Modulation of the intramolecular hydrogen bonding and push–pull electron effects toward realizing highly efficient organic room temperature phosphorescence†

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The exploitation of ultralong organic room temperature phosphorescence (UORTP) materials lags far behind the need because of the lack of general design strategies. Here we proposed a facile design strategy based on the structural control of intramolecular hydrogen bonding (IHB) and push–pull electron effects (PPEEs) to construct highly efficient UORTP materials. Two series of carbazole derivatives with different IHBs and PPEEs were designed accordingly. By enhancing the IHB interactions of the luminophores, the molecular planarity, intermolecular interactions and packing mode were effectively tuned, facilitating the intermolecular electron coupling. PPEEs, enhanced by introducing heteroatoms and heavy atoms, strengthened the intramolecular charge transfer states, which changed the orbital transition configuration of excited states, thus boosting the intersystem crossing (ISC) and spin–orbit coupling (SOC). Consequently, CzPM and CzPMBr with dual IHBs and the strongest PPEEs exhibited ultralong lifetimes (τph) of 1.31 s and 233 ms with the highest phosphorescence quantum yields (ΦP) of 1.7% and 48.6% in their series, respectively. Theoretical investigations revealed that the high-lying intersystem crossing (HISC) between excited singlet states (Sm, m > 1) and triplet states (Tn, n > 1) occurred and played a vital role in enhancing the ΦP values of UORTP materials. Significantly, the SOC matrix elements between S3 and T7 (ε[S3,T7]) of CzPMBr reached up to 39.95 cm⁻¹. Finally, CzPMBr was successfully used as an anti-counterfeiting ink in calligraphy and painting due to its excellent RTP properties. The design strategy based on the structural control of IHBs and PPEEs will greatly widen the design platform of UORTP materials. Meanwhile, the discovery of the HISC process will also provide a new insight for the design of UORTP materials.

Introduction

In the last decade, ultralong organic room temperature phosphorescence (UORTP) materials with durations ranging from several seconds to hours have become the focus of scientific research for their potential applications in optoelectronic technologies, such as anti-counterfeiting, information storage, chem/biosensors and bioimaging. Being superior in terms of structural versatility, flexibility, processability and biocompatibility, UORTP materials have displayed broader development prospects and are ideal alternatives to inorganic phosphors. However, different from the well-developed inorganic counterparts, the design and formulation of pure organic room temperature phosphorescence (RTP) luminophores with bright and long-lived emissions remain to be further explored, due to the inherent problems of organic molecules including inefficient intersystem crossing (ISC) and rapid nonradiative decay rate.

According to the first-order perturbation theory, Fermi Golden Rule and Marcus–Levich–Jortner theory, the rate constants of ISC (κISC) are positively correlated with the spin–orbit coupling (SOC) Hamiltonian and the energy gap (ΔERET) between the lowest excited singlet (S1) and triplet states (T0). Thus, boosting SOC or minimizing the ΔERET of organic compounds is
an effective approach to obtaining highly efficient UORTP luminophores.\textsuperscript{37–40} Common strategies to promote SOC focus on introducing heavy atoms or heteroatomic groups (e.g. C=O, N, S, P, etc.) with lone pair electrons.\textsuperscript{41–43} For example, Kim et al. found that the halogen bonding in crystals can activate the heavy atom effect, achieving strong RTP emission with a phosphorescence quantum yield ($\Phi_t$) of up to 55%.\textsuperscript{44} Chi and coworkers proposed the intermolecular electronic coupling of n electrons and $\pi$ units with different excited-state configurations, which can facilitate the ISC process.\textsuperscript{45} In terms of reducing $\Delta E_{ST}$, methods including intramolecular donor-acceptor interactions and polymerization have been employed. Tang et al. reported an efficient UORTP lumiphore with a lifetime of 795 ms and $\Phi_t$ of 2.1% by structural isomerism tuning in $\Delta E_{ST}$ and the first excited triplet state ($T_1$) configuration.\textsuperscript{46} Zhang et al. proposed polymerization-induced energy splitting to create small $\Delta E_{ST}$ and thus to promote ISC.\textsuperscript{46} On the other hand, suppression of nonradiative deactivation pathways of triplet excitons, such as crystallization,\textsuperscript{47,48} polymer–matrix assistance,\textsuperscript{49–51} host–guest interactions,\textsuperscript{52–58} H-aggregation,\textsuperscript{59} intermolecular halogen bonding,\textsuperscript{60} ionic crystals,\textsuperscript{61} and self-assembly,\textsuperscript{62,63} was also found to play critical roles in constructing UORTP luminophores. Although these strategies have largely promoted the development of UORTP materials, most of them are based on the modulation of intermolecular interactions with poor openability. Therefore, a facile design strategy of UORTP materials, which directly correlates molecular structure with phosphorescence performance, is highly desired.

