Continuous Tuning of Organic Phosphorescence by Diluting Triplet Diffusion at the Molecular Level

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ABSTRACT: Organic long-persistent phosphorescent materials are advantageous due to the cost-effectiveness and easy processability. The organic phosphorescence is achieved by the long-lived triplet excitons, and the challenges are recognized regarding the various nonradiative pathways to quench the emission lifetime. Taming long-lived phosphorescence is generally engaged with the charge-transfer or exciton diffusion in molecular stacking to stabilize triplet excitons or form a

photo-induced ionized state. Herein, we elucidate that the triplet-diffusion can cause a significant quenching that is not thermally activated by using a system of perfluorinated organic complexes. Hence, we suggest a co-evaporation technique to dilute a single phosphorescence-emitting molecule with another optically-inactive molecule to suppress the diffusion-induced quenching, tuning the phosphorescence lifetime and spectral features continuously. The work successfully suggests a general semi-theoretical method of quantifying the population equilibrium to elucidate the loss mechanisms for organic phosphorescence.

TOC GRAPHICS

Continuous Tuning of Phosphorescence Lifetime:
~ 0.09 s to ~ 0.2 s

Dilution in Co-Doped Thin Film
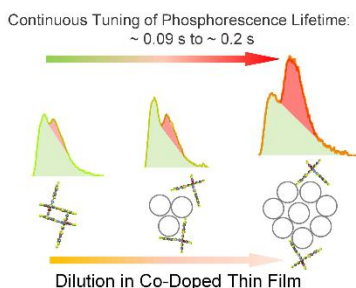
KEYWORDS Spectroscopy, Thin-film, Triplet-triplet annihilation, Perfluorinated Compounds, Co-doping Method, Population Equilibrium

Organic phosphorescence has become of great interest in functional and cost-effective optical applications such as energy storage, advanced anti-counterfeiting, bioimaging, and sensors, *etc*. The phosphorescence is emitted from a triplet-to-singlet ground state transition that is spin-forbidden, and the long-persistence tends to make triplet excitons to suffer from several non-radiative deactivation pathways to fade the phosphorescence. Thermally activated quenching[1] has been a known problem, although the cryogenic temperature can suppress this nonradiative pathway, which restricts practical applications. Hence, several approaches regarding material design have been suggested to realize ultralong phosphorescence, up to hours lifetime, at room temperature by introducing H-aggregation[2], photo-induced ionized state[3], molecular packing[4,5], chemical cross-linking[6], and halogen bonding[7]. These approaches commonly rely on molecular aggregation[8–10], where triplet exciton diffusion becomes a considerable consequence[11]. The improved exciton diffusion could favor the possibility of an exciton-interaction that might cause self-quenching, for instance, triplet-triplet annihilation (TTA) that is intrinsic rather than a thermally-activated process. However, this quenching effect and mechanism are less evident in this field. Herein, our study elucidates that TTA is a considerable loss for the phosphorescence. Nonetheless, we provide a simple co-evaporation technique to dilute the exciton diffusion to suppress the loss. Consequently, it is realized that the phosphorescence emission lifetime and spectral features are tuned continuously on a single perfluorinated organic compound.

At photoexcitation, triplet excitons are formed via intersystem crossing (ISC). Two mechanisms can lead to the ISC. One is the heavy atom effect, where the coordinated metallic ions and the halogen atoms can both improve spin-orbit coupling. Alternatively, the ISC can be triggered by inter-molecular interaction[12] that is also responsible for the exciton diffusion. We thus choose an organic metallic complex, Zinc (II)

tetrafluoro(hydroxyphenyl)tetrafluorobenzothiazoles: Zn(FBTZ)$_2$, where two F-BTZ$^-$ ligands in a single molecule nearly are perpendicular in orientation with a poor inter-ligand packing[13]. This would allow the ISC to be mainly activated by the heavy-atom effect of a large number of fluorine atoms that can interact with the excited states instead of the inter-ligand packing. A deposited film of the pure material is likely to form some molecular stacking. This might explain the slight shift of the absorption maxima and additional trivial absorption band over a range of ~ 550 nm to 700 nm, which would form some trapped singlet states[14] compared to the absorption of the complex diluted in solution, shown in **Figure 1a**.

