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Time-dependent and clustering-induced phosphorescence, mechanochromism, structural-function relationships, and advanced information encryption based on isomeric effects and 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

- Three new carbazole isomers were designed and synthesized.
- The isomers show high-contrast RTP and mechanochromism.
- The isomers show time-dependent RTP by host-guest doping.
- The isomers show unusual anti-Kasha behaviors.
- Lo-CzAD and Lp-CzAD simultaneously show RTP and TADF emission in PPh₃ matrix.

ARTICLE INFO

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ABSTRACT

To explore the intrinsic mechanism of pure organic room temperature and clustering-induced phosphorescence and investigate mechanochromism and structural-function relationships, here, 4-(2-(9H-carbazol-9-yl)phenyl)-2amino-6-methoxypyridine-3,5-dicarbonitrile (Lo-CzAD), 4-(3-(9H-carbazol-9-yl)phenyl)-2-amino-6-methoxypyridine-3,5dicarbonitrile (Lp-CzAD) and 4-(4-(9H-carbazol-9-yl)phenyl)-2-amino-6-methoxypyridine-3,5dicarbonitrile (Lp-CzAD) were designed and synthesized by choosing self-made carbazole and 3, 5-dicyanopyridine (DCP) unit as electron acceptor and electron donor in sequence. Compared with crystals Lm-CzAD and Lp-CzAD, crystal Lo-CzAD shows better room temperature phosphorescence (RTP) performance, with RTP lifetimes of 187.16 ms, as well as afterglows 1s, which are attributed to twisted carbazole unit and donor–acceptor (D-A) molecular conformation, big crystal density and spin orbit coupling constant ξ (S₁ \rightarrow T₁ and S₁ \rightarrow T₂), as well as intermolecular H type stacking and small ξ (S₀ \rightarrow T₁). By choosing urea and PPh₃ as host materials and tuning doping ratio, four doping systems were successfully constructed, significantly improving RTP performance of Lo-CzAD and Lp-CzAD, as well as showing different fluorescence and RTP. The lifetimes and afterglows of pure organic Urea/Lo-CzAD and Urea/Lp-CzAD systems are up to 478.42 ms, 5 s, 261.66 ms and 4.5 s in turn. Moreover, Lo-CzAD and Lp-CzAD show time-dependent RTP in doping systems due to monomer and aggregate

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dispersion, as well as clustering-induced phosphorescence. Based on the different luminescent properties, multiple information encryptions were successfully constructed.

1. Introduction

Ultralong organic room temperature phosphorescence (UORTP) materials have broad application prospects in many high-tech fields such as data storage, biological imaging, sensors, and anti-counterfeiting due to good biocompatibility and low toxicity [1–8]. The harm caused by counterfeit and pirated drugs is progressively escalating in today's information age, with the proportion of counterfeit drugs within the global drug market steadily rising. This poses a significant threat to both human health and social stability. Consequently, there is an urgent imperative to develop novel optical materials that can facilitate enhanced levels of anti-counterfeiting measures and information storage technology [9]. Overall, the construction of phosphors mainly includes two aspects: boosting intersystem transition and suppressing nonradiative decay of triplet excitons [10,11]. The former relies on molecular design by introducing carbonyl groups, heteroatoms, and heavy atoms, as well as reducing band gaps (ΔE_{ST}) between the lowest singlet (S1) and triplet (T1), while the latter usually depends on crystal engineering and host-guest doping [12-15]. Thereby, many twisted D-A or D-A-D/A-D-A luminogens show excellent room temperature phosphorescence (RTP) performance due to small ΔE_{ST} [16,17]. Among of them, carbazole, triphenylamine, and phenothiazine are often used as electron donors, which are conjugated with electron acceptors such as benzoic acid, benzaldehyde, and cyanobenzene by nitrogen atoms, forming distorted D-A molecular configurations [18-30]. However, DCP unit is rarely used as an electron acceptor for D-A phosphors. Furthermore, DCP unit not only contains multiple electron-withdrawing and electrondonating groups such as cyan, pyridine units, methoxy, and amino, possibly producing clustering induced phosphorescence by spatial conjugation of functional groups, but also has the characteristics of feasible preparation, high yields, and mild reaction conditions. Therefore, UORTP materials with DCP unit are worth looking forward to.

In addition to suppressing the non-radiative decay of triplet excitons, crystal engineering also plays a crucial role in exploring the intrinsic mechanisms of RTP [31]. Crystals have ordered molecular arrangements and stacking forms, which can be easily obtained by single crystal X-ray diffraction. Crystal analysis combined with theoretical calculations can reveal the key parameters of photophysical properties, thereby obtaining the key factors affecting RTP performance [32–34]. Isomers have identical molecular formulas but different molecular configurations, intermolecular arrangements and stacking modes, frequently leading to high-contrast optical performance [35,36]. Therefore, a series of isomers with excellent crystallinity contribute to construct structure-function relationships, and thereby reveal internal mechanism behind RTP and mechanochromism in depth [37,38]. The existing literatures indicate that carbazole isomers are the focus of molecular design in the fields of mechanochromism and RTP, but most of them were prepared by commercial carbazole containing trace 1H-benzo[f]indole (Bd), possibly leading to incorrect structure-function relationships [39]. Therefore, it is necessary to conduct in-depth structure-function relationships derived from pure carbazole isomers.

To explore the above issues, three carbazole isomers named as Lo-



Fig. 1. (a) The molecular structures of Lo-CzAD, Lm-CzAD and Lp-CzAD. (b) Fluorescence and phosphorescence emission spectra of Lo-CzAD, Lm-CzAD, and Lp-CzAD crystals (delayed time: 1 ms, λ_{ex} : 365 nm). (c) Time-resolved phosphorescence decay curves of three crystals excited at 365 nm. (d) Fluorescence and phosphorescence spectra of Lo-CzAD, Lm-CzAD and Lp-CzAD in DCM (1 × 10⁻⁵ mol/L) at 77 K (delayed time: 1 ms).

