

# Activating efficient phosphorescence from purely organic materials by crystal design

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**Phosphorescence is among the many functional features that, in practice, divide pure organic compounds from organometallics and inorganics. Considered to be practically non-phosphorescent, purely organic compounds (metal-free) are very rarely explored as emitters in phosphor applications, despite the emerging demand in this field. To defy this paradigm, we describe novel design principles to create purely organic materials demonstrating phosphorescence that can be turned on by incorporating halogen bonding into their crystals. By designing chromophores to contain triplet-producing aromatic aldehydes and triplet-promoting bromine, crystal-state halogen bonding can be made to direct the heavy atom effect to produce surprisingly efficient solid-state phosphorescence. When this chromophore is diluted into the crystal of a bi-halogenated, non-carbonyl analogue, ambient phosphorescent quantum yields reach 55%. Here, using this design, a series of pure organic phosphors are colour-tuned to emit blue, green, yellow and orange. From this initial discovery, a directed heavy atom design principle is demonstrated that will allow for the development of bright and practical purely organic phosphors.**

Purely organic materials that are also phosphorescent are very rare. The few that are known are very inefficient emitters. In contrast to electrons in metal-containing materials, the highly bonded nature of electrons in metal-free organic materials leaves them little freedom and less impetus to emit from triplet states<sup>1</sup>. Phosphorescence is therefore generally regarded as a solely inorganic or organometallic property. So weak is the emission from metal-free organic materials and so ineffective have been the few attempts at using them in this way<sup>2</sup> that purely organic materials now fail to enter discussions on modern phosphorescent applications<sup>3</sup>. Phosphorescent materials are commonly used in organic electronics<sup>4,5</sup>, as well as chemical<sup>6</sup> and biological<sup>7,8</sup> detection, but because of a lack of practical, efficient and versatile metal-free organic phosphors, the range of materials in use has narrowed to include only organometallic chelates<sup>9,10</sup>. Purely organic materials have been widely considered to be non-phosphorescent in character.

In this Article, we present a phenomenon that uniquely combines three factors to initiate bright phosphorescence from purely organic crystals: aromatic carbonyls, the heavy atom effect, and halogen bonding. Aromatic carbonyls exhibit a degree of spin-orbit coupling at the carbonyl oxygen that allows for intrinsic triplet generation through intersystem crossing<sup>11,12</sup>. This makes them unique among light-element organic compounds, although it does not normally afford bright or even, in many cases, detectable phosphorescence<sup>13</sup>. Despite being considered of scientific value for decades, the demonstration of reasonably efficient phosphorescence from these compounds has only been possible in low-temperature, strictly dilute and de-oxygenated environments, as well as under other impractical conditions<sup>14,15</sup>. Ambient solid-state efficiencies are so low that they are seldom reported, if indeed measurable.

The second phenomenon, the heavy atom effect, promotes singlet-triplet conversion and has long been used externally<sup>16</sup> and internally<sup>17</sup> to make improvements, usually modest, in the phosphorescence and triplet character of organic compounds. This effect works by enhancing spin-orbit coupling between the excited-state

