Three Highly Fluorescent Iridium(III) Unit Based Coordination Polymers: Coordinated Solvent-Dependent Photoluminescence

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Supporting Information

ABSTRACT: Three highly luminescent coordination polymers were solvothermally synthesized in three different solvents, i.e., H2O, DMF (DMF = N,N-dimethylformamide), and DEF (DEF = N,N-diethylformamide) based on a superiorly luminescent Ir(III) unit (L, L = Ir(ppy)2(Hdcbpy)2−, ppy = 2-phenylpyridine, dbcpy = 2,2'-bipyridine-4,4'-dicarboxylate). The three CPs, [MgL2(H2O)2]−·3.5H2O [1], [MgL2(DMF)2]−·3H2O [2], and [MgL2(DEF)(H2O)]−·3H2O [3], exhibit intense emissions, long fluorescence lifetimes, and high quantum yields. In particular, compound 2 shows a very long fluorescence lifetime up to 11.3 μs and high quantum yield up to 18.1%. Attractively, it was found that the luminescence of 1–3 varied from yellow to orange under the irradiation of UV light. The distinct luminescence of 1–3 probably is due to different coordinated solvents in the three compounds.

INTRODUCTION

Explorations of coordination polymers (CPs) have developed into a hot issue, since CPs can be designed as various functional materials with useful tailor-made properties,†−3 which have flourished in gas storage,‡ gas separation,§ photocatalysis,∥ and luminescent sensors.¶ Thereinto, fluorescent CPs (FCPs) exhibit superior properties, including high thermal stability, strong emission, and tunable colors, which make them promising materials as light-emitting diodes,‡ biomolecular probes,¶ and sensors.∥ Until now, chemists have synthesized amounts of FCPs, including lanthanide metal ions based FCPs, organic luminescent ligands based FCPs, and organometallic units based FCPs. Importantly, noble-metal complexes, particularly Ir(III) polypyridine complexes, show long excited-state lifetimes and high luminescent quantum yields, resulting from efficient intersystem crossing between the singlet and triplet excited states via strong spin-orbit coupling of Ir(III) metal ion.¶ The long-lived excited state of Ir(III) polypyridine complexes derives from (1) An electron is promoted from a metal to one of the ligands leading to metal-to-ligand charge transfer (MLCT),∥ and (2) An electron is promoted from a phenyl substituent on the ppy ligand to a bipyridine ligand leading to ligand-to-ligand charge transfer (LLCT).¶ Furthermore, their photophysical properties can be easily modified and tuned via metal-to-ligand charge-transfer (MLCT) excitation and ligand-to-ligand charge-transfer (LLCT) excitation.‡ Therefore, the CPs with promising luminescent properties can be constructed by incorporating Ir(III)-polypyridine complexes. For example, based on Ir(ppy)3 derivatives, Lin et al. synthesized a series of luminescent CPs which can efficiently and reversibly sense oxygen via luminescence quenching.¶ Recently, we developed a coordination polymer Y(L)2(OH) acting as both a photosensitizer to harvest the visible light and a catalytic active for CO2 photoreduction.∥ We also designed three iridium–lanthanide heteronuclear coordination polymers [(LnL)2(OH)2(H2O)]− (Ln = Yb, Er, Nd), which exhibit highly sensitized near-infrared luminescence.‡ To the best of our knowledge, the study of CPs based on Ir(III)-based complexes are still in their infancy; thus it deserves much more efforts on systematic studies.

The metal ions are crucial to the coordination environment and the structural architectures of CPs. Amounts of CPs have been constructed from the multifunctional carboxylate ligands based on alkaline earth metals. These metals possess a large radius, low polarizability, and high affinity for oxygen donors, and thus exhibit strong coordination capacity and high coordination number.∥ Foo’s groups synthesized three baryum coordination polymers with one-, two-, and three-dimensional frameworks based on biphenyl carboxylic acid ligands.‡ Guo’s groups reported a magnesium CP based on biphenyl-3,4′,5-tricarboxylate, exhibiting superior hydrogen-sorption hysteresis at medium pressure.‡