To interrupt the molecular stacking, we employ a co-evaporation technique[15] to co-dope Zn(FBTZ)$_2$ with an inactive molecular complex that can be treated as a molecular barrier[12] to prevent the exciton diffusion among Zn(FBTZ)$_2$ molecules. The molecular barrier we chose is the tetrakis(pentafluorophenyl)imidodiphosphninimidic complex of yttrium, Y(F-TPIP)$_3$, which is optically inactive at UV-visible-IR wavelengths.[16] The co-evaporation technique is described in the Supporting Information (SI), and it allows two complex molecules to be composited at the molecular level with accurate control of the doping ratios. In a series of co-doping films, the Zn(FBTZ)$_2$ can be continuously diluted from a molar ratio of 91% to 20%.

In a 20% Zn(FBTZ)$_2$ co-doped film, decreasing temperature gradually introduces additional photoluminescence (PL) band at long wavelength, shown in **Figure 1b**. Meanwhile, its intensity reduces when the temperature increases to 300 K. At 80 K, the time-resolved PL curve recorded at 550 nm wavelength gives an average emission lifetime of ~ 225 ms, indicating that the emission results from phosphorescence compared to a ~ 10 ns fluorescence recorded at 500 nm wavelength. In a fully fluorinated material system, the phonon energy due to bond vibration[16,17] and inter-molecular vibration[18] is < 1360 cm^{-1}, which is inconsistent with the emission energy of

> 18,000 cm^{-1}. According to the energy gap law, we can exclude the possibility of a thermal quenching for the $T_1 \rightarrow S_0$ transition. The phonon energy is approximately resonant with the energy gap between the S_1 and T_1 level. Therefore, the thermal quenching for the $T_1 \rightarrow S_0$ transition can be dominated by the thermal-activated delayed fluorescence, which is rational to be eliminated at a low temperature.

With the dilution gradually tuned by controlling the doped Y(FTPIP)$_3$ concentration, we found a continuous tuning of the phosphorescence lifetime and spectral features at 80 K. shown in **Figure 2**. This modulation allows a continuous tuning of the average emission lifetimes from ~ 96 ms to ~ 225 ms. The nearly linear response of the average emission lifetimes to the Zn(FBTZ)$_2$ concentration below 60% might imply the uniformity of the molecular-level composition of two materials within the dilution region. The fitting data are listed in **Table S1**. The temperature dependent PL of the 20% Zn(FBTZ)$_2$ film allows us to calculate that the ISC rate (R_{ISC}) is ~ 3.9 × 10^7 s^{-1} corresponding to the order of ~ 25 ns. This value is comparable to the fluorescence lifetime of ~ 10 ns. The calculation details can be found in the SI. At 80K, the reverse-ISC rate is estimated to be small enough to be negligible. Thus the quenching effect for the T_1 states can be dominated by the TTA rate, R_{TTA}, which will partially repopulate the S_1 states (SI). In Figure 2, the R_{TTA} value for the 91% Zn(FBTZ)$_2$ doped film is ~ 5.76 s^{-1}, which is similar to the estimated triplet emission rate (R_T) of ~ 4.75 s^{-1}, indicating the TTA can significantly quench the T_1 state population leading to shortening of the phosphorescence lifetime. However, once the Zn(FBTZ)$_2$ is diluted linearly to 20%, the molecular stacking is spatially interfered to reduce the R_{TTA} to be < ~ 0.22 s^{-1}, shown in Figure 2 and **Table S2**. This rate is reduced to be within the experimental error of measured phosphorescence emission rate, and it is negligible for the quenching mechanism. Using the fitted

parameters can give the calculated phosphorescence peak intensities, indicated by the empty circles in **Figure 3**, which agree with the experimentally extracted PL data.

The time-resolved PL curves shown in **Figure S1** indicate there are two exponential components in the decays which can both be tuned by the dilution. It is rational to consider that molecular grains can form for each material when they are co-deposited onto a room-temperature substrate.[16,19] Thus, even for 20% Zn(FBTZ)$_2$, we believe that the TTA pathway might be still valid inside some Zn(FBTZ)$_2$ grains that lead to the short-lifetime component ($\sim$ 8 ms to 33 ms). These trivial stacking might also explain the small blue-shift of the phosphorescence peak for 91% Zn(FBTZ)$_2$ and small distortions of the phosphorescence spectral features at various dilutions, shown in Figure 3. Nevertheless, this short-lifetime component takes up $\sim$ 10%, implying the most of Zn(FBTZ)$_2$ molecules are spatially separated.