Based on the above considerations, we proposed a facile strategy for modulating intramolecular hydrogen bonding (IHB) and push–pull electron effects (PPEEs) to construct UORTP luminophores with high $\Phi_t$. We envisaged that molecular planarization can be manipulated by IHB, thus conducive to promoting conjugation and inducing intermolecular $\pi$$\cdots$$\pi$ interactions. In addition, the intramolecular PPEEs improved by the introduction of heteroatoms and heavy atoms can probably lead to decreased $\Delta E_{ST}$ and increased SOC. Meanwhile, the $\pi$$\cdots$$\pi$ interactions induced by IHBs and PPEEs are expected to promote intermolecular electron coupling, thus obtaining efficient UORTP materials (Scheme 1). To verify our hypothesis, six compounds were designed and synthesized in two series (with and without heavy atoms), namely 9-phenyl-9H-carbazole (CzPh), 9-[pyridin-2-yl]-9H-carbazole (CzPy), 9-[pyrimidin-2-yl]-9H-carbazole (CzPM), 9-[4-bromophenyl]-9H-carbazole (CzPhBr), 9-[5-bromopyridin-2-yl]-9H-carbazole (CzPyBr), and 9-[5-bromopyrimidin-2-yl]-9H-carbazole (CzPMBr). As shown in Fig. 1A, each compound contained a donor group (carbazole) and an acceptor group (phenyl, pyridinyl or pyrimidinyl derivatives). The experimental results demonstrated that IHBs and PPEEs gradually intensified with increasing numbers of nitrogen atoms in the acceptor group. As a result, the molecular structure became planar and intermolecular $\pi$$\cdots$$\pi$ interactions were remarkably enhanced. In particular, CzPM and CzPMBr with dual IHBs and the strongest PPEEs exhibited the phosphorescence lifetimes ($\tau_p$) of 1.31 s and 233 ms with $\Phi_t$ values of 1.7% and 39.7%, respectively. Theoretical calculations revealed that IHB-induced planarization together with PPEEs greatly contributed to the increased SOC. More interestingly, high-lying intersystem crossing (HISC) from excited singlet states ($S_m, m > 1$) to triplet states ($T_n, n > 1$) was found in the compounds CzPM and CzPMBr with strong IHBs and PPEEs, accounting for higher $\Phi_t$ values. In short, this work demonstrates that highly efficient UORTP materials can be successfully achieved by structural control of IHBs and PPEEs, promoting the rapid development of UORTP materials.

### Results and discussion

#### Synthesis and characterization

Six carbazole derivatives were synthesized via a one-step reaction in high yields (Schemes S1–S6, ESI†) and characterized by standard spectroscopic methods with satisfactory results (Fig. S1–S18, ESI†). All compounds were purified multiple times by high-performance liquid chromatography and recrystallization (Fig. S19, ESI†). Their single crystals were obtained by slow solvent evaporation of ethyl acetate and characterized crystallographically (Table S1, ESI†).

#### Photophysical performance

First, the absorption spectra of the obtained six compounds were recorded as shown in Fig. S20 (ESI†). The experimental results showed that they have similar absorption bands. All
triplet excitons in three compounds. This implies that at low temperatures, the \( S_1 \) without passing through \( T_1 \) via internal conversion. Notably, different from CzPh and CzPy, some unique features were observed for CzPM. An emission band at 360–450 nm with a lifetime of 435 ms at 298 K was recorded in the delayed PL spectrum (Fig. 1C and Table S10, ESI†). The emission intensity remarkably enhanced at 340 K, but almost completely disappeared at 240 K (Fig. S31 and S32, ESI†), which can be attributed to triplet-triplet annihilation (TTA).

