

General Design Strategy for Aromatic Ketone-Based Single-Component Dual-Emissive Materials

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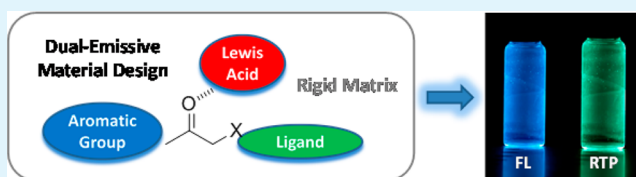
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S Supporting Information

ABSTRACT: Materials with both fluorescence and room-temperature phosphorescence (RTP) can be useful in the field of optoelectronics. Here we present a general strategy, taking advantage of carbonyl compounds, which have been known to possess efficient intersystem crossing with high triplet state yield, as well as a strongly fluorescent intramolecular charge-transfer (ICT) state, to produce materials with both fluorescence and RTP at the same time, or dual-emission. In the presented model systems, in order to generate a suitable ICT state, Lewis acid binding to aromatic ketone derivatives has been proved to be a viable method. We have selected AlCl₃, BCl₃, BF₃, and GdCl₃ as binding Lewis acids, in that they exhibit sufficiently strong binding affinity toward the aromatic ketone derivatives to afford stable complexes and yet do not possess low-lying electronic transitions vs the ligands. We have successfully observed dual-emission from these designed complexes in polymers, which act to suppress competitive thermal decay at room temperature. One of the complexes is particularly interesting as it is dual-emissive in the crystalline state. Single-crystal XRD reveals that the molecule forms multiple hydrogen bonds with its neighbors in crystals, which may significantly enhance the rigidity of the environment.

KEYWORDS: aromatic ketone, Lewis acid, charge-transfer state, fluorescence, room-temperature phosphorescence, dual-emission



1. INTRODUCTION

Dual-emissive photoluminescent materials with distinct fluorescence and room-temperature phosphorescence (RTP) are highly desirable in practical applications such as sensing,^{1–3} imaging,^{4–6} and data storage.⁷ RTP is generally very susceptible to the external microenvironment⁸ and is therefore highly responsive to changes in temperature,^{9,10} solvent viscosity,¹¹ and the presence of quenchers.^{12–14} In contrast, fluorescence is relatively robust and can be used as the calibration signal when combined with RTP for ratiometric sensing.¹⁵ For example, some dual-functional nanosensors carry a fluorescent-RTP dye pair, the intensity ratio of which is employed to simultaneously report multiple physical parameters such as pH and oxygen levels.⁶ Among luminescent ratiometric sensors, single-component dual-emissive materials (SDMs) are preferred since they do not suffer from limitations such as stoichiometric imbalance^{16,17} between fluorescent and RTP dyes. Strategies involving covalent linking of a fluorophore to a metal phosphor for fluoride, copper ion, and oxygen sensing have been reported by Wang,¹ Lippard,² and Nocera,³ respectively. More recently, Kim et al.¹⁸ reported highly efficient dual-emitting feature of purely organic molecules via directed heavy atom (halogen bonding) effects. Using an alternate approach to promote RTP

by combining heavy atom and molecular-weight effects, Fraser et al.⁵ described the design, synthesis, and imaging applications of a biocompatible polymer, iodine-substituted difluoroboron dibenzoylmethane-terminated polylactide, BF₂dbm(I)PLA, where the glassy polymer matrix at room temperature restricts competitive thermal decay pathways and allows for strong RTP. The tunable SDM design concept has enabled real-time and in vivo tumor hypoxia imaging with excellent temporal and spatial resolutions.⁵

Judging from the chemical structures of the dual-emissive BF₂dbm derivatives, it is possible that boron chelation to the β -diketone (bdk) ligands can boost a suitable charge-transfer (CT) state with strong fluorescence.¹⁹ On the other hand, the strong RTP is likely intrinsic to carbonyl compounds due to the small singlet–triplet energy splitting and thus enhanced intersystem crossing (ISC) rates.^{18,20} Based on the structure–property relationship analysis, dual-emitting molecules should not be limited to BF₂dbm complexes. Instead, *aromatic ketones in general should possess dual-emissive behaviors when a strongly*

