Tunable Full-color Room Temperature Phosphorescence of Two Single-Component Zinc(II) Complexes

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Abstract

Tunable full-color room temperature phosphorescence (RTP) is charming due to its potentials in multiple anti-counterfeitings, all-color displays, and multichannel biomarkers. However, it is a huge challenge to acquire excitation-dependent continuously adjustable full-color RTP from a single-component compound. Herein, we report two Zn(II)-based organic complexes, which are the first examples that present blue, cyan, green, yellow, orange, and red continuously tunable phosphorescence with decent quantum efficiency in response to variation of excitation energy at ambient conditions. The unique photoluminescence property is induced by multiple triplet decay pathways, i.e. $^3$ligand-centered* and $^3$charge transfer*. The population and stabilization of the triplet excitons benefit from heavy atom effect of Br ions and restriction of molecular motion due to crystallization. This work contributes an insight for the construction of full-color RTP materials and endows Zn(II)-based organic complexes with fresh features for extensive applications.

Introduction

Room-temperature phosphorescence (RTP), also characterized as discernible afterglow luminescence, is a fascinating optical phenomenon and caused by long-lived molecular triplet excited state. Persistent luminescence characters empower RTP materials with wide applications in emergency lighting, encryption, anti-counterfeiting, sensing, and biological imaging. Comparing with inorganic afterglow materials doped with rare-earth or noble transition metals, pure organic systems with RTP have received considerable achievements. Generally, the lifetime and quantum efficiency are difficult to exceed 10 milliseconds and 20% for pure organic materials because the intersystem crossing (ISC) is inherently inefficient and the active triplet state is readily exhausted through non-radiative relaxation. To address this issue, most contributions focused on designing organic RTP molecules with ultra-long lifetime and/or higher quantum efficiency. For instance, organic phosphorescence with a lifetime of 2.81 seconds and efficiency of more than 76% has been recently obtained by a synergistic enhancement (polymerization and complexation) strategy. On the other hand, the dynamic modulation of phosphorescence color of RTP materials has also attracted enormous attention very recently. For example, a series of phosphors with color variation from cyan (502 nm) to orange-red (608 nm) have been achieved by a host-guest approach. Compared with the multi-color phosphorescence realized by modulating different chromophore guests, single component phosphors with tunable multi-color RTP are extremely attractive because of the potential superiorities in simple fabrication and device stability for practical applications. Nonetheless, it is well known the observed emission is generally determined by the lowest excited state according to Kasha’s rule, thus it remains challenging to achieve multi-color RTP from single-component materials. To date, only scattered examples were reported on multicolor single-component RTP, in which feasible strategies were tried including construction of chromophores in isolated or aggregated states, and multi-chromophore cross-linked copolymerization. A single-component RTP material with dynamic color tuning from violet to green, for instance, was firstly reported
by mixing molecular phosphorescence and H-aggregation phosphorescence, analogous color-tunable RTP from blue to yellow was achieved through the incorporation of multiple organic phosphorescence emitting centers into one polymer. However, achieving single-component phosphorescence emission across the entire visible spectrum remains highly challenging.

Paralleling to the pure inorganic or organic system to quest excellent RTP with wide color-tunable range, inorganic–organic hybrid system hold promise as a preferable candidate platform for constructing desirable RTP materials, within which the organic moieties, metal centers, and charge transfer all can potentially generate luminescence and furthermore the active triplet excitons can be well populated and stabilized owing to the restricted molecular motion on the basis of coordination crystallization. We have endeavored to develop RTP materials in hybrid zincophosphite system in the last few years. Considering that halogens (e.g., Cl, Br, I) with lone pair electrons can well coordinate with metals and simultaneously act as heavy atoms to facilitate effective ISC and even induce newborn phosphorescence, we introduce Br ions into the hybrid system to optimize the performance of resulting RTP materials. Herein, two hybrid compounds \([\text{Zn}_2(\text{HCOO})(\text{tib})\text{Br}_3]\) (tib = 1,3,5-tris(1-imidazolyl)benzene), denoted as QDU-21a), and \([\text{Zn}_2(\text{CH}_3\text{COO})(\text{tib})\text{Br}_3]\) (QDU-21b) were synthesized, both of which presented continuously tunable afterglow from blue/cyan to orange/red, almost covering the whole visible spectrum, by changing the excitation wavelengths from 240 nm to 460 nm.

