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Highly efficient room-temperature phosphorescent materials with a heavy-atom effect of bromine[†]

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Room-temperature phosphorescent (RTP) materials with long luminescence lifetimes have stimulated considerable interest. However, pure organic molecules with persistent room-temperature phosphorescence are still rarely reported. In this work, we study two molecules, DCzMPh and TCzMPh, in which persistent room-temperature phosphorescence in the amorphous state is achieved *via* the heavy-atom effect of bromine atoms in their structure. Their final quantum yields are found to be as high as 90 and 93%, respectively, at the phosphorescence lifetimes of 0.27 and 0.28 s, respectively. Moreover, both molecules are shown to be appropriate for security protection applications.

Over the past few years, organic afterglow materials have attracted a considerable amount of attention due to their unique properties that find application in optoelectronic devices,¹ data security protection,² molecular sensing,³ and mass spectrometric analysis.⁴ Among these materials, the most effective are inorganics and organometallic room-temperature phosphorescence (RTP) compounds.^{5–7} However, metal materials exhibit shortcomings such as instability, high cost, toxicity and poor flexibility. Furthermore, high non-radiative deactivation rates along with weak intersystem crossing (ISC) impede the efficient RTP in pure organic luminogens.^{8–10} Thus, designing organic (RTP) materials with lower toxicity and longer emission lifetimes is one of the important tasks of researchers.

In recent years, synthesis of organic materials with ultralong phosphorescence has been presented by various strategies such as host–guest design,^{11,12} H-aggregation,^{13,14} (*co*)crystallization,^{15,16} chelation,^{17,18} and polymerization.^{19,20} Meanwhile, achieving highly efficient phosphorescence in pure organic materials under ambient conditions is a challenging task because of a weak spin–orbit coupling (SOC)²¹ between the singlet and triplet states. In this respect, the phosphorescence efficiency in metal-free

organic compounds can be multiplied by introducing halogen atoms (Br or I) that are favorable to enhance the intersystem crossing process²² due to a pronounced heavy-atom effect.^{23,24}

In the present work, carbazole and benzene are linked by methylene, which increases distortion and activates crystalinduced phosphorescence.²⁵ Such a combination of a heavy atom as a π -acceptor with a carbazole unit aims to improve the phosphorescence efficiency of these compounds. The chemical and structural analysis of both molecules was performed using nuclear magnetic resonance (NMR) and single-crystal X-ray diffraction (XRD) techniques. Their photophysical properties such as quantum yields and phosphorescence lifetimes were evaluated by ultraviolet-visible (UV/Vis) absorption spectroscopy in a tetrahydrofuran (THF) solution and steady-state fluorescence and phosphorescence spectrophotometry in the crystalline state under ambient conditions (at atmospheric pressure and room temperature).

DCzMPh and **TCzMPh** compounds were prepared from trimethyl bromide benzene 1 through a two-step process (Scheme 1). First, 2 and 3 were prepared *via* the routes described in the literature.²⁶ The substitution reactions of 2 and 3 with carbazole were performed under KOH conditions and DMSO was used as the solvent. **DCzMPh** and **TCzMPh** were recrystallized with dichloromethane and *n*-hexane until the colorless crystals were obtained. The final quantum yields of these molecules are found



Scheme 1 Synthesis of DCzMPh and TCzMPh



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to be as high as 90 and 93%, respectively. The thermal properties of **DCzMPh** and **TCzMPh** were studied by thermogravimetric analysis (TGA). **DCzMPh** and **TCzMPh** have good thermal stability, the 5% weightlessness temperature (T_d) is 363.3 °C and 394.0 °C, respectively (Fig. S2, ESI†). To characterize the frontier molecular orbital distributions of **DCzMPh** and **TCzMPh**, density functional theory (DFT) calculations were carried out on the ground state by using density functional theory (DFT) with the B3LYP/6-31G* basis set. As shown in Fig. S3 (ESI†), the LUMO is clearly confined in the carbazole and benzene ring, respectively, and the HOMO is also similarly distributed on the carbazole, indicating a good overlap between the HOMO and LUMO.