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fluorescent state is induced. For aromatic ketones, the lowest singlet excited states can be $^1(n-\pi^*)$ or $^1(\pi-\pi^*)$ in nature; however, their fluorescence is typically weak because of rapid ISC to a dark $^3(n-\pi^*)$ state.²¹ In theory, $^1(n-\pi^*)$ state can be replaced with a fluorescent ^1CT state if the lone-pair electrons on the carbonyl oxygen are bound to electron acceptors such as Lewis acids. As such, the $n-\pi^*$ state energy levels will be raised, and the more emissive CT or $\pi-\pi^*$ states will become the new lowest transitions. This way, intraligand dual-emission (fluorescence and RTP) should be expected. A workable design is to use electron rich aromatic ketones (donor) to complex with Lewis acids (LAs, acceptor) and can thus generate a low-lying, emissive ^1CT state, which has been known to facilitate efficient ISC as well.^{22,23} As shown in Figure 1, SDMs may be readily

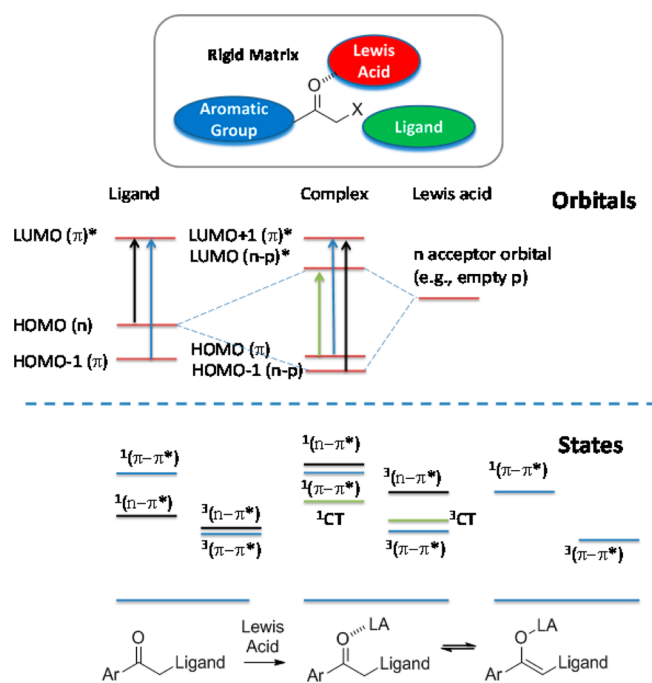


Figure 1. Schematic illustration of the design of aromatic ketone-based single-component dual-emissive materials. Exemplar electronic orbitals and simplified Jablonski diagrams are also provided: the lone-pair orbital of the aromatic carbonyl can interact with an acceptor orbital from the Lewis acid, and the resulting orbitals can enhance CT emission and facilitate ISC.

achievable by subjecting these aromatic ketones to a few simple rules: (1) binding LAs may not be “colored” since active transitions in the visible range can cause complicated energy- or electron-transfer processes;²⁴ (2) for practical applications, LAs require extra stabilization such as chelation with bidentate ligands since monocoordination is not stable;²² (3) rigid matrices are necessary for RTP such as polymers and crystals.^{18,19} In this initial communication, the proof-of-concept SDM design involves primarily α -substituted aromatic ketones (Figure 1), where X can be hydrogen, alkyl amine, carbonyl, aryl imine, or ester. Optically “transparent” B(III), Al(III), and Gd(III) are used as model LAs since none of them possesses electronic transitions in the visible-light region. It was also found that when α -ketone-LA complexes energetically favor the enol form, phosphorescence is significantly suppressed, which could be due to the loss of triplet-generating carbonyl moiety. The reported strategy has significant implications for the design

of next generation of organic phosphors and might also intrigue renewed synthetic interests in ketone chemistry.