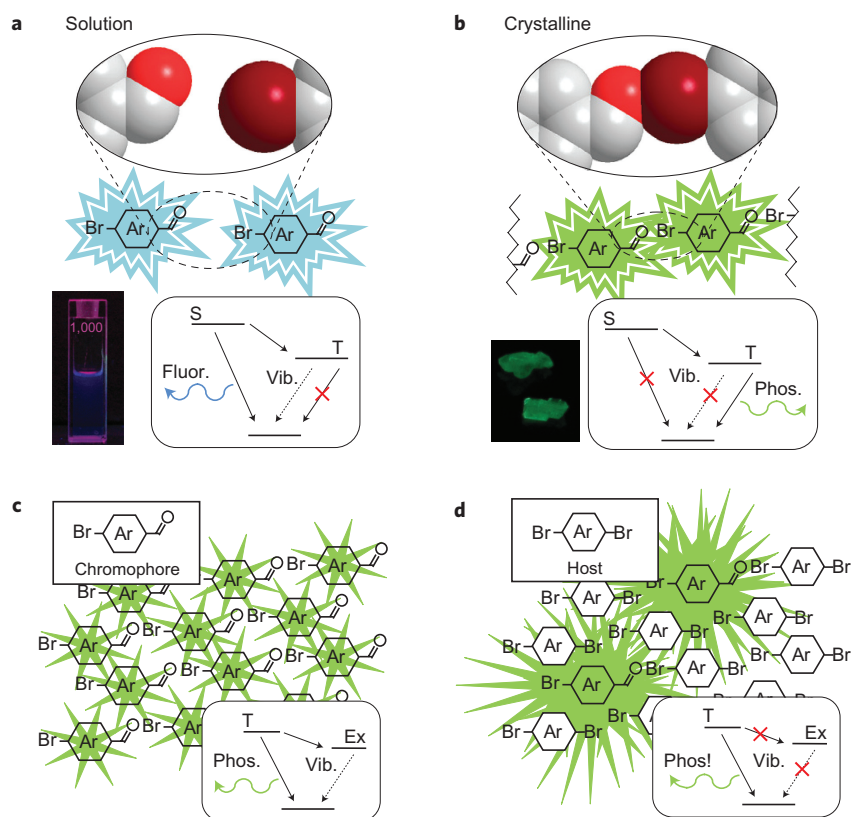
electrons of a compound and the massive nucleus of the heavy atom<sup>18</sup>. Proximity to the heavy atom promotes mixing of the singlet and triplet states of the excited chromophore to promote both singlet-to-triplet and triplet-to-singlet intersystem crossing.

The third component, halogen bonding<sup>19</sup>, brings aromatic carbonyls and the heavy atom effect together in an unprecedented synergy. Chromophores designed to contain both aromatic aldehyde and bromine can exhibit strong halogen bonding in their crystal state. This bonding joins the bromine to the aldehyde oxygen of neighbouring molecules in a non-covalent interaction that delocalizes the oxygen electrons partially onto the bromine. This puts the heavy atom effect to work at the very site where the triplets are produced, amplifying triplet generation and activating triplet emission, phosphorescence. This net and unique effect is notably stronger than the typical heavy atom effect, and is considered a 'directed' heavy atom effect.

The directed heavy atom effect can be used as a design principle for metal-free organic phosphors (Fig. 1). Figure 1a shows aromatic aldehyde chromophores in solution (or any disordered phase), where there is no halogen bonding. Triplet generation is not optimal, which leads to fluorescence, and the vibrational loss of triplets is strong, making triplet emission inefficient or inactive. In Fig. 1b the same chromophore is now crystalline, with halogen bonding coupling the bromine and aldehyde. Triplets are now generated very efficiently, which suppresses fluorescence, and phosphorescence is activated by enhanced spin-orbit coupling to the ground state and reduced vibrational freedom of the aldehyde.

Figure 1c,d shows how more efficient directed heavy atom organic phosphors can be achieved by using a mixed crystal design. In Fig. 1c, crystals of pure chromophore emit directed heavy atom-enabled phosphorescence, but the quantum yield is modest, because self-quenching is rampant in this condensed phase. In Fig. 1d, a suitable host compound is designed to be a bi-halogenated, non-carbonyl analogue to the chromophore. This compound exhibits a similar crystal structure to the chromophore,

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**Figure 1 | Directed heavy atom organic phosphorescence and its design principle.** **a**, Halogenated aromatic aldehydes produce fluorescent emission in solution and disordered states. Triplets are generated, but not efficiently enough to prevent fluorescent singlet decay. Triplets are lost to vibration and no phosphorescence is emitted. **b**, In crystal form, halogen bonding between these chromophores delocalizes the electrons of the carboxyl oxygen partially towards the neighbouring halogen. Triplet generation is promoted, essentially quenching fluorescence. Vibrational freedom of the aldehyde is limited by tight packing, allowing triplets to decay emissively. Phosphorescent emission is achieved. **c**, The chromophore, a brominated aromatic aldehyde. In its highly ordered crystal, the directed heavy atom suppresses fluorescence and generates phosphorescence. Excimer formation is rampant, however, and self-quenching limits quantum yield. **d**, The host, a dibrominated analogue to the chromophore. The chromophore is diluted by substitution into the host crystal. The directed heavy atom effect again activates phosphorescence, but here the chromophores are isolated, preventing excimer-induced self-quenching. Quantum yield becomes much higher.

but does not interfere optically to contribute to self-quenching. When substituted into the host crystal matrix the chromophore is diluted, emitting much more efficient phosphorescence. The host provides a halogen-bonding, but non-quenching, scaffold for the chromophore. This design will be demonstrated empirically here.

