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Arylene Diimide Phosphors: Aggregation Modulated Twin Room Temperature Phosphorescence from Pyromellitic Diimides

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Abstract: Arylene diimide derived ambient organic phosphors are seldom reported despite their potential structural characteristics to facilitate the triplet harvesting. In this context, highly efficient room temperature phosphorescence (RTP) from simple, heavy-atom substituted pyromellitic diimide derivatives in amorphous matrix and crystalline state is reported here. Multiple intermolecular halogen bonding interactions among these phosphors, such as halogen-carbonyl and halogen- π resulted in the modulation of phosphorescence, cyan emission from monomeric state and orange-red emission from its aggregated state, to yield twin RTP emission. Remarkably, the air-stable phosphorescence presented here own one of the highest quantum yield ($\approx 48\%$) among various organics in orange-red emissive region.

Design of ambient organic phosphors is one of the most actively pursued research in recent times as promising alternative to the toxic, metal-based organometallic phosphors for various applications.^[1] One of the important challenges in realizing the RTP from organic molecules is to stabilize the triplet states by minimizing the vibrational and oxygen mediated triplet quenching.^[1a] Recently, very elegant design strategies in this direction have been reported to achieve ambient RTP from organic phosphors both in their crystalline states^[2] and by embedding them in polymeric matrix^[3] or in various supramolecular scaffolds.^[4] However, new molecular designs with high quantum yield phosphors are required for the further advancement in this field. Since phosphorescence is a spin-forbidden process, a strong spinorbit coupling (SOC) is considered as a basic design to promote the intersystem crossing process (ISC) between a singlet (S_n) and triplet state (T_n) .^[1a,5] In this respect, we envisage that arylene diimides present an important class of

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molecules to be explored, with its multiple carbonyl groups in the backbone and with the diverse synthetic strategies available for their core-substitution with heavy atoms to increase the SOC and thus the resultant ISC efficiency.^[6] Although arylene diimides have been extensively investigated for various optoelectronic applications as electron-deficient semiconductors, their ambient triplet harvesting properties are rarely explored.^[7] While arylene monoimides such as naphthalene monoimides and phthalimide derivatives are recently shown to exhibit ambient RTP, corresponding diimide derivatives are seldom exploited for triplet harvesting.^[8] In this context, we have recently reported the ambient triplet harvesting of core-substituted naphthalene diimides via RTP^[4h] and thermally activated delayed fluorescence (TADF).^[9]

Further we envision that, well-studied supramolecular chemistry of arylene diimides would give an opportunity to realize multimode phosphorescence via tunable intermolecular interactions. Recently, (supramolecular) aggregation of organic phosphors has been elegantly used by the groups of Huang^[2c,10] and Yang^[11] for realizing dual-mode phosphorescence, which is of great importance for various applications such as white-light phosphorescence.^[3i,12] Herein we report novel heavy-atom core-substituted pyromellitic diimide (**PmDI**) derivatives, as efficient orange-red ambient RTP emitters stable in air (Figure 1). Such intense RTP emission



Figure 1. a) Molecular structures of **BrPmDI** and **IPmDI**. b) Simplified Jablonski diagram to explain the monomer and aggregated phosphorescence and other photophysical process. Inset: Monomeric and dimeric optimized geometry of **BrPmDI** at the first triplet excited state. Photographs of the monomer fluorescence in solution, phosphorescence in the polymer matrix and phosphorescence in crystal of **BrPmDI** under 365 nm light is also shown.

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with one of the highest quantum yield ($\approx 48\%$) in the longwavelength region of the visible spectrum is unprecedented. Further, we show that the phosphorescence emission could be modulated from cyan of the monomeric state to orange-red of aggregated state of the phosphors, by exploiting various intermolecular halogen bonding interactions such as halogen- π and halogen-carbonyl interactions, which facilitates the stacking of the phosphors and increases the SOC significantly. Although triplet harvesting of **PmDI** has recently been explored as polymer phosphors, small molecule-based phosphors are not yet reported.^[13]

