s, while RTP and TADF lifetimes of 1 % o-AMBT@PMMA film were up to 727 ms and 606 ms in sequence. Finally, a series of data encryption were successfully constructed based on different afterglow lifetimes of the doping systems, and a dynamic anti-counterfeiting pattern was prepared by using different temperature responses of TADF and RTP emissions. Most importantly, the underlying mechanism of TR emission were deeply discussed based on theoretical calculations.

#### 2. Results and discussion

# 2.1. Preparations of hosts and guests

As shown in Scheme-1, o-CBM, m-CBM, and P-CBM were prepared by the condensation reaction of o/m/p-cyanobenzaldehyde and malononitrile, as well as the reduction reaction of borane ammonia complex [39], while o-AMBT, m-AMBT, and p-AMBT were synthesized (Scheme-2) by one pot multi-step reactions under the catalysis of sodium hydroxide, with yields of 80-87 %. The high-purity target compounds were obtained by column chromatography combining with recrystallization, and then characterized and verified with NMR and HR-MS spectra, whose purities were further confirmed by high performance liquid chromatography (HPLC) (Fig. S9-S32). Owing to low melting points (80-130 °C), excellent crystallinity, and short conjugate structures, o-CBM, m-CBM, and p-CBM were utilized as hosts, while o-AMBT, m-AMBT, and p-AMBT were chosen as guests due to longer conjugate structures. Subsequently, a series of host-guest doping systems (o-CBM/ o-AMBT, o-CBM/m-AMBT, o-CBM/p-AMBT, m-CBM/o-AMBT, m-CBM/ m-AMBT, m-CBM/p-AMBT, p-CBM/o-AMBT, p-CBM/m-AMBT, and p-CBM/p-AMBT) were constructed by a melting-cooling treatment, whose room temperature phosphorescence (RTP) intensities and afterglow lifetimes were investigated and optimized by tuning the mass ratios between host and guest materials from 10:1, 100:1, 1000:1 to 10,000:1. As control groups, CBM and AMBT series compounds were doped in polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA) at different mass ratios respectively. Taking the o-CBM/PMMA mass ratios of 1:10 and 1:100 as examples, the two doping systems were named as 10 % o-CBM@PMMA film and 1 % o-CBM@PMMA film in sequence, while 10 % o-CBM/o-AMBT meant that o-AMBT was doped in o-CBM at the doping concentration of 10 % by melting.

#### 2.2. Photophysical properties

Fig S1 indicated that o-AMBT, m-AMBT, and p-AMBT had two

absorption bands at 225-300 nm and 300-400 nm in DCM solution, with faint bathochromic-shifts for p-AMBT than o-AMBT and m-AMBT due to the increasing conjugation effect, while emission maxima of o-AMBT, m-AMBT, and p-AMBT were located at 405 nm, 405 nm and 413 nm respectively, exhibiting more obvious bathochromic-shifts for p-AMBT than o-AMBT and m-AMBT, which illustrated that p-AMBT had the increased dipole moment for the excited state relative to the ground state. Powers of AMBT series compounds relative to their solutions presented conspicuous bathochromic shifts due to intermolecular interactions and stacking, but they were unable to present visible RTP by switching on/off a 365 nm UV lamp. By contrast, AMBT series compounds had longer absorption and fluorescence emission maxima than CBM series compounds in solution and solid state, and thereby CBM and AMBT series compounds were used as host and guest materials respectively. The phosphorescence nature of AMBT series compounds were confirmed by cooling their DCM solution to 77 K, with phosphorescence emission maxima of 480 nm, 500 nm, and 515 nm for o-AMBT, m-AMBT, and p-AMBT in sequence (Fig. 1c), indicating tunable phosphorescence emission by molecular isomers. Different from AMBT series compounds, crystal m-CBM showed persistent green RTP, with fluorescence ( $\Phi_{FI}$ ) and RTP ( $\Phi_{P}$ ) quantum yields of 0.19 and 0.03 in turn (Table S1), whose phosphorescence emission maxima, RTP and afterglow lifetimes were 500 nm, 212 ms and 3 s respectively (Fig. 1b and Fig. 1e). Crystals o-CBM and p-CBM presented invisible afterglow at room temperature, but their RTP spectra and lifetimes could be detected by instruments, with phosphorescence emission maxima at 530 nm and 510 nm, as well as RTP lifetimes of 59 ms and 71 ms in turn. Of note, phosphorescence emission maxima between CBM (crystals) and AMBT series compounds (DCM solution at 77 K) had small Stokes shifts (Fig. 1c), especially for m-CBM, p-CBM, o-AMBT, and m-AMBT, as well as o-CBM and p-AMBT, indicating close triplet energy levels. Besides, fluorescence spectra of CBM series compounds in crystalline state overlapped absorption spectra of AMBT series compounds in solution very well (Fig. S1), which would trigger FÖster resonance energy

