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Reversible control of triplet dynamics in metal-organic framework-entrapped organic emitters via external gases

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Triplet excitons play an important role in the physics of organic emitters used in organic light-emitting diodes, bio-imaging, and security inks. Triplet exciton dynamics is influenced by the emitters and the environment surrounding them, but there is no effective way to alter triplet dynamics using external triggers. Here we demonstrate rapid and reversible control of the triplet dynamics of the emitter coronene via an external heavy-atom effect induced by external gases. Strong interaction between the emitter molecule and gases is achieved by encapsulating the emitter in a metal organic framework. Exposure to xenon, which has a large spin-orbit coupling, accelerates the radiative decay of triplets, leading to a stronger phosphorescence that decays more quickly than under vacuum. By contrast, excitons can be non-radiatively quenched through exposure to oxygen. This fast and reversible regulation of triplet dynamics may provide a new platform for responsive photo-switches, optical storage, and molecular computers.

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Triplet excitons of organic molecules used as phosphors^{1,2} and photo-absorbers^{3,4} play an important role in the physics of optoelectronic devices, such as organic light-emitting diodes^{5–7} and photovoltaics⁸. Devising new ways to control triplet excitons will help advance the development of a wide variety of emitters⁷, photo reactions^{9,10}, and organic semiconductor devices^{11–13}. In a simple system undergoing photoluminescence, the key processes affecting triplet excitons are the generation process of intersystem crossing (ISC) from a singlet excited state to a triplet excited state and the deactivation processes of radiative (phosphorescence) and non-radiative transition from a triplet excited state to the singlet ground state. The rate constants of ISC (k_{isc}) and of radiative emission from triplets (k_p) are strongly influenced by the chemical structure of the emitting molecules and can be tuned from 10^{-2} to 10^6 s^{-1} by exploiting spin-orbit coupling through the inclusion of heavy atoms like bromine¹⁴, iridium^{15–17}, and platinum^{18,19}. The rate constant of non-radiative decay from triplet excited state ($k_{nr}(T)$) is affected by factors related to the environment surrounding the emitters, such as the host matrix^{20,21}, emitter concentration²², and temperature (T) through processes such as energy transfer to other molecules²³ and thermal deactivation²⁴. Minimization of $k_{nr}(T)$ by using rigid host matrices like steroids²¹, polymers²⁵, clathrate compounds^{20,26}, mixed crystals¹⁴, and metal organic frameworks (MOFs)^{27–29} has been reported.

Because of the competing radiative and non-radiative recombination processes, precisely designed molecules and optimized molecular environments are required to obtain efficient room-temperature phosphorescence (RTP) from organic molecules. RTP can easily be reduced by increasing temperature²⁴, introducing triplet quenchers²³, or enhancing molecular motion to increase $k_{nr}(T)$. However, no effective way exists to enhance RTP by increasing k_p via simple external triggers. Although several approaches, such as the use of photochromic emitters³⁰ and pH-sensitive molecules³¹ and the introduction of potassium iodine³² or xenon (Xe)³³ to induce an external heavy-atom effect, have been reported, these systems exhibit very slow responsivity and poor reversibility.

In general, the external heavy-atom effect is used to describe the changes in the optical properties of an organic emitter caused by the presence of heavy atoms that are not incorporated in the emitter molecules. Although this effect increases all spin-flipping processes k_{isc} , k_p , and $k_{nr}(T)$ ³⁴, the degree of enhancement depends on various factors such as the spin-orbit coupling constants^{35,36}, the distance between a heavy atom and an organic emitter^{37,38}, the concentration of the heavy atoms^{32,35,39}, the presence of ionic interactions⁴⁰, and the formation of charge transfer complexes between a heavy atom and emitter⁴¹. In some cases, the external heavy atom increases $k_{nr}(T)$ more than k_p ⁴¹. However, in most cases, the heavy-atom effect enhances phosphorescence more than non-radiative processes⁴⁰. For example, sodium halide more effectively enhances the k_p than the $k_{nr}(T)$ of 2-naphthalenesulfonate³⁵. Thus, k_p of an emitter can be reversibly controlled by introduction and removal of external heavy atoms.

Recently, we demonstrated long-lived RTP with an observed phosphorescence lifetime (τ_{phos}) of 22 s under vacuum by embedding deuterated coronene (coronene- d_{12}) into the zeolitic imidazolate framework ZIF-8²⁷. The large surface area of ZIF-8 and low-doping concentration of coronene- d_{12} in ZIF-8 allow for gas adsorption and desorption.