Table 1

	λ_{em}			τ		Φ	
	Fluo. (nm)	Phos./Exp. (nm)	Phos./Cal. (nm)	Fluo. (ns)	Phos. (ms)	PL. (%)	Phos. (%)
Lo-CzAD	441	492	510	20.44	187.16	31.51	2.13
Lm-CzAD	446	494	500	14.97	40.27	26.09	0.25
Lp-CzAD	428	521	510	3.56	32.04	39.07	0.31
1 % Lo-CzAD@PMMA	450	455	-	21.34	77.13	46.33	1.72
10 % Lo-CzAD@PMMA	453	460	-	23.03	80.05	42.47	2.21
1 % Lp-CzAD@PMMA	424	429	-	5.43	92.37	40.05	4.72
10 % Lp-CzAD@PMMA	424	427	-	4.67	128.48	36.87	4.97
Urea/Lo-CzAD	442	510	_	17.43	478.42	15.96	10.47
Urea/Lp-CzAD	467	514	-	5.26	261.66	19.48	9.78
PPh ₃ /Lo-CzAD	462	483	-	16.24	293.35	16.35	10.43
PPh ₃ /Lp-CzAD	450	509	-	4.37	240.15	13.39	7.51

CzAD, Lm-CzAD, and Lp-CzAD were designed and synthesized by choosing self-made carbazole and DCP as electronic acceptors and electron donors, respectively. Among of crystals Lo-CzAD, Lm-CzAD, and Lp-CzAD, crystal Lo-CzAD presents the best RTP performance, with lifetimes of 187.16 ms, as well afterglows of 1 s. Lp-CzAD shows mechanochromic activity before/after grinding, but Lo-CzAD and Lm-CzAD present mechanochromism inertness. In different host-guest doping systems, Urea/Lo-CzAD displays the best RTP performance, whose lifetime and afterglow are up to 478.42 ms and 5 s in turn. More importantly, four doping systems display time-dependent RTP, and Urea/Lo-CzAD and Urea/Lp-CzAD systems have wider phosphorescence spectra than PPh₃/Lo-CzAD and PPh₃/Lp-CzAD systems. Moreover, Urea/Lo-CzAD, Urea/Lm-CzAD, and Urea/Lp-CzAD present faint afterglows by switching on-off UV lamp of 380 nm and 400 nm due to clustering induced RTP, but not for PPh3/Lo-CzAD, PPh3/Lm-CzAD, and PPh₃/Lp-CzAD. The doping systems display similar color in sunlight, but different fluorescence and phosphorescence by the on-off switching of UV lamp, which is beneficial for building multiple digital encryptions.

2. Results and discussion

2.1. Photophysical and mechanochromism properties

As shown in Scheme S1, Lo-CzAD, Lm-CzAD and Lp-CzAD were successfully prepared by two-step synthesis reactions and using selfmade carbazole as raw material, and characterized by ¹H NMR, ¹³C NMR, HR-MS, and X-ray single crystal diffraction (Figs. S22–S30), whose purity was confirmed by high-performance liquid chromatography (Fig. S31). In various solutions, the UV–Vis absorption spectra Lo-CzAD, Lm-CzAD and Lp-CzAD show two absorption bands at 275–300 nm and 320–400 nm respectively, corresponding to π - π * transition and intramolecular charge transfer (Fig. S1a–c). Different from UV–Vis absorption spectra, fluorescence emission spectra of Lo-CzAD (30 nm), Lm-CzAD (60 nm) and Lp-CzAD (70 nm) present prominent bathochromicshifts as the polarity of the solvent increases (Fig. S1d–f), indicating larger dipole moment for excited state than ground state, as well as more significant Stokes shift for p-CzAD than o-CzAD and m-CzAD. In THF-H₂O solution, Lm-CzAD and Lp-CzAD form aggregates at water fraction



Fig. 2. (a) Comparison pictures of crystals Lo-CzAD and Lp-CzAD before and after grinding. (b) Fluorescence spectra of Lp-CzAD in different states. (λ_{ex} : 330 nm). (c) Phosphorescence emission spectra of crystal Lp-CzAD before and after grinding (delayed time: 1 ms, λ_{ex} : 365 nm). (d) X-ray diffraction patterns of Lp-CzAD in different states.



Fig. 3. (a) Photographs of Urea/Lo-CzAD, Urea/Lp-CzAD, PPh₃/Lo-CzAD and PPh₃/Lp-CzAD at optimal doping concentration by the on–off switching of 365 nm lamp. Fluorescence and phosphorescence spectra of (b) Urea/Lo-CzAD, (c) Urea/Lp-CzAD, (d) PPh₃/Lo-CzAD and (e) PPh₃/Lp-CzAD at optimal doping concentration (λ_{ex} : 365 nm). (f) Time-resolved phosphorescence decay curves of four doping systems excited at 365 nm.

(f_w) of 80 %, accompanied by blue shifts of emission maxima and enhancement of emission intensity, while Lo-CzAD shows the strongest fluorescence emission at $f_w = 40$ %, which rapidly decreases at $f_w = 80$ % after slowly decreases (Fig. S2). Generally, Lm-CzAD shows aggregation-induced enhanced emission (AIEE) activity, but aggregation caused quenching for Lo-CzAD and Lp-CzAD, indicating obvious isomeric effects, which may be attributed to different intermolecular arrangement and stacking modes.

 λ_{em} (Phos./Exp) and λ_{em} (Phos./Cal) are room temperature phosphorescence emission maxima, and $\Phi(PL)$ is the total quantum yield containing fluorescence and room temperature phosphorescence quantum yields.