transfer (FRET) from hosts to guests in host-guest doping systems.

Based on the reported literatures, the phosphorescence performance of host-guest doping system was mainly affected by the following factors: (1) excellent crystallinity of host materials [40]; (2) strong intermolecular interactions and compatibility between host and guest materials [41]; (3) matching singlet and triplet energy levels for host and guest materials [42]. The above photophysical properties indicated that CBM series compounds had good crystallization ability and lower melting points. By melt blending, non-radiative energy loss of the hostguest doping systems could be effectively suppressed. Considering their molecular structures with multiple functional groups (CN, NH<sub>2</sub>), the hosts and guests might have excellent compatibility due to strong intermolecular interactions between functional groups. Duo to very close triple state energy levels between CBM and AMBT series compounds, the doping systems were expected to exhibit dual-state afterglow emissions according to the reported literature [43]. Firstly, o-CBM/o-AMBT, m-CBM/m-AMBT, and p-CBM/p-AMBT were constructed and optimized based on the similar molecular structures. The RTP intensity and afterglow lifetime showed that the optimal doping mass ratios of o-CBM/o-AMBT, m-CBM/m-AMBT, and p-CBM/p-AMBT were 10:1,100:1, and 1000:1 respectively, with afterglow lifetimes of 3.5-5 s (Fig. 2a and Fig. S2-S4). 10 % o-CBM/o-AMBT and 1 % m-CBM/ m-AMBT had dual-band and persistent emission at 420-440 nm and 500 nm, corresponding to TADF and RTP lifetimes of 356-430 ms and 356-460 ms respectively (Fig. 2b and Fig. 2c). The TADF and RTP characteristics would be confirmed by variable temperature phosphorescence spectra of 0.1 % m-CBM/o-AMBT in the following research (Fig. 3b). However, 0.1 % p-CBM/p-AMBT only gave a long-lived (356 ms) RTP peak at 520 nm, while TADF emission peak at 420-440 nm was difficult to perceive. Theoretical calculation indicated that the energy gap between T1 of p-CBM and T2 of p-AMBT was 0.13 eV, but the corresponding energy gaps between o-CBM and o-AMBT, as well as m-CBM and m-AMBT were 0.27 eV and 0.31 eV in turn (Fig. 6). The smaller energy gap facilitated Dexter energy transfer (DET) from T<sub>2</sub> of p-AMBT



**Fig. 1.** (a) The synthesis routes of CBM and AMBT series compounds. (b) Digital photos of o-CBM, m-CBM, and p-CBM by the switching on–off of 365 nm UV lamp. (c) Phosphorescence spectra of CBM and AMBT series compounds at 77 K in DCM solution  $(1 \times 10^{-5} \text{ mol/L})$ . (d) Phosphorescence spectra of crystals o-CBM, m-CBM, and p-CBM at room temperature; (e) Room temperature phosphorescence decay curves of crystals o-CBM, m-CBM, and p-CBM.