First, we have synthesized BrPmDI and IPmDI, from a durene derivative and were fully characterized by NMR, mass spectrometry, single crystal X-ray diffraction and HPLC (See Supporting Information, Scheme S1). Spectroscopic characterization of these molecules in solution and solid states was subsequently performed using steady-state and time-resolved emission experiments. In solution state (THF, 0.05 mM), absorption spectra of BrPmDI and IPmDI showed characteristic S_0 - S_2 (π - π *) transition with a maximum at 360 nm and 380 nm, respectively (Figure S1).^[13] In solution, both molecules exhibited only weak fluorescence emission in the 400-550 nm regions with a short average lifetime of ≈ 0.8 ns (Figure S1, Table S1). On the other hand, when the experiments were performed at 77 K (THF) in the glassy matrix to reduce the vibrational dissipation, red-shifted emission in the 425 to 700 nm region with an emission maximum at 504 and 507 nm for **BrPmDI** ($\tau_{avg} = 7.7 \text{ ms}$) and **IPmDI**, ($\tau_{avg} = 1.9 \text{ ms}$), respectively was observed (Figure 2b,e, S1 and Table S2). The high lifetime of this redshifted emission suggests its phosphorescence origin. In order to harvest the triplets by minimizing the vibrational dissipation under ambient conditions, we first dispersed the molecules in poly(methylmethacrylate) (PMMA) matrix, an amorphous polymeric host known to stabilize RTP, at very low concentrations (1 wt. % with respect to PMMA).^[3a] Remarkably, a strong cyan emission was observed for both PMMA films with maximum at 480 and 487 nm along with very weak fluorescence emission for BrPmDI and IPmDI, respectively under ambient conditions (Figure 2b,e, Figure S2, Table S3). High lifetime of these red-shifted emissions (1.4 ms and 6.3 µs for BrPmDI and IPmDI, respectively) and its similarity with that of the emission of the pure molecules in frozen THF at 77 K clearly suggests the phosphorescence origin from monomeric states (Figures 2 c,f, S1 and Tables S2, S4). The absolute phosphorescence quantum efficiencies of BrPmDI and IPmDI in 1 wt. % PMMA matrix were 18% and 2%, respectively under air (Table S5). Therefore, it is evident that a strong internal heavy-atom effect is operative in these derivatives to facilitate substantial ISC and subsequent efficient RTP in amorphous matrix (Table S6). We hypothesized that higher phosphorescence efficiency of the BrPmDI compared to the IPmDI in 1 wt. % PMMA matrix is due to higher ISC rate $(k_{\rm ISC})$, lower non-radiative decay rate $(k_{\rm nr})$ and the more number of ISC channels present in monomeric state (Figure S3, Table S6). It is worth mentioning that 1 wt.% amorphous films of BrPmDI when under vacuum displayed an impressive phosphorescence quantum yield of 54% (Table S5). Interestingly, on increasing the concentration of these phosphors in the PMMA matrix (5 to 50 wt.%



Figure 2. Steady-state emission spectra of PMMA films with different wt.% of a) **BrPmDI** and d) **IPmDI**. Normalized emission spectra of b) **BrPmDI** and e) **IPmDI** in frozen THF at 77 K, in PMMA films with 1 wt.% and 50 wt.% of phosphors and in crystalline state (Inset: photographs of **BrPmDI** and **IPmDI** in PMMA films with 1 wt.% and 50 wt.% of phosphors and in crystalline state under 365 nm UV-lamp excitation, λ_{exc} = 330 and 350 nm for **BrPmDI** and **IPmDI**, respectively). Phosphorescence lifetime decay profiles of c) **BrPmDI** and f) **IPmDI** in PMMA films with 1 wt.% of phosphors and in crystalline state (λ_{exc} = 330 and 350 nm for **BrPmDI** and f) **IPmDI** in $\lambda_{collected} = 500$ nm for monomer and 650 nm for aggregate/crystal, all experiments were performed in air).