Three crystals were successfully grown by slow evaporation of the mixed solution of ethyl acetate and n-hexane. As shown in Figs. 1a and S3a, Lo-CzAD, Lm-CzAD, and Lp-CzAD emit deep blue fluorescence under UV irradiation, with single emission maxima at 428, 441, and 446 nm. Note RTP maxima of crystals Lo-CzAD, Lm-CzAD and Lp-CzAD are located at 492 nm, 494 nm, and 521 nm in turn when the delayed time is 1 ms, instead of multiple phosphorescence peaks at 500-660 nm, demonstrating without trace Bd in crystals (Table 1). By switching on-off UV lamp, only crystal Lo-CzAD displays yellow afterglow visible to the naked eyes, whose RTP and afterglow lifetimes are 187.16 ms and 1s in turn. By contrast, RTP lifetimes of crystals Lm-CzAD and Lp-CzAD are shortened to 40.27 ms and 32.04 ms sequentially, outlining significant isomer effect (Fig. 1b and S3a). Moreover, Lo-CzAD (2.13 %) presents higher phosphorescence quantum yields than Lm-CzAD (0.25 %) and Lp-CzAD (0.31 %) (Table S2). Furthermore, nature phosphorescence of three dyes were confirmed in DCM solution at 77 K (Fig. 1c), emitting bright blue afterglows after stopping UV radiation of 365 nm, phosphorescence emission maxima show continuous whose bathochromic-shift from Lo-CzAD, Lm-CzAD to Lp-CzAD, illustrating longer unimolecular conjugation for Lp-CzAD than Lo-CzAD and Lm-CzAD. Of note, fluorescence emission maxima of Lo-CzAD, Lm-CzAD and Lp-CzAD showed obvious blue shifts compared with their phosphorescence emission maxima, illustrating three compounds with unusual anti- Kasha behaviors (Fig. 1d).

By grinding, fluorescence emission maxima of Lp-CzAD generates red shifts of 20 nm, accompanied by a noticeable color transition from deep blue to light blue (Fig. 2a and b). The reversibility of mechanochromism is investigated by heating and DCM fuming, and the results show that Lp-CzAD has reversible mechanochromism by heating, but not for DCM fuming. Moreover, phosphorescence maxima of Lp-CzAD also undergoes a blue shift of 25 nm after grinding (Fig. 2c), which should be attributed to destruction of intermolecular interactions. In contrast, fluorescence emission maxima of Lo-CzAD and Lm-CzAD coincide very well before/after grinding, illustrating mechanochromism inertness (Fig. S3). X-ray diffraction (XRD) patterns show crystal Lp-CzAD has strong XRD signals, which almost completely disappeared after grinding, demonstrating the occurrence of phase transition from crystalline to amorphous state. Furthermore, the main diffraction signals are restored by heating rather than DCM fuming (Fig. 2d). Overall, Lp-CzAD shows reversible mechanochromism by grinding and heating due to phase transition between crystalline and amorphous state. Mechanochromism inertness of Lo-CzAD and Lm-CzAD should be due to the excellent crystallizability. Taking Lo-CzAD as an example, there are still strong XRD signals after grinding (Fig. S3d). The absolute fluorescence quantum yields (Φ_F) of Lo-CzAD, Lm-CzAD and Lp-CzAD were obtained by an integrating sphere before and after grinding (Fig. S3e). Ground Lp-CzAD (0.45) gave higher Φ_F compared with crystal Lp-CzAD (0.39) possibly due to the denser molecular packing induced by grinding, better inhibiting molecular motions, while $\Phi_{\rm F}$ of Lo-CzAD and Lm-CzAD basically maintained constant because of stable crystal phase (Fig. S3d).

2.2. Urea and triphenylphosphine doped systems

In addition to polymer matrix, many efficient host-guest doping systems adopted small molecules such as benzophenone, triphenylphosphorus (PPh₃), triphenylamine, and urea as host materials. Owing to excellent crystallinity, low melting point and cost, and distorted molecular configuration, the small molecules show good compatibility with guest materials, and effectively suppress non-radiative deactivation



Fig. 4. (a) The spatial conformations and (b) intermolecular distances, and pitch angles of Lo-CzAD, Lm-CzAD and Lp-CzAD. (c) The energy level diagram and SOC coefficient of Lo-CzAD. (d) The HOMO and LUMO of Lo-CzAD, Lm-CzAD, and Lp-CzAD.

of guest molecules, even serve as an energy bridge between the triplet and singlet of guests. However, the selection of host materials still relies more on experience and luck due to complex influencing factors and the lack of unified rules. Here, Urea/Lo-CzAD, Urea/Lm-CzAD, Urea/Lp-CzAD, PPh₃/Lo-CzAD, PPh₃/Lm-CzAD, and PPh₃/Lp-CzAD doping systems were constructed by using triphenylphosphorus (PPh₃) and urea as host materials, which were further optimized by tuning doping ratios between host and guest. When the doping ratio between host and guest is 100:1, the doping systems exhibit the best RTP performance (Fig. S8). Switching off UV lamp of 365 nm, Urea/Lo-CzAD (5 s), Urea/Lm-CzAD (2.5 s), and Urea/Lp-CzAD (4.5 s) systems display the longer afterglow than PPh₃/Lo-CzAD (3 s), PPh₃/Lm-CzAD (1.5 s), and PPh₃/Lp-CzAD (3 s) systems, and they are all superior to the corresponding PMMA systems as well crystals Lo-CzAD and Lp-CzAD (Fig. 3a and Fig. S5). By contrast, Urea/Lm-CzAD and PPh3/Lm-CzAD show shorter RTP and afterglow lifetimes, as well as weaker emission intensity compared with that of Urea/Lo-CzAD, Urea/Lp-CzAD, PPh3/Lo-CzAD, and PPh3/Lp-CzAD. Therefore, the following discussion will mainly be conducted by four doping systems of Lo-CzAD and Lp-CzAD. The RTP lifetime of Urea/Lo-CzAD is almost six times that of 10 % Lo-CzAD@PMMA film, while RTP lifetime of Urea/Lp-CzAD also increase to more than twice that of 10 % Lp-CzAD@PMMA film (Fig. 3f and Fig. S5). Meanwhile, phosphorescence quantum yields of the doping systems are also significantly improved, especially for Urea/Lo-CzAD (0.10) and PPh₃/Lo-CzAD (0.10) (Table 1 and S5). Of note, the fluorescence peaks of Urea/Lo-CzAD, Urea/Lp-CzAD, PPh3/Lo-CzAD and PPh3/Lp-CzAD are 442 nm, 467 nm, 462 nm, and 450 nm respectively, and their phosphorescence peaks are 510 nm, 514 nm, 483 nm, and 509 nm in turn when the delay lifetime is 0.2 ms (Fig. 3b-e). Obviously, urea and PPh₃ not only affect fluorescence emission maxima of Lo-CzAD and Lp-CzAD, but also change their RTP, which is extremely beneficial for anti-counterfeiting patterns and digital encryption. Compared to phosphorescence peaks of Lo-CzAD and Lp-CzAD in DCM solution at 77 K (Fig. 1d), RTP maxima of the doping systems are closer to that of the luminogens in the crystalline state. Thereby, we infer that Lo-CzAD and Lp-CzAD are not

