Organic color-tunable and bright phosphors

Onas Bolton and Jinsang Kim

A new molecular design principle makes highly emissive, tunable, and metal-free phosphorescent materials.

When the spin of an excited electron is reserved it is referred to as an excited singlet state. Alternatively, if the electron spin is reversed during excitation, the molecule is described as the triplet state. Fluorescence is the rapid energy emission (as light) from the singlet state, whereas phosphorescence is the slow emission phenomenon from the triplet state. Most organic (i.e., non-metallic) compounds are very poor phosphorescent emitters and typically achieve efficiency of mere single percentages. The reason for this is the highly bonded nature of electrons in these compounds, which leaves little freedom for emission from triplet states. As a result, the field of phosphorescence research has focused almost exclusively on organometallic compounds.

In contrast to organic phosphors, metal-containing compounds can be extremely efficient phosphors, with many approaching unity (i.e., 100% emission efficiency). However, organic phosphors are increasingly in demand for applications such as cancer detection and organic LEDs because organic materials are inexpensive. Despite this, the infinite design flexibility of purely organic compounds has largely been left unexplored as researchers labor to push the limits of organometallic compounds. In contrast to organic phosphors, metal-containing compounds can be extremely efficient phosphors, with many approaching unity (i.e., 100% emission efficiency). However, organic phosphors are increasingly in demand for applications such as cancer detection and organic LEDs because organic materials are inexpensive. Despite this, the infinite design flexibility of purely organic compounds has largely been left unexplored as researchers labor to push the limits of organometallic compounds.

Here, we describe a new design principle to create purely organic materials that demonstrate tunable phosphorescence using in-crystal halogen bonding.

While phosphorescence from purely organic materials is not impossible, it is currently impractical. Achieving emission from metal-free, purely organic compounds requires chemical functionalities—such as aromatic carbonyl, halogens, and arenes—to generate triplet states. Additionally, these functionalities must be contained in environments that restrict vibration to prevent the generated triplets from being lost as heat. To realize the latter, temperatures of liquid nitrogen (77K, −196°C) are typically required. These stringent requirements have thus precluded organic phosphors from consideration in commercial applications. To circumvent this, we have designed rigid crystals that restrict the vibration of the phosphorescent functionalities, thus preventing triplet state loss as heat.

We chose brominated benzaldehydes as our chromophores because aromatic carbonyls efficiently generate triplets. We included bromine in the structure because halogens—when in proximity to a phosphorescent chromophore (for example, benzaldehydes)—are known to promote phosphorescence generation in a phenomenon known as the heavy atom effect. Within the crystal, halogen bonding occurs between the aldehyde oxygen and bromine atoms of adjacent molecules, bringing the two functional groups in close contact (see Figure 1).

Our prototype chromophore, 2,5-dihexyloxy-4-bromobenzaldehyde (Br6A)—see Figure 2—emits blue fluorescence when in solution, but green phosphorescence when crystalline. The extended network of halogen bonding both enhances the heavy atom effect as well as binds the molecules tightly to prevent vibration. The result is a brightly phosphorescent crystalline material. We observed that the phosphorescence efficiency was correlated to the crystal quality, where the highest quality crystals of Br6A benefit from improved packing of the molecules. This

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gives improved halogen bonding and subsequent phosphorescent quantum yields of 2.9%. Our result was modest relative to organometallic phosphors, but several orders of magnitude higher than most purely organic emitters.

In its crystalline form, Br6A is highly condensed and thus suffers from concentration self-quenching. Dilution is generally seen as a remedy to this problem. However, to maintain the ordered nature of the Br6A crystals, we required a compound that features the same halogen bonding motif. Furthermore, the diluting compound should not interfere optically with the phosphorescence of the chromophore. To that end, we selected 2,5-dihexyloxy-1,4-dibromobenzene (Br6) as the host (see Figure 2). This host substitutes the aldehyde moiety of Br6A with a bromine atom, which is of comparable size so as to not disturb the crystal structure. Br6 also allows for phosphorescence-enhancing halogen bonding while isolating the chromophores so that they do not suffer from self-quenching. With contents of roughly 1% by weight Br6A, the mixed crystals produced improved quantum yields of ~55%.

Based on our success with Br6A and Br6, we established a general molecular design principle for purely organic phosphors. We found that a halogenated aromatic aldehyde chromophore doped in an analogous bis-halogenated aromatic host can produce a bright organic phosphor. We can change the electron density by varying the side chain or extending the conjugation of the aromatic core, allowing us to tune the color of the phosphorescent emission. We designed, synthesized, and realized blue, yellow, and orange purely organic phosphors, demonstrating the applicability of this design principle for future organic phosphor research (see Figure 3).

In summary, we have designed and synthesized purely organic phosphorescent crystals that demonstrate the highest quantum yields to date for non-metallic compounds. Our flexible molecular design principle promises purely organic phosphors may soon be competitive and practical alternatives to organometallic compounds. We are currently developing these prototype compounds into materials more suitable for electronic and sensing applications.

**Author Information**

Onas Bolton and Jinsang Kim  
Department of Materials Science and Engineering  
University of Michigan  
Ann Arbor, MI

Onas Bolton received his PhD in 2009 under the supervision of Jinsang Kim. He is currently working as a postdoctoral researcher in the laboratory of Adam Matzger.

Jinsang Kim earned his PhD from Massachusetts Institute of Technology and underwent postdoctoral training at the California Institute of Technology. He is currently an associate professor.

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References