In conclusion, the TTA process is competitive to consume the population of excited triplet states to quench the phosphorescence. Thus the TTA needs to be considered as a significant quenching effect for a long-persistent organic triplet emitting material. Our study demonstrates that diluting the phosphorescent materials at the molecular level using a co-evaporation technique is an effective way to suppress the TTA-induced quenching. The results demonstrate a continuous tuning of the phosphorescence lifetime and spectral feature using a single organic triplet emitting material in a solid-state film. Our results also provide a semi-theoretical modeling and experimental method to simulate the quenching effect for the newly synthesized long-persistent organic emitting materials in future.
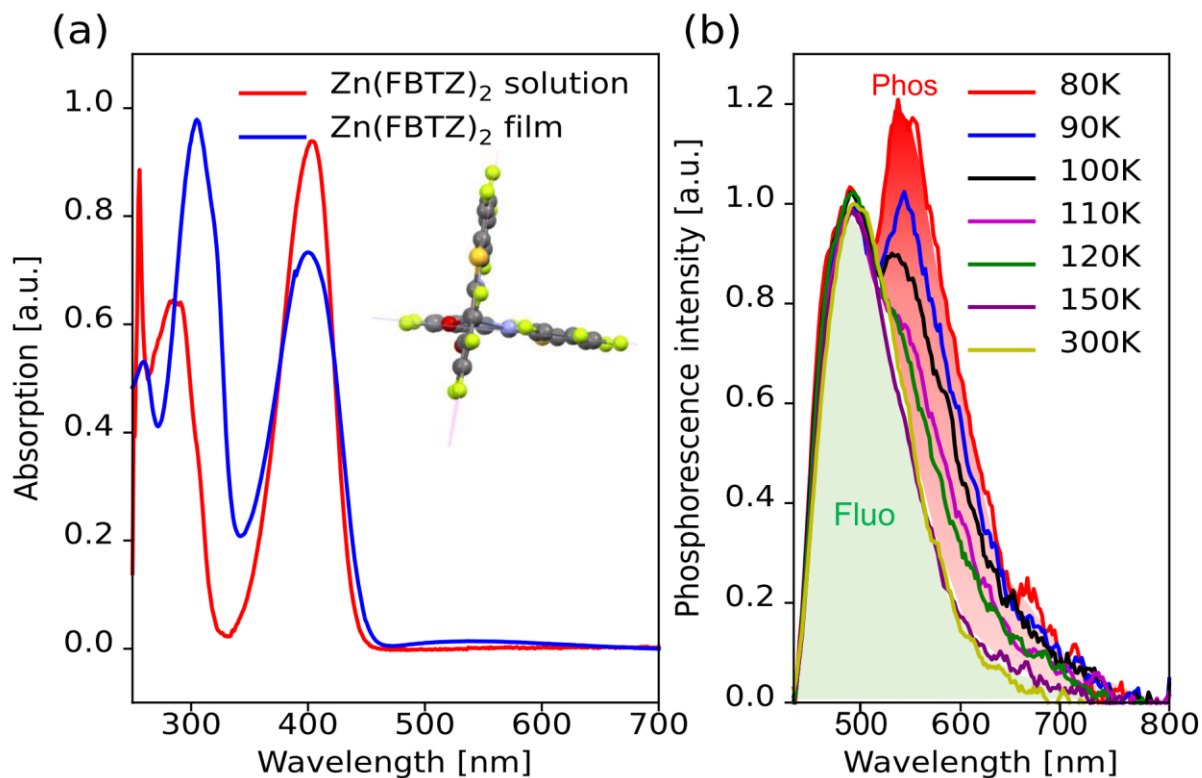
Figures and Captions:

Figure 1. (a). Absorption spectra of the Zn(FBTZ)$_2$ in CHCl$_3$ (2.34×10^{-6} M) and a 250 nm Zn(FBTZ)$_2$ film. The inset is the Zn(FBTZ)$_2$ molecular structure extracted from a crystallographic data (CCDC number: 873937). (b) The temperature dependent PL spectra of a 20%-Zn(FBTZ)$_2$-80%-Y(FTPIP)$_3$ film. The green region indicates the fluorescence (Fluo) and the red region indicates the phosphorescence(Phos). Photoexcitation: 405 nm CW laser, 10 mW. The smoothed PL spectra are provided, and the original spectral data are provided in the SI.
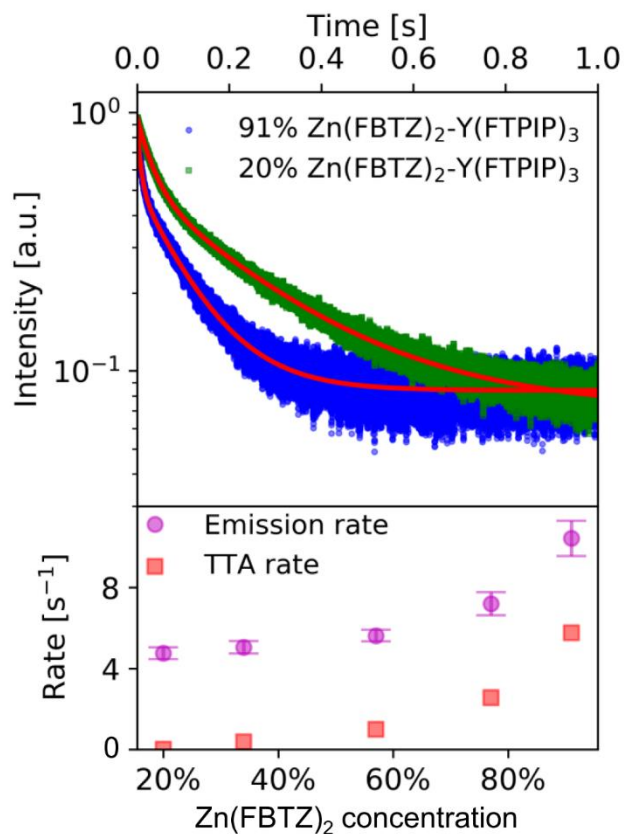
Figure 2. Upper Plot: The time-resolved PL decay of a 20%-Zn(FBTZ)$_2$ and 91%-Zn(FBTZ)$_2$ film at 80 K. The red lines are the dual exponential fits to the data. The original spectral data for all samples are provided in the SI. Lower Plot: the phosphorescence emission rate, $1/\bar{\tau}_T$, which is calculated from the average emission lifetimes, and the TTA rate, R_{TTA}, which is obtained from the fitting (SI), are plotted with the Zn(FBTZ)$_2$ concentration in molar ratios.
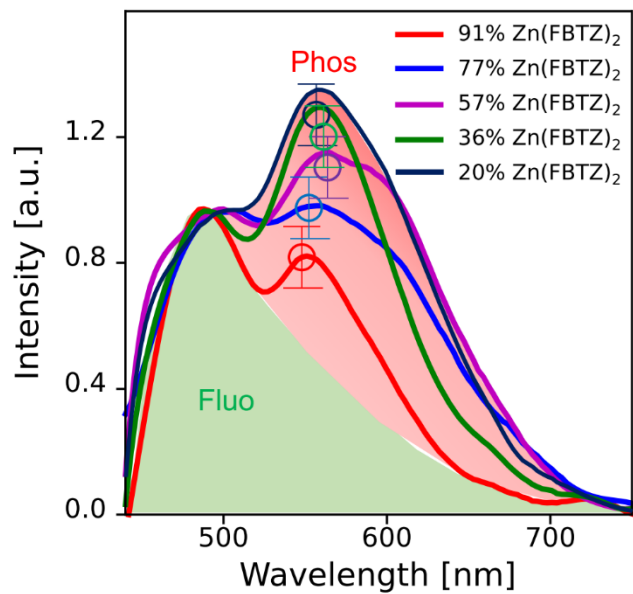
Figure 3. The Zn(FBTZ)$_2$ dilution dependent PL spectra measured at 80 K. The green region is the fluorescence (Fluo) and the phosphorescence (Phos). The colored empty circles indicate the calculated phosphorescence peak intensities.

ASSOCIATED CONTENT

Supporting Information. Further details of material information, population equilibrium modeling, Table S1-to-S2, and Figure S1-to-S3 are available in the supporting information.

AUTHOR INFORMATION

Notes

J.X.H and H.Q. Ye contributed equally to this work.

The authors declare no competing financial interests.

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