Here we report a rapid and reversible enhancement of k_p in emitters encapsulated in MOFs by introducing heavy-atom gases as an external trigger (Fig. 1a). We expose coronene- d_{12} encapsulated in ZIF-8 (coronene- d_{12} @ZIF-8) to the gas argon (Ar) mixed with various concentrations of Xe, which has a large spin-orbit coupling constant, at room temperature, and investigate the

dependence of the emission spectra, phosphorescence quantum yield (Φ_{phos}), and τ_{phos} on the concentration of Xe and the timing of the gas exposure. Both k_p and $k_{nr}(T)$ can be tuned by introducing Xe and air, allowing for the full control of long-lived triplet excitons.

Results

Optical properties of coronene- d_{12} @ZIF-8 under various conditions. A thin film of coronene- d_{12} encapsulated in ZIF-8 (coronene- d_{12} @ZIF-8) was fabricated according to the literature²⁷. The concentration of coronene- d_{12} in ZIF-8 is 1.03 wt%, which means that coronene- d_{12} @ZIF-8 still has enough space to accommodate extra molecules²⁷. The emission spectra under steady-state excitation and the emission decay profiles of the film were obtained in ambient air, Ar, and Xe and under vacuum at room temperature (Fig. 1). Because phosphorescence is quenched by the oxygen in air²³, only fluorescence was observed in air under steady-state excitation. On the other hand, dual steady-state emission from fluorescence and phosphorescence was observed under vacuum and in Ar and Xe (Fig. 1b), and a slowly decaying phosphorescence was observed after stopping the excitation.

The large surface area originating from the porous structure of ZIF-8 leads to a good affinity for the gases^{42,43}, so the external gas molecules can easily interact with the solid-state coronene- d_{12} in ZIF-8²⁷. While air easily quenched the phosphorescence, the inert gas Ar does not affect the emission spectra or the observed phosphorescence lifetime (τ_{phos}), which were nearly identical to those under vacuum (Fig. 1c). On the other hand, both the phosphorescence spectra and τ_{phos} were drastically different in Xe even though it is also an inert gas (Fig. 1b, c).

Because, the ZIF-8 pores can adsorb Xe molecules⁴⁴, this result can be attributed to an external heavy-atom effect induced by Xe. The yellow phosphorescence with peaks of 487, 509, 527, 539, 563, and 608 nm in Ar changes into green phosphorescence with peaks of 517, 525, 529, 563, 594, and 609 nm in Xe. Interestingly, the phosphorescence peak maximum under Xe is at 517 nm, which corresponds to the 0-0 transition of coronene- d_{12} ³². Thus, the symmetry forbidden 0-0 transition of coronene- d_{12} becomes partially allowed because of spin-orbit coupling with Xe. A similar phenomenon was reported by combining aromatic hydrocarbons with heavy atoms, such as coronene with potassium iodide in ethanol³² or benzene with Xe^{33,45}. Moreover, the delayed fluorescence observed in Ar at 300 K disappeared in Xe because of the faster k_p ²⁷.

In addition to accelerating k_p , the heavy-atom effect also increases k_{isc} . Thus, the phosphorescence component in the steady-state emission increases compared to that in Ar, and the ratio of phosphorescence to the total emission (I_{phos}/I_{total}) for 100-ms-long photo-excitation (see the Methods section for measurement details) increases from 0.26 in Ar to 0.70 in Xe (Table 1). The τ_{phos} of coronene- d_{12} @ZIF-8 in Xe was 4.7 s, which is one-fifth of that in Ar (20.2 s). Although an acceleration of $k_{nr}(T)$ is often the origin of a reduction in τ_{phos} , the phosphorescent quantum yield (Φ_{phos}) calculated from the total photoluminescence quantum yield (Φ_{total}) and I_{phos}/I_{total} was found to be 6.2%, which is much larger than that in Ar (3.7%) (Table 1 and Supplementary Figure 1). Therefore, the shorter τ_{phos} originates from an enhanced k_p .

Altering the concentration of Xe provides a simple method to control τ_{phos} . We measured the film in mixtures of Ar and Xe with Xe concentrations of 25, 50, and 75% (Fig. 1c, d). Phosphorescence intensity shows a linear relationship with the concentration of Xe (Supplementary Figure 2). Increasing the concentration of Xe increased Φ_{phos} because of the accelerated k_p , but Φ_{total} decreased since k_{isc} also accelerated, leading to a

