

Enhancing Organic Phosphorescence by Manipulating Heavy-Atom Interaction

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Supporting Information

ABSTRACT: Achieving highly efficient phosphorescence in metal-free materials under ambient conditions remains a major challenge in organic optoelectronics. Herein, we report a concise approach to obtaining pure organic phosphorescence with high quantum efficiency of up to 21.9% and millisecond-scale lifetime by manipulating heavy-atom interaction based on a class of dibromobenzene derivatives in the solid state under ambient conditions. By comparing two pairs of the organic compounds designed, the one with two more bromine atoms on the alky terminals (PhBr₂C₆Br₂/PhBr₂C₈Br₂) showed



higher luminescence efficiency than the other one (PhBr₂C₆/PhBr₂C₈). From the single-crystal analysis, it was proposed that the enhancement of phosphorescence resulted from increased intermolecular heavy-atom interaction in the organic crystals. Furthermore, a temperature sensor was demonstrated by using a model probe of this kind of organic phosphorescent crystals. This work not only provides a concise alternative to enhance phosphorescence in metal-free materials but also extends the scope of pure organic phosphorescent materials with high luminescent efficiency in a single component.

INTRODUCTION

Organic phosphorescent materials have evoked considerable interest due to their potential applications in organic lightemitting diodes,¹ photovoltaics,^{2,3} photocatalytic reactions,⁴ and bioimaging.⁵ So far, most room temperature phosphorescent materials are typically limited to heavy-metal-containing complexes, such as Ir³⁺, Pt²⁺, and Ru³⁺ complexes,⁶ which can facilitate intersystem crossing to enhance phosphorescence generation.⁴ These metals are not only costly but also resourcelimited, which have hindered the development of the organic phosphorescence. Phosphorescence from organic metal-free materials under ambient conditions has been widely considered to be impossible due to weak spin-obit coupling and highly forbidden triplet-singlet transitions, despite the emerging demand in the optoelectronics.⁷ To defy this imprisonment, many efforts have been made to investigate the metal-free organic phosphorescence recently.⁷⁻²⁸ Crystallization-induced phosphorescence based on pure organic luminogens was observed at room temperature by Tang and co-workers.²⁹ Kim et al. largely enhanced pure organic phosphorescence efficiency by impurity doping method and introducing organic compounds into an amorphous polymer matrix.^{7,10,22} The triplet-promoting heavy-atom and rigid solid-state conditions could enhance the spin-forbidden singlet-to-triplet excited-state transition. Adachi and co-workers showed phosphorescence with a lifetime of above 1 s by using a doping method along with deuteriation substitutions.⁸ Very recently, our group proposed a rational design strategy by stabilization of triplet excited states through H-aggregation to realize ultralong phosphorescence with a lifetime of 1.35 s and a lasting time of up to 56 s.¹⁹ Nevertheless, the exploration of new strategies to enhance phosphorescence in organic metal-free materials is still of great importance and challenge.

Phosphorescence is usually not seen in fluid solutions because there are many deactivation processes that compete with the emission, such as nonradiative decay and collisional quenching by oxygen and other impurities.³⁰ As shown in Figure 1a, a certain amount of additives with heavy atoms, such

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Figure 1. Schematic presentation for the manipulation of heavy-atom interaction to enhance organic phosphorescence. (a) Typical approach to enhance phosphorescence by replenishing additives with heavy atoms in solution. (b) Proposed strategy of manipulating heavy-atom interaction in the solid state. (c) Synthetic routes of pure organic phosphorescence molecules.

Table 1. Structure Data of Single Crystals^a

name	$PhBr_2C_6$	$PhBr_2C_6Br_2$	$PhBr_2C_8$	$PhBr_2C_8Br_2$
formula	$C_{18}H_{28}Br_2O_2$	$C_{18}H_{26}Br_4O_2$	$C_{22}H_{36}Br_2O_2$	$C_{22}H_{34}Br_4O_2$
wavelength (Å)	1.54184	1.54184	1.54184	1.54184
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	6.9534 (8)	8.0564 (19)	6.7829 (5)	8.4619 (9)
b (Å)	8.2493 (14)	8.5752 (13)	9.6771 (6)	9.0000 (5)
c (Å)	9.7157 (12)	9.5028 (13)	9.6955 (7)	9.5811 (7)
α (deg)	107.062 (13)	66.877 (14)	74.616 (6)	115.671 (6)
β (deg)	106.936 (10)	87.324 (16)	85.034 (6)	92.610 (6)
γ (deg)	99.153 (12)	66.414 (19)	73.541 (6)	99.466 (5)
vol (Å ³)	491.107	548.533 (2)	588.411	643.072
Z	2	2	2	2
density (g/cm ³)	1.475	1.798	1.3893	1.6786
F(000)	222	287.8	253.1622	319.8326
h_{\max} , k_{\max} , l_{\max}	8, 10, 8	9, 10, 11	8, 11, 11	10, 9, 11