Fig. 1 displays the UV/Vis absorption spectra of both molecules. Except for a difference between the methyl and carbazole at the adjacent positions, the structures of **DCzMPh** and **TCzMPh** are close to each other, resulting in almost similar UV/Vis absorption spectra of the two materials. Both compounds exhibit two pronounced absorption peaks at 239 and 293 nm and signatures at 240 and 295 nm, respectively, with a small acromion, which are the π - π * characteristic absorption peaks of the carbazole group and the phenyl conjugated double bond. The absorption peaks at 327, 340, 329 and 342 nm possess low absorption intensities at higher absorption wavelengths and refer to the $n \rightarrow \pi$ *absorption from the solitary electron pairs to the empty orbitals on carbazole and bromine atoms (Fig. 1).

Fig. 2 displays the steady-state fluorescence and phosphorescence spectra of crystalline **DCzMPh** and **TCzMPh** under ambient conditions. As shown in Fig. 2a, **DCzMPh** in a crystalline state exhibits a delayed luminescence in a wide wavelength range ($\lambda_{max} = 431$ nm) with an ultralong lifetime τ_p of up to 0.27 s and a quantum yield Φ_p of 6.58% (Fig. 4), along with a fluorescence signal at $\lambda_{max} = 408$ nm ($\lambda_{ex} = 356$ nm). The large Stokes shift between fluorescence and RTP emission of **DCzMPh** is around 150 nm. Meanwhile, compared with a fluorescence emission ($\lambda_{max} =$ 408 nm), the maximum emission redshift in a phosphorescence mode ($\lambda_{max} = 431$ nm) is 23 nm, which is testimony to the fact that the afterglow is rather associated with phosphorescence than with delayed fluorescence. For the crystalline **TCzMPh** (Fig. 2b) a delayed luminescence is observed within a wide wavelength region ($\lambda_{max} =$ 430 nm) with an ultralong lifetime τ_p of up to 0.28 s and a quantum



Fig. 1 UV/Vis absorption spectra of DCzMPh (black) and TCzMPh (red) in THF.



Fig. 2 Steady-state fluorescence (black) and phosphorescence (red) spectra of crystalline (a) **DCzMPh** and (b) **TCzMPh** under ambient conditions.

yield $\Phi_{\rm p}$ of 13.77% (Fig. 4), almost the same as the fluorescence spectrum ($\lambda_{\rm ex}$ = 400 nm).

The information available from UV-Vis absorption spectroscopy data in Fig. 1 and 2 enabled one to assess the photophysical parameters of **DCzMPh** and **TCzMPh** under ambient conditions. Table 1 summarizes the fluorescence and phosphorescence characteristics for both molecules, including quantum yields and phosphorescence lifetimes. The quantum yield Φ_p of crystalline **DCzMPh** was found to be 6.58% at an ultralong lifetime τ_p of up to 0.27 s. The appropriate values for **TCzMPh** in a crystalline state were 13.77% and 0.28 s, respectively.

The afterglow decay curves of both samples are plotted in Fig. 3 at various lifetimes. To elucidate the origin of ultralong phosphorescence in both compounds, a single-crystal X-ray diffraction analysis was performed to thoroughly study their molecular packing models and interaction. Fig. 4 shows the crystal packing models of crystalline **DCzMPh** and **TCzMPh** under ambient conditions. As seen in Fig. 4a, a **DCzMPh** molecule is presented

| Table 1 Photophysical data of DCzMPh and TCzMPh at 298 K | | | | | | | |
|--|--|---------------------------------|--|--------------|------------------|------------------------|------------------------|
| Compoun | λ _{ex} d [nm] ^a | $\lambda_{ m Fluo} \ [nm]^{ab}$ | $\lambda_{	ext{Phos}} [ext{nm}]^{ab}$ | $[ns]^a$ | $[\mathbf{s}]^a$ | $\Phi_{ m F}(\%)^{ac}$ | $\Phi_{ m p}(\%)^{ac}$ |
| DCzMPh TCzMPh | 356 400 | 408 430 | 431 430 | 9.12 4.88 | 0.27 0.28 | 6.58 13.77 | 0.98 3.43 |

 a In a crystalline state. b Emission maximum upon excitation at the longest absorption maximum. c Absolute quantum yield.



