

Ultralong Organic Phosphorescence: A Molecular Design Challenge

Justin Malme

Literature Seminar

October 14, 2021

Materials that exhibit long-lived, intense and efficient phosphorescence are desirable for their potential applications in optoelectronics, chemical sensing, and data security, but most substances with these properties contain metals, reducing biocompatibility and increasing cost compared to purely organic systems.¹ Purely organic materials generally do not exhibit phosphorescence because the weak spin-orbit coupling is unable to overcome the energy barrier of the prohibited triplet-singlet transition required for photoemission, so that relaxation occurs instead by nonradiative, thermal decay pathways.² Still, with effective molecular design, these internal barriers can be overcome, and highly efficient, long-lived phosphorescence has been attained with purely organic systems. Design schema include restricted motion from crystallization,³ aromatic carbonyls, heavy atoms,⁴ and donor-acceptor pairing.⁵

A surprising feature of ultralong organic phosphorescence materials is their tendency to exhibit the longest-lived, most intense emissions when in the crystalline phase. This behavior is a departure from a generally-accepted phenomenon known as aggregation-induced quenching, in which a photoluminescent material exhibits weaker emission when made into a solid, owing to the formation of excimers.⁶ These long-lived emissions are thought to arise from a mechanism similar to that responsible for the ability of some molecules that exhibit phosphorescent emission when cooled rapidly to low temperatures,⁷ in which molecular vibrations, as well as intermolecular interactions with ambient molecules are suppressed, eliminating nonradiative decay pathways.

Yuan et al. demonstrated the above phenomenon with a variety of benzophenones and their halogen-substituted derivatives (Figure 1), exhibiting emissive lifetimes of up to 4.8 ms with quantum yields of up to 12%.⁴ Solutions of these benzophenones were not emissive at room temperature, nor were they emissive when adsorbed on a TLC plate or doped into a polymer film, but became strongly emissive when cooled in solution to 77 K.⁴ When crystallized, unsubstituted benzophenone exhibited strong blue phosphorescence at room temperature, with a lifetime of 316.5 μ s.⁴ The photoluminescence spectrum of the crystalline benzophenones contained the same peaks at 420, 449, and 483 nm as the 77 K solution-phase molecule, suggesting that the mechanism responsible for the emission was the same in both.⁴ X-ray crystallography studies demonstrate that the molecules assume a twisted conformation, and are locked in place by strong C-H...O interactions, as well as C-H...X (X= Cl, Br) and unusual C-Br...Br-C interactions in the case of halogen-substituted derivatives.

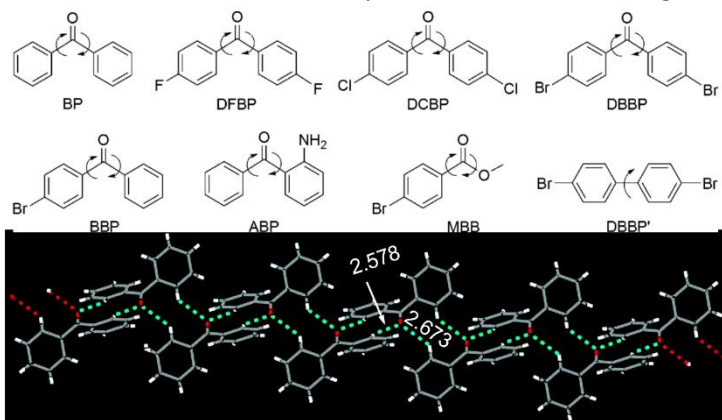


Figure 1: Benzophenone derivatives and view of molecular packing of benzophenone from Yuan, et al.⁴

The incorporation of heavy halogens into these aromatic carbonyl compounds resulted in the longest lifetimes, and Bolton et al. extended this strategy by designing molecules with both aromatic

aldehydes and nearby aromatic bromines that combine the spin-orbit coupling of an aromatically-positioned oxygen atom with the heavy atom effect.³ The resulting molecules pack with strong ordering from halogen bonding, and enhance singlet-triplet mixing near to the oxygen, resulting in increased triplet generation and emission.³ Impressively, some of Bolton's compounds exhibit a surprisingly 55% quantum yield and a lifetime of 8.3 ms.³

The heavy atom effect and spin-orbit coupling alone, however, are not enough to cause a substance to become phosphorescent. Gong, et al. studied bromine substitution in certain carbazole-derivatized benzophenones; their idea was that these electron donor-acceptor molecules combined the desirable high triplet energy of carbazole with the crystal-induced phosphorescence of benzophenone.¹ Surprisingly, they found that bromine substitution caused a nearly thousand-fold decrease in phosphorescent lifetime. Specifically, the unsubstituted molecule exhibits a phosphorescence lifetime of 517.87 ms with a 1.4% quantum yield, whereas the di-brominated molecule exhibits a lifetime of 0.16 ms and a 7.5% quantum yield.¹ Their explanation of this difference was that the unsubstituted molecule packs more tightly and forms larger crystals than the bromine-substituted molecules. This result implies that spin-orbit coupling plays a large role in quantum efficiency, but that crystal packing and the suppression of molecular motion is the dominant factor in determining the lifetime of a phosphorescent organic molecule.