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with respect to PMMA) gradual appearance of a red-shifted emission (orange-red region) with maximum at 576 and 585 nm for BrPmDI and IPmDI respectively with the concomitant disappearance of monomeric cyan phosphorescence, was observed (Figures 2a and d). The lifetime in the millisecond time scale for these films suggests the phosphorescence modulation of these phosphors via intermolecular interactions ($\tau_{avg.} = 5.2, 0.32 \text{ ms}$ and $\Phi_p = 17.5\%, 30\%$ for BrPmDI and IPmDI respectively in 50 wt. % with respect to PMMA under air) (Figures 2 c,f, S4 and Tables S5, S7). Dropcasted films of BrPmDI and IPmDI showed similar emission features with lower quantum yield, which confirms the emission from aggregated phosphors (Figure S5 and Table S8). Aggregation of phosphors in the polymer matrix at higher wt. % is further evident from the increased scattering and red-shift in the absorption spectra as well as redshifted excitation spectra monitored at 650 nm (Figure S6, S7). We envisage that the presence of multiple non-covalent interactions in the aggregated state stabilizes the triplet energy level.^[10,11]

In an attempt to characterize the various intermolecular interactions in the stacked state of these phosphors, single crystals of BrPmDI and IPmDI were further investigated. Interestingly, single crystals of **BrPmDI** and **IPmDI** showed intense orange-red phosphorescence emission with a maximum at 576 and 585 nm for BrPmDI and IPmDI, respectively similar to that of the PMMA films with aggregated phosphors (Figure 2b,e). The high lifetimes of 11.4 ms and 0.61 ms for BrPmDI and IPmDI crystals, respectively and gated emission spectra (delay time = 0.5 ms) confirms the phosphorescent nature of the emission (Figures 2 c,f, S8 and Table S9). Selective excitation of the aggregated absorption also resulted in similar red-sifted phosphorescence emission suggesting the assembled state of the phosphors in crystals (Figure S9 and Table S10). Remarkably, both BrPmDI and IPmDI crystals showed high absolute phosphorescence quantum efficiencies of 26% and 48% (statistical data presented in Table S11), respectively under air, which is the highest phosphorescence quantum yield in the arylene diimide family and also one of the highest phosphorescence quantum yield reported in the orange-red region among various ambient organic phosphors (Tables S5, S12 and Scheme S2). Remarkably, the phosphorescence quantum yield of **IPmDI** crystals has increased to 68% under vacuum (Tables S5). Higher phosphorescence quantum efficiency of **IPmDI** crystals compared to the **BrPmDI** could be attributed to a stronger SOC and high ISC rate (k_{ISC}) in the former, which is also supported by its faster phosphorescence lifetime (Figures 2 c,f and Table S6, S9), as expected in heavy-atom organic phosphors.

X-ray diffraction analysis of the crystals further provided insights into the molecular organization of the phosphors in the aggregated state. Single crystals of BrPmDI exhibited a layered slip-stacked molecular organization with an interlayer distance of 3.8 Å (Figures 3 a,b and Table S13) which justifies the stabilization of orange-red emissive, red-shifted phosphorescence of the aggregated state in the crystalline phase. Further stacked arrangement of phosphors is stabilized by the halogen- π (C. Br, 3.5 Å) and the interdigitated alkyl chains between molecules of adjacent layers. In addition, within each layer, these molecules are connected by C=O...Br intermolecular non-covalent interactions (3.1 Å) (Figure 3c). It has been well-established that halogen bonding can enhance the SOC by external heavy-atom effect.^[2a] We envisage that, rigid 3D network due to the various noncovalent interactions specially halogen bonding help the triplet stabilization via minimizing the vibrational dissipation and by enhancing the SOC. In addition, strong intramolecular C=O...Br (3.2 Å) (Figure 3b) interactions can also contribute to high SOC even in the molecular dispersed and glassy matrix. Similar organization was also observed in the crystals of IPmDI (Figure S10, Table S13). Since the crystal packing is similar in both molecules with closely matching short-contact distances, we envision that the extent of external/internal heavy-atom effect determines the differences in their RTP intensity. To validate the stabilization of triplets in the crystal state we have performed time-dependent density functional theory (TDDFT) calculations. The calculated energy levels of the optimized geometry of the first



Figure 3. a) Unit cell, b) slipped stacked arrangement showing various intermolecular interactions, c) intramolecular and intermolecular halogencarbonyl interaction of **BrPmDI** single crystal.