^{*a*}The obtained crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1404734 (PhBr₂C₆), 1404733 (PhBr₂C₆Br₂), 1405036 (PhBr₂C₈), and 1405039 (PhBr₂C₈Br₂).

as 1-ethyl iodide³¹ and propyl halide,³² as well as sodium iodide,³³ was added into the solutions to enhance the phosphorescence quantum yield, which is acknowledged to be one of the most efficient alternatives for increasing phosphorescence generation.³³ The enhancement of the spincoupling by surrounding heavy atoms, with the consequent increase in the probability of $T_1 \rightarrow S_0$ transition, can be affected by external perturbation of heavy atoms within the absorbing or emitting molecules. Inspired by such an effective strategy, we thus made our efforts on tailing molecular alkyl groups with various numbers of bromine atoms to enhance the phosphorescence in pure organic materials in the solid state (Figure 1b), providing an alternative approach for enhancing the phosphorescence efficiency. The bromine atoms at the end of the alkyl units play the same role as the isolated heavy atoms shown in Figure 1a.

In this study, we designed a modification of alkyl terminal groups with bromine atoms to enhance the phosphorescence efficiency by manipulating heavy-atom interaction, as illustrated in Figure 1b. Bright green phosphorescence was observed for all of the compounds in the solid state under ambient conditions due to the heavy-atom effect. By comparing the two pairs, the ones with four bromine atoms showed higher luminescence efficiency than the ones with two bromines. As observed from the single-crystal structures, there are three Br–Br interaction pairs for $PhBr_2C_6Br_2$ and two Br-Br interaction pairs for $PhBr_2C_8Br_2$ between every two molecules, while there is only one for $PhBr_2C_6$ and $PhBr_2C_8$. Therefore, we proposed that more efficient phosphorescence could be obtained by increasing the intermolecular heavy-atom interaction ratio in the solid state. To the best of our knowledge, this is the first system that the enhancement of phosphorescence in organic metal-free materials was realized by manipulating molecular heavy-atom interaction through tailoring terminal groups of alkyl substituents with bromine atoms.

RESULTS AND DISCUSSION

In order to validate our hypothesis, a type of dibromobenzene derivatives, namely, 1,4-dibromo-2,5-bis(hexyloxy)benzene (PhBr₂C₆), 1,4-dibromo-2,5-bis(octyloxy)benzene (PhBr₂C₈), 1,4-dibromo-2,5-bis((6-bromohexyl)oxy)benzene (PhBr₂C₆Br₂), and 1,4-dibromo-2,5-bis((8-bromooctyl)oxy)benzene (PhBr₂C₈Br₂), were synthesized in high yields of above 70% by following a concise one-step approach shown in Figure 1c. These molecules were fully characterized by ¹H NMR, ¹³C NMR (Figures S1–S8 in the Supporting Information (SI)), elemental analysis, and single-crystal X-ray diffraction (Table 1). The melting points of PhBr₂C₆ and PhBr₂C₈ were around 63.5 and 66.8 °C (SI Table S1). It was noteworthy that compounds of PhBr₂C₆Br₂ and PhBr₂C₈Br₂

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with alkyl groups substituted by bromines exhibited a higher thermal feature with melting points of around 89 °C.

In a further set of experiments, photophysical properties of the four compounds were investigated in detail through measuring both steady-state and time-resolved emission spectra in solution and the solid state. For these dibromobenzene derivatives in dilute dichloromethane solutions, the same profiles of the absorption spectra with peaks at around 300 nm were presented in Figure 2a. No emission was observed in



Figure 2. Photophysical characteristics of pure organic phosphorescent molecules. (a) Normalized absorption spectra in dilute dichloromethane solutions. (b) Normalized steady-state photoluminescence spectra in crystal state excited at 325 nm. (c) Luminescent images of the four compounds under hand-held UV lamp excitation at 365 nm.

solution, ascribing to the enhancement of the singlet-to-triplet transition induced by the heavy atoms. In the solid state when excited at 325 nm, the chromophores of PhBr₂C₆ and PhBr₂C₈ showed intense green emissions with major emission bands at around 500 nm and small blue bands at about 380 nm, where the blue emission area occupied only about 5% of the total emission. After one of the terminal hydrogen atoms in alkyl chains was substituted with a bromine atom, the blue emissions disappeared completely, leaving only strong green emission bands for both PhBr₂C₆Br₂ and PhBr₂C₈Br₂ (Figure 2b). With excitation by a hand-held UV lamp at 365 nm under ambient conditions, intense green luminescence was observed for all of the crystals, particularly for PhBr₂C₆Br₂ (Figure 2c).