Results And Discussion

X-ray Crystal Structures. Complexes QDU-21a and QDU-21b feature similar structures with differences only in the bridging carboxylate group (formate vs. acetate). Single-crystal X-ray diffraction (SCXRD) reveals that QDU-21a crystallizes in triclinic \(P\) space group. The asymmetric unit contains two \(\text{Zn}(\text{II})\) cations, three \(\text{Br}^-\) anions and one formate anion, and one neutral tib ligand (Figure 1a). All the \(\text{Zn}(\text{II})\) centers are co-coordinated by the O-atoms from formate, \(\text{Br}^-\) ions, and N-atoms from tib, forming tetrahedral \([\text{ZnBrN}_2\text{O}]\) and \([\text{ZnBr}_2\text{NO}]\) configuration. The tridentate bridging mode of tib, together with the \(\text{syn,anti}\)-formate, connect zinc ions to yield paralleling hybrid chains along the \(c\) axis (Figure 1b). Notably, the non-coplanar tib moieties feature dihedral angles (30.119-44.678°) between the imidazole and the benzene rings, which inhibits \(\pi-\pi\) stacking to some degree. However, 3D supramolecular architecture (Figure 1c) was available with the assistance of intermolecular interactions, such as C-H...Br, C-H...N, Br...\(\pi\), and C-H...\(\pi\) between the chains. The detailed structure data, selected bond lengths, and bond angles of the two compounds are tabulated in Supplement Tables S1–S3, respectively. The phase purity of the two compounds was confirmed by powder XRD (Supplement Figure S1). Thermogravimetric analysis (TGA) reveals that QDU-21a and QDU-21b can be respectively stable up to 473 K and 623 K (Supplement Figure S2). As expected, blue-white, green, and red luminescence can be clearly seen when taken a single crystal of QDU-21a under UV, blue, green light irradiation, respectively (Figure 1d).

Full-color RTP. The photophysical properties of compound QDU-21a and QDU-21b under ambient conditions were studied in detail. Figures 2a/b display the phosphorescence excitation-emission
mapping, in which the emission wavelengths bathochromic shift with increasing excitation wavelengths, demonstrating that both compounds exhibit the excitation-dependent phosphorescence. However, the wavelength range of excitation and emission is different and the optimal excitation/emission of QDU-21a and QDU-21b are respectively located at 275/465 nm and 340/520 nm. Resolved phosphorescence emission spectra can better exhibit the excitation-dependent phosphorescence characteristic. The main emission peaks shift gradually from 466 to 568 nm when the excitation wavelengths change from 280 to 420 nm for QDU-21a. Correspondingly, the afterglow colors can be finely regulated from blue, cyan, green, yellow, to orange (Figure 2c). By comparison, red-shifts of main emission peaks can be observed for QDU-21b, which varies from 490 to 600 nm upon the excitation changing from 280 to 460 nm, along with the afterglow colors present a fine modulation from cyan, green, greenish-yellow, yellow, orange, to red (Figure 2d). As far as we know, such wide range of phosphorescence colors in a single-component material has only been achieved in 77 K. QDU-21a and QDU-21b are the first examples that feature continuously tunable excitation-dependent full-color phosphorescence at room temperature.

**Mechanism of Full-color RTP.** To explore underlying luminescent species, time-resolved emission spectra were measured under ambient conditions. Figure 2e reveals that QDU-21a has different phosphorescence lifetimes at disparate emission wavelengths upon excitation at 340 nm, with examples of emissions at 485 and 502 nm possessing a lifetime of 15 and 20 ms, respectively (Supplement Figure S3). Besides the dynamic phosphorescence lifetimes, the quantum efficiency also exhibits excitation-dependence with yield varying from 4.7 to 13.8%. (Supplement Table S4). Similarly, the phosphorescence lifetimes and quantum efficiencies of QDU-21b also show dynamic performance under different monitored wavelengths (Figure 2f and Supplement Figure S4 and Tables S4,5). We have also investigated the phosphorescence excitation spectra of the two compounds. Figure 2g and Supplement Figure S5 show that the excitation bands present the characteristics of multiple peaks, and the main excitation peaks together with the effective excitation range exhibit apparent bathochromic shift trend on the basis of the regularly red-shifted monitored wavelengths. Combined with the emission spectra (Figures 2c,d), the excitations (≤ 300 nm) give rise to solid phosphorescence emission at 470 nm for QDU-21a and 490 nm for QDU-21b. By contrast, the continuous excitations from 300 to 475 nm lead to concomitant multicolor phosphorescence emission. The multiple excitation peaks, together with dynamic lifetimes and quantum efficiencies at disparate monitored bands, imply that multiple excited states may exist in the two compounds.

