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Boosting the triplet activity of heavy-atom-free difluoroboron dibenzoylmethane *via* sp³ oxygen-bridged electron donors[†]

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Purely organic phosphors have important applications in imaging, sensing, informatics and illumination. Methoxy-substituted difluoroboron dibenzoylmethane (BF₂dbm) complexes exhibit intense fluorescence with an almost unity quantum yield. Here we show that by simply introducing an sp³ oxygen-bridged methoxylphenyl group as a pendant to BF₂dbm, the boron complex exhibits a triplet quantum yield of 0.16, a more than 100-fold increase compared to that of BF₂dbm.

Photoluminescent organoboron molecules are routinely investigated for their exceptional photophysical properties and have found applications in optical sensing^{1,2} and light-emitting devices.^{3–7} Among these reports on organoboron materials, difluoroboron diketonates (BF₂bdks)⁸⁻¹⁰ have received tremendous attention due to their strong interaction with visible light, high fluorescence quantum yields, tunable emission features, long-lived phosphorescence in polymer matrices, and mechanochromic luminescence (ML) in the solid state.¹¹⁻¹⁵ In order to increase the relative quantum yield of the oxygen-sensitive, emissive triplet excited state of BF2bdks, halogen-substitution has been used in various applications such as tumour oxygen imaging,¹⁶⁻²⁰ wound recovery monitoring^{21,22} and ML quenching²³⁻²⁷ due to the enhanced heavy-atom effect with boosted triplet activity. Otherwise, the nearly unity fluorescence from BF₂bdks would have precluded most applications based on a balanced ratio between fluorescence and phosphorescence. In addition, the halogen atom can be photochemically unstable, toxic and unfriendly to the environment, which makes heavyatom free BF2dbm with high triplet activity an attractive substitute. Here we show a new methodology, where the fluorescent species can be transformed into phosphorescent ones by minor alterations in the molecular structure. The strategy employs no

heavy atoms, nor does it require functional groups strongly enhancing spin–orbit coupling (SOC) such as carbonyl, nitro or amine substitution. Instead, the sp³ oxygen-bridged electron donor moiety significantly boosts the triplet state yield *via* a combination of SOC related to transition angular momentum and charge-transfer (CT) mediated intersystem crossing (ISC).^{28,29}

Three BF₂dbm model complexes **1–3** (Fig. 1a) were readily synthesized by Claisen condensation and subsequent coordination with boron trifluoride in high yield (overall yields > 50%, Scheme S1; for synthetic procedure and characterization, see Fig. S10–S18 in ESI†), where the oxygen atom is linked to methyl, phenyl and *p*-methoxylphenyl to produce **1**, **2** and **3**, respectively, and provides a twist angle between the BF₂dbm core and the



Fig. 1 (a) Chemical structures of BF₂dbm model complexes **1–3**; (b) UV/Vis absorbance and steady-state emission ($\lambda_{ex} = 372$ nm) spectra of model complexes **1–3** in *m*-THF at room temperature, inset: image showing PL emission in *m*-THF at RT at an identical concentration of 4.95 μ M; (c) steady-state emission spectra of model complexes **1–3** in *m*-THF at low temperature (77 K, LT) ($\lambda_{ex} = 372$ nm), inset: image showing steady-state PL emission in *m*-THF at 77 K; (d) delayed ($\Delta t = 100$ ms) emission spectra of model complexes **1–3** in *m*-THF at 77 K inset: image showing afterglow 100 ms after excitation (using a 365 nm handheld lamp) had ceased with the aid of a mechanical shutter.



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pendant group. The absorption and emission spectra in dilute solutions (2-methyl-tetrahydrofuran, m-THF, 4.95 µM) are presented in Fig. 1b, where complex 1 has been investigated by many research groups including us, both in solutions and in the solid state.^{13,30} All three compounds have almost the same absorption between 350 and 420 nm (λ_{max} = 396, 393 and 395 nm, respectively); the slight blue shift for 2 is likely due to the electronic conjugation between the oxygen lone pair and the phenyl group, which reduces the donating ability of the lone pair. Both 1 and 2 emit strong blue photoluminescence (PL, $\lambda_{\rm em}$ = 420 nm, $\Phi_{\rm F}$ = 0.97 and 0.81) at room temperature under UV irradiation at 372 nm, whereas, interestingly, 3 exhibits extremely attenuated blue PL as shown in the inset ($\Phi_{\rm F}$ < 0.001, Fig. 1b and Table 1). It is not uncommon for PL molecules to show reduced fluorescence yield with more substituent groups due to extra vibrational and rotational modalities that could dissipate the energy in the excited state. In this case, however, the reduction in PL quantum yield from 2 to 3 (from nearly unity to nothing) is far too significant to attribute to nuclear motions. A more reasonable explanation would be fluorescence quenching from a dark, CT-mediated ISC process, as has been noted from other donor-sp³-acceptor systems.²⁸ As shown in Fig. 1c, 3 exhibited strong photoluminescence at 77 K with a strong phosphorescence peak at \sim 500 nm ($\tau_{\rm P}$ = 1.41 s) and a calculated phosphorescence yield of 0.16, while the value for 1 was almost negligible.