To confirm the applicability of our design strategy, CzPhBr, CzPyBr and CzPMBr were designed by introducing bromine atoms. As expected, their \( \Phi_P \) increased to 1.8%, 14.1% and 48.6%, respectively (Fig. 1A), compared to their heavy atom-free counterparts CzPh, CzPy and CzPM. Interestingly, \( \Phi_P \) was proportional to the number of nitrogen atoms in the acceptor moiety. This indicated that the anticipatory design strategy of UORTP materials is of certain universality. The steady-state PL spectra showed that the three brominated compounds possessed a stronger phosphorescence emission band at 500–720 nm than their counterparts (Fig. 1D). In particular, for CzPyBr and CzPMBr, even in the prompt PL spectrum, there was still a stronger phosphorescence band than the fluorescence band, which can be ascribed to more efficient SOC between the \( S_m \) and \( T_n \) promoted by the heavy atom effect and PPEE. The \( \tau_P \) of these brominated compounds is shortened to 293 ms (CzPhBr), 65 ms (CzPyBr) and 233 ms (CzPMBr), respectively (Fig. 1A and F). The brominated compounds also displayed temperature and oxygen dependent phosphorescence behaviours (Fig. S34–S44 and Tables S16–S27, ESI†). Additionally, a new phosphorescence band (\( T_n \rightarrow S_0 \)) at 450–500 nm with \( \tau_P \) values of 150 ms (at 460 nm) for CzPhBr and 60 ms (at 470 nm) for CzPyBr appeared and increased gradually, which is similar to that of their heavy atom-free counterparts (Fig. S35, S39 and Tables S17, S21, ESI†).

The phosphorescence spectra of all compounds exhibited excitation wavelength-dependence (Fig. S45, ESI†). Time-resolved
emission spectra further showed that CzPy displayed an intense phosphorescence emission band around 450 nm even at room temperature (Fig. S46, ESI†). This may be due to the fact that CzPy has more triplet states lower than S1. For CzPM, a TTA emission band centered at 400 nm was clearly observed, indicating that TTA could easily occur due to the longest τp of 1.31 s and efficient population of Tπ states.

**Single crystal diffraction analyses**

Single crystal X-ray diffraction analyses were carried out to further uncover the origin of enhanced ΦP. As shown in Fig. 2A, two molecular conformations were observed in the single crystal structures of CzPh and CzPy, while only one conformation was recorded for the other four compounds. For CzPh, the dihedral angles between the carbazole and benzene rings in two conformations were 77.60° and 53.46°, respectively. For CzPy with pyridine as the acceptor moiety, a single hydrogen bond between the carbazole and pyridine rings was found at distances of 2.771 Å and 2.630 Å for each conformation, leading to decreased dihedral angles of 56.93° and 47.20°. When pyrimidine served as the acceptor, CzPM was almost planar with a dihedral angle of 5.87°, accompanied by shorter IHB distances of 2.291 Å and 2.312 Å. Similar tendencies were found in CzPhBr, CzPyBr and CzPMBr. Their dihedral angles between the donor and acceptor were found to be 48.44°, 38.13°, and 4.93°, respectively. IHB interactions were not observed in CzPhBr. For CzPyBr, the distance of the IHB was 2.498 Å, and stronger IHB interactions at 2.316 Å and 2.320 Å were observed for CzPMBr. This elucidated that the molecular conformation was driven to be planar by progressively strengthened IHBs. Since intermolecular packing modes of organic phosphors are directly correlated with their molecular structures and conformations, the intermolecular packing of the six phosphors was further investigated. As depicted in Fig. 2B and Fig. S47, S48 (ESI†), the intermolecular interactions of CzPh and CzPhBr were mainly C–H···π interactions, with the absence of π–π interactions. In addition, dual Br–H interactions between adjacent CzPhBr molecules were also observed. These C–H···π and Br–H interactions efficiently suppressed the non-radiative transition of triplet excitons, which contributed a lot to their phosphorescence behaviours. In the single crystal of CzPy, apart from plentiful C–H···π interactions, weak π–π (3.438 Å) and intermolecular hydrogen bonding (N–H 2.574 Å) interactions were observed (Fig. 2B and Fig. S49, ESI†). Compared to CzPy, stronger dual π–π interactions (3.423 Å and 3.456 Å) rendered the two adjacent CzPyBr molecules in an antiparallel head-to-tail arrangement in their crystal structures (Fig. 2B), and the two adjacent layers were locked by intermolecular hydrogen bonding (N–H 2.720 Å) and Br···Br interactions (3.304 Å) (Fig. S50, ESI†). We assumed that the antiparallel arrangements coupled with the stronger intermolecular PPEE of CzPyBr dominantly contributed to its layered stacking pattern and needle-like crystal shape. CzPM and CzPMBr with dual IHB interactions and near-planar structure presented parallel head-to-tail arrangements with strong π–π interactions, forming J-aggregates as a result (Fig. 2B and Fig. S51, S52, ESI†). Also, the intermolecular PPEEs between the carbazole and pyrimidine of adjacent molecules may enhance the intermolecular electronic coupling which greatly promoted the ISC rate. Together, the synergistic effect of J-aggregates and intermolecular electronic coupling induced by π–π stacking and intermolecular PPEEs endowed CzPM and CzPMBr with the highest Φp in their series. These results again manifested that highly efficient UORTP can be achieved by enhanced IHBs and PPEEs through regulating the planarity and packing mode of molecular structures.