To gain deeper insight into the nature of the green emissions, time-resolved excitation and emission spectra were collected under ambient conditions. As shown in Figure 3, only green emissions were observed with the excitation at 350 nm, and the emission band at ~380 nm thoroughly disappeared after 0.2 ms time delay for all of the compounds. The excitation peaks monitoring the green emission bands at 500 nm were around 350 nm for all of the compounds. Furthermore, the luminescence decay curves were recorded at around 500 nm as shown in Figure 3 (right part). A lifetime at green emission was as long as several microseconds, which further verified that the green emission originated from the radiative decay of the triplet excited state. The fluorescence feature of the emission at 380 nm was proven by the data of short lifetimes in nanosecond scale from photoluminescence decay curves shown in Figures S13 and S14 of the SI. The absolute quantum efficiencies (AQEs) of the phosphorescence for $PhBr_2C_6$ and $PhBr_2C_8$ were only 3.4% and 8.9%, respectively. With an increase of the heavy atoms at the end of alkyl chain units, the corresponding AQEs of PhBr₂C₆Br₂ and PhBr₂C₈Br₂



Figure 3. Phosphorescent characteristics of four organic phosphorescent molecules in crystal state. (Left) Phosphorescence excitation and emission spectra of the four compounds with time delay in crystal state at room temperature excited at 350 nm (total decay time, 0.02 s; delay time, 0.20 ms; gate time, 5.0 ms). (Right) green band luminescence decay of the four compounds under ambient conditions.

compounds were significantly enhanced up to 21.9% and 13.1%, respectively. This increase may be attributed to the influence of the heavy atoms at the end of the alkyl groups. To prove the effect of the bromine heavy atoms on the generation of phosphorescence, a control experiment using two compounds without any bromine atoms (Scheme S1 in the SI) was conducted. It was found that the crystals of PhC₆ and PhC₈ showed fluorescence emission with short lifetimes of around 2.9 and 6.1 ns, respectively, but not phosphorescence (Figure S15 in the SI).

To further understand the origin of enhanced pure organic phosphorescence in this study, the single-crystal structures and molecular packing modes of the four compounds were examined by X-ray diffraction analysis. In crystals, all of these organic phosphors are arranged in layers with a distance of around 3.7 Å between neighboring layers presented in Figure S16 of the SI. In the same layer, all luminogens are locked by various intermolecular forces including C-Br...Br-C and C-H…Br interactions (Figure 4). In both $PhBr_2C_6$ and $PhBr_2C_8$ single-crystal systems, there are only Br…Br short-range interactions with the distances of 3.405 and 3.380 Å, respectively. For PhBr₂C₆Br₂ and PhBr₂C₈Br₂ single crystals, analogous bromine clusters near benzene chromophores were observed. Within the allowable interaction distance of <4.4 Å,³⁴ it is important to note that there are triple Br…Br interactions for a single chromophore in PhBr₂C₆Br₂ single crystal, double Br...Br interactions for PhBr₂C₈Br₂, and only one Br...Br interaction for PhBr₂C₆ and PhBr₂C₈, which lead to different phosphorescence efficiency among these four compounds. The improvement of the phosphorescence quantum yields for both PhBr₂C₆Br₂ and PhBr₂C₈Br₂ solids may be ascribed to the synergistic effects from the promotion of Br-cluster interaction



Figure 4. Perspective views of the heavy-atom interaction in single crystals of dibromobenzene derivatives.

and the suppression of triplet-triplet annihilation between adjacent molecules. The hypothesis was further proven by multimolecule triplet spin density distribution simulated by density functional theory (DFT) calculation. As shown in Figure S17 of the SI, the spin density distribution of PhBr₂C₆ was localized on two adjacent molecules for every four molecules, while it was only distributed on one molecule for PhBr₂C₆Br₂. Thus, the lowest phosphorescence efficiency of PhBr₂C₆ solid was expected because of the accessorial triplettriplet quenching process. By comparing the spin density distribution of PhBr₂C₆ and PhBr₂C₈, it was found that the spin density was only localized on one molecule for PhBr₂C₈ (Figure S17 in the SI), which may lead to higher phosphorescence efficiency by suppressing triplet-triplet annihilation.

