

Tuning the Photophysical Properties of Metal-Free Room Temperature Organic Phosphors via Compositional Variations in Bromobenzaldehyde/Dibromobenzene Mixed Crystals

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Supporting Information

ABSTRACT: Spurred by several recent discoveries and a broad and largely unexplored design space, purely organic phosphorescent materials are starting to garner interest for potential applications in organic optoelectronics and sensors. One particularly promising class of purely organic phosphor is the family consisting of bromobenzaldehyde emitters doped into crystals of dibromobenzene hosts. These stand out by featuring bright, robust, and color-tunable room temperature phosphorescence. However, despite these attractive qualities, the mixed crystal motif defining these materials puts complex



demands on crystal packing, chemical structure, and sample preparation in ways that are not yet well understood. Here we report a detailed study on these materials to optimize emission efficiency and fine-tune color. Overall, data suggest that achieving efficient inclusion of the emitter into the host crystal is critical to optimizing quantum efficiency. Phosphorescent emission from the mixed crystals is polarized, indicating that bromobenzaldehyde guest is ordered in the dibromobenzene host crystal. While host compounds tolerate a surprising variety of emitter sizes, both oversized and undersized, maximum quantum efficiency is reached when emitters and hosts are identically sized and the former is present at 1-10 wt % of total solids. The optimum quantum efficiency for these systems appears, empirically, to be in the range of 45-55%. To fine-tune emission color, altering the halogen substitution of the emitter molecule affords sequential 5-30 nm changes to emission maxima within the green region. The relatively minor impact these alterations have on the overall chemical structure affords color tuning with minimal detriment to mixing efficiency.

INTRODUCTION

Until recently phosphorescence from metal-free purely organic materials was regarded as an intractably inefficient phenomenon, leading these compounds to receive little attention from relevant applications,¹ such as phosphorescent organic light emitting diode (PhOLED)²⁻⁶ and photovoltaic fields.⁷⁻⁹ More recently, however, reports have begun to awaken interest in purely organic phosphorescence for applications in sensing $^{10-13}$ and potential uses in optoelectronic devices.14-19 Several families of purely organic phosphors including fluorobor-ons,^{20–22} acenes,^{23–25} thiones,^{26,27} and classic aromatic ketones^{28,29} are emerging or re-emerging with promise for use in optical applications. One such family of purely organic phosphors that has emerged from the growing field of crystal engineering³⁰⁻³⁶ and has received recent attention is that of bromobenzaldehyde/dibromobenzene-style crystal phosphors reported recently by our group.¹⁴ These materials feature robust high room temperature quantum efficiency and tunable emission color from simple small molecules. Realizing the attractive functional qualities of these materials, however, depends greatly on optimizing crystal and chemical structures, a combination that is nontrivial. Here we report phosphorescent quantum efficiency and fine color tuning of the first

members of this family of organic phosphor by varying compositions and chemical structures. These organic materials consist primarily of an emitter compound that features an aromatic aldehyde with bromine substitution. These emitters are nonphosphorescent when in solution or liquid states, but they produce photoluminescent phosphorescence when crystallized. This, we have hypothesized, is because the bromine atoms in their structures both promote intersystem crossing via the heavy atom effect and prevent carbonyl vibration via a halogen bond.^{37–39} This hypothesis is built upon the existing understanding of the heavy atom effect,⁴⁰ the spin–orbit coupling activity of aromatic carbonyls,⁴¹ and the fact that all phosphorescent crystal structures in this family feature such halogen-carbonyl oxygen contact. Also, the phosphorescent efficiency of these materials has been observed to correlate with crystal quality, suggesting that the emission mechanism is influenced by the solid state condition of this compound.¹⁴

When these aldehyde emitters are condensed into their pure crystals, they suffer greatly from self-quenching and produce

