Room-Temperature Phosphorescence and Low-Energy Induced Direct Triplet Excitation of Alq₃ Engineered Crystals

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ABSTRACT: Crystal engineering is a practical approach for tailoring material properties. This approach has been widely studied for modulating optical and electrical properties of semiconductors. However, the properties of organic molecular crystals are difficult to control following a similar engineering route. In this Letter, we demonstrate that engineered crystals of Alq₃ and Ir(ppy)₃ complexes, which are commonly used in organic light-emitting technologies, possess intriguing functional properties. Specifically, these structures not only process efficient low-energy induced triplet excitation directly from the ground state of Alq₃, but also can show strong emission at the Alq₃ triplet energy level at room temperatures. We associate these phenomena with local deformations of the host matrix around the guest molecules, which in turn lead to a stronger host−guest triplet−triplet coupling and spin−orbital mixing.

Engineered crystals—spatially ordered structures with the packing controlled by the growth process—allow for efficient modulation of optical and electrical properties of semiconductors.¹−³ However, organic crystals show low tolerance to foreign materials because of the weak intermolecular interactions.⁴⁻⁵ Different types of organic molecules prefer to pack forming a new lattice structure, while barely inducing the deformation of the host lattice.⁶⁻⁸ Despite the general paradigm, electronic states in organic crystals are quite localized at the molecular entities and are barely affected by proximal molecules.⁹⁻¹⁰ Modulation of the organic crystal optical properties relies on both the inherent electronic states of the molecular entities as well as the delocalization of the molecular states.¹⁰⁻¹⁴

Electronic states of molecular entities can be of a spin-singlet or a spin-triplet character, depending on the presence of paired or unpaired electrons, respectively. Population of molecular triplet states, which is usually optically forbidden because of the requirement of an additional spin flip, can be ordinarily accomplished via inter-system crossing (ISC).¹⁵⁻¹⁷ Recently, radiative decay of triplet states, which yields room-temperature phosphorescence, has become the subject of active research.¹⁸⁻²¹ For example, including heavy atoms in the molecular structure²²⁻²³ or inducing stronger intermolecular coupling²⁴ in the crystalline structure can promote the phosphorescence process. However, this mechanism still requires the excitation to higher-lying singlet states from the ground state with a subsequent ISC process to yield triplet excitons, which hinders the development of organic phosphorescence materials. Hence, direct excitation of the low-lying triplet state in the organic material, especially without involving the higher-lying singlet states, represents an intriguing strategy for modulating optical properties of organic semiconductors.²⁰,²⁵,²⁶

We report here two types of engineered crystals that are produced by doping foreign molecules into the molecular crystalline structure. The engineered structures efficiently emit light in a broad range of the optical spectrum, which is associated with the room-temperature phosphorescence. Moreover, the emission is maintained even when the crystals are excited with incident energy below the singlet band edge of the crystals. This contrasts with pure crystals of the host or guest molecules where no photoluminescence is observed for the sub-band edge excitation. We suggest that local lattice deformations in the engineered crystals can lead to singlet−triplet intensity borrowing due to the external heavy-atom effect.²⁷⁻²⁹ In turn, this results in the enhanced triplet optical absorption by both the host and guest complexes, as well as efficient excitation relaxation to the lowest triplet states of the host−guest system.

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Materials based on tris(8-hydroxyquinoline) aluminum (Alq₃) and tris(2-phenyl-pyridine) iridium (Ir(ppy)₃) complexes (Figure 1a) are most frequently used in organic light-emitting technologies. Both structures are metal chelates, enabling molecular spatial reorganization for packing. Their performance in the optoelectronic properties,29,30 polycrystalline phases,31,32 and nanostructures33,34 is widely studied both experimentally and theoretically.35,36 The iridium complex, Ir(ppy)₃, exhibits the efficient long-lived triplet emission due to an internal heavy-metal effect.37 In contrast, Alq₃ mainly exhibits fluorescence, and its triplet state is hardly populated for radiative emission. Even if doped with Ir(ppy)₃ in the amorphous film, phosphorescence of Alq₃ can hardly be obtained at room temperatures.33,38