Purely organic, heavy-atom-free RTP molecules have wide applications in optical sensing, bioimaging and illumination.³¹⁻⁴¹ Many applications require that small molecular phosphors be embedded into rigid polymer matrices as an efficient approach to achieve RTP due to suppression of molecular motions in these systems (restriction of non-radiative relaxations).42,43 All three molecules were dissolved in PMMA films (film thickness $\sim 200 \ \mu\text{m}$, solute 0.1% by weight) and the steady-state PL emissions in air and under vacuum were measured as shown in Fig. 2a and b, respectively. The PL emissions of 1 and 2 are similar with a single fluorescence peak at 433-434 nm ($\tau_{\rm F}$ = 2.2–2.3 ns, Table 2) in PMMA films while that of 3 is significantly broadened in the lower energy region (450-650 nm). We ascribed the broadening to the enhanced ISC and subsequently boosted RTP with polymer protection. Indeed, a lifetime of 250 µs (Fig. 2c inset) was recorded for 3 in the low energy

Table 1 Luminescence properties of 1, 2 and 3 in m-THF											
	λ_{F}^{a} (nm)	$\lambda_{\mathrm{P}}{}^{b}$ (nm)	$\tau_{\rm F}^{\ c}({\rm ns})$	$\tau_{\mathrm{LP}}^{d}(\mathbf{s})$	${\Phi_{ ext{PL}}}^e$	${\varPhi_{\mathrm{PL}}}^f$	${\Phi_{\mathrm{P}}}^g$				
1	420	502	1.75	1.25	0.97	0.97	< 0.01				
2	414	497	1.60	1.30	0.81	0.82	0.045				
3	415	539	h	1.41	< 0.001	0.30	0.16				

^{*a*} Fluorescence emission maximum from steady-state emission spectra ($\lambda_{ex} = 372 \text{ nm}$) in *m*-THF at 77 K. ^{*b*} LP maximum at 77 K ($\lambda_{ex} = 372 \text{ nm}$). ^{*c*} FL lifetime fitted from single-exponential decay ($\lambda_{ex} = 374 \text{ nm}$, nanoLED) at 77 K ^{*d*} Phosphorescence lifetime fitted from single-exponential decay ($\lambda_{ex} = 372 \text{ nm}$, spectraLED) at 77 K. ^{*e*} Absolute quantum yield from 400–600 nm at RT. ^{*f*} Absolute quantum yield from 400–600 nm at 77 K. ^{*s*} Calculated phosphorescence quantum yield at 77 K by spectral subtraction. ^{*h*} Signal too weak for accurate measurement.



Fig. 2 Steady-state emission spectra of model complexes **1–3** in thin PMMA films at room temperature in air (a) and under vacuum (b) ($\lambda_{ex} = 372$ nm); (c) time-resolved emission decay curves of **3** at 510 nm in air and under vacuum; delayed ($\Delta t = 100$ ms) emission spectra of model complexes in PMMA at RT (d) and 77 K (e) and emission spectra of model complexes **1** (f), **2** (g), and **3** (h) in PMMA at RT (Ss: steady state emission, DE in air: delayed emission in air ($\Delta t = 50 \mu$ s), DE in vacuum: delayed emission in vacuum ($\Delta t = 50 \mu$ s)).

Table 2 Luminescence properties of ${\bf 1},\,{\bf 2}$ and ${\bf 3}$ in PMMA films (0.1% by weight) at room temperature

	λ_{F}^{a} (nm)	$\lambda_{\mathrm{RTP}}^{b}$ (nm)	$\tau_{\rm F}^{\ c}$ (ns)	$\tau_{\mathrm{RTP}}^{}d}$ (µs)	$\tau_{\mathrm{RTP}}^{e}(\mathbf{s})$
1	434	510	2.27	_	0.70
2	433	510	2.15		0.58
3	440	510	2.00	250	0.31

^{*a*} Fluorescence emission maximum from steady-state spectra (λ_{ex} = 372 nm) in PMMA at room temperature. ^{*b*} RTP maximum at RT (λ_{ex} = 372 nm). ^{*c*} FL lifetime fitted from single-exponential decay (λ_{ex} = 372 nm, nanoLED) at RT. ^{*d*} RTP lifetime fitted from single-exponential decay (λ_{ex} = 370 nm, spectraLED) at RT in air, note that RTP emissions of **1** and **2** in air are too weak (if any) to measure. ^{*e*} RTP lifetime fitted from single-exponential decay (λ_{ex} = 370 nm, spectraLED) at RT in air, note that RTP emissions of **1** and **2** in air are too weak (if any) to measure. ^{*e*} RTP lifetime fitted from single-exponential decay (λ_{ex} = 370 nm, spectraLED) at RT in vacuum.