2. RESULTS AND DISCUSSION

To test the SDMs design strategy, we first examined whether monoketone-Lewis acid complexes would possess dual-emissions in polylactide (PLA) matrix at room temperature. Commercially available monoketones and a strong Lewis acid, BCl_3 , were added to CH_2Cl_2 , presumably forming labile complexes **1a-1c** (Figure 2a),²² as evidenced by the absorption spectra. The structureless shoulder peaks in the lower energy region are characteristic of CT bands (Figures S1–S3 in the Supporting Information). The monoketones were weakly or not fluorescent in CH_2Cl_2 ; upon BCl_3 addition, fluorescent emissions could be observed (Figures S4–S7). It was noted that complexes **1b** and **1c** exhibited much stronger fluorescence emission than did **1a**, which is probably due to better electron-donating ability for aromatic ketones with more extended π systems. After PLA was codissolved in **1a-1c** solutions, polymer films (~ 0.5 wt %/wt dye content) were fabricated by casting inside a glass vial and dried under vacuum. Under N_2 , the PLA films exhibited bright fluorescence under UV excitation (Figures 2 and S8); even after UV irradiation had ceased, the RTP “after-glow” (~ 1 s) was still present. The films were scraped off from the vials and then transferred to individual quartz tubes, which were sealed on hydrogen flames when being degassed with an oil pump for dual-emission measurements (Figures 2b, 2c, and 2d). Despite the similarity in fluorescence emissions ($\lambda_{\text{max}} \sim 450$ nm), the RTP of **1a** is much higher in energy ($\lambda_{\text{max}} \sim 460$ nm) compared to that of **1b** ($\lambda_{\text{max}} \sim 550$ nm), suggesting the lowest triplet state could be ligand-localized ($\pi-\pi^*$) and highly dependent on the size of the aromatic moiety. The small singlet–triplet energy differences for the three monocoordinated complexes (~ 5 – 7 kcal/mol) determined from the spectra further indicates the two lowest excited states may not be both $\pi-\pi^*$ transitions, which tend to have much larger singlet–triplet energy splitting.²⁵ The results are also consistent with the El-Sayed rules,²⁶ which states that the rate of intersystem crossing is relatively large if the radiationless transition involves a change of orbital type. In this case, the lowest singlet state is most likely of CT transition involving n, p orbitals, while the triplet counterpart is of $\pi-\pi^*$ nature (Figure 1). The negative controls, with only the monoketones embedded in PLA under N_2 at the same loading (0.5% w/w), showed much weaker emissions (Figure S8).

Although monoketone-LA complexes exhibit interesting dual-emission capability at room temperature, they are nonetheless impractical for sensing and imaging purposes considering their poor stability.²² We next tested more stable structures (with an additional binding site) such as Mannich bases, β -diketones, and β -iminoketones. In these cases, increased stability is at the cost of reduced electron-accepting ability of LAs and thus weaker CT states. Complex **2** (MB1, Figure 2e), in which tertiary ammonium (proton) serves as the LA, was obtained via a routine, one-step Mannich reaction.²⁷ Dual-emission was observed under N_2 when **2** was dispersed in PLA matrix. Fluorescence and RTP maxima were determined to be at 421 and 534 nm, respectively. It was noted that positively charged **2** is soluble in water ($\lambda_{\text{max}} = 455$ nm, $\tau_{\text{F}} = 5.05$ ns) and has a high fluorescence quantum yield of 0.43 (Figure 2e). The emission spectrum in water is red-shifted by ~ 1800 cm^{-1} compared to that in the PLA matrix, indicating the CT character of MB1 fluorescence. These findings indicate that

