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Reversible Switching between Phosphorescence and Fluorescence in a Unimolecular System Controlled by External Stimuli

Jing Xu,[†] Hui Feng,[†] Hao Teng, Guilin Chen, Saifei Pan, Jianrong Chen and Zhaosheng Qian*

Abstract: Manipulation of the emission properties of pure organic molecules through external stimuli is attractive but challenging. Herein, we report a dual-emissive hexathiobenzene-based molecule with significant aggregation-induced phosphorescence characteristic, and demonstrate reversible switching among blue fluorescence, green fluorescence and yellow phosphorescence by controlling molecular aggregation state or protonation state. Variation of solvent or pH value manipulates the interconversion between fluorescence and phosphorescence, while the change in protonation state in organic solvent switches two short-lived emissions in a controllable manner. Such a controlled manipulation is achieved by rational design of combining twisted structure and proper arrangement of energy gaps among different excited states. This work provides a new design principle for organic molecules with efficient room-temperature phosphorescence and tunable singlet-triplet emissive properties, and contributes to design and development of smart materials and intelligent optoelectronic devices.

Precious photoluminescence of organic materials has shown great power in a variety of areas including organic light-emitting diodes, sensors and life sciences.[1] Fluorescence from emissive singlet of a molecule has long dominated in diverse applications by the way of various traditional organic dyes with rigid conjugated structures,[2] and recent discovery and flourishing of aggregation-induced emission (AIE) have further boosted the development of fluorescence.[3] However, room-temperature phosphorescence (RTP) originated from molecular triplet state has only observed from a small portion of particular organic molecules.[4] Recently proposed crystallization-induced phosphorescence (CIP) provided a promising strategy to construct organic materials with efficient room-temperature phosphorescence by enhancing intersystem crossing process and suppressing nonradiative deactivation pathways of triplet excitons.[5] Under such a background, it is still extremely difficult to achieve organic materials with dual emissions from two singlets[6] or two triplets[7] via rational structural design and molecular packing. More challenging work is to achieve controllable manipulation of phosphorescence and fluorescence at single molecule level.

First example of organic molecules with phosphorescence-fluorescence dual emission was reported by Fraser and coworkers,[8] which demonstrated smart modulation of fluorescence and phosphorescence for a single component through systematic variation of poly(lactic acid) chain length combined with heavy atom substitution. Singlet-triplet emissive switching in single molecular system was accomplished by helical self-assembly and dissociation of a hexathiobenzene-based single luminophore in a recent study,[9] and helical self-assembly driven by intermolecular hydrogen bonding and π-π stacking interactions are responsive for the reversible switching between fluorescence and phosphorescence,[10] which further inspired the design of a single luminophore with dual emissions controlled by molecular stacking.[11] For such a unimolecular system, crystallization-induced self-assembly is required for simultaneous emission of phosphorescence and fluorescence, which makes the shift between phosphorescence and fluorescence in a non-controllable way. Precise manipulation of the switch between phosphorescence and fluorescence in a single molecule controlled by external stimuli still remains a great challenge.

Persulfurated arenes have long been exploited for designing redox sensors, coordination polymers and organic conductors due to their conformational patterns of the sulfur ligands,[12] but their unique solid-state phosphorescence was reported by Bergamini et al. till 2013,[13] uncovering unique room-temperature phosphorescence[14] and extremely high quantum yields of persulfurated benzene molecules.[15] This specific property was further employed to develop a phosphorescence turn-on sensor for magnesium ion.[16] These distinctive molecules with significant aggregation-induced phosphorescence (AIP) characteristic provide an ideal platform to manipulate phosphorescence and fluorescence in the unimolecular system in a controlled manner. In this work, a novel dual-emissive molecule with significant aggregation-induced phosphorescence characteristic was designed and synthesized, and reversible switching between phosphorescence and fluorescence can be achieved by external stimuli such as aggregation state and pH value. As shown in Scheme 1, the twisted structure of hexakis(3-hydroxy-1-phenylthio)-benzene (compound 1, HHPB) contributes to its efficient room-temperature phosphorescence in aggregated state, and this molecule also shows appreciable blue fluorescence or green emission under different conditions. The shift between phosphorescence and blue or green fluorescence can be realized by controlling aggregation state of HHPB via variation in solvent or pH value, while the switching between blue fluorescence and green emission is conducted by modulating the protonation state of isolated molecules. Except for the contribution from twisted structure of HHPB, a proper arrangement of energy gaps of S_1 and T_1 or the neighboring T

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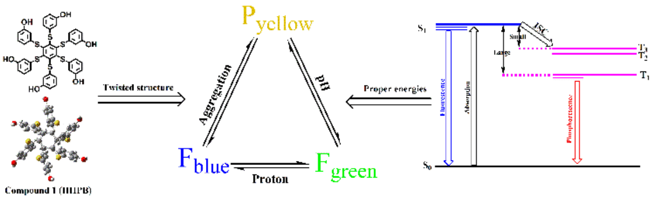

Scheme 1. Schematic Illustration of Reversible Switching between Phosphorescence and Fluorescence Controlled by External Stimuli and Underlying Contributions from Twisted Structure and Proper Energy Arrangement.