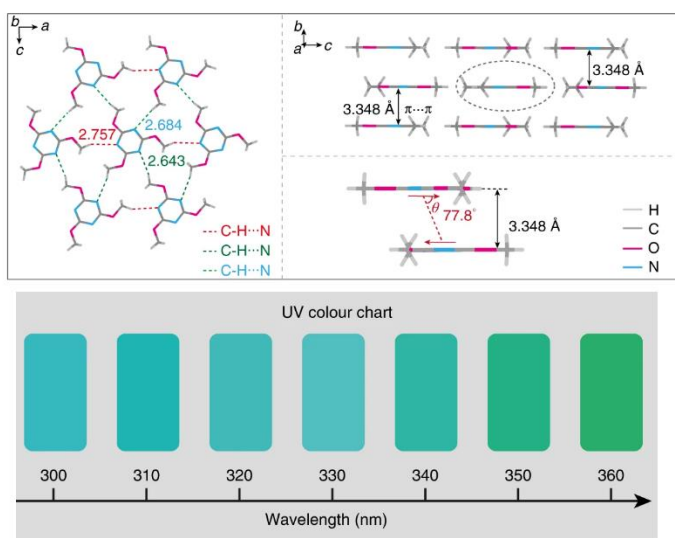


Figure 2: Packing (top) and wavelength-dependent emission (bottom) of triazine derivatives from Gu, et al.¹⁰

In a survey of other boronic esters, they found that 14 of the 19 they studied exhibited phosphorescence at room temperature, but the effects of the crystal structure on the phosphorescence of these molecules remained unclear.⁹

Gu, et al. demonstrated a triazine-based molecule capable of wavelength-dependent phosphorescence of different colors, ranging from blue to green (Figure 2) with a maximum lifetime of 0.75 s and a maximum quantum efficiency of 31.2%.¹⁰ Similar to the behavior seen in carbon dots, the

Pan, et al. observed similar results in a supramolecular assembly, in which the quantum efficiency of their π - π stack-based packing system was enhanced from >1% to 17% by the introduction of heavy atoms, but the emission lifetime plummeted from 420 ms to 9.0 ms.⁸

Other types of organic molecules can also exhibit long phosphorescent lifetimes. Shoji, et al. demonstrated that a crystalline phenylboronic ester exhibits low-efficiency phosphorescence with a lifetime of 1.79 s.⁹ In a computational study, they found that this long lifetime likely arises from the high spin-orbit coupling constant of a structurally-deformed triplet state, stabilized by the boron functionality.⁹ In a

color variation is attributed to different emission centers forming at different wavelength due to the strong H-aggregation, a type of packing in which molecules are oriented with molecular planes parallel to each other,¹¹ which is also responsible for the long room temperature phosphorescence.¹⁰ Cai, et al. demonstrated a bovine gelatin-based porous foam exhibiting a surprising lifetime of 485.8 ms, in which the phosphorescence was attributed to carbonyl aggregates in the gelatin structure (Figure 3).¹² They argued that the luminescent centers of the foam were vibrationally restricted by the multiple hydrogen bonds formed, leading to the long lifetime.¹²

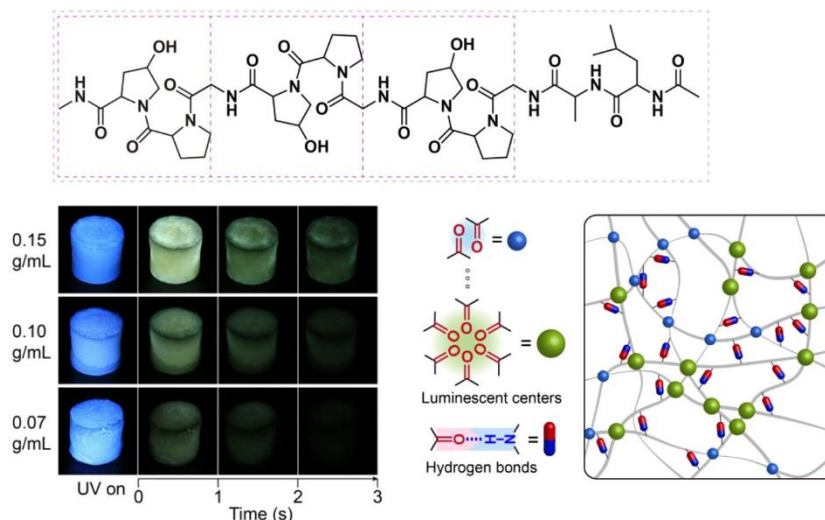


Figure 3: Molecular structure of Bovine gelatin foam (top), phosphorescence of foam (bottom left), and packing of the foam with attribution of phosphorescent centers from Cai, et al.¹²

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Although ultralong organic phosphorescent materials have been studied for just over a decade, there is still much room to design new phosphorescent organic molecules, guided by these earlier works. Seconds-long lifetimes have been attained thus far, albeit with low quantum efficiency. Whereas a rigid, tightly-packed structure seems to be a requirement for making the requisite triplet state accessible,¹ utilizing the heavy atom effect and other triplet-stabilizing or singlet-triplet mixing design features is key to creating systems with high quantum efficiency.³ Furthermore, more focused X-ray crystallographic and computational studies ought to be undertaken to elucidate the exact mechanisms by which these crystals dampen molecular vibrations, and whether or not crystal packing itself can result in more fine spin-orbit coupling and singlet-triplet mixing.

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