Fig. 3 Afterglow decay curves vs. lifetimes of DCzMPh and TCzMPh under ambient conditions.

by three types of intramolecular interactions, including C-H···N (2.469 and 2.557 Å). Strong C-Br···N and C-Br··· π interactions effectively limit the molecular rotations and thus decrease the nonradiative decay. Intramolecular Br bonds promote the spin-orbit coupling (SOC) between the excited singlet and triplet states. Each molecule in a crystalline **DCzMPh** is surrounded by two types of intermolecular interactions (C-Br··· π , 3.698 Å), as shown in Fig. 4b. Moreover, a small overlap of the carbazyl group with a formed π ··· π stacking (3.452 Å) is highlighted for a **DCzMPh** molecule pair *s* in the crystal (Fig. 4c). In the crystalline **TCzMPh** (Fig. 4d), there are three types of intramolecular interactions, including C-H···N (2.433, 2.484, 4.046 and 2.512 Å). Compared with a **DCzMPh** structure, **TCzMPh** possesses a carbazole



Fig. 4 Crystal packing models of crystalline (a–c) DCzMPh and (d–f) TCzMPh under ambient conditions.

group, which reduces to a large extent the changes in the indicated intramolecular interactions. Since the C-H...N interaction is characterized by four values, this also suppresses the molecular motions, protecting triplet excitons from the nonradiative transitions. Each molecule in a crystalline TCzMPh is surrounded by the two types of intermolecular interactions that are shown in Fig. 4e (C–Br $\cdot \cdot \pi$, 3.906 Å). Simultaneously, a small overlap of the carbazyl group with a formed $\pi \cdots \pi$ stacking (3.393 Å) is found for a pair of TCzMPh molecules in the crystalline state (Fig. 4f). A great deal of intermolecular and intramolecular interactions results in a relatively small rate of relaxation from T_1 to S_0 , which explains the ultralong lifetimes obtained for both molecules. The persistent phosphorescence originates from the carbazoles involved in the electronic interactions between the Br atoms and carbazole.27 In particular, the H-aggregation formed in both crystalline compounds can stabilize the triplet excitons for an ultralong lifetime under ambient conditions.13

RTP materials with ultralong lifetimes may find applications in anti-counterfeiting technology and encryption.²⁸ For example, Fig. 5 depicts a secure code pattern where **DCzMPh** serves as a "J" part and **TCzMph** is used as the "N" part (Daylight mode). Under UV irradiation of 365 nm (UV light on mode), the pattern exhibits white-light emission, which can act as the fluorescent security protection mode. After turning off the UV excitation (UV light off mode), it can be seen by the naked eye that "J" and "N" show yellow RTP, thus making it difficult to distinguish each part.

In 2020, Yan's group reported the synthesis of compound $(Ph_4P)_2Cd_2Br_6$, which was synthesized difficultly, and with a low overall yield, with the room temperature phosphorescence quantum yield of 62.79% and lifetime of 37.85 ms.²⁹ Our synthesized materials **DCzMPh** and **TCzMPh** have lifetimes of 0.27 s and 0.28 s, respectively. Compared with the above materials, we have achieved better phosphorescence lifetime and higher yield materials.

In summary, we developed a concise and very simple chemical approach to construct amorphous, heavy-atom containing pure organic RTP materials, where the triplet exciton stabilization is achieved through a combination of the bromine atom and carbazole. For this, we produced **DCzMPh** and **TCzMph** molecules with bromine as halogen atoms, in which carbazole and benzene

Daylight

UV light on

UV light off



Fig. 5 Example of the use of **DCzMPh** and **TCzMPh** in data security protection. Here, the "J" pattern is made of **DCzMPh** (powder) and the "N" pattern is obtained using **TCzMPh** (powder). The UV light excitation wavelength is 365 nm.

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were linked by methylene, thus increasing molecular distortions and activating crystal-induced phosphorescence. In these structures, weak intermolecular interactions were found to strongly influence the luminescence efficiency, resulting in quantum yields above 90% and ultralong lifetimes up to 0.27–0.28 s. Furthermore, the suitability of both materials for anti-counterfeiting and cryptographic purposes was demonstrated as well. Thus, the method we propose can be used as a new platform to design highly efficient RTP materials for data security, molecular imaging, and LED applications.

Conflicts of interest

The authors declare that there is no conflict of interest.

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Authorship agreed by all authors except for Mark G. Humphrey who could not be contacted.

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