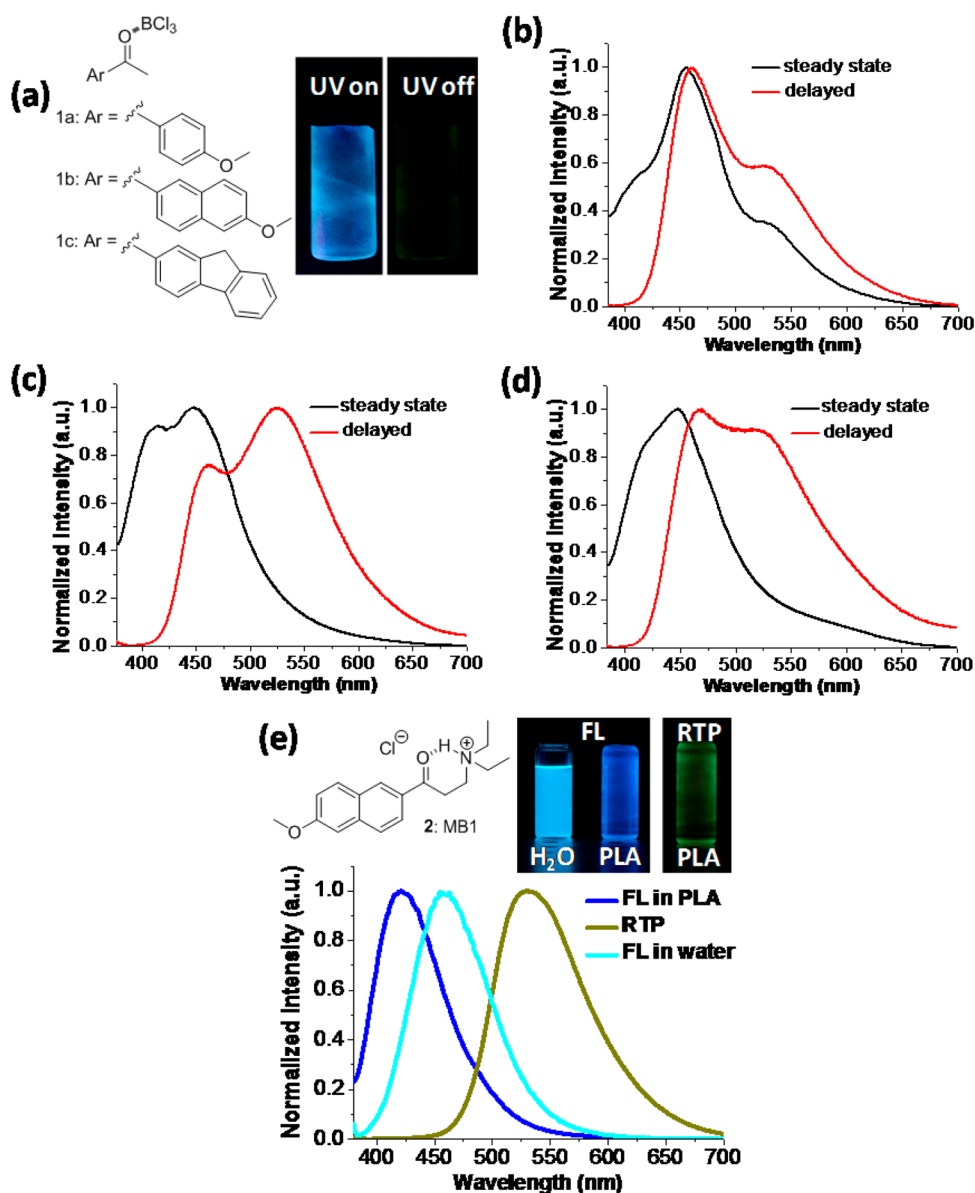


Figure 2. (a) Chemical structures of complexes 1a-1c, photos showing 1b in PLA film under UV light ($\lambda_{\text{ex}} = 365$ nm) and after UV light has ceased. Steady-state and delayed emission spectra of 1a (b), 1b (c), and 1c (d) in the PLA matrix at room temperature in vacuo. (e) Chemical structure of Mannich base MB1 (2, top left); photos showing fluorescence (FL) of MB1 in water and in PLA film, and RTP in PLA film (top right); corresponding emission spectra of MB1 under these conditions (bottom). For all measurements, $\lambda_{\text{ex}} = 365$ nm and delayed emission spectra were recorded at a delay time $\Delta t = 25$ ms in a sealed quartz tube in vacuo.

Mannich bases are promising for developing new dual-emissive biomarkers.