To further study the potential mechanism for the color-tunable phosphorescence emission, we first focus on the luminescent characteristics of the chromophore ligands. Supplement Figure S6 shows the influence of excitation wavelengths on phosphorescence of tib in DMF solution at 77K. The result indicates that the phosphorescence peak possesses excitation-independence in the excited range of 260-330 nm, which excludes the contribution of tib moieties to the dynamic phosphorescence emission. Then, we investigate the possibilities of the co-existence of single molecule and aggregate states in both compounds. However, the tib moieties with twisted molecular conformation hinder intermolecular π–π stacking in part, and the large centroid-to-centroid distance (> 4 Å) of adjacent tib molecules also exclude
the existence of π⋯π stacking in QDU-21a (Supplement Table S6). Obviously, the present excitation-dependent phosphorescence in this work is distinct from those originated from the single molecule and aggregate state.\textsuperscript{18-20} The presence and roles of ordinary Br\textsuperscript{−} ion were subsequently considered. Besides acting as heavy atoms, Br\textsuperscript{−} ions may play a subtle effect on the generation of color-tunable phosphorescence emission. Structural analysis shows that the distances between Br and C/N of tib around the central metal ions are 3.482-3.948 Å in QDU-21a and 3.538-3.826 Å in QDU-21b (Figure 1b and Supplement Figure S7), which may be responsible for potential bond/space-driven charge transfer (CT) and result in phosphorescence.\textsuperscript{30,32} Compared with the electrophilic tib moieties as potential acceptors, the coordinated Br\textsuperscript{−} ions with available isolated electrons can appropriately serve as electron donors. We contend that the CT between Br\textsuperscript{−} ions and adjacent tib units may be helpful to the triplet decay and the resulting superior phosphorescent performance. Such triplet decay pathways induced by CT transition have also been reported by Zhang et al. in the quinolinium halides system.\textsuperscript{33,34}

Theoretical calculations based on periodic density functional theory (PDFT) were conducted for QDU-21a and QDU-21b. As illustrated in Figure 3a and Supplement Figures S8 and S9, the highest occupied molecular orbitals (HOMOs) mainly distributed in the Br\textsuperscript{−} ions and tib ligands, while the lowest unoccupied molecular orbitals (LUMOs) are contributed by the tib ligands. Total and partial densities of states (DOS) show that Br\textsuperscript{−} ions can lose their electrons under relatively low energy (Figure 3b). These results demonstrate that both ligand-centered and charge transfer transitions may give birth to photoemissions. The variable distances between Br\textsuperscript{−} ions and tib molecules may offer multiple paths for CT, which coupled with the local emission of tib and finally lead to the excitation-dependent multicolor RTP. For QDU-21b, the acetate, instead of formate groups, present a stronger intermolecular interaction among Br\textsuperscript{−} ions, acetate groups and tib ligands, and π⋯π stacking is observable with a centroid-to-centroid distance of 3.685 Å (Figure 1b, Supplement Figure S7 and Table S6). The formation of aggregate state may be the main reason for the red-shifted excitation and emission bands of QDU-21b compared to QDU-21a.

**Thermostability and application**

Figure 3c displays the variable-temperature phosphorescence of QDU-21b excited at 360 nm. The phosphorescence intensity gradually decreased with the increasing temperature. Notably, QDU-21b still presented a modest intensity even heated to 453 K. For QDU-21b, the cycling stability of afterglow to temperature has been examined by alternately transforming the temperature between 293 and 453 K. Figure 3d shows the reversible variation of the phosphorescence, wherein the afterglow could still be detected even at 453 K after five runs and could recover the brightness as initial at 293 K. The stable phosphorescence up to 450 K is very scarce, which may benefit from the well protected environment of metal-organic complexes to triplet excitons. A polymethyl methacrylate (PMMA) film containing QDU-21a powder (5 wt\%) was prepared and the phosphorescence emission spectra are shown in Figure 3e. The emission wavelengths of the as-synthesized hybrid film at 466 and 500 nm with excitation at 300 and 360 nm are identical with those in QDU-21a, which demonstrates the good maintain of RTP properties in the resultant hybrid film. Furthermore, the hybrid film possesses high transparency under ambient light.
and presents blue, cyan, to green afterglow upon excitation from 280 to 360 nm, indicating their potential applications in coatings and multicolor displays.

In summary, two metal-organic complexes with continuously tunable RTP have been synthesized. QDU-21a presents blue, cyan, green, yellow, to orange afterglow based on excitation varying from 280 to 420 nm. QDU-21b shows cyan, green, greenish-yellow, yellow, orange, to red afterglow upon excitation changing from 280 to 460 nm. Both compounds exhibit disparate lifetimes (e.g. 11.5-40.3 ms for QDU-21b) and quantum efficiencies (e.g. 4.7-13.8% for QDU-21a) on the basis of different monitored wavelengths. Structural analyses and theoretical calculations show that the local emission of chromophore ligands coupled with multiple charge transfer induces the wide-range finely adjustable phosphorescence. The phosphorescence of this kind of compound possesses well thermostability and the afterglow can still be detected up to 453 K. The compounds can be mixed with PMMA to prepare film with satisfying transparency and multicolor phosphorescence. RTP studies of this model compound indicate that plentiful metal–organic complexes can be designed and synthesized by rational assembly of chromophore ligands and electron-donating and electron-accepting moieties.