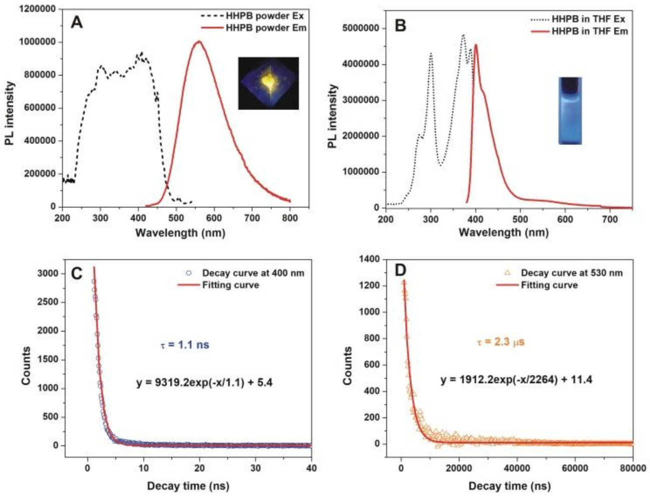

Figure 1. (A) Excitation and emission spectra of HHPB powder. Inset: Photograph for HHPB powder excited by UV light. (B) Excitation and emission spectra of HHPB in THF. Inset: image for HHPB solution in THF irradiated by UV light. (C) Time-resolved luminescence decay curve of HHPB in THF at 400 nm. (D) Time-resolved luminescence decay curve of HHPB in THF at 530 nm.

state of S_1 is required to attain a large population of triplet excitons, promoting the generation of intense phosphorescence. The revealing of underlying nature in photophysical process is helpful and valuable to design such an efficient S-T interconversion approach in a controllable manner.

The synthetic route in Scheme S1 and procedures for target compound HHPB were shown in the Supporting Information. Hexakis(3-methoxy-1-phenlthio)benzene (HMPB) as the intermediate product illustrates an emission band around 528 nm and a long lifetime of 13.6 μs as shown in Figure S1. Similar to its precursor HMPB, the solid powder of HHPB exhibits extremely bright luminescence under the irradiation of UV light, suggesting its significant aggregation-induced room-temperature phosphorescence (RTP) nature. Figure 1A shows PL spectra of HHPB powder, and its bright yellow luminescence is readily observed by naked eyes. Its emission maximum is located around 558 nm with a substantial red-shift relative to that of HMPB powder, and can be efficiently excited by a wide light range of 300 − 450 nm. The long lifetime of 8.8 μs from time-resolved luminescence decay curve in Figure S2 and a high emission efficiency of 0.13 demonstrated its excellent phosphorescence characteristic. HHPB can be well dissolved in most polar organic solvent like THF and ethanol, but has poor solubility in water. As seen from Figure 1B, HHPB shows an intense blue emission around 400 nm with a small emission peak at 530 nm, which largely differs with that of its solid. The quantum yield for the emission at 530 nm is lower than 0.001, implying its long-lived nature. After carefully measuring and analyzing their time-resolved decay curves in Figure 1C and 1D, we found that the intense blue emission and the weak green-yellowish luminescence belong to fluorescence and phosphorescence, respectively, in terms of their extremely different lifetimes by three orders of magnitude. These results clearly suggest HHPB in THF possesses a dual fluorescence-phosphorescence emission, but its solid only shows an intense phosphorescence band, which provides the opportunity to modulate their emission intensity in a controlled way.