Fig. 1 Photoluminescence properties of coronene- d_{12} @ZIF-8 under various conditions. **a** Schematic image of coronene- d_{12} @ZIF-8 adsorbing xenon with the different radiative and non-radiative pathways. **b** Steady-state photoluminescence spectra (solid lines) and delayed decay spectra (dashed lines), which correspond to phosphorescence, of coronene- d_{12} @ZIF-8 in air, Ar or vacuum, and Xe. **c** Phosphorescence decay curves under vacuum and in various gas mixtures. **d** Phosphorescence spectra under vacuum and in various gas mixtures. **e** Steady-state phosphorescence intensity at 563 nm of coronene- d_{12} @ZIF-8 exposed to multiple cycles of vacuum, Xe, and air

reduced fluorescence contribution (Table 1). These results clearly indicate that the strength of the external heavy-atom effect can be tuned with the concentration of the external gas. Even though the atomic size (4.4 Å) of Xe is slightly larger than the window size of ZIF-8 (3.4 Å), Xe atoms can pass through the windows of ZIF-8 and interact with the coronene- d_{12} because the window size can

be expanded by the rotation of the imidazole linkers⁴⁴. Since there is no strong encapsulation effect between the Xe atoms and the pores of ZIF-8, Xe atoms can be removed by exposing the film to a different gas or placing the film under vacuum. Therefore, the effects of the external gases on coronene- d_{12} @ZIF-8 are highly reversible.

To demonstrate this reversibility, the steady-state phosphorescence intensity of the coronene- d_{12} @ZIF-8 film was observed over multiple cycles of sequential exposure to vacuum, Xe, and air (Fig. 1e). Each environment had a distinct phosphorescence intensity that was nearly constant over the multiple cycles. Moreover, the phosphorescence intensity did not change even after we stored the film in air for several months. These results indicate that the modification of the triplet dynamics is fully reversible.

Responsivity of triplet excitons to external gases. The response of the emission to the external gases is rapid and reversible, enabling the direct control of accumulated triplet excitons via the external heavy-atom effect. The emission of the film under vacuum exhibited a clear response within 1 s of introducing Xe after stopping the photo-excitation, and the response time was largely determined by the time it takes to manually open and close the gas valves of the measurement system and not the migration speed of the gas (Supplementary Figures 3 and 4). The response of the emission decay of coronene- d_{12} @ZIF-8 film to the introduction of Xe after stopping the excitation along with the decay in Xe and under vacuum are shown in Fig. 2 and Supplementary Movies 1–3.

Long-lived phosphorescence from coronene- d_{12} @ZIF-8 under vacuum is clearly visible more than 1 min after stopping the excitation light (Fig. 2a and Supplementary Movie 1). Because the

Xe gas accelerates both k_{isc} and k_p , an initially more intense phosphorescence with a faster decay was observed in Xe (Fig. 2b and Supplementary Movie 2). When we introduced Xe after stopping the excitation under vacuum, the phosphorescence intensity rapidly increased and the emission color became greener. (Figs. 2c, 3a and 3d and Supplementary Movie 3).

Introduction of Xe accelerates k_p , so the accumulated triplet excitons are more rapidly converted into phosphorescence, leading to a phosphorescence intensity that quickly increases before beginning to decay at a faster rate than under vacuum (Fig. 3d). Because introducing Xe increases k_p , the integrated phosphorescence decay when exposed to Xe after being under vacuum was slightly larger than that in a constant Ar atmosphere by 1.1 times (Supplementary Figure 5), which also indicates that k_p is accelerated more than the $k_{nr}(T)$ in the presence of Xe. By contrast, the long-lived phosphorescence was completely quenched when we introduced air (Fig. 3d). In general, triplet exciton quenching by oxygen in the solid matrix is much slower than that in solution because of the slow migration speed of gases²³. However, MOFs adsorb oxygen into their cavities in a moment because of its large surface area, leading to fast-response time. The enhanced emission intensity and shorter τ_{phos} indicate that we can regulate the phosphorescence by the introduction of Xe at arbitrary times (Fig. 3e and Supplementary Figure 6). The τ_{phos} can also be easily controlled by varying the concentration of Xe gas (Fig. 3f and Supplementary Figure 6). All of these results indicate that both the phosphorescence intensity and τ_{phos} can be easily and rapidly regulated through the introduction of a controlled amount of heavy atoms.