## Results

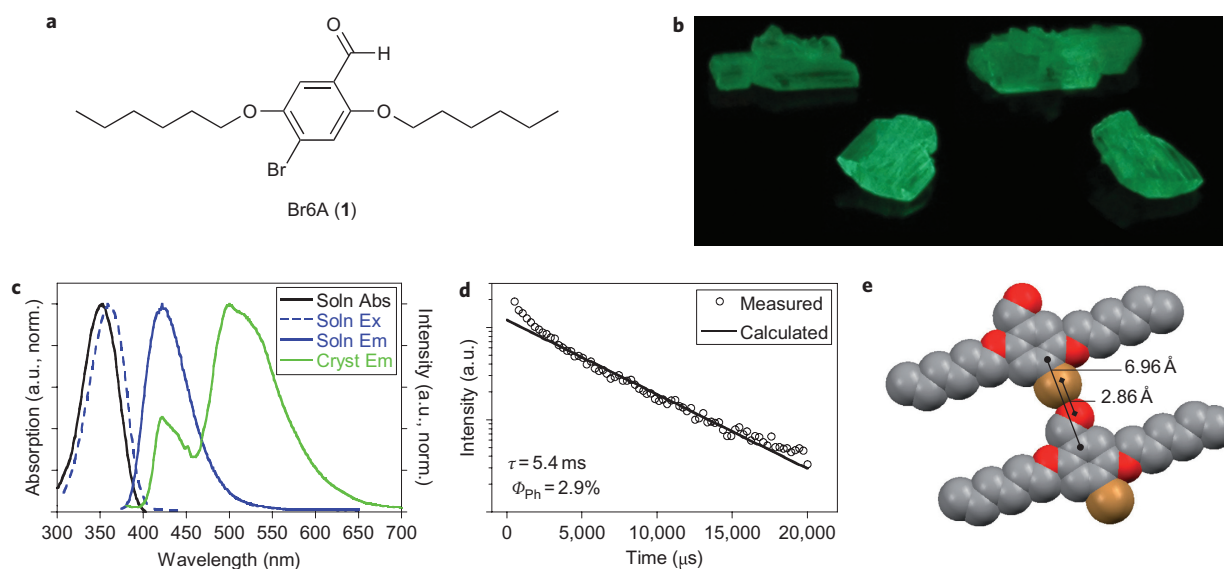
2,5-Dihexyloxy-4-bromobenzaldehyde (Br6A, **1**; Fig. 2a) is a simple and easily synthesized small molecule. The UV absorption spectrum of Br6A has its  $S_0 \rightarrow S_2$  band (Fig. 2c; commonly the lowest energy absorption for aromatic carbonyls,  $\pi - \pi^*$ ) at 360 nm. When in solution in chloroform and excited at 360 nm, this chromophore is weakly fluorescent, emitting at 420 nm with a quantum yield of 0.5% and lifetime of 0.5 ns. However, when again excited at 360 nm but in its crystal form, Br6A emits distinct green phosphorescence at 500 nm, with a phosphorescent quantum yield of 2.9% and lifetime of 5.4 ms (see Fig. 2b for a photograph, Fig. 2c for the spectrum, and Fig. 2d for the emission dynamics).

Single-crystal X-ray diffraction (XRD) was used to reveal the halogen bond that appears to be responsible for the green phosphorescence of Br6A crystals. Figure 2e shows the packing motif of Br6A, highlighting the extremely close contact between the carbonyl oxygen and the bromine of the neighbouring molecule. The  $C=O \cdots Br$  angle of  $126^\circ$  falls within the range of reported halogen bonds and is very close to the ideal of  $120^\circ$  (ref. 20). Measuring 2.86 Å, this is among the shortest bromine–oxygen halogen bonds

ever reported<sup>21</sup>, and clearly indicates a definite electronic interaction between the two atoms. So short is this distance that it is very reasonable to assume that such contact is rare in non-condensed states (that is, solutions). This, we hypothesize, is why phosphorescence is strong from Br6A crystals, but not detected from Br6A in solution (see Supplementary Movie for a demonstration of this; as crystals grow from the molten liquid phase the phosphorescence is activated in real time).