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Figure 1. Bromobenzaldehyde purely organic phosphorescent crystals. (a) Benchmark aldehyde emitter and host, Br6A and Br6, respectively. (b) Schematic illustration of dim Br6A (emitter) crystals, nonemissive Br6 (host) crystals, and bright phosphorescent Br6A/Br6 (mixed crystals).

host combinations in this young family of phosphors. Pure Br6A crystals are only weakly emissive, but when Br6A is doped into crystals of Br6, which are otherwise completely nonemissive, phosphorescent emission from Br6A becomes very bright (Figure 1b). Our hypothesis that Br6A becomes included into the Br6 crystal lattice by substitution, and thus experiences the same order and halogen contact, is supported by the fact that phosphorescent emission from Br6A/Br6 mixed crystals is polarized, indicating that Br6A is ordered in the Br6 crystal (Figure 2).

Unfortunately, the emitter/host relationship that gives these materials their high quantum efficiency also complicates optimization. An ideal system features emitter substituted





perfectly into a high quality host crystal, and, unfortunately, though the emitter is very similar to the host, it is not identical. It is an impurity in the host crystal and, thus, not thermodynamically favored in the host crystal. This renders these mixed crystal phosphors susceptible to a number of emission-reducing conditions (Figure 3). Optimizing quantum efficiency thus requires optimizing mixing so that the maximum population of emitters present are isolated and ordered within the host crystal.



Figure 3. Sources of reduced quantum efficiency in mixed crystal pure organic phosphors (upper three) and the emissive outcome of a perfectly included and isolated emitter (bottom).

EXPERIMENTAL SECTION

All chemicals used were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents for NMR (nuclear magnetic resonance) were purchased from Cambridge Isotope Laboratories. Proton NMR was conducted on a Varian Inova 500 equipped with a Varian indirect detection probe using CDCl₃ solvent with chemical shifts identified relative to 0.05 v/v% tetramethylsilane standard (0.00 ppm). ¹³C NMR was conducted on a Varian MR400 equipped with a Varian 5 mm PFG AutoX Dual Broadband probe using CDCl₃ for which the solvent peak was used to calibrate. Anhydrous tetrahydrofuran was generated by distilling over sodium metal and benzophenone, collected only from deep purple solution.

UV-vis electronic absorption measurements were collected using a Varian Cary 50 Bio spectrometer with solution samples held in a quartz cuvette. Photoluminescent (PL) emission, excitation, and quantum yield data were collected using a Photon Technologies International (PTI) Quantamaster system equipped with an integrating sphere. Gated photoluminescence was collected with a delay time of 150 μ s after 365 nm excitation of each sample at room temperature. X-ray diffraction for dropcast mixed crystals was carried by a Rigaku Rotating Anode X-ray Diffractometer (X-ray wavelength: 1.54 Å). Microscope images were collected on an Olympus BX51 W/ DP71 fluorescent microscope equipped with cross-polarizers.

Quantum yield (QY) was measured using an integrated sphere whose accuracy was verified using a 10 mM Rhodamine 6G/ethanol solution.⁴² Samples for quantum yield measurement were prepared by dropping 0.1 g/mL chloroform solutions of the desired compounds, mixed in the weight ratios reported, onto an unmodified glass substrate. Crystal "films" would form as the solvent evaporated. Each sample had a total mass of 2 mg. Absorption and emission inside the sphere was determined by comparison to a blank sample (glass only). A neutral density filter was used to allow for maximization of the emission signal without saturating the photomultiplier tube detector with excitation light. Each sample type was run in quadruplicate (or more) with each quantum yield measurement coming from a freshly dropcast sample. Measurements proved highly repeatable, and errors are given as ± 1 standard deviation.