**Theoretical calculation**

To further reveal the essence of the UORTP design strategy, time-dependent density functional theory (TD-DFT) calculations were performed to investigate the energy level information and SOC matrix elements (ξ) of the six UORTP luminophores. In Fig. S53

![Fig. 2](image-url)
(ESI†), as the number of nitrogen-atom increased from CzPh to CzPM, the energy gaps between S1 and S0 decreased gradually. Three UORTP materials with bromine atoms exhibited the same tendency (Fig. 3A and Fig. S54, ESI†). This is due to the better molecular planarity and conjugation degree resulting from enhanced IHBs and PPEEs. The energy level of the excited state indicated that CzPy possessed more transition pathways from S1 to Tn than CzPh, accounting for its higher \( \Phi_P \) (Fig. S53A and S53B, ESI†). Even so, both the compounds showed negligible \( \tilde{\xi}(S_mT_n) \) between S_m and T_n demonstrating their poor ISC efficiency. Surprisingly, CzPM with higher \( \Phi_P \) exhibited fewer transition pathways compared to CzPy. In order to find out the reason, the \( \tilde{\xi}(S_mT_n) \) values of CzPM Br was analysed (Fig. S53C, ESI†). The results displayed that its \( \tilde{\xi}(S_mT_n) \) can be up to 1.576 cm\(^{-1}\) and \( \Delta E_{STT} \) is only 0.09 eV. Therefore, ISC may exist in CzPM due to the perturbation of the charge transfer state and the small \( \Delta E_{STT} \), leading to its higher \( \Phi_P \). To verify the occurrence of ISC, the energy levels and \( \tilde{\xi} \) values of CzPhBr, CzPyBr and CzPMBr were then calculated. The results further confirmed the ISC pathways with larger \( \tilde{\xi} \) values (Fig. 3A and Fig. S54, ESI†). For example, \( \tilde{\xi}(S_mT_n) \) and \( \tilde{\xi}(S_nT_3) \) of CzPMBr are as high as 39.95 cm\(^{-1}\) and 6.737 cm\(^{-1}\), respectively. Thus, the dual influences of the heavy atom effect and PPEE on the orbital transition configuration and the charge transfer strength resulted in a more efficient ISC. The calculated natural transition orbitals demonstrated that almost all of the electronic configurations of excited states in CzPh and CzPy are dominated by \( \pi \rightarrow \pi^* \) transition (Fig. S55 and S56, ESI†). Hence, a small \( \tilde{\xi} \) was observed because the ISC from \( S_m (\pi \rightarrow \pi^*) \) to \( T_n (\pi \rightarrow \pi^*) \) is spin-forbidden. In contrast, the \( S_m \) involved in the ISC of CzPM and CzPMBr possesses an \( n \rightarrow \pi^* \) configuration due to the presence of a heteroatom and heavy atom, while \( T_n \) still exhibits a predominant \( \pi \rightarrow \pi^* \) configuration (Fig. S57–S60, ESI†). Thus, efficient SOC occurs and the ISC process opens up for the spin-allowed transition from \( n \rightarrow \pi^* \) to \( \pi \rightarrow \pi^* \). In addition, \( \Phi_P \) \( (\pi \rightarrow \pi^*) \) also guarantees the generation of RTP with long lifetimes. Together, with the aid of IHBs and PPEEs, the efficient ISC breaks through the limitations of the highly efficient RTP caused by the spin-forbidden ISC process.