Difluoroboron- β -diketone complexes have been previously found dual-emissive in polymer matrices at room temperature.⁵ Here we show that SDMs built from bdks can be further extended to more LA systems, such as Al (III) and Gd (III). Avobenzone (AVB) and oxybenzone (OBZ) were used to chelate with AlCl_3 given their commercial availability and potential for large-scale applications. As active ingredients used in sunscreens, aromatic ketone derivatives have been found largely devoid of radiative triplet states when used alone at room temperature.^{28,29} Here however we use the two model ligands, AVB and OBZ, to show that potentially harmful radiative triplet states (which can effectively generate singlet oxygen) might arise, given that the body is a large reservoir of LAs that can bind to the two ligands. As such, LA chelation

might also induce photodegradation³⁰ of the sunscreen compounds and thus could reduce their actual sun protection factor (SPF) values. For AVB, stable and well-defined Al(III) triscomplex 3 (Figure 3a) could be obtained via complexation with AlCl_3 in CH_2Cl_2 , as has been characterized by EA, HRMS, and ^1H NMR (their absorption spectra are provided in Figure S9). Dual-emission peaks at 422 and 491 nm are obtained for fluorescence and RTP in the PLA matrix under N_2 . The vibronic shoulder in 3 indicates significant $\pi-\pi^*$ nature for the lowest singlet excited state. This can be explained by decreased CT strength (AlCl_3 being a much better electron acceptor vs AlAVB_2) and increased π conjugation size (lower $^1(\pi-\pi)^*$ energy level).

Tris-complex 4 was also obtained under a similar reaction condition and was characterized by ^1H NMR, EA, HRMS, and MALDI-TOF MS spectra, respectively. Again, strong fluo-

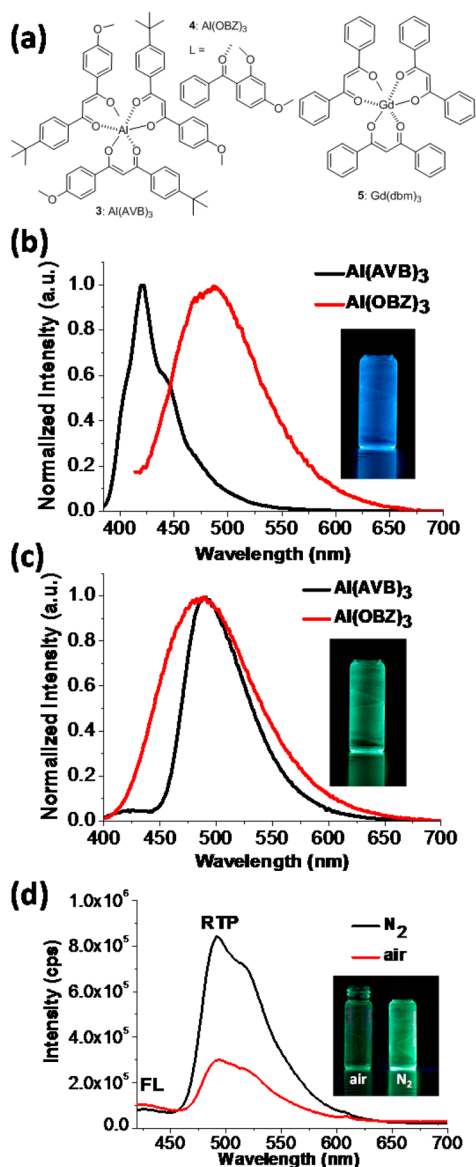


Figure 3. (a) Chemical structures of complexes 3, 4, and 5. (b) Normalized fluorescence emission spectra of complexes 3 and 4 in PLA films; inset: photo of 3 in PLA film under UV excitation ($\lambda_{\text{ex}} = 365$ nm). (c) Delayed emission spectra of complexes 3 and 4 in PLA films with a delay time of $\Delta t = 25$ ms; inset: photo of 3 in PLA film under N₂ after UV excitation has ceased ($\lambda_{\text{ex}} = 365$ nm). (d) Relative steady-state emission spectra of 5 in PLA in air (red line) and under N₂ (black line); inset: photos showing 5/PLA blends in air and under N₂ under UV irradiation ($\lambda_{\text{ex}} = 365$ nm).

rescence ($\lambda_{\text{max}} = 487$ nm) and delayed emission ($\lambda_{\text{max}} = 489$ nm) were observed in PLA (0.5%) under N₂, indicating that Al binding still induces dual-emission from OBZ (Figures 3b and 3c). In this particular case, delayed fluorescence instead of RTP is obtained presumably due to the more efficient back-population from triplet to singlet excited states, suggesting a different energy landscape from that of complex 3. Finally, we performed excitation spectra for both complexes 3 and 4 (Figure S10) and found that the spectra for fluorescence and RTP are quite similar, which suggests the two emissive states are originated from the same complex.