Table 1 Photophysical properties of coronene- d_{12} @ZIF-8 under various conditions

Ar:Xe gas ratio	λ_{max} (nm)	$I_{phos}/$ I_{total}	τ_{phos} (s)	Φ_{total} (%)	Φ_{flu} (%)	Φ_{phos} (%)
1:0	563	0.26	20.2	13.8	10.1	3.7
3:1	563	0.54	8.4	9.1	4.2	4.9
1:1	517	0.62	6.4	8.7	3.3	5.4
1:3	517	0.66	5.5	8.9	3.0	5.9
0:1	517	0.70	4.7	8.9	2.7	6.2

λ_{max} the peak of phosphorescence spectra, I_{flu} the fluorescence intensity, I_{phos} the phosphorescence intensity, Φ_{flu} the fluorescent quantum yield, Φ_{phos} the phosphorescent quantum yield

Discussion

In summary, we demonstrated the use of the external heavy-atom effect to achieve fast, rapid, and reversible control of triplet excitons in organic semiconductors. A host matrix of ZIF-8 provides not only a rigid environment for the guest emitter but also a high affinity for external gases. According to the combination of these functions, we can easily regulate the conversion of the accumulated triplet excitons into emission. The timing and speed of extraction of accumulated excitons as emission can be controlled by introducing gas mixtures with various concentrations of Xe.

Fig. 2 Photographs of time-dependent phosphorescence of coronene- d_{12} @ZIF-8. **a** Under vacuum. **b** In Xe. **c** Excited under vacuum followed by introduction of Xe 15 s after stopping excitation

Fig. 3 Responsivity of emission to external gases. **a–c** Phosphorescence spectra for various times after stopping excitation (**a**) in Ar, (**b**) under vacuum with Xe injection starting at 2 s, and (**c**) in Xe. **d** Phosphorescence decay profiles in Ar, under vacuum with air injection starting from 2 s, in Xe, and under vacuum with Xe injection starting from 2 s. **e** Phosphorescence decay curves in Ar without Xe introduction and with Xe introduction starting at 3, 10, and 20 s. **f** Phosphorescence decay curves under vacuum with the introduction of a various gas mixtures of Xe and Ar starting at 2 s

Alternatively, the accumulated excitons can be completely extinguished through non-radiative processes by introducing air. This fast and reversible control of triplet excitons in a MOF matrix could open a new platform for fast-response photo-switches, reversible optical storage, and molecular computers.

Methods

Preparation of coronene- d_{12} @ZIF-8 film. A coronene- d_{12} @ZIF-8 film was prepared by using ship-in-a-bottle synthesis following the procedure from literature²⁷. A dimethylformamide (DMF) solution of coronene- d_{12} , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 2-methylimidazole (H-Melm) was heated at 140 °C for 24 h in a Teflon-lined autoclave reactor. After cooling to room temperature, the activation steps were performed under low pressure ($<10^{-3}$ Pa) using a turbo molecular pump. The doping concentration of coronene- d_{12} into ZIF-8 was calculated according to the method in a previous report.

Optical measurements. The long-lived photoluminescence spectra and decay profiles under various conditions were obtained using a measurement system with the configuration shown in Supplementary Figure 4. A coronene- d_{12} @ZIF-8 film was first activated by the turbo molecular pump (HiPace80, Pfeiffer vacuum), then a gas mixture, the concentration of which was controlled by a gas mixer (Kofloc, PMG-1A), was introduced into the sample chamber. Notably, this system contains several manual gas valves used for the introduction of the external gases. The coronene- d_{12} @ZIF-8 film was placed in a sample chamber with a quartz window and excited by a UV light source (MORITEX MUV-202U) with a bandpass filter (340 ± 5 nm). The emission spectra and emission decay profiles were recorded using a multichannel spectrometer (PMA-12, Hamamatsu Photonics) with a longpass filter (370 nm).

The Φ_{total} of coronene- d_{12} @ZIF-8 in various environments were measured with an absolute photoluminescence quantum yield spectrometer (Quantaurus-QY, Hamamatsu Photonics) at room temperature under a vacuum (10^{-3} Pa). Here, Φ_{flu} (photoluminescence quantum yield of the fluorescence) and Φ_{phos} were calculated

from the emission intensity at all wavelengths obtained using the PMA-12. The PMA-12 was used to measure the emission integrated over 100-ms intervals. The total emission intensity (I_{total}) for 100-ms-long photo-excitation was measured by integrating all of the measurements from the PMA-12 with the first measurement starting at the same time as the photo-excitation. The fluorescence intensity (I_{flu}) was estimated by subtracting the intensity from the second 100-ms measurement interval, which roughly corresponds to the phosphorescence during the first 100-ms measurement interval, which includes the photo-excitation period. The phosphorescence intensity (I_{phos}) was measured from the integrated intensity for all of the measurements from the second 100-ms measurement interval on with the intensity of the second 100-ms measurement interval counted twice to roughly account for the phosphorescence during excitation.

Data availability. The authors declare that the data support the findings of this study are available from the authors upon reasonable request.

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Author contributions

R.K. conceived the project. H.M. and R.K. conducted the experiments. H.M., R.K., and C. A discussed the results and co-wrote the manuscript.

Additional information

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