**Anti-counterfeiting**

Given the superior ultralong RTP properties of CzPMBr, its potential application as a security ink for anti-counterfeiting in calligraphy and painting was investigated. As shown in Fig. 4, a seven-character quatrain and a painting containing fluorescence area and phosphorescence area were made. The quatrain is an acrostic poem that contained four sentences, and the first word of each sentence is composed of the Chinese words “室温磷光”, namely, “room temperature phosphorescence”. The painting was entitled “Cat and Mouse”. The fluorescence areas were written by an aggregation-induced emission lumino- gen TTAPE-Me dissolved in aqueous solution. In contrast, the phosphorescence areas were drawn by using the THF solution of TPE with 5% of CzPMBr (Fig. S61, ESI†). When exposed to 365 nm UV light, the whole poem was seen with bright blue emission. When turning off UV excitation, however, only yellow-emissive Chinese words “室温磷光” were observed, and it lasted for several seconds benefiting from the ultralong RTP lifetime of CzPMBr. Similarly, a blue-emissive cat emerged in the painting under UV irradiation. Upon switching off the light source, a mouse giving yellow emission appeared instead. These results demonstrated that the UORTP properties of CzPMBr made it a promising candidate for a security ink material for anti-counterfeiting.

**Conclusions**

In summary, we proposed a facile design strategy based on the structural control of IHBs and PPEEs to construct highly efficient UORTP materials. Accordingly, two series of carbazole derivatives with a D–A structure were designed and synthesized. When the acceptor changed from phenyl, pyridinyl to pyrimidinyl, their molecular conformations became planar with strengthened IHB interactions and PPEEs. This further led to the changes in intermolecular interactions from C–H…π to π–π interactions. The strong π–π interactions combined with intermolecular D–A interactions are in favour of the formation of J-aggregates and intermolecular electron coupling, promoting the ISC rate. Consequently, CzPM and CzPMBr with dual IHBs and the strongest PPEEs exhibited \( \Phi_P \) of 1.31 s and 233 ms and highest \( \Phi_F \) of 1.7% and 48.6%. Theoretical investigations revealed that the heavy atom effect and PPEE strengthened the intramolecular charge transfer states to change the orbital transition mode of \( S_m \). This makes ISC possible, which plays a crucial role in preparing UORTP materials. Specifically, \( \tilde{\xi}(S_mT_n) \) of CzPMBr reached up to 39.95 cm\(^{-1}\), and thus CzPMBr
exhibited the highest $\Phi_\text{P}$. Finally, CzPMBr has been successfully used as a multifunctional ink for anti-counterfeiting in calligraphy and painting due to its excellent RTP properties. Collectively, the design strategy based on the structural control of IHBs and PPEEs will greatly widen the design platform of UORTP materials. Meanwhile, the discovery of the HISC process will also provide a new idea for the design of UORTP materials.

Author contributions

Guoyu Jiang: conceptualization, validation, formal analysis, investigation, data curation, methodology, funding acquisition, and writing – original draft, review and editing. Qiyao Li: visualization, formal analysis, and writing – review and editing. Anqi Lv: visualization, investigation, and data curation. Lingxiu Liu: investigation. Jianye Gong: investigation. Huili Ma: investigation, methodology, conceptualization, and writing – review and editing. Jianguo Wang: conceptualization, validation, formal analysis, methodology, writing – review and editing, and supervision. Ben Zhong Tang: writing – review and editing, and supervision.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