entirely monomer dispersed in urea and PPh3 matrix. Furthermore, four doping systems show time-dependent RTP (Fig. 3b-e), especially for Urea/Lo-CzAD and PPh₃/Lp-CzAD, which can be perceived by the naked eyes. By extending the delay time from 0.2 ms, 30 ms to 50 ms, RTP maxima of Urea/Lo-CzAD and Urea/Lp-CzAD yield continuous blue shifts, while phosphorescence spectra of PPh3/Lo-CzAD and PPh3/Lp-CzAD transform into dual band RTP emission, with a main peak at around 450 nm and a shoulder peak at around 507 nm. Combined phosphorescence emission of Lo-CzAD and Lp-CzAD in DCM solution at 77 K and crystalline state, in PPh₃/Lo-CzAD and PPh₃/Lp-CzAD systems the main peak comes from Lo-CzAD and Lp-CzAD monomers, while the shoulder peak belongs to Lo-CzAD and Lp-CzAD aggregates. Compared with PPh3/Lo-CzAD and PPh3/Lp-CzAD systems, Urea/Lo-CzAD and Urea/Lp-CzAD present wider phosphorescence spectra, possibly containing more emission centers besides monomers and aggregates by spatial interactions of multifunctional groups of Lo-CzAD and Lp-CzAD with amino and carbonyl groups of urea. To further verify the above speculation, the afterglows of Urea/Lo-CzAD and PPh3/Lo-CzAD were first investigated by the on-off switching of 380 nm, 400 nm, and 420 nm lamps. The results indicate Urea/Lo-CzAD presents faint afterglows after switching off 380 nm and 400 nm lamps, whose afterglows even last 0.5 s after switching off the 400 nm lamp, while PPh₃/Lo-CzAD does not give visible afterglow (Fig. S10). The similar situation also happens to Urea/Lm-CzAD, PPh₃/Lm-CzAD, Urea/Lp-CzAD, and PPh₃/Lp-CzAD. Moreover, Lo-CzAD, Lm-CzAD, Lp-CzAD, PPh₃, and Urea does not emit visible afterglow by the on-off switching of 380 nm and 400 nm lamps (Fig. S10). Thereby, the faint afterglows in urea doped systems should derive from RTP induced by spatial conjugation between multifunctional groups (CN, NH2 and OCH3) of the luminogens and amino/ carbonyl groups of urea. Subsequently, XRD patterns of the hosts and doping systems were recorded and analyzed. Before/after doping, XRD signals of urea are hardly changed, indicating excellent crystallinity, while XRD signals of PPh₃ show obvious changes (Fig. S11), illustrating that the guests change intermolecular arrangement and stacking mode of PPh₃. As speculation, PPh₃ has a twisted molecular conformation, which is beneficial for enhancing the compatibility between host and guest. To further explore the interactions between hosts and guests, we tested solid-state UV-vis absorption spectra of the hosts, guests, and doping systems (Fig. S12a and d). Compared with urea, Lo-CzAD and Lp-CzAD, Urea/Lo-CzAD and Urea/Lp-CzAD don't generate new absorption peaks, ruling out appearance of exciplexes. It is worth noting that there is partial overlap between the emission spectra of Urea and the absorption spectra of Lo-CzAD and Lp-CzAD (Fig. S12b), which may lead to Föster resonance energy transfer (FRET). Therefore, the phosphorescence emission spectra of Urea/Lo-CzAD and Urea/Lp-CzAD were investigated by using different excitation wavelengths (Fig. S12c). The results indicate that the two doping systems show the strongest phosphorescence intensities under 365 nm excitation, followed by 410 nm and 200 nm. Owing to 200 nm mainly corresponds to the absorption of urea, while Lo-CzAD and Lp-CzAD have stronger absorption at 365 nm compared to 410 nm, and thereby RTP of the two doping systems comes from excitation of guests rather than FRET. Using the same method, RTP mechanism of PPh3/Lo-CzAD and PPh3/Lp-CzAD were analyzed and discussed, which is attributed to excitation of guests (Fig. S12e-f). Furthermore, phosphorescence spectra of the doping systems were measured at different temperatures (Fig. S13). The results indicated that phosphorescence spectra of PPh₃/Lo-CzAD and PPh₃/Lp-CzAD showed significant differences, with stronger emission at 450 nm for 298 K than 77 K, which was attributed to thermally activated delayed fluorescence (TADF) emission, while the emission peaks near 490 nm came from phosphorescence emission. By contrast, TADF emission were invisible in phosphorescence spectra of Urea/Lo-CzAD and Urea/Lp-CzAD. As speculation, the lowest triplet energy level (T1) of PPh3 sandwiched T1 and lowest singlet energy levels (S1) of Lo-CzAD and Lp-CzAD, leading to the reduced energy gap between T₁ of PPh₃ and S₁ of Lo-CzAD and Lp-CzAD.