Methods

Synthesis of QDU-21. All chemicals are reagent grade and can be purchased without further purification.

QDU-21a: ZnBr$_2$ (0.11g, 0.49mmol), HNO$_3$ (0.25mL, 68%), tib (0.02g, 0.07mmol), DMF (N,N-dimethylformamide) (1mL) and H$_2$O (2mL).

QDU-21b: ZnBr$_2$ (0.11g, 0.49mmol), HNO$_3$ (0.35mL, 68%), tib (0.02g, 0.07mmol), DMA (N,N-dimethylacetamide) (1mL) and H$_2$O (2mL).

Above reagents were well mixed and sealed in a polytetrafluoroethylene-lined autoclave (20 mL) and heated to 120°C for 3 days, then cooled to room temperature.

Characterization. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert-MPD diffractometer by using Cu-Kα1 radiation (λ = 1.54076 Å). A NETZSCH STA 449 F5 instrument was employed to carry out the thermogravimetric measurements with the temperature being in the range of 30–800 °C. UV-vis adsorption spectra were obtained on a PERSEE TU-1901 spectrophotometer. Steady-state phosphorescence and excitation spectra were measured using Hitachi F4700. The lifetime, time-resolved emission spectra and variable temperature luminescence were measured on an Edinburgh FLSP 920 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe900), a microsecond flash-lamp (uF2). Photoluminescence efficiency was collected on a Hamamatsu Absolute PL Quantum Yield Spectrometer C11347.

Crystallography. The crystallographic data of QDU-21a and QDU-21b were collected on a XtaLAB-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by w scan mode. The structures were
solved by the SHELX-2016 software. Detailed crystallographic data are summarized in Table S1 and the selected bond lengths and angles are given in Table S2 and Table S3.

**Calculation methods.** All calculations were performed with the periodic density functional theory (DFT) method by using Dmol3 module in Material Studio software package (Accelrys Inc., San Diego, 2003). The initial configurations were fully optimized by the Perdew-Wang (PW91) generalized gradient approximation (GGA) method with the double numerical basis sets plus polarization function (DNP). The core electrons of metals were treated by effective core potentials (ECP). The self-consistent field (SCF) converged criterion was within $1.0 \times 10^{-5}$ hartree per atom and the converged criterion of the structure optimization was $1.0 \times 10^{-3}$ hartree per bohr. The Brillouin zone was sampled by $1 \times 1 \times 1$ $k$-points, and test calculations reveal that the increase in $k$-points does not affect the results.

**Data availability**

The datasets generated and/or analyzed in the current study are available from the corresponding authors upon reasonable request, and are also included with the manuscript as Supplementary Information. The crystal structure data of QDU-21a and QDU-21b have been deposited in Cambridge Structural Database as CCDC 2053640, and 2053641, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Declarations**

**Author Contributions**

G.M.W., and J.H.L. conceived and designed the experiments. Z.X.L., and Y.M. conducted the synthesis and PL measurement. X.Y.F. performed calculations. J.P., and Q.W. analyzed the crystal structures. Y.M., S.D.H., and G.M.W. co-wrote the manuscript.

**Competing Financial Interests**

The authors declare no competing financial interests.

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**Figures**
Figure 1

Crystal structure of compound QDU-21a. (a) Asymmetric unit and coordination mode of Zn centre. (b) Self-assembled 1D chain. (c) 3D accumulation along [100] direction. (d) Fluorescence microscope photographs of a single crystal of QDU-21a taken under UV (left), Blue (middle), Green (right) light excitation, respectively.
Figure 2

Photoluminescence characterization of QDU-21 under ambient conditions. Phosphorescence excitation–emission mapping of QDU-21a (a) and QDU-21b (b). Normalized phosphorescence emission spectra of QDU-21a (c) and QDU-21b (d) with excitation at displayed wavelengths. The upper inset images show the afterglow photographs taken following excitation as indicated. (e) Time-resolved emission spectra with excitation at 340 nm. (f) The dependence of lifetimes on monitored wavelengths for QDU-21b. (g) Normalized phosphorescence excitation spectra of QDU-21b with emission at displayed wavelengths.
Figure 3

Theoretical calculations and applications of QDU-21. Frontier orbitals (a) and total and partial DOS (b) of QDU-21a and QDU-21b. The Fermi level is set at 0 eV. c) Phosphorescence emission spectra of QDU-21b with excitation at 360 nm at various temperatures from 293 to 453 K. d) Reversible variation of the phosphorescence intensity at 293 and 453 K. The inset images show the afterglow photographs taken under corresponding temperature. e) Normalized phosphorescence emission spectra of QDU-21a thin films with excitation at 300 and 360 nm. The upper inset images show photographs taken under ambient light and after excitation at indicated wavelengths.

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