Synthesis of 2,5-Dihexyloxybenzaldehyde (H6A). 2-Bromo-1,4-dihexyloxybenzene (1 equiv) was loaded into a two-neck round bottomed flask and vacuum purged with argon three times. Anhydrous

tetrahydrofuran was added by syringe (ca. 25 mL solvent/g reagent), and the vessel was placed into a bath of dry ice and 2-propanol at -78°C. A solution of *n*-butyllithium in hexanes (2.5 M, 1 equiv) was added dropwise via syringe, and the reaction was then stirred at -78 °C for 1 h. Anhydrous DMF (4 equiv) was then added, and the reaction was allowed to warm to 23 °C for 3 h. The reaction was quenched carefully with water and extracted with diethyl ether. The organic layer was collected and dried over MgSO₄ before being filtered, and the solvent was removed by rotary evaporation. Products were purified by column chromatography with ethyl acetate/hexane (1:30) eluent. Viscous oil eventually crystallizing into a white solid was collected at a yield of 79%. ¹H NMR (500 MHz, CDCl₃): δ 10.47 (s, 1H, CHO), 7.31 (d, ${}^{4}J_{(H-H)} = 3.0$ Hz, 1H, Ar-H), 7.11 (q, ${}^{4}J_{(H-H)} = 3.0$ Hz, ${}^{3}J_{(H-H)} = 4.0$ Hz, 1H, Ar-H), 6.92 (d, ${}^{3}J_{(H-H)} = 4.0$ Hz, 1H, Ar-H), 4.03 (t, ${}^{3}J_{(H-H)} = 6.5$ Hz, 2H, OCH₂), 3.94 (t, ${}^{3}J_{(H-H)} = 6.5$ Hz, 2H, OCH₂), 1.81 (m, 2H, CH₂), 1.55 (m, 2H, CH₂), 1.42 (m, 4H, CH₂), 1.32 (m, 8H, CH_2), 0.91 (t, ${}^{3}J_{(H-H)} = 6.0$ Hz, 6H, CH_3). ${}^{13}C$ NMR (100 MHz, CDCl₃): δ 14.0, 22.5, 25.6, 29.2, 31.5, 68.7, 69.2, 110.8, 114.4, 124.1, 125.1, 153.0, 156.3, 189.8. HRMS (ESI)⁺ m/z 307.2273 (C₁₉H₃₁O₃ $[M + H]^+$ requires 307.2268).

Synthesis of 4-Chloro-2,5-dihexyloxybenzaldehyde (Cl6A). Cl6A was made by formylation of 4-chloro-2,5-dihexyloxy-1iodobenzene in a method similar to that used to produce H6A. White crystals were collected at a yield of 59%. ¹H NMR (400 MHz, CDCl₃): δ 10.41 (s, 1H, CHO), 7.36 (s, 1H, Ar-H), 7.04 (s, 1H, Ar-H), 4.02 (t, ³J_(H-H) = 6.4 Hz, 2H, OCH₂), 4.01 (t, ³J_(H-H) = 6.4 Hz, 2H, OCH₂), 1.82 (m, 4H, CH₂), 1.48 (m, 4H, CH₂), 1.34 (m, 8H, CH₂), 0.91 (t, ³J_(H-H) = 6.0 Hz, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 14.0, 22.5, 25.6, 29.0, 31.4, 69.4, 69.7, 111.1, 115.4, 123.6, 131.0, 148.9, 155.8, 188.8. HRMS (ESI)⁺ *m*/*z* 341.1884 (C₁₉H₃₀ClO₃ [M + H]⁺ requires 341.1878).