In this study, these two complexes are used for the design of engineered crystals. The energy diagrams in Figure 1a show the band gaps of the two molecules.31,36,39 The absorption and photoluminescence (PL) spectra of these two molecules in the crystalline superstructure. The modified double-film annealing method34 is employed for the fabrication of engineered crystals at 573 K. This method allows for a fast high-temperature crystallization of the molecular material, which in turn facilitates the crystallization with the dopant. The doping percentage of the guest molecule inside the engineered crystal is controlled by the initial weight ratio of the doping percentage of the guest molecule inside the engineered crystal with the dopant. The emission lifetime of Alq₃-I is 3.01 ± 0.32 μs and of Ir(ppy)₃-A

![Figure 1](https://dx.doi.org/10.1021/acs.jpclett.0c02416)
Crystalline structures of the doped materials with 10% of doping concentration are characterized by the X-ray diffraction (XRD). As shown in Figure 3a, the obtained Alq3-I and Ir(ppy)3-A structures are in a crystalline form, with fewer diffraction peaks as compared to pure crystals. By comparing these XRD profiles with those of the Alq3 and Ir(ppy)3 crystalline microwires, the prepared Alq3-I have a clear (010) diffraction peak, which is the same as the Alq3 crystalline structure, but with ~0.09° of shift. The prepared Ir(ppy)3-A shows a (220) diffraction peak which is the same as the Ir(ppy)3 crystalline structure, but with 0.45° of shift. We conclude that the engineered crystals keep the crystalline structures similar to the corresponding host materials. The dopant molecules induce small shifts of the diffraction peaks, corresponding to the reduction or expansion of the crystalline lattices, which is the evidence of lattice deformation.

To compare with our engineered crystals, a homogeneous lattice deformation of pure Ir(ppy)3 and Alq3 crystals can be induced by high hydrostatic pressure. It was shown that such a deformation further affects photoluminescence properties of the materials. These changes in photoluminescence have been explained in terms of the enhancement of molecular interactions as intermolecular distances decrease. Specifically, pure Ir(ppy)3 crystals with a compressed lattice have been characterized by the occurrence of a shoulder at 507 nm at the high-energy side of the main maximum at 545 nm emission peak profile. The computational results suggest that the short-wavelength shoulder peak can correspond to the 0–0 transition, but this vibrionic structure of the triplet emission spectra is rarely observed at ambient conditions. The Ir(ppy)3-A, where the Ir(ppy)3 lattice disorder is induced by the Alq3 dopant, shows P2 with the shoulder peak profile which is similar to the PL spectrum of the Ir(ppy)3 crystal under high pressure, verifying that P2 is the triplet emission Ir(ppy)3. In contrast, we have not observed a shoulder peak for the Alq3-I crystal. The pure Alq3 crystal with lattice distortion under high pressure shows a significant shift to longer wavelength due to the higher proportion of triplet emission. This agrees well with the triplet emission of Alq3 (P2) in both engineered crystals. We hypothesize that the PL behavior of engineered crystals can be associated with the enhancement of molecular interactions as the crystal lattice is distorted by the doping molecules.
The low-energy level structure of engineered crystals is further characterized using a transient absorption technique by exciting the samples below the P1 peak, which are pumped at 520 nm and probed at 780 nm. Under the sub-bandgap excitation, the decay profiles for both the engineered crystals exhibit the dual decay component. The best-fit curves for the decay of two engineered crystals are shown in Figure 3b. For Alq3-I, the decay dynamics are well fit by a double exponential $\tau_1 = 1.98 \text{ ps}$ and $\tau_2 = 29.89 \text{ ps}$. For Ir(ppy)3-A, we obtain $\tau_1 = 2.37 \text{ ps}$ and $\tau_2 = 29.99 \text{ ps}$. The transition time scale is comparable with the ultrafast dynamics of electronic excitations in Ir(ppy)3 and the quinolinolate complexes. It can be associated with the excitation transfer between states of the same symmetry. In contrast, the pure Alq3 or Ir(ppy)3 does not exhibit any photon absorption under sub-band edge excitation (see Supporting Information SI.4 for detail). For the engineered crystals, such transitions are permitted without the excitation of their S1. The absorption of a photon of 2.38 eV leads to the excitation of intermediate triplet states which subsequently relax to the lowest triplet state T1. As suggested earlier, the host–guest coupling in the engineered crystals permits the intersystem crossing which is forbidden for the molecular entity or the pure crystals.