Fig. 2. (a) Digital photos of 10 % o-CBM/o-AMBT, 1 % m-CBM/m-AMBT, and 0.1 % p-CBM/p-AMBT by switching on/off 365 nm UV lamp; (b) Phosphorescence spectra of 10 % o-CBM/o-AMBT, 1 % m-CBM/m-AMBT, and 0.1 % p-CBM/p-AMBT; (c) Room temperature phosphorescence decay curves of 10 % o-CBM/o-AMBT and 1 % m-CBM/m-AMBT at 410 nm and 430 nm respectively. (d) Room temperature phosphorescence decay curves of 10 % o-CBM/o-AMBT, 1 % m-CBM/m-AMBT, and 0.1 % p-CBM/p-AMBT; (c) Room temperature phosphorescence decay curves of 10 % o-CBM/o-AMBT, 1 % m-CBM/m-AMBT, and 0.1 % p-CBM/p-AMBT at 500 nm.

to T<sub>1</sub> of p-CBM, thereby accelerating phosphorescence radiation and leading to the reduced I<sub>TADE</sub>/I<sub>RTP</sub>. Further comparison indicated the doping systems showed doping concentration dependent intensity ratios (I<sub>TADF</sub>/I<sub>RTP</sub>) between TADF and RTP. As shown in Fig. S2d and Fig. S3e, o-CBM/o-AMBT and m-CBM/m-AMBT presented bigger  $I_{TADF}/I_{RTP}$  at a doping concentration of 10 % compared to other doping concentrations, accompanied by obvious red shifts for their TADF emission maxima, which leaded to the reduced  $\Delta E_{ST}$ , but 10 % p-CBM/p-AMBT gave more obvious TADF emission relative to other doping systems (Fig. S4f). Owing to  $T_1$  of the hosts sandwiching  $T_2$  and  $T_1$  of the guests, the increasing doping concentration for guests was more conducive to reducing phosphorescence radiation in theory, and thereby yielding TADF emission, which was consistent with the experimental result of 10 % p-CBM/p-AMBT, while the completely different results for 10 % o-CBM/o-AMBT and 10 % m-CBM/m-AMBT should be attributed to the reduced  $\Delta E_{ST}$ , boosting the reversible intersystem transitions (RISC) and TADF emission. More interestingly, o-CBM/m-AMBT and o-CBM/p-AMBT showed two decay emission peaks at doping mass ratios of 100:1-10,000:1, but they presented three decay emission peaks at doping mass ratios of 10:1, which came from TADF and RTP of unimolecular and aggregated m-AMBT or p-AMBT respectively due to the increased doping concentration (Fig. S2e, Fig. S2f). Furthermore, solidstate UV-Vis absorption spectra of o-CBM, p-AMBT and 10 % o-CBM/p-AMBT were examined, which indicated that new absorption peak was

invisible, eliminating the exciplex (Fig. S5). 10 % o-CBM/p-AMBT presented variable phosphorescence spectra with the increasing temperatures from 77 K to 298 K, with a single phosphorescence peak at 77 K, two continuously lessened phosphorescence peaks from 248 to 288 K, as well as one TADF peak and two phosphorescence peaks at 298 K (Fig. S6). Of note, temperature responsive phosphorescence emission of aggregated p-AMBT was different from excimer phosphorescence, which presented enhanced emission intensity as the temperature increased. Temperature responsive afterglows of 10 % o-CBM/p-AMBT were also investigated, showing green afterglow at 0  $^\circ C$  and 30  $^\circ C$ , yellow afterglow at 50 °C and pale-yellow afterglow at 65 °C (Fig. S7). The persistent dual-band or triple-band TADF and RTP emissions are scarce, but RTP lifetimes of 460 ms and afterglow of 4 s are not outstanding for the doping systems. We know that the selection of host and guest materials has diversity and flexibility in doping systems, and significantly affects luminescence performance. To further enhance TADF and RTP lifetimes and quantum yields, as well as explore their structural-functional relationships, new doping systems need be constructed and optimized by cross doping the host and guest materials.