3. Crystal analysis and theoretical calculations

To understand the luminescent properties of the compounds, crystal structures, intermolecular stacking, and arrangement modes, the highest occupied molecular orbitals (HOMO), and the lowest unoccupied molecular orbitals (LUMO) distribution of Lo-CzAD, Lm-CzAD and Lp-CzAD were investigated. As shown in the Fig. 4a, carbazole ring and pyridine ring maintain non-planar configurations in crystals Lo-CzAD (CCDC 2322927), Lm-CzAD (CCDC 2322928), and Lp-CzAD (CCDC 2322931), yielding a dihedral angle of 3.16° between plane C1C4N1 and ring A (ring A is composed of C₁, C₂, C₃ and C₄), as well as dihedral angle of 4.34° between plane C₅C₉N₂ and ring C (ring C is composed of C₅, C₆, C₇, C₈ and C₉) for crystal Lo-CzAD, which are 1.81° and 5.24° for crystal Lm-CzAD, as well as 0.61° and 2.13° for crystal Lp-CzAD. The protrusion of N_1 from ring A is beneficial for boosting n- π transitions and producing more triplet excitons, which is consistent with the better RTP performance for Lo-CzAD than Lm-CzAD and Lp-CzAD. Furthermore, dihedral angles of ring A-B, B-C and A-C are 59.35°, 74.28° and 64.94° respectively in crystal Lo-CzAD, while the corresponding dihedral angles are 46.07°, 48.13° and 46.16° for crystal Lm-CzAD, as well as 49.66°, 49.03° and 1.18° in turn for crystal Lp-CzAD. Among of the three dyes, Lo-CzAD exhibits the most distorted molecular conformation, followed by Lp-CzAD and Lm-CzAD. Theoretically, the twisted D-A luminogens have small ΔE_{ST} , contributing to promote ISC transitions. In one unit cell, two Lo-CzAD molecules form an antiparallel π - π stacking mode (Fig. S14), with a centroid-to-centroid (Cg-Cg) distance of 3.618 Å and a plane-toplane (C_P-C_P) distance of 3.283 Å between two adjacent benzene rings on carbazole unit, corresponding to a pitch angle of 65.1° and intermolecular H type stacking (Fig. 4b). For Lm-CzAD, there are two molecules in one unit cell, and they adopt an antiparallel arrangement mode without π - π stacking (Fig. S15), but face-to-face stacking modes between two adjacent carbazole units can be observed by molecular expansion along the a-axis, with a Cg-Cg distance of 4.270 Å and a CP-CP distance of 3.545 Å, corresponding to a pitch angle of of 56° (Fig. 4b). One unit cell

of Lp-CzAD contains two Lp-CzAD molecules and two EtOAc molecules, showing a head (carbazole unit) to tail (pyridine unit) stacking mode between two Lp-CzAD molecules (Fig. S16), with a Cg-Cg distance of 4.624 Å and a centroid-to-plane (C_g - C_P) distance of 3.537 Å (Fig. 4b). The reported literatures indicated that intermolecular H type stacking is beneficial for stabilizing triplet excitons, and thereby crystal Lo-CzAD shows the longest phosphorescence lifetime [40]. There are various intermolecular hydrogen bonding and weak interactions in crystals Lo-CzAD, Lm-CzAD, and Lp-CzAD, contributing to fasten molecular conformations and suppress non radiative energy loss. By contrast, Lo-CzAD has weakest and least intermolecular hydrogen bonding, but with the strongest π - π stacking (Fig. S14 and S17). Besides, Lo-CzAD (1.346 g cm⁻³) has the biggest crystal density, followed by Lp-CzAD (1.303 g cm⁻³) and Lm-CzAD (1.281 g cm⁻³), meaning more effective non radiation suppression for crystal Lo-CzAD than crystals Lp-CzAD and Lm-CzAD (Table, S2). Based on the above crystal analysis, Lo-CzAD, Lm-CzAD and Lp-CzAD have significant differences in twisted degree of carbazole unit, molecular conformation, crystal density, intermolecular arrangement and stacking mode, which can provide some theoretical explanations for different RTP performance induced by molecular isomerism, but which are still insufficient. By adopting ORCA software and extracting molecular structures from single crystals, molecular structures of three dyes were further optimized at the PBE-SVP level by twisting and bending intramolecular dihedral angles. Then, energy calculation of phosphorescence and fluorescence were achieved at the PBE-TZVP level. The results indicate the dihedral angles between plane $C_1C_4N_1$ and ring A are 1.009°, 0.165°, and 0.039° in turn for Lo-CzAD, Lm-CzAD, and Lp-CzAD, whose order is consistent with experimental results (Fig. 4a). Meanwhile, Lo-CzAD (63.58°) possesses the biggest dihedral angle between ring A-B, while Lm-CzAD (53.47°) and Lp-CzAD (52.36°) have equivalent dihedral angle between ring A-B. Phosphorescence emission maxima of Lo-CzAD, Lm-CzAD, and Lp-CzAD are 509.5 nm, 500.2 nm, and 510.3 nm respectively (Table S1), which show deviations of 6-11 nm from the crystal test data. Notably, phosphorescence emission of Lo-CzAD, Lm-CzAD, and Lp-CzAD come from $T_3 \rightarrow S_0$ or $T_4 \rightarrow S_0$ rather than $T_1 \rightarrow S_0$, conforming to the Anti-Kasha's rule. According to the reported literature, MeO- and -CN located on paraposition of aromatic ring easily lead to Anti-Kasha phosphorescence emission [41]. Taking Lo-CzAD as an example, theoretical calculations show that oscillator strength (Table S1) and radiative rate of $T_3 \rightarrow S_0$ (1.1×10^8) are two and three orders of magnitude higher than that of T₁ \rightarrow S₀ (6.0 \times 10⁵) in turn, illustrating the internal conversion process between T_1 and T_3 was inhibited due to a large energy gap [42,43]. Subsequently, energy levels and spin-orbit coupling contants (ξ) between singlet and triplet states of Lo-CzAD, Lm-CzAD, and Lp-CzAD were calculated (Fig. 4c and Fig. S20). Theoretical calculations show all three dyes have tiny ΔE_{ST} (0.01–0.04 eV), whose $\xi(S_1 \rightarrow T_1)$ are 0.08 cm^{-1} , 0.10 cm^{-1} and 0.13 cm^{-1} in turn for Lo-CzAD, Lm-CzAD, and Lp-CzAD. Besides, three dyes also have one triplet excited state (T_2) around the S₁ state, with energy gaps of 0.43–0.45 eV and ξ of 0.04–0.19 cm⁻¹. Due to almost identical ΔE_{ST} and ΔE_{S1T2} , generation of triplet excitons are mainly affected by $\xi(S_1 \rightarrow T_1)$ and $\xi(S_1 \rightarrow T_2)$. By contrast, Lo-CzAD has the biggest ξ (0.27 $\mbox{cm}^{-1}\mbox{)},$ followed by Lm-CzAD (0.17 cm⁻¹), and Lp-CzAD (0.17 cm⁻¹) based on the summation of $\xi(S_1 \rightarrow T_1)$ and $\xi(S_1 \rightarrow T_2)$. Moreover, Lm-CzAD (1.22 cm⁻¹) and Lp-CzAD (1.06 cm⁻¹) show bigger $\xi(T_1 \rightarrow S_0)$ than Lo-CzAD (0.46 cm⁻¹). Thereby, Lo-CzAD shows the best RTP performance due to the biggest $\xi(S_1 \rightarrow T_1 \text{ and }$ $S_1 \rightarrow T_2$) and the smallest $\xi(T_1 \rightarrow S_0)$, which accelerate the generation of triplet excitons and reduce the radiation rate of triplet excitons respectively, leading to simultaneous improvement of RTP quantum yield and lifetime. As expected, HOMO of the luminogens is mainly concentrated on 3, 5-dicyanopyridine unit rather than carbazole unit (Fig. 4d), illustrating 3, 5-dicyanopyridine unit plays the role of an electron donor.