shoulder band area (500–550 nm). Under vacuum, the relative intensity of the broad shoulder band is further increased, which confirms the oxygen-sensitive nature of the RTP from **3**. The RTP lifetime exhibits a concomitant increase by more than 1000 fold to 310 ms (Fig. 2c). Although the relative RTP intensity is much lower for **1** and **2**, their lifetimes are nonetheless much longer, which can be explained by Fig. 2d and e. The delayed emission spectra recorded not only show the main RTP band at 510 nm but also the thermally activated delayed fluorescence (TADF)^{44–47} band at around 430 nm, which disappears at 77 K (Fig. 2e). The RTP bands for all three complexes **1–3** are almost super-imposable,

indicating the identical origin from the localized π - π * state from the BF2dbm core structure, as has been previously reported.^{13,30,48} The fact that **3** alone exhibits the most intense TADF peak strongly suggests multiple energy pathways for ISC, most likely a combination of localized (\sim 430 nm) and other mediating states (>440 nm), such as CT, in between ${}^{1}\pi-\pi^{*}$ and ${}^{3}\pi$ - π^{*} . ^{44,45} Higher TADF ratios generally promise shorter RTP lifetimes, irrespective of thermal activation or triplet-triplet annihilation. In addition, the similarity in TADF peak intensity of 1 and 2 also points to the fact that vibrational coupling caused by the additional phenyl ring plays a minor role in effectuating the ISC process. Fig. 2f-h compare the steady-state and delayed emission spectra of 1-3, respectively. It is evident that RTP is dramatically more sensitive to oxygen quenching vs. TADF given that air quenches most RTP while TADF persists. We were also able to record the TADF spectra in different solvents (Fig. S33 and S34, ESI⁺); it was found that the TADF intensity is the lowest in the most polar solvent. This observation is attributed to increased non-radiative decay rate in polar solvents as has been previously reported by Adachi et al.49

To further understand the photophysics of the sp³-bridged donor effects, we performed quantum chemical calculations and modelled their molecular geometries in the ground and excited states (singlet and triplet) using a previously established method.^{50,51} Theoretical modeling for this sequence was accomplished with the functional B3PW91 and the basis 6-311+G(d), proved by Barlow and co-workers to be effective in describing the charge-transfer excitations.⁵² The medium was modeled by the polarizable continuum defined by Tomasi, with parameters for THF.⁵³ Charge transfer plays a crucial role in populating the triplet excited states as indicated in Fig. 3a–c

and Tables S1-S3 (ESI⁺). Briefly speaking, the energy gaps between the S₁ state (localized $\pi - \pi^*$) and the neighbouring lowest triplet state for both 1 and 2 are almost identical (~ 0.22 eV), while that of 3 (¹CT) exhibits a sharp decrease to 0.025 eV, readily bifurcating to T₃ and T₂. Specifically, MO analysis (Fig. 3a) shows little if any CT character in 1's reddest transition. There is also substantial splitting between S1 and T1 dominated by the HOMO-LUMO excitation. This is consistent with a large exchange integral K (HOMO-LUMO). Strong fluorescence emission (f = 1.04, experimentally $\Phi_{\rm F} \sim 1$) probably also helps to hinder effective passage to the nearest triplet state. When O-phenyl replaces O-methyl to form 2, the reddest (HOMO-LUMO) transition in the absorption spectrum is hardly shifted, and the MOs (Fig. 3b) involved are still confined to the core defined by 1. Little CT character is seen in the transition. The further substitution of a para MeO-fragment moves the MO on the O-phenyl-OMe up in energy; which becomes the new HOMO (Fig. 3c). The LUMO is still located at the BF₂dbm core, so the HOMO-LUMO transition has a substantial CT character. This is illustrated by the small exchange splitting between the singlet and triplet states defined by those two MOs (only 0.025 eV) and the relative weakness of the lowest singlet-state transition (f = 0.016). These features of 3 are preserved in the excited S₁ state (Fig. 3c, splitting 0.01 eV and f < 0.01). This defines a diradical character and implies a long lifetime for the S₁ state. All these features suggest efficient passage to the triplet state and subsequent strong RTP emission of 3.

In summary, we have successfully synthesized three difluoroboron dibenzoylmethane derivatives with the methyl, phenyl and p-methoxylphenyl as the "pedant" groups to the BF₂dbm core, respectively. Despite the subtle structural change, the molecules



Fig. 3 Calculated molecular orbitals for the lowest singlet-state transition for all three boron complexes. Schematic diagrams of the TD-DFT calculated energy levels and possible ISC channels of $\mathbf{1}$ (a), $\mathbf{2}$ (b) and $\mathbf{3}$ (c) at the singlet (S₁) and triplet (T_n) states. H and L represent the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. The insets are the Kohn–Sham frontier orbitals obtained from all three complexes; and (d) calculated molecular geometries at the ground state (S₀), first triplet excited state (T₁) and first singlet excited state (S₁) for all three complexes.

show substantial difference in the photophysical and photochemical properties, particularly for the *p*-methoxylphenyl substituted BF_2 dbm complex, **3**, where the enhanced triplet excited state activity, including RTP and TADF, reveals that the chargetransfer mediated ISC process can also be realized in the oxygenbridged donor-sp³-acceptor systems. The report broadens the application potential of the donor-sp³-acceptor systems and can serve as a working strategy to construct heavy-element free organic phosphors.

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Conflicts of interest

There are no conflicts to declare.

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