It is well-known that heavy-atoms can increase phosphorescence emission via spin-orbit coupling.³¹ Here we also tested

whether a heavy LA, Gd (III) for instance, could induce enhanced RTP emission from the ketone-LA pair. Complex 5 was obtained as crystals (Figure S11) via one-step chelation between dibenzoylmethane and GdCl₃ in ethanol using NaOH as the deprotonating agent³² (5-8: known compounds synthesized from the literature).³³ Elemental analysis reveals that the crystal is in fact a monohydrate or Gd(dbm)₃ H₂O. As shown in Figure 3, almost exclusive RTP ($\lambda_{\text{RTP}} = 491$ nm) was observed for Gd(dbm)₃/PLA film under N₂, which indicates rapid ISC rate and triplet radiative decay rates. The RTP could not be quenched entirely even when exposed to air (Figure 3d). Compared to the second-long “after-glow” ($\tau_{\text{RTP}} \sim 400$ ms) observed for Al(AVB)₃, the RTP lifetime of Gd(dbm)₃ was measured to be ~ 1.3 ms. However, RTP emission spectra of Al and Gd complexes are very similar, once again suggesting that the origin of RTP could be mainly from ligand-localized states, $^3(\pi-\pi^*)$.

Iminoketones were also investigated (6 and 7), and both complexes possess strong fluorescence. In PLA films, complexes 6 and 7 have fluorescence maxima at 482 and 474 nm, respectively. However, 6 shows barely detectable RTP and complex 7, the synthesis of which was recently reported by Matsui et al.,³⁴ is to our surprise not dual-emissive at all. A plausible explanation is that the ligands of 6 and 7 have a stable enol-imine form and a much less stable keto-amine form (Figure 4a). Previously reported crystal structures indeed revealed that the derivatives of 6 favor the enol form.³⁵ For 7,

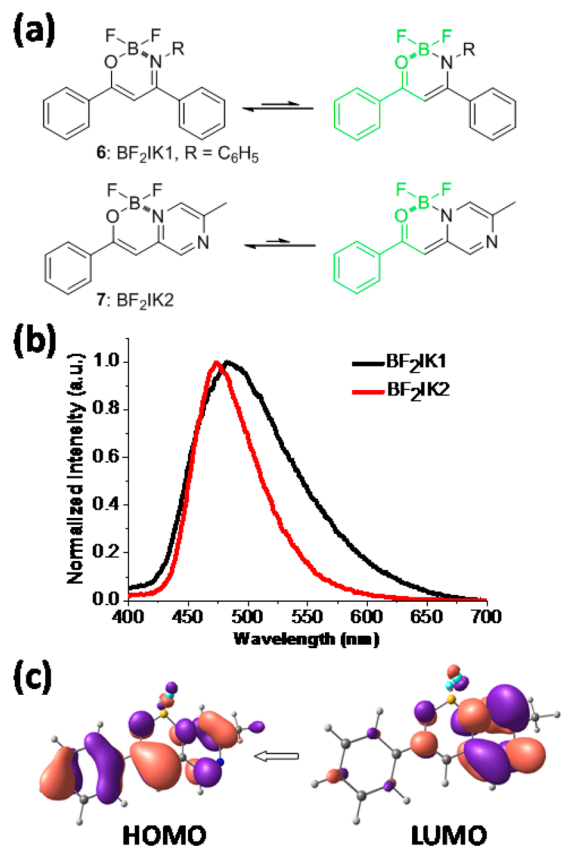


Figure 4. (a) Chemical structures of complexes 6 and 7 and essential resonance structure (green) for SDMs from carbonyl compounds. (b) Normalized fluorescence emission spectra of 6 (black line) and 7 (red line) in PLA. (c) Calculated HOMO and LUMO for 6 indicating significant ICT character.