Fig. 5. Information encryption using the outline of Urea and PPh_3 doped systems.

4. Applications

Based on different fluorescence and phosphorescence emission characteristics of the doping systems, a high-level digital encryption was designed. As shown in Fig. 5, two filter papers were soaked in molten urea and PPh3 respectively, and then Lo-CzAD and Lp-CzAD were dissolved separately in ethyl acetate and used as inks. By using the same template and the treated filter papers, a series of maple leaves were depicted, which were cropped and arranged in proper order. Under sunlight, only white maple leaves are seen due to the main absorption bands of the host and guest are below 400 nm, but they show deep blue or light blue fluorescence under UV irradiation of 365 nm. When the UV lamp is turned off, three different afterglows including orange, deep blue, and yellow can be observed, which are respectively used to represent "horizontal", "dot" and "blank". Therefore, correct information cannot be obtained under both sunlight and ultraviolet lights. Taking the first row as example, we can obtain the information of "horizontal", "dot", "horizontal" and "dot" when the UV lamp is turned off, which is used as the correct reading information. Compared the correct information with the international password table (Fig. S21), the first row can be interpreted as letter "C". Using the same strategy, the remaining four rows are decrypted into "H", "I", "N", and "A" in sequence. Finally, the complete encrypted information is decrypted into "CHINA".

5. Conclusions

In summary, three novel luminogens named Lo-CzAD, Lm-CzAD and Lp-CzAD were prepared based on isomeric effects. The AIE experiment indicates Lm-CzAD has AIEE activity, but for Lo-CzAD and Lp-CzAD with ACQ behaviors, showing obvious isomeric effects. By grinding and heating, Lp-CzAD shows reversible mechanochromism (20 nm) due to phase transition between crystalline and amorphous state. Lo-CzAD and Lp-CzAD and Lp-CzAD show phosphorescence nature in DCM solution at 77 K, whereas only Lo-CzAD emits visible afterglow to the naked eyes in the crystalline states, with afterglows of 1 s, displaying isomeric effects. Compared with Lm-CzAD and Lp-CzAD, crystal analysis indicates that Lo-CzAD has more twisted carbazole unit and D-A molecular conformation, as well as the biggest crystal density and π - π stacking, contributing to boost K_{ISC} and reduce non-radiative energy loss, as well as stabilize triplet excitons. Theoretical calculations further confirm Lo-

CzAD relative to Lm-CzAD and Lp-CzAD possesses a faster rate of triplet exciton generation and a lower radiation rate, leading to better RTP performance for Lo-CzAD than Lm-CzAD and Lp-CzAD. By choosing different host materials and tuning doping ratio, RTP performance of Lo-CzAD and Lp-CzAD were significantly improved. The lifetimes and afterglows of pure organic Urea/Lo-CzAD and Urea/Lp-CzAD systems are up to 478.42 ms, 5 s, 261.66 ms and 4.5 s in turn, with RTP quantum yields of 0.10. XRD and phosphorescence spectra with different delay times indicate monomers and aggregates of Lo-CzAD and Lp-CzAD are simultaneously dispersed in urea and PPh3 matrix, leading to timedependent phosphorescence emission. The afterglows at different excitation wavelengths further show the existence of spatial interactions between functional groups of Lo-CzAD/Lm-CzAD/Lp-CzAD and urea, which present faint afterglows by the on/off switching of ultraviolet lamp of 380 nm and 400 nm. Based on different fluorescence and phosphorescence emission characteristics of the dyes and their doping systems, high-level information encryptions were successfully achieved. The work not only provides a series of novel pure organic RTP and mechanochromism materials, but also contributes to boost deep understanding of the structure-functions relationships. Meanwhile, dynamic RTP is achieved by monomers, aggregates, and clustering induced RTP.

CRediT authorship contribution statement

Jianmei Guo: Visualization, Software, Methodology, Investigation, Formal analysis, Conceptualization. Jiaqi Liu: Software, Methodology. Yupeng Zhao: Software, Methodology. Yongtao Wang: . Lei Ma: Supervision. Jianfeng Jiang: Visualization.

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 material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.saa.2024.124449.