The ratio of phosphorescence to fluorescence is correlated to the quality of the crystal. As Fig. 3 shows, crystals grown from quick dropcasting predominantly exhibit fluorescence. As crystals are grown more slowly, and are thus of greater quality and higher order, phosphorescence increases to dominate fluorescence.

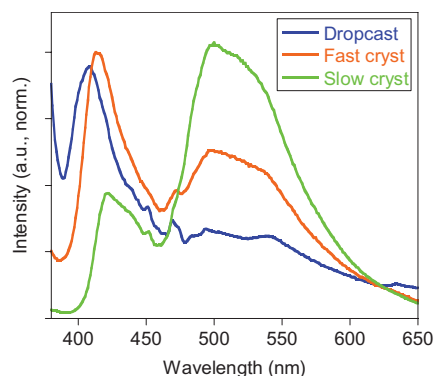
We suggest that the unusually short  $O \cdots Br$  interaction leads to a combination of effects that promote triplet emission. It may delocalize the excited-state electrons from the carbonyl oxygen to the outer orbitals of the heavy atom bromine, bringing those electrons closer to the bromine nucleus, promoting spin–orbit coupling and therefore singlet-to-triplet and possibly triplet-to-singlet ( $T_1 \rightarrow S_0$ ) intersystem crossing. This short bond may also prevent any vibrational freedom of the carbonyl by packing it tightly, preventing loss of the triplet to heat. Although the degree to which these individual effects contribute to the overall phenomenon is still unclear, the optical and crystallographic observations made here, in combination with the established understanding of the photophysics of aromatic carbonyl compounds and heavy atom effects, provide



**Figure 2 | Photophysical properties of Br6A (1).** **a**, Chemical structure of Br6A. **b**, Photograph of crystals of Br6A under 365 nm UV light. **c**, Normalized UV absorption of Br6A in chloroform (black solid trace), photoluminescence excitation of Br6A in chloroform (blue dashed trace), photoluminescence emission—fluorescence—of Br6A in chloroform (blue solid trace), and photoluminescence emission—mixed weak fluorescence and strong phosphorescence—of pure crystals of Br6A (green solid trace). **d**, Time-resolved measurement of 530 nm emission from Br6A crystals with fit to long-lived component. Lifetime and phosphorescent quantum yield are indicated. **e**, Diagram of Br6A crystal packing, highlighting the carbonyl oxygen-bromine distance defining the halogen bond. It is believed that this contact is responsible for the phosphorescence observed from Br6A crystals. Aromatic ring spacing is highlighted for later reference.

strong circumstantial evidence that a directed heavy atom effect is responsible for the bright phosphorescence observed.

Like other organic chromophores, Br6A suffers greatly from self-quenching. The metal-free organic phosphors that have been reported to date are strictly diluted to achieve the highest possible quantum yields, otherwise producing extremely weak or undetectable phosphorescence. Br6A crystals, in remarkable contrast, emit phosphorescence of appreciable efficiency despite being in the densest possible state of the chromophore. However, like those reported phosphors, Br6A does become a much more efficient emitter when diluted. Achieving this requires Br6A to be diluted into a crystal that features the same halogen-bonding motif without interfering optically. Luckily, as the bromine atom is similar in size to the aldehyde moiety, a simple approach exists for designing such a host material.