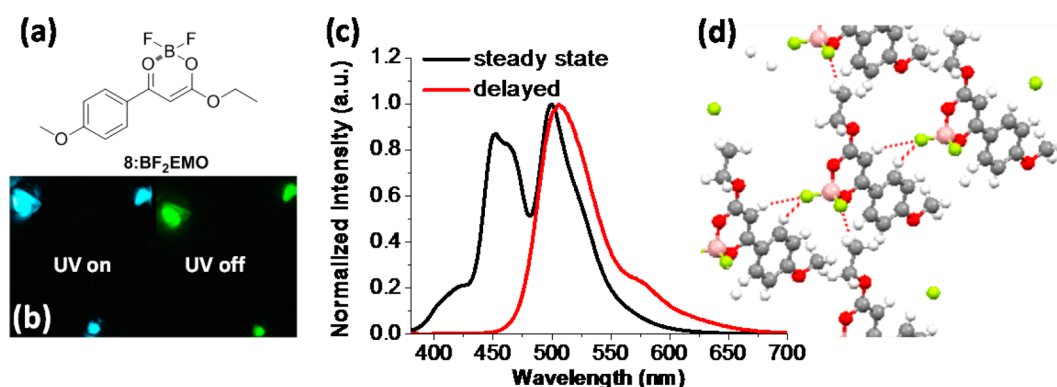


Figure 5. (a) Chemical structure of difluoroboron ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (BF₂EMO, **8**). (b) Emission of BF₂EMO crystals at room temperature in air under UV light (left) and after UV light stops (right, $\lambda_{\text{ex}} = 365$ nm). (c) Steady-state (black line) and delayed emission spectra (red line) of BF₂EMO at room temperature in air ($\lambda_{\text{ex}} = 370$ nm), delayed emission recorded at a delay time of $\Delta t = 25$ ms. (d) Single-crystal XRD structure suggesting that every molecule has at least four weak interactions (H bonding) with the surrounding ones.

the ketone resonance structure involves dearomatization of the pyrazine ring and is thus highly unfavorable. A calculated value of ΔE_{ST} of the enol form suggests inefficient ISC (~ 11 kcal/mol, $\lambda_{\text{F}} = 477$ nm and $\lambda_{\text{RTP}} = 590$ nm, consistent with steady-state fluorescence measurements, Figure 4b), despite its significant ICT character for the lowest electronic transition (Figure 4c). These two exceptions may in fact agree well with the design strategy from a different perspective, that ketone form instead of the enol one is key to the dual-emission feature.

Finally, we demonstrate that crystals can also serve as a viable medium for SDM design. Compared to polymer embedding, pure dye crystals are generally weakly emitting largely due to more prominent aggregates quenching of radiative states.¹⁸ However, we have identified that some of the ester-substituted aromatic ketones exhibit strong fluorescence and RTP as crystals. Figure 5 gives such an example, where the crystals of difluoroboron ethyl 3-(4-methoxyphenyl)-3-oxopropanoate³⁶ (BF₂EMO, **8**) exhibit long “after-glow” at room temperature when UV excitation stops even in air. The steady-state emission spectrum clearly shows that the peaks of fluorescence ($\lambda_{\text{max}} = 452$ nm; $\tau_{\text{F}} = 14.0$ ns) and RTP ($\lambda_{\text{max}} = 500$ nm; $\tau_{\text{RTP}} = 215$ ms) are separated by 6.2 kcal/mol, a suitable energy gap for efficient ISC. The fashion of molecular stacking has been known to influence the emission properties of crystals,³⁷ and it is therefore crucial to perform structural determination for **8** in the solid state. Single crystal XRD data reveal that multiple weak interactions among the molecules may have rigidified the crystal matrix and thus effectively shut down thermal decay (Figure 5d). Unlike polymer matrices, crystals can generate dual-emission that does not require oxygen-free conditions.

3. CONCLUSION

In conclusion, by employing a variety of ketone-Lewis acid model complexes, we have demonstrated that conventionally considered rare dual-emission phenomenon can be made easily accessible following a general design principle, where Lewis acid binding to an aromatic ketone is crucial. The simultaneous fluorescence and room-temperature phosphorescence are thought to originate from Lewis-acid-induced charge-transfer state and carbonyl-enhanced intersystem crossing, respectively. The reported strategy is highly facile and versatile and may find important applications in the field of optoelectronics.

■ ASSOCIATED CONTENT

Supporting Information

Materials, methods, experimental details, characterization of new compounds, and single-crystal data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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