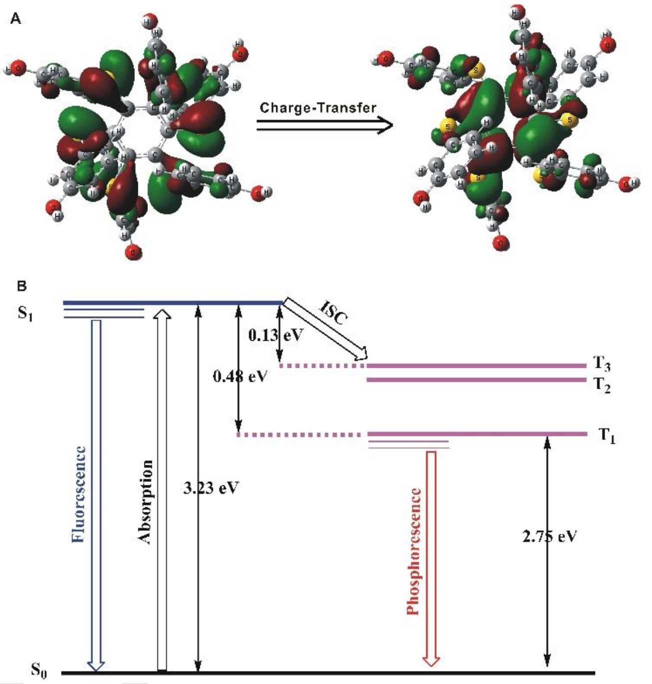

Figure 2. (A) HOMO and LUMO of HHPB molecule with charge-transfer feature. (B) A Jablonski diagram of HHPB molecule with labelled excitation energies.

Among a diversity of organic materials with room-temperature phosphorescence, hexathiobenzene-based organic molecules showed the most precious features because their RTP does not require the introduction of heavy atoms and the occurring of strictly crystalline state. [15,17] To gain a deep insight into the efficient aggregation-induced room-temperature phosphorescence of HHPB, we performed first- principle density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations on HHPB molecule. The optimized structure in Figure S3 demonstrates that six 3-hydroxy-benzene subunits are perpendicular to central benzene showing as a twisted structure in whole. Such a propeller-like conformation, similar to that of the famous AIEgen tetraphenylethylene, is responsible for its apparent AIE behavior because nonradiative deactivation pathways can be efficiently blocked under a constrained

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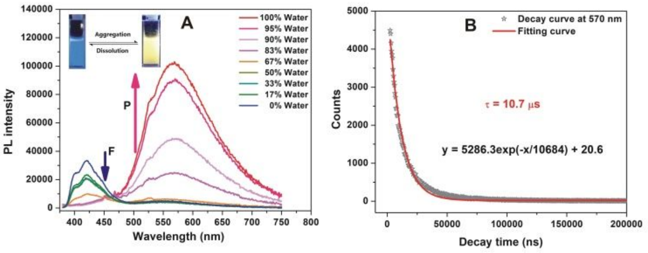

Figure 3. (A) The change of PL spectra of HHPB versus the ratio of ethanol/water. (B) Time-resolved luminescence decay curve of HHPB in water at 570 nm.

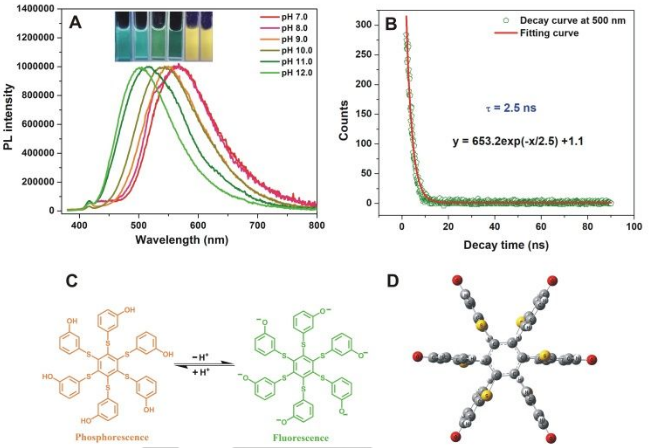

Figure 4. (A) The change of PL spectra of HHPB in varied pHs. Inset: Photoimages of HHPB solution at different pHs when excited by UV light. (B) Time-resolved luminescence decay curve of HHPB in pH 12 solution at 500 nm. (C) Schematic illustration of phosphorescence-fluorescence switching controlled by pH and optimized structures of HHPB and its deprotonated form. (D) Optimized structure of deprotonated form of HHPB.