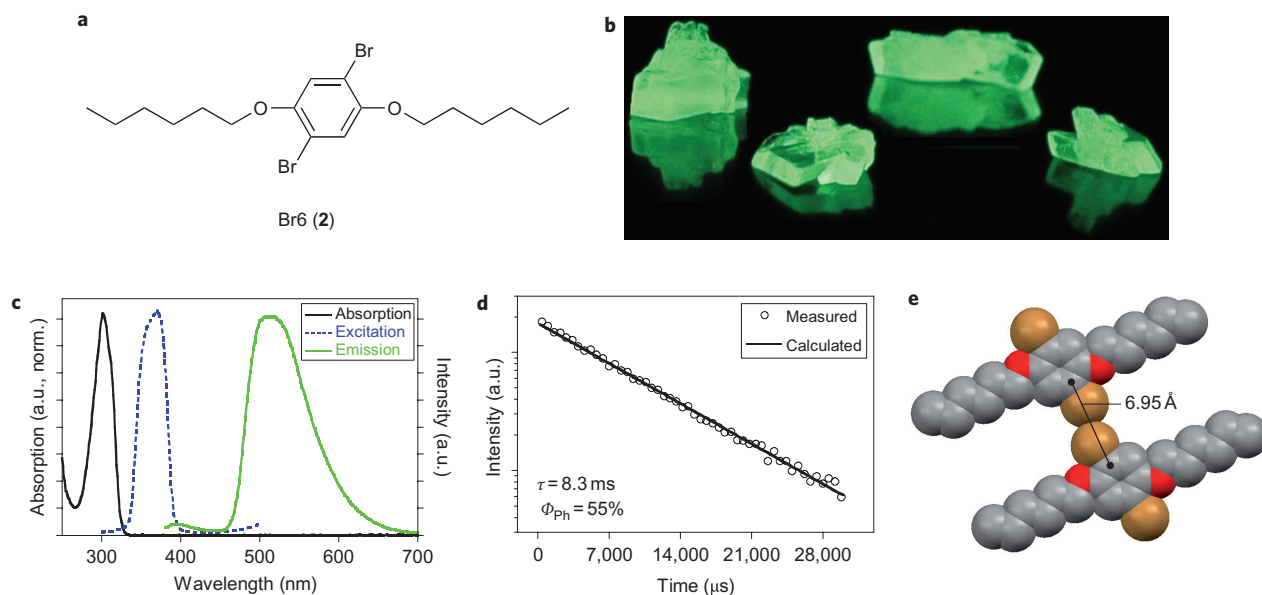


**Figure 3 | Dependence of emission on crystal growth.** Three crystal samples were prepared by different methods, and their emission spectra measured: dropcasting (poor order, blue trace), fast crystallization from methanol at  $-12\text{ }^{\circ}\text{C}$  (moderate order, orange trace), and slow crystallization from methanol at  $23\text{ }^{\circ}\text{C}$  (high order, green trace). Phosphorescence intensity increases as crystal order improves.

2,5-Dihexyloxy-1,4-dibromobenzene (Br6, **2**) is a bi-halogenated analogue to Br6A. As shown in Fig. 4a, Br6 is the same as Br6A, but with a second bromine in place of its aldehyde. Figure 4b shows that Br6 absorbs a narrow band at 300 nm, which is significantly higher in energy than the UV absorption of Br6A (360 nm). Br6 is also completely non-emissive in any form at room temperature. When Br6A and Br6 are crystallized together, the resulting mixed crystals exhibit green phosphorescence very similar to the phosphorescent portion of the spectrum from pure Br6A crystals but with a much higher quantum yield, as shown in Fig. 4c. As Fig. 4b also shows, these mixed crystals are excited only by a narrow band at 360 nm, which falls within the UV absorption band of Br6A, but not Br6, indicating that the emission comes from the Br6A in the crystal. When dropcast from chloroform solution onto glass, mixed crystals of Br6A/Br6 (with a composition optimized for quantum yield) exhibit phosphorescent quantum yields of  $55 \pm 3\%$  and lifetimes of 8.3 ms. This is shown in Fig. 4c,d. These mixed crystals contain  $\sim 0.001\text{ wt}\%$  and  $\sim 1\text{ wt}\%$  Br6A, respectively.

Investigation of the Br6 crystals using XRD revealed a motif very similar to that of Br6A. Figure 4e shows the crystal packing in the plane of the aromatic rings. A halogen-halogen interaction is observed, very similar to the halogen bonding seen in Br6A. Using the nearest aromatic carbons as a comparable trait, both Br6A and Br6 exhibit aromatic ring distances that are nearly identical (6.96 and 6.95 Å, respectively). This makes it highly plausible that Br6A is included into Br6 by substitution. XRD analysis of Br6A/Br6 mixed crystals containing  $\sim 10\text{ wt}\%$  Br6A revealed a unit cell identical to that of pure Br6 crystals.