Taking advantage of the temperature sensitivity of phosphorescence,³⁵ a temperature sensor was developed on the basis of PhBr₂C₆Br₂ crystal with the highest phosphorescence yield of 21.9%. As shown in Figure 5, upon increasing temperature from 20 to 90 °C, the phosphorescence intensity of PhBr₂C₆Br₂ crystal decreased gradually along with fixed emission profiles, which are attributed to the enhanced nonradiative transition of the excited states at elevated temperature. Unexpectedly, despite the relative low melting point (88.6 °C) for PhBr₂C₆Br₂ solid, the phosphorescence intensity fell about 50% when the temperature reached 90 °C, suggesting that the compound still showed strong phosphorescence even in the melting state. The relationship between the



Figure 5. Phosphorescent spectra of $PhBr_2C_6Br_2$ crystal at different temperatures.

phosphorescence intensity changing rate (*I*) and the temperature (*T*) can be accurately fitted by a parabola equation of $(I_0 - I)/I = 3.24T^2 + 3.04 \times 10^{-3}T - 0.07$, which revealed the quantification possibility of temperature sensing in the range of 20–90 °C using the pure organic phosphors.

CONCLUSIONS

In summary, a series of pure organic phosphorescent compounds with concise molecular structures have been designed and prepared. Pure organic phosphorescence with high quantum efficiency of up to 21.9% and millisecond-scale lifetime has been obtained by manipulating heavy-atom interaction. The relationship between molecular structures and phosphorescence feature has been studied through singlecrystal analysis and DFT calculation, indicating that the phosphorescence generation could be promoted by increasing bromine-cluster interactions and decreasing triplet-triplet annihilation chance. Furthermore, the potential application of these kinds of materials as temperature sensors has been demonstrated by using PhBr₂C₆Br₂ solid as a model probe, which revealed the possibility of the quantification of temperature sensing in the range of 20-90 °C. This work outlines a fundamental approach to enhance pure organic phosphorescence under ambient conditions, providing a major step forward expanding the scope of pure organic phosphorescence applications.

EXPERIMENTAL SECTION

General Methods. The steady-state photoluminescence and excitation spectra in solution and the solid state were measured by Shimadzu RF5300 equipment with a xenon lamp as an excitation light source. The phosphorescence spectra at room temperature were obtained by a Varian Cary Eclipse fluorescence spectrophotometer with the following detailed settings: total decay time, 0.02 s; delay time, 0.20 ms; gate time, 5.0 ms; excitation and emission slits, 10 nm. Emission lifetime and absolute quantum efficiency were measured by Edinburgh FL 920 fluorescence spectrometer with a μ F900 μ s flash lamp and an integrated sphere at room temperature. The lifetimes (τ) of the luminescence were obtained by fitting the decay curve with a multiexponential decay function of

$$I(t) = \sum_{i} A_{i} e^{-t/\tau_{i}}$$

where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multiexponential decay profiles, respectively. UV– visible absorption spectra in solution were detected by UV-3600 Shimadzu. ¹H and ¹³C NMR spectra were recorded on Bruker BBFO-400 and -100 MHz spectrometers, respectively. Tetramethylsilane was chosen as the internal standard. Elemental analysis was performed on an Elementar Vario MICRO elemental analyzer. The crystal luminescent photographs were taken by a Cannon EOS 700D camera under the excitation at 365 nm with a hand-held UV lamp at room temperature.

The X-ray crystallography was carried on an Agilent Technologies Super Nova diffractometer using microfocus graphite-monochromated Cu K α radiation (λ = 1.5418 Å) at room temperature. The structure was solved by direct methods and refined by full matrix least-squares analyses on SHELXTL-97S3.

Calculation Method. The DFT simulations were performed to study the electronic properties of singlet and triplet states of $PhBr_2C_8$ and $PhBr_2C_8Br_2$ crystals by using exchange-correlation functional B3LYP and the unrestricted formalism (UB3LYP), respectively, together with basis sets 6-31G(d,p). The spin density distribution of triplet states was plotted in SI Figure S17 with isovalue of 0.02 e/Å³, where green and blue areas represent the positive and negative spin densities, respectively. All of the DFT calculations were based on the experimental crystal structures without further crystal optimizations.