Synthesis of 2,5-Dihexyloxy-4-iodobenzaldehyde (I6A). I6A was made by lithiation of 1,4-diiodo-2,5-dihexyloxybenzene in a method similar to that used to produce H6A and Cl6A. White crystals were collected at a yield of 31%. ¹H NMR (400 MHz, CDCl₃): δ 10.42 (s, 1H, CHO), 7.46 (s, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 4.02 (t, ${}^{3}J_{(H-H)} = 6.0$ Hz, 2H, OCH₂), 4.00 (t, ${}^{3}J_{(H-H)} = 6.0$ Hz, 2H, OCH₂), 1.82 (m, 4H, CH₂), 1.49 (m, 4H, CH₂), 1.35 (m, 8H, CH₂), 0.91 (t, ${}^{3}J_{(H-H)} = 6.8$ Hz, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 14.0, 16.2, 22.5, 22.6, 25.6, 25.7, 29.0, 31.4, 69.5, 69.9, 108.8, 124.5, 125.1, 152.1, 155.8, 189.3. HRMS (ESI)⁺ m/z 433.1232 (C₁₉H₃₀IO₃ [M + H]⁺ requires 433.1234).

RESULTS AND DISCUSSION

The limits of inclusion efficiency were probed via a size exclusion experiment. In order to perturb mixing, a series of analogous aldehydes and hosts were synthesized with alkoxy chain lengths variable from five to eight carbon atoms (Figure 4a). These were intermixed in crystals grown by dropcasting chloroform solutions containing 1 wt % aldehyde, and their photoluminescence quantum efficiencies were measured using an integrating sphere. As expected, emission was brightest when aldehyde and host were the same size. Mismatched emitter and host combinations were seen to mix surprisingly well, though distinctly worse than ideally matched pairs, with quantum efficiency dropping as the size difference grows. This was true for both undersized and oversized emitters, though when the emitter was larger than the host the quantum efficiency was markedly lower than in the opposite case. This can be seen in Figure 4b, where the lower left corner of the image is qualitatively darker and quantitatively weaker than the upper right.

The fact that phosphorescence is generated from mismatched emitter-host pairs, some dramatically mismatched, indicates that inclusion is kinetically quite favorable, even if not thermodynamically so. This is made especially clear when oversized emitters, in some cases six methylene carbons and 7.5



Figure 4. Emitter inclusion perturbed by size exclusion. (a) Chemical structures of emitters Br(5-8)A and hosts Br(5-8). (b) Photograph of dropcast crystals made of mixed aldehyde and host compounds illuminated by 365 nm light. Quantum efficiencies measured from samples of the same compositions and growth conditions.

Å longer than their hosts, produce appreciable emission even when mixed with undersized hosts. This experiment also suggests, for these compounds and this growth method, a possible optimum empirical quantum efficiency of ca. 45-55%, as each ideally matched combination is in near agreement. XRD was performed for mixed crystals grown from each emitter Br(5-8)A as a guest in Br6 host in order to examine how the size mismatch affects the crystal packing of host Br6. XRD data were analyzed based on the XRD pattern of Br6 single crystal. As shown in Figure 5, they show three characteristic peaks appearing at 10.15, 20.5, and 23.7° corresponding to (001) plane from Br-Br contact, (110) plane from H-Br contact, and (020) plane from H-Br contact, respectively, which indicates that by the inclusion of 1 wt % mismatched guest emitter the crystal structure of Br6 is not significantly altered to be responsible for the reduced quantum efficiency. The



Figure 5. XRD pattern of mixed crystal with different emitters in Br6 prepared by dropcast on a glass substrate. Data were analyzed based on the XRD pattern of Br6 single crystal. Doping concentration was 1 wt % for all experiments.

emission lifetime of bromobenzaldehyde guests also remains in a similar range regardless of the size mismatch as shown in Table S1 in the Supporting Information.

In order to determine an optimal mixing ratio of emitter and host, several samples were made with varying concentrations of Br6A in Br6. Both compounds were mixed in a chloroform solution to the desired amounts before being dropcast onto unmodified glass slides. Br6A content was varied from 0.0001 wt % to 100 wt %, as total solids. No fewer than four samples were made from each combination, and these were measured for quantum efficiency in an integrating sphere. Efficiencies were charted showing a mixing ratio of 1 wt % Br6A to produce the brightest samples, though samples of 10 wt % Br6A were in close agreement (Figure 6). A rapid reduction in quantum