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excited triplet state of monomeric and dimeric **BrPmDI**s supports the observed red shift in phosphorescence in the aggregated state (Figure S11, Table S14). Further, reduced density gradient (RDG) plot of the dimeric triplet state also clearly shows the intra- and intermolecular non-covalent interactions observed in the crystalline state, which can enhance the ISC/SOC efficiency (Figure S12).

The fundamental prerequisite for the triplet emission in arylene diimide based systems is to access the triplet excited state. Therefore, in order to have a qualitative understanding of ISC efficiency in PmDI derivatives reported here, we investigated their excited state characteristics by detailed TDDFT calculations using CAM-B3LYP exchange-correlation functional (Figure S13-S18, Table S15). The rate of ISC is dependent on the SOC strength and this is estimated quantitatively by calculating the SOC matrix element (SOCME) between S_1 and its closely lying triplet states (T_n) (Table S16). In both these cases, multiple triplet states are present below the S₁ excited state and thus provide a thermodynamically favorable ISC route (Figure S3). In BrPmDI, there are two main contributing pathways for ISC according to corresponding SOC matrix element (Figure 4, S3, S13 and S15). These are S_1 (n- π^*) to T_6 (π - π^*) and S_1 to T_2 , where corresponding calculated SOCME are 16 and 523 cm⁻¹, respectively (Figures 4, S13 and Table S16). It is important to note that the closely-lying T_5 and T_4 possess the similar molecular orbital (MO) configuration as that of S₁ and this does not follow El-Sayed rule; therefore, the magnitude is much lower than that between S_1 and T_2 having different electron-hole configurations (Figure S15). In addition, both these transitions are also facilitated by the presence of heavy Br atoms. For IPmDI monomers, the ISC pathway is facilitated by close-lying S1-T2 which follow El-Sayed rule and since Iodine is expected to show a stronger heavy-atom effect as compared to Br, the magnitude of SOCME is three



Figure 4. Ground state geometries, relative excitation energies and their corresponding hole, electron wavefunctions and SOC matrix elements for both monomeric and dimeric **BrPmDIs** (Hole and electron wavefunctions are shown below and above in the schematic, respectively. Inset: monomeric and dimeric structure of **BrPmDIs** obtained from crystal structure).

times higher than **BrPmDI** (Figure S3, S16 and Table S16). Upon aggregation, number of intersystem crossing channels increases significantly as evident from the ground state optimized geometries of **BrPmDI** dimers (Figure 4, S13 and S17) which could be one of the reasons for the high phosphorescence efficiency in the crystalline state compared to the monomeric state. As a control, we also investigated the un-substituted **HPmDI**, and the only possible ISC pathway in this case is between S₁ and T₁ state with substantially low SOCME (Figure S18 and Table S16).

In conclusion, we have introduced a new class of small organic molecule based efficient, ambient organic phosphors from the smallest member of arylene diimide family, that is, pyromellitic diimides, by a rational "heavy-atom" substitution strategy. The PmDI derivatives reported here showed high phosphorescence quantum yield ($\approx 48\%$ and $\approx 68\%$, in air and vacuum, respectively) with exceptional air stability. Further the tunable phosphorescence emission could also be achieved by the stacking of phosphors using multiple intermolecular halogen bonding interactions. Although many organic room temperature phosphors are reported recently, the present system is unique with respect to its new molecular design, high quantum yield and halogen bonding induced tunable phosphorescence.^[1f] We envisage that arylene diimide phosphors, with its rich chemistry of core-substitution and appropriate molecular structure conducive for efficient SOC and ISC, offers plethora of opportunities in the frontier research area of organic phosphors.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aggregation · dual phosphorescence · noncovalent interactions · photochemistry · pyromellitic diimide

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Communications

Tuneable Phosphorescence

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Arylene Diimide Phosphors: Aggregation Modulated Twin Room Temperature Phosphorescence from Pyromellitic Diimides



Highly efficient room-temperature phosphorescence, stable in air, from the simplest class of arylene diimides, i.e., pyromellitic diimides, is achieved. Aggregation modulated, colour tuneable phosphorescence emission from cyan to orange-red in amorphous film and crystalline state is observed. The role of molecular design and weak intermolecular interactions in the observed properties is explained.

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