environment.[18] NBO analysis provides visualized HOMO and LUMO of HHPB shown in Figure 2A, and it is easily noted that HOMO is mainly comprised of atomic orbitals of six sulfur atoms whereas LUMO consists of atomic orbitals from central benzene. Such a separated location of LUMO and HOMO clearly indicates a significant charge-transfer character, and also implies a relatively small S-T slitting energy resembling organic thermally activated delayed fluorescence materials.[19] However, a Joblonski diagram with labeled excitation energies for HHPB in Figure 2B shows that the energy gap between S_1 and T_1 (ΔE_{ST}) is estimated to be 0.48 eV, which is much larger than those of typical organic molecules with thermally activated decayed fluorescence (around 0.1 eV).[20] The large energy gap between S_1 and T_1 blocks the reverse intersystem crossing for T_1 to S_1. A close examination on these excitation energies of singlets and triplets from calculated data in Table S1 leads to the conclusion that the small energy gap between S_1 and T_3 states (0.13 eV) promotes intersystem crossing process between them, appreciably increasing the population of triplet excitons. Effective suppression of nonradiative deexcitaiton pathways under constrained environments allows T_3 triplet to reach T_1 triplet via internal conversion, finally releasing photons in the form of phosphorescence. Thus, charge-transfer character at the lowest singlet and triplet states and small energy difference between the lowest singlet and its neighboring triplet dominantly contribute to the occurring of aggregation-induced phosphorescence and its dual emission behavior in solution, and these findings are promising to develop as a design guideline for efficient RTP materials without the presence of heavy atoms.

Twisted molecular structure and specific electronic configuration of HHPB result in its efficient RTP in solid state, and thus the change in physical state would be used to modulate its fluorescence and phosphorescence. This hypothesis was verified by the observation in Figure 3A, which shows the variation of fluorescence and phosphorescence of HHPB by gradually aggregating HHPB molecules in ethanol solution using a poor solvent water. A moderately intense blue emission of HHPB in ethanol can be observed without the addition of water, but the blue fluorescence progressively decreases as the rise in ratio between water and ethanol. A new intense yellow emission centered at 570 nm is generated when the ratio is 83%, and its intensity reaches the top when pure water is used as the solvent. It is readily noticed that aggregation of HHPB is enhanced as more water content is introduced by naked eyes. The lifetime of the generated yellow emission was determined to be 10.7 μs from Figure 3B, clearly revealing its phosphorescence nature. Time-resolved PL decay curves in Figure S4 shows the huge change in lifetimes of these solutions from 1.1 ns to 10.7 μs, which confirms the gradual conversion from fluorescence to phosphorescence. To further verify water-caused aggregation of HHPB, dynamic light scattering was used to characterize the size change during this process. When water content in THF solution of HHPB is lower than 67%, no substantial nanoparticles in hundreds nanometer are detected, but appreciable amount of aggregates with the size at 300±100 nm appears when the water content reaches 83%. A gradual rise in average size of generated aggregates as water ratio is also observed from Figure S5, which verifies the progressive aggregation of HHPB molecules as the addition of water into THF. These results suggest aggregation or dissolution induced by variation in solvent is capable of switching fluorescence and phosphorescence in a single HHPB molecule.

Six hydroxyl groups of HHPB allow this hydrophobic molecule to dissolve in alkaline aqueous solution by adjusting pH value, and thus the occurring state of HHPB molecules can be controlled between aggregation and dissolution by external pH value. The hypothesis of pH-mediated aggregation-induced phosphorescence was tested by changing pH value of HHPB suspension from pH 7.0 to 12.0 in Figure 4A. However, it is surprisingly found that yellow phosphorescence of HHPB suspension is progressively turned to an intense green emission as pH value varies from pH 7.0 to 12.0, and the suspension finally becomes a homogenous solution. The aggregation state of HHPB molecules at pH 7 and 8 was also confirmed by dynamic light scattering as shown in Figure S6, where average diameters fall in the range of 100 – 400 nm. The generated green emission is quite bright since its absolute quantum yield is determined to be 0.08. A short lifetime on the order of nanoseconds (2.5 ns) determined from time-resolved

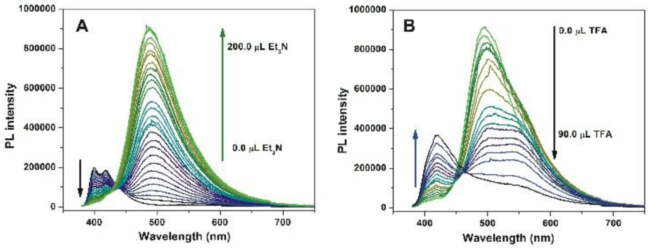

Figure 5. (A) The change of PL spectra of HHPB in THF versus the content of triethylamine (Et_3N). (B) The change of PL spectra of HHPB in THF in the presence of 200.0 µL triethylamine versus the content of trifluoroacetic acid (TFA).