Figure 6. Phosphorescent quantum efficiency versus weight percentage of Br6A in Br6A/Br6 mixed crystal sampled from dropcast. Error bars represent \pm one standard deviation.

efficiency was observed as Br6A concentration was either increased or decreased. Quantum efficiency tapered from a maximum of 55% at 1 wt % Br6A to 0.1% at 100 wt % Br6A and 0.4% at 0.0001 wt % Br6A. Gated phosphorescence spectra (Figure S1) of the samples used for this mixing ratio study confirm that the green emission is phosphorescence emission from the embedded Br6A. Regardless of the side chain length the same trend was observed in all cases where emitter from Br5A to Br8A was intermixed at varying concentration from 0.01 wt % to 30 wt % with its matching host from Br5 to Br8 (Figure 7). Substituting different solvents for drop casting and dropcast solution concentration and changing substrate temperature and hydrophobicity did not make any meaningful change in the maximum phosphorescence quantum yield of 55% (Figure S2).

While it is not unexpected that quantum efficiency would drop as Br6A content increases, a drop as Br6A content decreases is surprising. At high concentrations of Br6A selfquenching is anticipated as Br6A-Br6A contact becomes more likely and the sample trends toward pure Br6A. The same is not true at low concentrations of Br6A where emitter isolation becomes extremely likely. Simple statistical analysis eliminates the possibility that this trend is evidence that a dimer or multialdehyde interaction is facilitating phosphorescence because, for example, at concentrations of 1 wt % Br6A the likelihood of Br6A-Br6A contact in the crystal is far below 55%, the quantum efficiency measured at that loading of Br6A. We hypothesize that quantum efficiency loss at low Br6A sparse Br6A into the increasingly pure Br6 crystals. Phosphorescence microscopy reveals that Br6A/Br6 crystals are brightest near nucleation sites (Figure 8) and often feature sharp drop-offs in emission brightness. This indicates that the inclusion rate is not constant throughout the growth of the host crystals. If Br6A molecules are not leaving solution soon enough to catch Br6 crystals in early growth in the dropcast films, as would likely be the case when Br6A concentrations are low, inclusion will suffer. So, just as recrystallization is done in the wet lab successively to purify crystalline materials, at these low levels of Br6A the emitter is less likely to become included into the relatively pure Br6 crystal formed from dropcast.

Note that because these samples were made by dropcast, crystal quality is worse than that of crystals grown slowly from supersaturated solution. This is why pure Br6A here (dropcast) measured a quantum efficiency of 0.1%, while Br6A reported in our earlier work, there measured as high quality single crystals, exhibited a quantum efficiency of 2.9%. While that trend is true for pure crystals, dropcasting is preferable to solution growth for mixed crystals because the likelihood of kinetically entrapped inclusion of the emitter into the host is much better in the faster process, dropcasting. Based on this understanding and our observations, it follows that inclusion, and thus quantum efficiency, appears to prefer fast crystal growth. Also supporting this hypothesis, attempts to thermally anneal Br6A/Br6 mixed crystals led to reduced quantum efficiency in all cases.

Achieving efficient inclusion also becomes an issue in color tuning. In earlier work broad changes to emission color were accomplished by altering the electron density of the emitter through the addition of electron deficient or rich atoms or extended conjugation.¹⁴ As these chemical structures strayed from the original models inclusion became more complicated and quantum efficiencies suffered. For example, in the case of the blue-emitting alkyl substituted compounds, inclusion efficiency was problematically low, in large part because the aldehyde had a freezing point below room temperature. A more elegant, and subtler, approach to color tuning would be to simply vary the halogen atom of the emitters. Such compounds were synthesized to explore the effects halogen variation would have on emission color. Alternative emitters 4-chloro-2,5dihexyloxybenzaldehyde (Cl6A) and 2,5-dihexyloxy-4-iodobenzaldehyde (I6A) have nonbromine halogens, while 2,5dihexyloxybenzaldehyde (H6A) was designed to be halogenfree (Figure 9a). Even though H6A is a halogen-free molecule it has the same core benzaldehyde unit that will form halogen bonding with a bromine of matrix Br6, which activates the heavy atom effect. We excluded the fluoride version because F does not form halogen bonding. These compounds alter the electron density of the emitter in ways that have less effect on the size, shape, and electronic character of the molecule and are thus less likely to alter pertinent materials properties such as the crystal growth mechanism and freezing temperature.