Subsequently, a series of new doping systems including o-CBM/m-AMBT, o-CBM/p-AMBT, m-CBM/o-AMBT, m-CBM/p-AMBT, p-CBM/o-AMBT, and p-CBM/m-AMBT were constructed and optimized. By contrast, 0.1 % m-CBM/o-AMBT showed the longest TADF (540 ms) and RTP lifetimes (721 ms), with fluorescence ( $\Phi_{FL}$ ), TADF ( $\Phi_{T}$ ) and RTP



Fig. 3. (a) Digital photos of 10 % o-CBM/o-AMBT, 0.1 % m-CBM/o-AMBT, 0.1 % p-CBM/o-AMBT by switching on/off 365 nm UV lamp; (b) Temperature-variable phosphorescence spectra of 0.1 % m-CBM/o-AMBT; (c) Phosphorescence spectra of 10 % o-CBM/o-AMBT, 0.1 % m-CBM/o-AMBT, 0.1 % m-CBM/o-AMBT, 0.1 % p-CBM/o-AMBT at room temperature; (d) Room temperature phosphorescence decay curves of 10 % o-CBM/o-AMBT, 0.1 % m-CBM/o-AMBT, 0.1 % p-CBM/o-AMBT at 420 nm; (e) Room temperature phosphorescence decay curves of 10 % o-CBM/o-AMBT, 0.1 % p-CBM/o-AMBT at 500 nm.

 $(\Phi_{\rm P})$  quantum yields of 0.11, 0.06 and 0.22 in sequence (Table S1), as well as afterglows lasting over 8 s (Fig. 3). More importantly, all the afterglow lifetimes of m-CBM/o-AMBT were up to 7 s or more when the doping mass ratio increased to 10,000:1 from 10:1, with excellent stability (Fig. S3). Moreover, 0.1 % m-CBM/o-AMBT presented timedependent dynamic afterglows from blue to green, which should be due to different TADF and RTP lifetimes and radiation rates (Fig. 3a). Furthermore, the doping systems with dual-band and long-lived emission are extremely rare. As documented, some luminogens could yield dual-band and persistent emission due to triplet-triplet annihilation (TTA) mechanism, but dual-band emission lifetimes of 0.1 % m-CBM/o-AMBT were close (Fig. 3d, Fig. 3e) [44], ruling out the TTA mechanism. Besides, some luminogens showed long-lived dual-band emissions due to Anti-Kasha's process, while other luminogens showed simultaneously persistent TADF and RTP emission because of proper  $\Delta E_{\text{ST}}.$  To ascertain the intrinsic mechanism of long-lived dual-band emissions, temperaturedependent decay spectra of 0.1 % m-CBM/o-AMBT were carried out (Fig. 3b), which indicated that emission intensity at 500 nm continued to decline from 77 K to 297 K, confirming RTP characteristics, whereas the emission peak at 420 nm began to appear until the temperature rose to 267 K, whose emission intensity continued to rise from 267 K to 297 K, outlining obvious TADF attributes. Of note, the dual-band emission might come from the matching energy levels between host and guest materials in doping systems, or from the host or guest molecular skeleton. Therefore, the luminescence performance of the three guests were further evaluated in PMMA and PVA films.

In host-guest doping systems, PMMA and PVA were often used as host materials, endowing the doping systems with good flexibility and transparency. o-AMBT, m-AMBT, and p-AMBT were doped in PMMA and PVA films by adopting the previous dissolution method and optimized by tuning the mass ratio (100:1 and 100:10) between guest and PMMA/PVA matrix [45] (Fig. 4 and Fig S8). The previous research results showed that PVA can form a large number of intermolecular and intramolecular hydrogen bonds, inhibiting the diffusion of oxygen, and thereby prolonging RTP lifetime of luminogens [43]. As expected, o-CBM, m-CBM and p-CBM showed stronger RTP intensity and longer afterglow in PVA films compared to PMMA films. Beyond expectation, o-AMBT, m-AMBT, and p-AMBT showed weak RTP emission and short afterglow in PVA films, but they provided significantly enhanced phosphorescence in PMMA films, which might be attributed to better compatibility between AMBT series compounds and PMMA. Furthermore, PVA is a hydrophilic polymer, while AMBT series chromophores are hydrophobic compounds. Therefore, it is difficult for AMBT series chromophores to be uniformly dispersed in PVA, which causes the molecular motion of AMBT series chromophores to not be well restrained and increases the chance of oxygen exposure, and thereby yields weak RTP emission. The optimized doping mass ratios of CBM and AMBT series compounds were 10:1 and 100:1 respectively, and the corresponding RTP performance was evaluated. As shown in Fig. 4, fluorescence emission maxima of 10 % o-CBM@PVA, 10 % m-CBM@PVA and 10 % p-CBM@PVA films were located at 400-460 nm, which were close to that of 1 % o-AMBT@PMMA, 1 % m-AMBT@PMMA and 1 % p-AMBT@PMMA films. For CBM series compounds, m-CBM still displayed the longest RTP (349 ms) and afterglow lifetimes (5 s), followed by p-CBM (273 ms and 4 s) and o-CBM (89 ms and 1 s). Moreover, RTP maxima of CBM series compounds showed obvious bathochromic shifts in PVA films compared to DCM solution in the glass state (Fig. 1c and Fig. 4d), indicating that it was not uniform monomer dispersion for the luminogens in PVA films, which might be attributed to the high doping concentration. Besides, RTP maxima of CBM series compounds maintained the same red shift law from o-CBM to p-CBM and m-CBM in PVA films and solid state due to aggregated phosphorescence emission (Fig. 1d and Fig. 4d). Different from the single RTP peak of CBM series compounds, o-AMBT, m-AMBT, and p-AMBT showed dual-emission coming from TADF and RTP in PMMA films, located at 418-427 nm and 495–510 nm respectively, corresponding to  $\Delta E_{ST}$  of 0.48 eV, 0.46