Following this design principle, a small series of additional directed heavy atom phosphors were synthesized. By varying the electron density of the chromophore, the triplet level, and thus emission colour, were successfully tuned. BrC6A (**3**)/BrC6 (**4**), BrS6A (**5**)/BrS6 (**6**), and Np6A (**7**)/Np6 (**8**) were each designed to achieve this end. Figure 5a shows the structure of these compounds. BrC6A had the alkoxy substituents of Br6A replaced with alkyl, a less electron-donating moiety, to reduce the electron density of the chromophore. BrS6A, on the other hand, included thiol ethers



**Figure 4 | Photophysical properties of mixed crystals of Br6A (1) and Br6 (2).** **a**, Chemical structure of Br6 (2). **b**, Photograph of mixed crystals grown from slow evaporation of a 0.001 wt% Br6A/Br6 mix in hexanes solution, under 365 nm UV light. **c**, UV absorption (black trace), photoluminescence excitation (blue dashed trace), and photoluminescence emission (green solid trace) of the crystals shown in **b**. UV absorption comes from Br6, which constitutes over 99.99 wt% of the crystal, but excitation comes from Br6A (Fig. 2c). **d**, Time-resolved measurement of 530 nm emission from crystals dropcast from chloroform solution containing a 1 wt% mixture of Br6A to Br6, with lifetime and phosphorescent quantum yield indicated. **e**, Diagram of Br6 crystal packing, highlighting the aromatic ring distance. Note that the aromatic ring distances of both Br6A (Fig. 2e) and Br6 are practically identical at 6.96 and 6.95 Å, respectively. From this, it is reasonable to assume that Br6A, following substitution into Br6 crystals, has O···Br distances comparable to those in pure Br6A crystals.

to shift the emission to the red. Finally, Np6A had a naphthyl core to increase electron density (and conjugation length) even further. For each, a suitable host compound was also designed and synthesized, replacing the aldehyde with a second bromine atom (in reality, the aldehyde was synthesized from the dibromo host; see Supplementary Information). As Fig. 5b shows, mixed crystals of each pairing produced distinct colours: blue, green (for reference), yellow and orange. Figure 5c shows the exact spectral emissions of each (with the green of Br6A/Br6 again included for reference). Figures 5d–f shows the time-resolved photoluminescence emission of each crystal, together with their phosphorescent lifetimes, which are in the micro/millisecond phosphorescent regime. Each material was mixed at ~1 wt% aldehyde-to-dibromo to mimic the best conditions for the Br6A/Br6 crystal. Although they were not optimized individually for quantum yield, the chromatic phosphorescence from these mixed crystals demonstrated the applicability of the directed heavy atom design principle. With appropriate crystal design, it could be used for the creation of new metal-free organic phosphorescent materials.