Each alternative aldehyde was included into Br6 host crystals and measured spectrally. Br6 was chosen as the host when it was observed to produce brighter samples than either 1,4dichloro-2,5-dihexyloxybenzene (Cl6) or 1,4-diiodo-2,5-dihexyloxybenzene (I6). Mixed crystals of Br6 were grown by dropcasting chloroform solutions of 1 wt % emitter/Br6 onto unmodified glass. As shown in Figure 9b, varying the halogen from chlorine to bromine to iodine shifts the emission spectrum in sequential 5 nm steps ($\lambda_{max, Cl6A}$: 510 nm, $\lambda_{max, Br6A}$: 515 nm, $\lambda_{max, I6A}$: 520 nm) commensurate with the varying



Weight % of Br(5-8)A in total solid

Figure 7. Phosphorescence quantum yield as a function of weight percentage of emitters Br(5-8)A in mixed crystal with hosts Br(5-8). Error bars represent \pm one standard deviation.



Figure 8. Markedly brighter regions surrounding apparent nucleation sites in Br6A/Br6 mixed crystals.



Figure 9. (a) Halogen-variable emitters for fine color tuning. (b) Emission (each excited at 365 nm) of crystals grown from solutions containing a 1 wt % ratio of the emitter in Br6. H6A (black), Cl6A (red), Br6A (blue), and I6A (green).

electron density afforded by the halogen. A halogen-free emitter, H6A, produces an emission spectrum with a more dramatic 30 nm blue shift ($\lambda_{max, H6A}$: 485 nm), which is because

of the more dramatically reduced electron density this emitter exhibits for having no halogen.

We measured phosphorescence lifetime of guest emitters (Cl6A, Br6A, and I6A) in their analogous hosts (Cl6, Br6, and I6) at room temperature (Table 1). The phosphorescence

Table 1. Phosphorescence Lifetime (ms) of Mixed Crystals Was Estimated at Room Temperature by Means of Time-Resolved Phosphorescence Measurement of 515 nm Emission with Single Decay Curve Fitting

	Cl6	Br6	16
Cl6A	6.62	6.19	4.76
Br6A	7.95	7.60	3.33
I6A	0.65	0.56	0.05

lifetime of guest emitters decreases when the halogen of the host becomes heavier from Cl6 through Br6 to I6 likely due to enhanced heavy atom effect between halogen atom of the host and oxygen of the emitter. This lifetime decrease was maximized at I6/I6A mixed crystals because it contains the heaviest atom, iodine, both in host and emitter. When combined with the broader color shifts presented in earlier work, these fine-tuning steps give this family of organic phosphors the capability to fine-tune emission color with both breadth and precision.

CONCLUSIONS

In summary, we have demonstrated the optimization of the quantum efficiency and fine-tuning of emission color from emerging metal-free purely organic phosphors. Quantum efficiency optimization relies on attaining efficient inclusion of the emitter into the host crystal, which is a kinetic equilibrium maximized when both components are similarly sized and the emitter is present at 1-10 wt %. Replacing or removing the halogen on the emitter facilitates sequential 5-30 nm steps in green emission region, allowing the designer to fine-tune the emission spectrum with minimal change to the chemical structure. These findings elucidate the complex optical and solid state behavior these materials exhibit and illustrate the extreme influence that material preparation has on their performance.

ASSOCIATED CONTENT

Supporting Information

Table S1 and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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