**Fig. 4.** (a) Digital photos of 10 % o-CBM@PVA, 10 % m-CBM@PVA and 10 % p-CBM@PVA films by switching on/off 365 nm UV lamp. (b) Digital photos of 1 % o-AMBT@PMMA, 1 % m-AMBT@PMMA and 1 % p-AMBT@PMMA films by switching on/off 365 nm UV lamp. (c) Fluorescence spectra of CBM series compounds in PVA films at the doping mass ratios of 10 % and AMBT series compounds in PMMA films at the doping mass ratios of 1 %. (d) Room temperature spectra of CBM series compounds in PVA films at the doping mass ratios of 1 %. (e) RTP decay curves of CBM series compounds in PVA films at the doping mass ratios of 10 %. (f) TADF decay curves of AMBT series compounds in PMMA films at the doping mass ratios of 1 %. (e) RTP decay curves of 1 %. (g) RTP decay curves of AMBT series compounds in PMMA films at the doping mass ratios of 1 %. (g) RTP decay curves of AMBT series compounds in PMMA films at the doping mass ratios of 1 %.

eV, 0.47 Ev in turn (Fig. 4d). By comparison, dual-emission maxima of AMBT series compounds basically maintained consistent in PMMA films and CBM series compounds, which further confirmed TADF and RTP emission should derive from AMBT series compounds rather than CBM series compounds in the doping systems of CBM/AMBT series compounds. Compared with PVA, PMMA has the weaker intermolecular and intramolecular hydrogen bonds, leading to poor inhibition ability for oxygen diffusion. Therefore, AMBT series compounds could not emit strong RTP until PMMA doped films were deoxygenated by UV photoactivation of 60–180 s. Of note, 1 % o-AMBT@PMMA film presented the longest RTP and TADF lifetimes, which were 727 ms and 606 ms in sequence, followed by 1 % m-AMBT@PMMA film (450 ms and 409 ms) and 1 % p-AMBT@PMMA film (441 ms and 331 ms). Consistent with RTP and TADF lifetimes,  $\Phi_{FL}$ ,  $\Phi_{T}$  and  $\Phi_{P}$  of 1 % o-AMBT@PMMA, 1 % m-AMBT@PMMA and 1 % p-AMBT@PMMA films decreased sequentially

from 0.17, 0.17, 0.23 to 0.13, 0.14, 0.16 and 0.11, 0.07, 0.13 (Table S1). Afterglows of 1 % o-AMBT@PMMA, 1 % m-AMBT@PMMA and 1 % p-AMBT@PMMA films lasted for 10 s, 9 s and 6 s in turn. Moreover, 1 % m-AMBT@PMMA film showed the bigger intensity ratio ( $I_{TADF}/I_{RTP}$ ) between TADF and RTP than 1 % p-AMBT@PMMA and 1 % o-AMBT@PMMA films due to small  $\Delta E_{ST}$  (Fig. 4), thereby emitting blue afterglow, but green afterglow for 1 % o-AMBT@PMMA film.