## Discussion

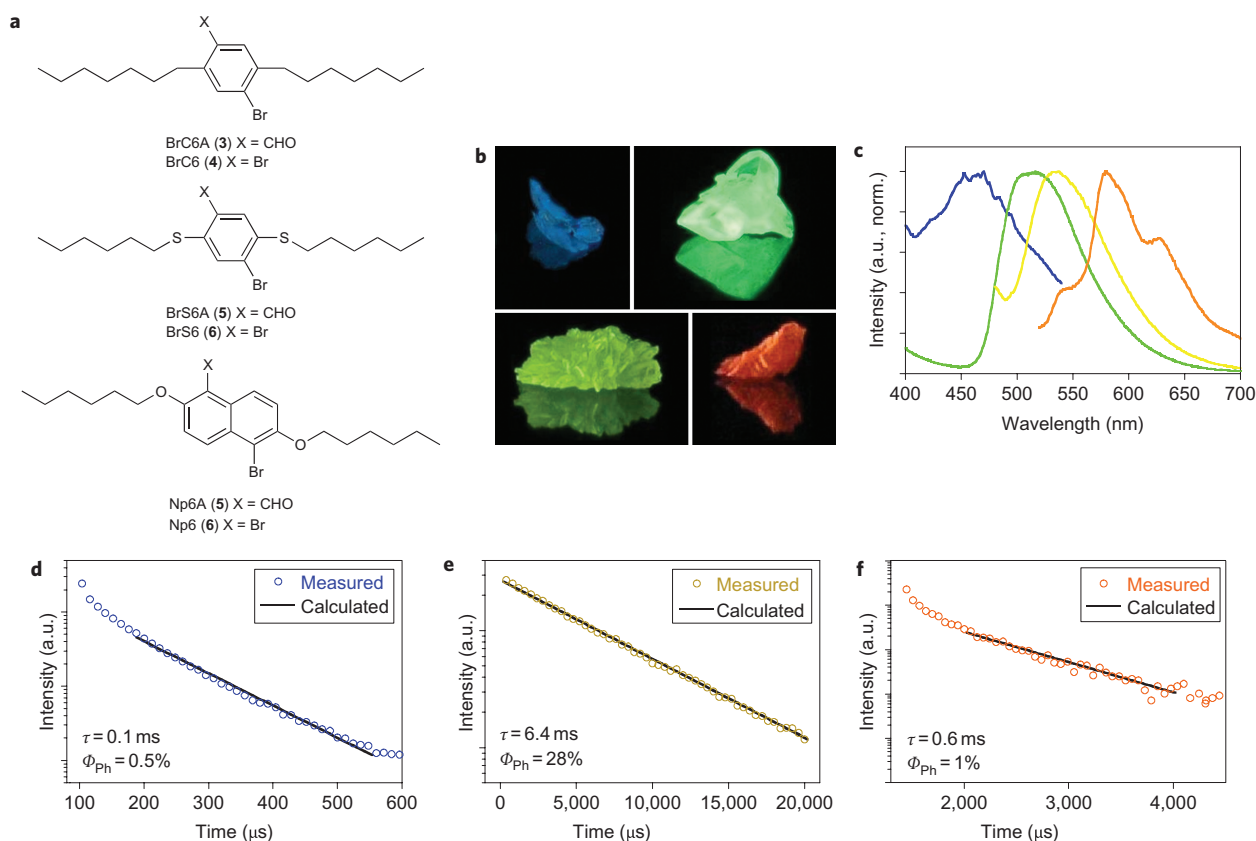
Although the accurate prediction of crystal structure from chemical structure is infamously difficult<sup>22</sup>, the examples given here offer a simple approach to creating novel directed heavy atom organic phosphors. Because of the similarity in size of the bromine atom and the aldehyde group, host–chromophore pairings can be designed from dibromo aromatics and their mono-aldehyde substituted analogues. As long as the dibromo compound exhibits a sufficient halogen–halogen interaction in its crystal, it is very likely that aldehyde will be a good candidate for substitution. Substituting aldehyde for a bromine atom in a halogen–halogen interaction creates the necessary halogen bond to enhance intersystem crossing and activate phosphorescent emission. Unfortunately, perfunctory attempts to use iodine in this capacity have failed to produce phosphorescent mixed crystals, presumably due to the larger size of the

atom preventing close contact to the aldehyde. The iodinated analogues of Br6 produced noticeably different crystal morphologies (when compared with Br6), and failed to yield phosphorescence when crystallized with their aldehyde counterpart.

It should be noted that although this design principle heralds a new class of phosphorescent materials for further exploration, those presented here were not designed with specific applications in mind. Br6A/Br6 crystals were discovered partially through serendipity, and the others were designed specifically for colour tuning and phenomenological assessment. These materials only represent the discovery of directed heavy atom phosphorescence and the first attempts at its application as a design principle. A list of potential applications for such materials would include organic electronics such as organic light-emitting diodes for display or ambient lighting, although more development would be needed to create directed heavy atom phosphors with higher conductivity and shorter exciton lifetime. Benefits for purely organic materials (as opposed to organometallics) may exist in terms of material cost, tunability (broader than organometallics, which struggle to achieve high-energy, blue phosphorescence) and device stability (there is no possibility of metallic impurities leading to defects or charge-traps). A more immediate application may lie in the field of sensors, where the conformational aspect of the directed heavy atom may be useful in detection motifs. The low-noise phosphorescent signal and potential reduced toxicity of purely organic structures may also give these materials a unique benefit in biosensing.