References

- J. Shi, W. Tao, Y. Zhou, G. Liang, Efficient room-temperature phosphorescence with tunable lifetime through light modulation from flexible polymer films, Chem. Eng. J. 475 (2023) 146178, https://doi.org/10.1016/j.cej.2023.146178.
- [2] 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, https://doi.org/10.1016/j.mtchem.2022.101297.
- [3] T. Zhu, T. Yang, Q. Zhang, W.Z. Yuan, Clustering and halogen effects enabled red/ near-infrared room temperature phosphorescence from aliphatic cyclic imides, Nat. Commun. 13 (2022) 2658, https://doi.org/10.1038/s41467-022-30368-7.
- [4] Y. Xie, Y. Ge, Q. Peng, C. Li, Q. Li, Z. Li, How the molecular packing affects the room temperature phosphorescence in pure organic compounds: ingenious molecular design, detailed crystal analysis, and rational theoretical calculations, Adv. Mater. 29 (2017), https://doi.org/10.1002/adma.201606829.
- [5] S.M.A. Fateminia, Z. Mao, S. Xu, Z. Yang, Z. Chi, B. Liu, Organic nanocrystals with bright red persistent room-temperature phosphorescence for biological applications, Angew. Chem., Int. Ed. 56 (2017) 12160–12164, https://doi.org/ 10.1002/anie.201705945.
- [6] 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. (2023) 111760, https://doi.org/ 10.1016/j.dyepig.2023.111760.
- [7] G. Baryshnikov, B. Minaev, H. Ågren, Theory and calculation of the phosphorescence phenomenon, Chem. Rev. 117 (2017) 6500–6537, https://doi. org/10.1021/acs.chemrev.7b00060.
- [8] Y. Lei, J. Yang, W. Dai, Y. Lan, J. Yang, X. Zheng, J. Shi, B. Tong, Z. Cai, Y. Dong, Efficient and organic host-guest room-temperature phosphorescence: tunable triplet-singlet crossing and theoretical calculations for molecular packing, Chem. Sci. 12 (2021) 6518–6525, https://doi.org/10.1039/d1sc01175h.
- [9] T.M. Figueira-Duarte, K. Müllen, Pyrene-based materials for organic electronics, Chem. Rev. 111 (2011) 7260–7314, https://doi.org/10.1021/cr100428a.
- [10] Y. Su, Y. Zhang, Z. Wang, W. Gao, P. Jia, D. Zhang, C. Yang, Y. Li, Y. Zhao, Excitation-Dependent Long-Life Luminescent Polymeric Systems under Ambient Conditions, Angew. Chem., Int. Ed. 59 (2019) 9967–9971, https://doi.org/ 10.1002/anie.201912102.
- [11] L. Xu, K. Zhou, X. Qiu, B. Rao, D. Pei, A. Li, Z. An, G. He, Tunable ultralong organic phosphorescence modulated by main-group elements with different Lewis acidity and basicity, J. Mater. Chem. C 8 (2020) 14740–14747, https://doi.org/10.1039/ d0tc02953j.
- [12] C. Han, R. Du, H. Xu, S. Han, P. Ma, J. Bian, C. Duan, Y. Wei, M. Sun, X. Liu, W. Huang, Ladder-like energy-relaying exciplex enables 100% internal quantum efficiency of white TADF-based diodes in a single emissive layer, Nat. Commun. 12 (2021), https://doi.org/10.1038/s41467-021-23941-z.
- [13] S. Jena, J. Eyyathiyil, S.K. Behera, M. Kitahara, Y. Imai, P. Thilagar, Crystallization induced room-temperature phosphorescence and chiral photoluminescence properties of phosphoramides, Chem. Sci. 13 (2022) 5893–5901, https://doi.org/ 10.1039/d2sc00990k.
- [14] Y. Gong, J. Yang, M. Fang, Z. Li, Room-temperature phosphorescence from metalfree polymer-based materials, Cell Rep. Phys. Sci. 3 (2022) 100663, https://doi. org/10.1016/j.xcrp.2021.100663.
- [15] Y. Chen, C.H. Wang, T.C. Chou, P.T. Chou, Comment on "Metal-Free Triplet Phosphors with High Emission Efficiency and High Tunability", Angew. Chem., Int. Ed. 61 (2022) 202109224, https://doi.org/10.1002/anie.202109224.
- [16] J. Yang, X. Zhen, B. Wang, X. Gao, Z. Ren, J. Wang, Y. Xie, J. Li, Q. Peng, K. Pu, Z. Li, The influence of the molecular packing on the room temperature phosphorescence of purely organic luminogens, Nat. Commun. 9 (2018) 840, https://doi.org/10.1038/s41467-018-03236-6.
- [17] K. Jiang, Y. Wang, C. Cai, H. Lin, Conversion of carbon dots from fluorescence to ultralong room-temperature phosphorescence by heating for security applications, Adv. Mater. 30 (2018) 1800783, https://doi.org/10.1002/adma.201800783.
- [18] A.J. Gillett, C. Tonnelé, G. Londi, G. Ricci, M. Catherin, D.M.L. Unson, D. Casanova, F. Castet, Y. Olivier, W.M. Chen, E. Zaborova, E.W. Evans, B.H. Drummond, P. J. Conaghan, L.-S. Cui, N.C. Greenham, Y. Puttisong, F. Fages, D. Beljonne, R. H. Friend, Spontaneous exciton dissociation enables spin state interconversion in delayed fluorescence organic semiconductors, Nat. Commun. 12 (2021) 6640, https://doi.org/10.1038/s41467-021-26689-8.