#### 2.3. Crystal structures analysis and theoretical calculation

Based on the excellent RTP performance of crystal m-CBM, single crystal growth of m-CBM was completed by slow solvent diffusion (CCDC 2353279). Crystal m-CBM was a triclinic system with the space group P-1[a = 8.3790(4) Å, b = 10.0451(5) Å, c = 12.3177(6) Å;  $\alpha = 67.078(2)^{\circ}$ ,  $\beta = 86.021(2)^{\circ}$ , and  $\gamma = 81.999(2)^{\circ}$ ]. There were two

different stacking modes named as head-to head (benzene ring) and tailto-tail stacking along a-axis (Fig. 5a), but only head-to head stacking could be observed along b and c a-axes (Fig. 5b and Fig. 5c), presenting obvious  $\pi$ - $\pi$  stacking with plane-plane (C<sub>P</sub>-C<sub>P</sub>) and centroid-centroid (Cg-Cg) distances of 3.510 Å and 4.441 Å, respectively (Fig. 5d), as well as typical H stacking, with CP-CP and Cg-Cg distances of 3.580 Å and 3.732 Å in sequence(Fig. 5e). The corresponding pitch angles of  $\pi$ - $\pi$  and H stacking were  $52^{\circ}$  and  $74^{\circ}$  respectively, contributing to stabilizing triplet excitons and prolonging phosphorescence lifetime [46]. Moreover, multiple intermolecular interactions were found in crystals, such as C-N…H (2.618, 2.670, 2.686, 2.422 Å), C-H…N (2.582, 2.637, 2.689, 2.601 Å), C-H…C(2.871 Å), C-N(3.241 Å) and C-N…C (3.160 Å), which inhibited the molecular motions to yield bright RTP in crystalline state (Fig. 5f). Host-guest doping was an important way to construct efficient RTP systems, whose mechanism mainly involved external heavy atom effects, compatibility between hosts and guests, good crystallization properties of host materials, triplet exciton formation ability of host materials, matching energy levels and strong interactions between host and guest materials, intermolecular arrangement and stacking modes of hosts, the regulation of ICT effect, and so on. Therefore, the intrinsic RTP mechanism of doping systems was very complex [47–51]. To clarify the intrinsic RTP mechanism of the luminogens and doping systems, the geometric configuration of CBM and AMBT series compounds were optimized at the B3LYP/def2-SVP level using D4 dispersion correction, whose HOMO and LUMO distribution, main energy levels and  $\xi$  were calculated (Fig. 6). The electron cloud density of HOMO and LUMO orbitals of CBM series compounds was distributed on cyanobenzene, indicating  $\pi$ - $\pi$  transition characteristics, while AMBT series compounds showed typical intramolecular charge transfer (ICT) characteristics, without electron cloud distribution on cyanobenzene for their LUMO orbitals. More interestingly, HOMO and LUMO energy levels of CBM series compounds increased sequentially from o-CBM, m-CBM to p-CBM, but HOMO and LUMO energy levels of AMBT series compounds decreased sequentially from o-AMBT, m-AMBT to p-AMBT. Moreover, HOMO and LUMO energy levels of AMBT series compounds embedded between HOMO and LUMO energy levels of CBM series compounds, confirming that FRET from CBM series compounds to AMBT series compounds in host-guest doping systems of CBM and AMBT series compounds. Furthermore, there were two triplet states (T<sub>3</sub> and T<sub>4</sub>) near