The intermolecular coupling is further investigated by varying the doping concentration in the engineered crystals (Figure 4). Under 405 nm excitation, the Alq3-I crystals exhibit mainly green PL (Figure 4a), which is barely affected by the doping concentration. In contrast, the PL images of Ir(ppy)3-A crystals vary from yellow-white to red with the change of the doping percentage from 10% to 1% (Figure 4d). As shown in Figure 4b,e, the intensity of the feature P1 relative to the feature P2 remains nearly the same for Alq3-I crystals but decreases significantly for Ir(ppy)3-A crystals when the doping concentration is reduced. As compared to the previous study, the emission from Alq3 triplet states is observed at room temperature for both types of engineered crystals and all studied concentrations of dopants. This supports our hypothesis of strong coupling between the triplet states of the host and the guest complexes, which in turn facilitates host–guest triplet exciton transfer.

The associated excitation dynamics is proposed as follows. In both types of the engineered crystals, the low-lying singlet states of either the Alq3 or Ir(ppy)3 molecular entity are optically populated, which further results in the intermolecular excitation transfer, intramolecular ISC, and the photon emission processes (Figure 4c,f). In Alq3-I crystals, the generated electronic excitations diffuse through the singlet manifold of the host complexes using Förster interaction until they get trapped by Ir(ppy)3 and subsequently converted into triplets. The following step, the triplet–triplet transfer between the guest Ir(ppy)3 and the host Alq3, is mediated by the Dexter interaction. In contrast, singlet electronic excitations in Ir(ppy)3-A crystals are quickly converted into triplets and then diffuse between the host complexes by means of the Dexter interaction until they get trapped by the Alq3 impurities. The described mechanisms are schematically outlined in Figure 4c,f, where we neglect the internal structure of the triplet and singlet bands for the sake of simplicity. The energies of the low-lying excited electronic states of the two molecules are calculated (see Supporting Information SI.5 for details) to a better understanding the energy landscape of the two systems. Both proposed processes allow the emission from the low-lying triplet states of Alq3.

It is important to emphasize that the intensity of the feature P1 in the PL spectra of the engineered crystals can correspond to singlet emission of Alq3 and the triplet emission of Ir(ppy)3.
Therefore, it can originate from both distant and proximal to the defect sites of the engineered crystals. In contrast, the feature P₂ is originated solely from the emission of Alq₃ triplet states. Because of the intrinsic asymmetry of the excitation and triplet (T) energy levels of Alq₃, and the vertical arrows show the studied engineered crystals. The black lines represent singlet (S) triplet transitions are forbidden in pure Alq₃, the presence of triplet states of Alq₃ complexes.

In conclusion, we designed and optically characterized two types of crystalline structures: Alq₃ crystals with Ir(ppy)₃ dopants and Ir(ppy)₃ crystals with Alq₃ dopants. The optical properties of the obtained organic semiconductor materials are successfully modulated by crystal engineering for the first time. Specifically, both crystals exhibit a broad range of photon absorption and emission properties. The triplet state of Alq₃ can be efficiently populated via crystal engineering. Efficient room-temperature phosphorescence of Alq₃ is observed in the engineered crystals. As compared to nondoped Alq₃ and Ir(ppy)₃ crystals, the engineered crystals efficiently emit light even with the excitation energy as low as 1.96 eV, which is far below the singlet bandgap of either molecule composing the crystal. The transitions between molecular energy levels within different manifolds which are otherwise forbidden by symmetry are resolved because of a stronger intermolecular coupling in the engineered crystals. We suggest that the ability to maintain the crystalline structure of the host organic materials in the engineered host–guest systems may advance multiple optoelectronic applications, including scalable crystalline solar cells, molecular photonics, and photosensitizers.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02416.

Additional details of the detailed experimental information, graphs and theoretical calculation methods (PDF)

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Figure 5. Schematics of the proposed external heavy-atom effect that can describe optical excitations of Alq₃ triplet states in the engineered crystals Alq₃-I and Ir(ppy)₃-A. While the singlet-to-triplet transitions are forbidden in pure Alq₃, the presence of heavy atoms in neighboring molecules can result in mixing of singlets and triplets (see Figure 5b). This, in turn, allows the intersystem crossing the Alq₃ as well as the direct optical excitation of the low-lying triplets. The strength of this effect should correlate with the number and the proximity of heavy-atom-containing molecules to the probed Alq₃.
The authors declare no competing financial interest.

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