- [19] J. Li, X. Li, G. Wang, X. Wang, M. Wu, J. Liu, K. Zhang, A direct observation of upconverted room-temperature phosphorescence in an anti-Kasha dopant-matrix system, Nat. Commun. 14 (2023) 1987, https://doi.org/10.1038/s41467-023-37662-y.
- [20] D. Malpicci, A. Forni, C. Botta, C. Giannini, E. Lucenti, D. Marinotto, D. Maver, L. Carlucci, E. Cariati, Dual fluorescence and RTP features of carbazole-cyclic triimidazole derivatives: the fluorophores' connectivity does matter, Dyes Pigm. 215 (2023) 111274, https://doi.org/10.1016/j.dyepig.2023.111274.
- [21] L. Huang, J. Liu, L. Liu, Q. Yang, Z. Ma, X. Jia, A D-A-D' type organic molecule with persistent phosphorescence exhibiting dual-mode mechanochromism, Dyes Pigm. 173 (2020) 107963, https://doi.org/10.1016/j.dyepig.2019.107963.
- [22] J. Xiao, J. Deng, Y. Bai, H. Liu, L. Yu, H. Wang, Persistent room-temperature phosphorescent triazole derivatives with high quantum yields and long lifetimes, Adv. Opt. Mater. (2023), https://doi.org/10.1002/adom.202301978.
- [23] J. Li, G. Xing, J. Wu, Y. Zhang, J. Wei, S. Liu, Y. Ma, Q. Zhao, Photoirradiationgated excitation-dependent room-temperature phosphorescence in through-space charge transfer molecules, Laser Photon. Rev. (2023), https://doi.org/10.1002/ lpor.202300704.
- [24] H. Sun, X. Wei, Y. He, Y. Xiao, Y. Wu, Z. Xie, T. Yu, Regulation of various photoactive UOPs in a polymer matrix by tuning intermolecular charge transfer, Mater. Chem. Front. 7 (2023) 3156–3163, https://doi.org/10.1039/d3qm00214d.
- [25] X. Song, G. Lu, Y. Man, J. Zhang, S. Chen, C. Han, H. Xu, Phosphine-manipulated pπ and π-π synergy enables efficient ultralong organic room-temperature phosphorescence, Angew. Chem., Int. Ed. 62 (2023) e202300980.
- [26] S. Jena, S.K. Behera, J. Eyyathiyil, M. Kitahara, Y. Imai, P. Thilagar, Modulating the room temperature phosphorescence by tweaking SOC and P = X interactions (X = O, S, and Se) in phosphoramides: magnetic circularly polarized luminescence from achiral phosphoramides, Adv. Opt. Mater. (2023), https://doi.org/10.1002/ adom.202300923.
- [27] M. Stanitska, D. Volyniuk, B. Minaev, H. Agren, J.V. Grazulevicius, Molecular design, synthesis, properties, and applications of organic triplet emitters exhibiting blue, green, red and white room-temperature phosphorescence, J. Mater. Chem. C 12 (2024) 2662–2698, https://doi.org/10.1039/D3TC04514E.
- [28] M. Ghasemi, M. Mahmoudi, D. Gudeika, K. Leitonas, J. Simokaitiene, A. Dabuliene, A. Panchenko, B. F. Minaev, D. Volyniuk, J. Vidas Grazulevicius, Effects of the change of isomers on room-temperature phosphorescence, thermally activated delayed fluorescence, and long persistent luminescence of organic holetransporting materials with the selective potential for the application in electronic devices and optical sensors of oxygen, Chem. Eng. J. 473 (2023) 145004, doi: 10.1016/j.cej.2023.145004.
- [29] K. Leitonas, B. Vigante, D. Volyniuk, A. Bucinskas, R. Keruckiene, P. Dimitrijevs, T.-L. Chiu, J.V. Grazulevicius, P. Arsenyan, 3,5-Dicyanopyridine motifs for electron-transporting semiconductors: from design and synthesis to efficient organic light-emitting diodes, J. Mater. Chem. C 11 (2023) 9514–9526, https:// doi.org/10.1039/D3TC00841J.
- [30] L. Skhirtladze, R. Keruckiene, O. Bezvikonnyi, M. Mahmoudi, D. Volyniuk, K. Leitonas, M. Ghasemi, J. Simokaitiene, F.H.A. Nasir, A. Ariffin, J. V. Grazulevicius, Switching thermally activated delayed fluorescence to room temperature phosphorescence for oxygen sensing: effect of donor substituents of trifluoromethylphenyl, Spectrochim. Acta, Part A 306 (2024) 123531, https://doi. org/10.1016/j.saa.2023.123531.
- [31] X. Shao, Molecular uniting set identified characteristic (MUSIC): a promising strategy for purely organic RTP luminogens, Sci. China Chem. 61 (2018) 975–976, https://doi.org/10.1007/s11426-018-9265-0.
- [32] Y. Gong, G. Chen, Q. Peng, W.Z. Yuan, Y. Xie, S. Li, Y. Zhang, B.Z. Tang, Achieving persistent room temperature phosphorescence and remarkable mechanochromism from pure organic luminogens, Adv. Mater. 27 (2015) 6195–6201, https://doi.org/ 10.1002/adma.201502442.
- [33] K. Zheng, X. Yang, F. Ni, Z. Chen, C. Zhong, C. Yang, Multicolor ultralong roomtemperature phosphorescence from pure organic emitters by structural isomerism, Chem. Eng. J. 408 (2021) 127309, https://doi.org/10.1016/j.cej.2020.127309.
- [34] W. Gao, Z. Liu, X. Dai, W. Sun, Q. Gong, J. Li, Y. Ge, Color-tunable ultralong organic phosphorescence: commercially available triphenylmethylamine for UVlight response and anticounterfeiting, Chem. – Asian J. 18 (2023) e202300450.
- [35] T. Zhang, X. Wang, Z. An, Z. Fang, Y. Zhang, W.Z. Yuan, Pure organic persistent room-temperature phosphorescence at both crystalline and amorphous states, ChemPhysChem 19 (2018) 2389–2396, https://doi.org/10.1002/cphc.201800310.
- [36] 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, https://doi.org/10.1016/j.mtchem.2023.101548.
- [37] S. Yi, S. Jiang, K. Wang, H. Wu, Y. Zhou, L. Qu, C. Yang, Electronic modulation induced luminescence from triphenylamine derivative and temperature sensor application, Adv. Opt. Mater. (2023), https://doi.org/10.1002/adom.202301601.
- [38] J. Deng, Y. Bai, J. Li, J. Jiang, C. Zhao, W. Xie, Y. Guo, H. Liu, D. Liu, L. Yu, H. Wang, Yellow and orange-red room-temperature phosphorescence from amorphous nonaromatic polymers, Adv. Opt. Mater. (2023), https://doi.org/ 10.1002/adom.202300715.
- [39] C. Chen, Z. Chi, K.C. Chong, A.S. Batsanov, Z. Yang, Z. Mao, Z. Yang, B. Liu, Carbazole isomers induce ultralong organic phosphorescence, Nat. Mater. 20 (2020) 175–180, https://doi.org/10.1038/s41563-020-0797-2.
- [40] D. Barman, P.K. Iyer, Aggregation-induced delayed fluorescence and phosphorescence from hot excitons via suppression of Kasha's rule in a stimuliactive molecular rotor, J. Phys. Chem. C 127 (2023) 2694–2704, https://doi.org/ 10.1021/acs.jpcc.2c08479.

J. Guo et al.

- [41] T. Itoh, Fluorescence and phosphorescence from higher excited states of organic molecules, Chem. Rev. 112 (2012) 4541–4568, https://doi.org/10.1021/ cr200166m.
- [42] H. Liu, Q. Mu, X. Zhao, Y. Wang, Y. Song, L. Lin, C.-K. Wang, J. Fan, Theoretical perspective for structural isomerism effect on photoelectric properties of organic room temperature phosphorescence molecules, Mater. Today Chem. 34 (2023) 4541–4568, https://doi.org/10.1016/j.mtchem.2023.101814.

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[43] S. Li, L. Fu, X. Xiao, H. Geng, Q. Liao, Y. Liao, H. Fu, Regulation of thermally activated delayed fluorescence to room-temperature phosphorescent emission channels by controlling the excited-states dynamics via J- and H-aggregation, Angew. Chem., Int. Ed. 60 (2021) 18059–18064, https://doi.org/10.1002/ anie.202103192.