Synthesis and Characterization. *Materials.* Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All of the solvents and chemicals were used as received from commercial sources.

General Procedure. These dibromobenzene derivatives were synthesized by referencing the previous literature.⁷ To a 50 mL round-bottomed flask with 2,5-dibromohydroquinone (1 equiv) and potassium carbonate (3 equiv) dissolved in dimethylmamide was added bromoalkanes (2.5 equiv). The mixture was stirred at 80 °C for 12 h. The product was purified by flash column chromatography with hexane and dichloromethane as the eluent to give target compounds with yields of 70–80%.

1,4-Dibromo-2,5-bis(hexyloxy)benzene (PhBr₂C₆). ¹H NMR (400 MHz, CDCl₃): δ 7.09 (s, 2H, ArH), 3.95 (t, 4H, CH₂O), 1.80 (m, 4H, CH₂), 1.48 (m, 4H, CH₂), 1.34 (m, 4H, CH₂), 0.91 (t, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 118.5, 111.1, 70.3, 31.5, 29.1, 25.6, 22.6, 14.0. Anal. Calcd for C₁₈H₂₈Br₂O₂: C, 49.56; H, 6.47; Br, 36.63; O, 7.34. Found: C, 49.45; H, 6.41.

1,4-Dibromo-2,5-bis((6-bromohexyl)oxy)benzene (PhBr₂C₆Br₂). ¹H NMR (400 MHz, CDCl₃): δ 7.08 (s, 2H, ArH), 3.96 (t, 4H, CH₂O), 3.43 (t, 4H, CH₂Br), 1.90 (m, 4H, CH₂), 1.82 (m, 4H, CH₂), 1.55 (m, 8H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 118.5, 111.2, 70.5, 33.8, 32.7, 28.9, 27.8, 25.2. Anal. Calcd for C₁₈H₂₆Br₄O₂: C, 36.40; H, 4.41; Br, 53.81; O, 5.39. Found: C, 36.48; H, 4.47.

1,4-Dibromo-2,5-bis(octyloxy)benzene (PhBr₂C₈). ¹H NMR (400 MHz, CDCl₃): δ 7.08 (s, 2H, ArH), 3.94 (t, 4H, CH₂O), 1.80 (m, 4H, CH₂), 1.48 (m, 4H, CH₂), 1.29 (m, 4H, CH₂), 0.89 (t, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 118.5, 111.2, 70.4, 31.8, 29.3, 29.2, 29.1, 25.9, 22.7, 14.1. Anal. Calcd for C₂₂H₃₆Br₂O₂: C, 53.67; H, 7.37; Br, 32.46; O, 6.50. Found: C, 53.49; H, 7.26.

1,4-Dibromo-2,5-bis((8-bromooctyl)oxy)benzene (PhBr₂C₈Br₂). ¹H NMR (400 MHz, CDCl₃): δ 7.08 (s, 2H, ArH), 3.95 (t, 4H, CH₂O), 3.41 (t, 4H, CH₂Br), 1.86 (m, 8H, CH₂), 1.50 (m, 8H, CH₂), 1.37 (m, 8H, CH₂). ¹C NMR (100 MHz, CDCl₃): δ 150.1, 118.5, 111.2, 70.2, 34.0, 32.8, 29.1, 28.7, 28.1, 25.9. Anal. Calcd for C₂₂H₃₄Br₄O₂: C, 40.64; H, 5.27; Br, 49.16; O, 4.92. Found: C, 40.48; H, 5.18.

Fabrication of Temperature Sensors. In this work, $PhBr_2C_6Br_2$ crystal was selected as a temperature probe because of its high phosphorescence yield of 21.9%. The organic phosphors were put into a cuvette with a volume of 0.35 mL. The capped cuvette was then placed in a holder of the fluorescence spectrophotometer with temperature-control equipment. To eliminate the effect of the external physical factors such as residual stress, the sample was first heated with a heating ratio of 5 °C/min to 90 °C and then cooled to the room temperature. After that, the phosphorescent spectra of the temperature probe at different temperatures were collected. The phosphorescence spectrophotometer with the following detailed settings: total decay time, 0.02 s; delay time, 0.20 ms; gate time, 5.0 ms; excitation and emission slit, 10 nm.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b01400.

Characterizations of the four compounds, DTF results, and absorption spectra (PDF)

Accession Codes

CCDC 1404733–1404734, 1405036, and 1405039 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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