luminescence decay curve in Figure 4B clearly implicates its fluorescence nature. These results lead to a hypothesis that the green emission probably originates from singlet of deprotonated form of HHPB due to such an alkaline environment. Figure 4C depicts the optimized structures of HHPB and its deprotonated form, and an appreciable difference in conformation can be concluded. HHPB as a neutral molecule exists a twist but compact configuration, whereas its deprotonated form shows a more spread conformation because of electrostatic repulsion among six phenoate subunits with a negative charge. This relatively rigidified structure facilitates the generation of fluorescence to some extent in comparison with HHPB. Table S2 lists excitation energies, oscillator strengths and contributions of molecular orbitals for the deprotonated form of HHPB. The accordance between theoretical and experimental values further confirms the origin of green emission from singlet of deprotonated form of HHPB. This unique pH-triggered phosphorescence-fluorescence switch is also reflected from a sharp decline from 10.7 μs to 2.5 ns as the rise of pH value from 7 to 12 as shown in Figure S7.

Two emissions from singlets were identified from the preceding results, and they originate from singlets of HHPB and its deprotonated form in the isolated state. As a result, triethylamine and trifluoroacetic acid were chosen as the organic base and acid, respectively, to achieve switching between blue and green fluorescence in organic solvents. As shown in Figure 5A, HHPB in THF only shows a blue emission around 400 nm initially, but the blue emission is gradually quenched as the addition of triethylamine in volume while a new emission at 500 nm is progressively enhanced. When 200.0 µL of trimethylamine is introduced, the blue fluorescence completely disappears while the green emission reaches the top. During this process, all the neutral molecules of HHPB have transformed to deprotonated forms, thus exhibiting intense green fluorescence. To further evaluate its reversibility of this emissive switch, different amounts of trifluoroacetic acid is continuously added into the above solution. The reverse process is demonstrated in Figure 5B, which shows the gradual enhancement of blue emission and progressive quenching of green fluorescence. These results prove fluorescence switching between two colors can be achieved by protonation and deprotonation in a reversible and controllable way.

The characteristics of AIP and emissive triplet-singlet switching controlled by external stimuli are extremely useful to design smart materials and intelligent devises.[21] We attempt to uncover underlying nature for such properties by analyzing and comparing optical properties of compound 1 and its isomer hexakis(4-hydroxy-1-phenylthio)benzene (compound 2). The schematic structure of compound 2 is shown in Figure S8, and Figure S9 demonstrates compound 2 has bright RTP in solid state and a long lifetime of 3.2 µs. The Joblonski diagram in Figure S10 shows that intersystem crossing process can be greatly promoted due to a very small energy gap between S_1 and T_9 (0.03 eV), but the relative energy difference between S_1 and T_1 effectively blocks the reverse process of intersystem crossing, facilitating the generation of phosphorescence. Both compound 1 and compound 2 meet such two requirements. In contract with compound 1, compound 2 has a weak fluorescence peak around 330 nm except for a long-lived emission at 580 nm as shown in Figure S11. The lacking of emissive singlet in the visible range excludes the possibility of manipulating phosphorescence and fluorescence. Such a small change in substitution position between compound 1 and compound 2 leads to extremely different behavior in photophysical properties, which suggests the rational design for organic luminogens with controllable emissions can be achieved by more efficient design of molecular structure with aid of theoretical analysis.

In summary, a twisted hexathiobenzene-based molecule with dual emissions was designed and synthesized, and it shows a significant aggregation-induced phosphorescence behavior and a regulation of singlet and triplet emissions by external stimuli. Switching between phosphorescence and fluorescence at the unimolecular level was realized by regulating the physical states of aggregation and dissolution. Twisted structure and the proper arrangement in excited energies mainly contribute to precise modulation of singlet and triplet emissions of the designed molecule. This work demonstrates an example of reversible switching among three colored emissions from a single molecule in a controlled way, which is extremely valuable to design smart materials and intelligent optoelectronic devices.

Experimental Section

Experimental details are included in Supporting Information.

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Keywords: Room-Temperature Phosphorescence • Aggregation-Induced Phosphorescence• Molecular Switch • Triplet-Singlet Switching• External Stimuli

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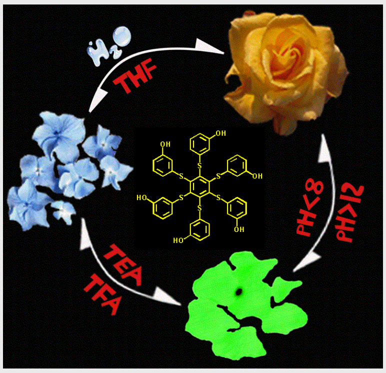
External Stimuli-Controlled Switching among Blue Fluorescence, Green Fluorescence and Yellow Phosphorescence in a Unimolecular System is Achieved.



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