## Conclusions

In summary, we have defined a new phenomenon and design principle for making bright and purely organic phosphors. This opens up the broad class of pure organic compounds to new applications in phosphor design. The halogen bonding present in crystals of brominated aromatic aldehydes directs the heavy atom effect to the active triplet site of the chromophore, enhancing intersystem crossing and reducing vibrational losses at the carbonyl to activate



**Figure 5 | Photophysical properties of colour-tuned aromatic aldehydes.** **a**, Structures of hosts/aldehydes designed to produce shifts in emission wavelength. **b**, Photographs of BrC6A/BrC6, Br6A/Br6, Np6A/Np6 and BrS6A/BrS6 (clockwise from top left) mixed crystals, each containing  $\sim 1$  wt% aldehyde chromophore and 99 wt% analogous host compound. Crystals are shown under 365 nm UV light. **c**, Normalized photoluminescence emission spectra of BrC6A/BrC6 (blue trace), Br6A/Br6 (green trace, repeated for reference), BrS6A/BrS6 (yellow trace) and Np6A/Np6 (orange trace) crystals. **d**, Time-resolved measurement of 460 nm emission from dropcast BrC6 crystals containing  $\sim 1$  wt% BrC6A. **e**, Time-resolved measurement of 540 nm emission from dropcast BrS6 crystals containing  $\sim 1$  wt% BrS6A. **f**, Time-resolved measurement of 580 nm emission from dropcast Np6 crystals containing  $\sim 1$  wt% Np6A.

phosphorescent emission. Diluting this aldehyde chromophore into an easily designed host crystal with a similar halogen-bonding motif allows for a pronounced increase in phosphorescent quantum yield through a reduction in self-quenching. Here, room-temperature phosphorescent quantum yields have already been seen to reach 55%, in this first report of such a material. Through the colour-tuning series presented here, this directed heavy atom design principle has been shown to hold promise as a versatile means with which to activate phosphorescent emission from pure organic materials, potentially toppling another barrier between the functionalities of pure organics and inorganics/organometallics.

## Methods

All reagents were purchased from Sigma-Aldrich, with the exception of di-*n*-hexyldisulfide and 1,4-dibromobenzene, which were purchased from Alfa Aesar. All reagents were used as purchased without additional purification. For more explanation of the synthetic methods, purity data and crystallography, see the Supplementary Information.  $^1\text{H}$  NMR (nuclear magnetic resonance) spectra were collected on a Varian Inova (500) equipped with a Varian indirect detection probe, and  $^{13}\text{C}$  NMR spectra were collected on a Varian MR400 equipped with a Varian 5 mm PFG AutoX Dual Broadband probe. Deuterated solvents were purchased from Cambridge Isotope Labs.

UV absorption data were collected on a Varian Cary 50 Bio spectrometer. Photoluminescent excitation and emission spectra, as well as quantum yields, were collected on a Photon Technologies International (PTI) QuantaMaster equipped with an integrating sphere. Phosphorescent lifetime data were collected using a PTI LaserStrobe using samples dropcast as described below for use in quantum yield measurements. Quantum lifetime calculations were carried out on the Felix32 software partnered with the PTI equipment.

Quantum yields were measured using an integrated sphere for which the accuracy was verified using a 10  $\mu\text{M}$  Rhodamine 6G/ethanol solution<sup>23</sup>. Samples for quantum yield measurement were prepared by dropping 0.1 g ml<sup>-1</sup> 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 were 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  $\pm 1$  s.d. (standard deviation).

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### Author contributions

O.B. synthesized all materials and crystals, made all photophysical measurements and analyses presented, and wrote the paper. K.L. made the initial discovery of phosphorescence. H.-J.K. assisted in early optical analyses. K.Y.L. conducted high-performance liquid chromatography to identify the aldehyde structure. J.K. designed and supervised the research and oversaw the writing of the paper.

### Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at [www.nature.com/naturechemistry](http://www.nature.com/naturechemistry). Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>. Correspondence and requests for materials should be addressed to J.K.

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After the publication of this Article the authors found a further relevant paper that they would like to cite. The paper reports crystallization-induced rotational restriction of benzophenone derivatives and ensuing phosphorescence enhancement: Yuan, W. Z. *et al.* Crystallization-induced phosphorescence of pure organic luminogens at room temperature. *J. Phys. Chem. C* **114**, 6090–6099 (2010).