the lowest singlet state  $(S_1)$  for o-CBM, which increased to three  $(T_3, T_4)$ and T<sub>5</sub>) for m-CBM and p-CBM, with energy gaps of 0.02-0.23 eV. Moreover, o-CBM gave tiny  $\xi(S_1 \rightarrow T_3)$  and  $\xi(S_1 \rightarrow T_4)$ , resulting in weak ISC and RTP.  $\xi(S_1 \rightarrow T_3)$  and  $\xi(S_1 \rightarrow T_5)$  of m-CBM were 0.091 cm<sup>-1</sup> and 0.151 cm<sup>-1</sup> in sequence, while  $\xi(S_1 \rightarrow T_3)$ ,  $\xi(S_1 \rightarrow T_4)$  and  $\xi(S_1 \rightarrow T_5)$  of p-CBM were 0.082 cm<sup>-1</sup>, 0.017 cm<sup>-1</sup> and 0.110 cm<sup>-1</sup>. By comparison, m-CBM showed the biggest  $\xi(S_1 \rightarrow T_3 \text{ and } S_1 \rightarrow T_5)$  in three CBM isomers, and thereby presented the strongest RTP in crystal and PVA film, while o-CBM gave an opposite result due to the small  $\xi(S_1 \rightarrow T_3 \text{ and } S_1 \rightarrow T_3 \text{$ T<sub>4</sub>). All three AMBT isomers had three triplet states (T<sub>2</sub>, T<sub>3</sub> and T<sub>4</sub>) near  $S_1$ , and with the biggest  $\xi$  for o-AMBT, as well as basically the same  $\xi$ between m-AMBT and p-AMBT. Comparing the energy gaps ( $\Delta E_{S1T2}$ ,  $\Delta E_{S1T3}$ , and  $\Delta E_{S1T4}$ ) of three isomers between the triplet states and S<sub>1</sub>, energy gaps of o-AMBT was the minimum, followed by m-AMBT and p-AMBT (Fig. 6d-f). Based on the big  $\xi$  and small energy gaps, o-AMBT can yield more triplet excitons than m-AMBT and p-AMBT, which should take responsible for longer RTP and afterglow lifetimes for 1 % o-AMBT@PMMA film than 1 % m-AMBT@PMMA and 1 % p-AMBT@PMMA films. Combined with bigger  $\xi(S_0 \rightarrow T_1)$  for o-AMBT than m-AMBT and p-AMBT, 1 % o-AMBT@PMMA film showed higher  $\Phi_P$  and Φ<sub>T</sub> than 1 % m-AMBT@PMMA and 1 % p-AMBT@PMMA films (Table S1). Apart from FRET from CBM series compounds to AMBT series compounds, Dexter energy transfer (DET) was also feasible due to higher T<sub>3</sub>, T<sub>4</sub> and T<sub>5</sub> energy levels for CBM series compounds than T<sub>2</sub>, T<sub>3</sub> and T<sub>4</sub> energy levels of AMBT series compounds. Besides, T<sub>1</sub> energy levels of AMBT series compounds were lower than that of CBM series compounds. Therefore, RTP of doping systems constructed by CBM and AMBT series compounds should come from AMBT series compounds. Overall, AMBT series compounds had dual-state long-lived RTP and TDAF, and 0.1 % m-CBM/o-AMBT and 1 % o-AMBT@PMMA films showed the highest  $\Phi_T$  and  $\Phi_P$ , as well as the longest RTP, TDAF, and afterglow lifetimes due to more efficient ISC for m-CBM and o-AMBT in CBM and AMBT series compounds. FRET and DET energy transfer, as well as excellent crystallinity endowed the doping systems with enhanced RTP and TADF. Compared with PMMA, CBM series compounds could increase the radiation rate ratio  $(k_{ph}/k_T)$  between RTP and TADF of AMBT series compounds (Table S1) due to T1 energy levels of CBM series compounds sandwiching T1 and T2 energy levels of AMBT series compounds, leading to the reduced I<sub>TADF</sub>/I<sub>RTP</sub>.



**Fig. 5.** The intermolecular stacking modes ignoring hydrogen atoms along (a) the a-axis, (b) the b-axis, (c) the c-axis. (d) The intermolecular  $\pi$ - $\pi$  stacking and (e) H type stacking. (f) The intermolecular weak interactions.



Fig. 6. Energy levels and spin orbit coupling constants (ξ) of (a) o-CBM, (b) m-CBM, (c) p-CBM, (d) o-AMBT, (e) m-AMBT, (f) p-AMBT. (g)HOMO and LUMO distribution of CBM and AMBT series compounds.

Data encryption can effectively reduce the risk of data leakage and information theft. For enterprises and government agencies, data encryption is also a necessary mean to ensure trade secrets and national security. By continuously innovating and improving encryption technology, privacy and security are expected to be fully guaranteed. Based on different afterglow lifetimes of the doping systems, a series of data encryption were successfully constructed. Three sets of numbers "869", "869", and "179" were cut out by using the common filter paper, which were immersed in a molten solution of m-CBM for one minute. Then three sets of numbers were removed and left at room temperature for 30 min. New three sets of numbers "653", "967", and "113" were drawn on the above numbers by using DCM solutions of p-AMBT, m-AMBT, and o-AMBT in turn. Under UV radiation of 365 nm, blue numbers "869", "869", and "179" were perceived (Fig. 7a). Switching off 365 nm UV lamp, blue numbers "869", "869", and "179" became green. After switching off 365 nm UV lamp for 3 s, green numbers "869", "869", and "179" transformed into green numbers "653", "967", and "113", indicating excellent data encryption performance. Based on the outstanding

dual-state afterglows of 1 % o-AMBT@PMMA film, a rabbit was outlined by using template. By the switching on/off of 365 nm UV lamp and tuning the ambient temperature around the rabbit, the rabbit showed dynamic color changes from deep blue via green, blue-green, and light blue to deep blue due to different temperature responses of TADF and RTP emissions (Fig. 7b), which is expected to be used for high-level pattern anti-counterfeiting.

### 3. Conclusions

CBM and AMBT series luminogens were successfully prepared, whose molecular structures and purity were characterized by NMR, HR-MS, HPLC, and single-crystal X-ray diffraction. In three CBM isomers, m-CBM showed the longest RTP (212 ms) and afterglow (3 s) lifetimes in crystalline state due to obvious intermolecular  $\pi$ - $\pi$  stacking, typical H stacking, and big  $\xi$ . CBM and AMBT series compounds had phosphorescence nature but failed to emit RTP for o-CBM and p-CBM because of small  $\xi$ , as well as for three AMBT isomers due to poor crystallinity.



Fig. 7. (a) Digital encryption by using m-CBM, m-CBM/o-AMBT, m-CBM/m-AMBT, and m-CBM/p-AMBT; (b) Digital photos of a rabbit constructed by 1 % o-AMBT@PMMA film at different temperatures.

Owing to FRET and DET energy transfer, as well as excellent crystallinity for hosts, a series of doping systems constructed by CBM and AMBT series compounds showed TR emission, even persistent triple-band emissions composed of TADF, unimolecular and aggregated AMBT series compounds. Furthermore, TR emission of CBM/AMBT series doping systems was attributed to host sensitized guest emission based on lower T<sub>1</sub> energy level for AMBT series compounds than CBM series compounds. In the doping systems of CBM/AMBT series compounds, 0.1 % m-CBM/p-AMBT showed the longest TADF (540 ms) and RTP lifetimes (721 ms), giving  $\Phi_{FL}$ ,  $\Phi_T$  and  $\Phi_P$  of 0.11, 0.06 and 0.22 in sequence, as well as persistent afterglow lasting for more than 8 s. Theoretical calculations and experimental results showed that m-CBM and o-AMBT had the highest ξ and longest RTP lifetimes in their respective isomers, which should take responsible for the best TR performance of 0.1 % m-CBM/p-AMBT. RTP and TADF lifetimes of 1 % o-AMBT@PMMA film were up to 727 ms and 606 ms in sequence, further confirming TR emission of AMBT series compounds. Compared with AMBT series compounds@PMMA films, CBM/AMBT series doping systems yielded the reduced  $I_{TADE}/I_{RTP}$  due to the increasing  $k_{ph}/k_T$ . Finally, a series of data encryption were successfully constructed based on different afterglow lifetimes of the doping systems, and a dynamic anti-counterfeiting pattern was prepared by using different temperature responses of TADF and RTP emissions. Of note, CBM and AMBT series compounds are suitable for kilogram level preparation based on short synthesis steps, mild reaction conditions (RT), and high yield (>80 %). This work will provide a novel understanding of long-lived dual-band/triple-band TADF and RTP and contribute to boosting the development of dynamic anti-counterfeiting and high-level digital information encryption.

#### 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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