We incorporated Ir(III) unit and alkaline-earth metal into a hybrid compound which not only kept the characteristic properties but also brought new performance. To the best of

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our knowledge, the CPs constructed from Ir(III) polypyridine complexes and alkaline-earth metals have not been reported yet. In this work, we report three luminescent CPs by reaction of organometallic chromophore, i.e., L-H, and alkaline-earth metals and Mg in three different solvents. The three designed CPs exhibit outstanding photophysical properties including intense emissions, long fluorescence lifetimes, and high quantum yields. Interestingly, three compounds exhibit distinct emissive peaks probably caused by different coordinated solvents.

### EXPERIMENTAL SECTION

**Materials and Methods.** All the solvents and reagents were of analytical grade and used as received without further purification. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm⁻¹ by using KBr pellets. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ range of 5–45° with a scan step of 0.05° in a sheet glass on a Rigaku MiniFlex diffractometer. Thermogravimetric analysis (TGA) measurements were carried out on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min. The UV absorptions in the solid state were collected at room temperature on a PE Lambda 900 UV fluorescence spectrometer. The photoluminescence spectra were collected on a FLS920 spectrophotometer. The photoluminescence spectra were collected on a FLS920 spectrophotometer. The photoluminescence spectra were collected on a FLS920 spectrophotometer.

**Synthesis of 1.** An aqueous solution of NaOH (20 μL, 1 M) was added to a mixture containing L-H (0.01 mmol, 7.4 mg), Mg(NO₃)₂·6H₂O (0.02 mmol, 5.1 mg), and 2 mL of H₂O in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container. The container was then placed under autogenous pressure and heated at 180 °C for 2 days. After being cooled to room temperature, the reaction mixture was filtered, washed with H₂O, and dried in air which produced bright yellow crystals of 1. The yield was 71% based on Mg. IR (cm⁻¹): 3430(m, br), 3111(w), 3039(w), 2920(w), 2849(w), 1606(vs), 1583(m), 1549(s), 1424(m), 1347(s), 1308(w), 1268(w), 1236(m), 1157(w), 1124(w), 1064(w), 1031(w), 934(w), 870(w), 835(w), 785(m), 760(s), 732(s), 698(m), 668(w), 629(w).

**Synthesis of 2.** An aqueous solution of HClO₄ (20 μL, 1 M) was added to a mixture of L-H (0.01 mmol, 7.4 mg) and Mg(NO₃)₂·6H₂O (0.02 mmol, 5.1 mg) dissolved in 3 mL of DMF/H₂O (2:1) in a 20 mL vial. After ultrasonication for about half an hour, the resulting solution was placed in an autoclave and heated at 90 °C for 4 days. After the solution was cooled to room temperature, a large amount of yellow crystals of 2 (yield 69% based on Mg) was obtained after filtration, washed with acetone, and dried in air. IR (cm⁻¹): 3420(m, br), 3111(w), 3039(w), 2922(w), 2848(w), 1606(vs), 1583(m), 1549(s), 1477(s), 1424(m), 1347(vs), 1307(w), 1268(w), 1236(m), 1157(w), 1124(w), 1064(w), 1031(w), 934(w), 870(w), 835(w), 785(m), 760(s), 732(s), 698(m), 668(w), 629(w).

**Synthesis of 3.** Compound 3 was synthesized with the same procedure as that of 2, except that DEF was used as the solvent in place of DMF. Orange crystals of 3 were obtained after filtration, washed with acetone, and dried in air. The yield was 51% based on Mg. IR (cm⁻¹): 3420(m, br), 3111(w), 3039(w), 2920(w), 2849(w), 1605(vs), 1582(m), 1547(m), 1477(s), 1422(m), 1382(w), 1312(w), 1268(w), 1235(w), 1159(w), 1015(w), 872(w), 784(m), 760(s), 731(s), 697(m), 630(m).

**Single Crystal Structure Determination.** Crystals of three compounds 1, 2, and 3 were selected and attached to a glass capillary under an optical microscope. Data collections of three compounds were performed in sequence at 173(2) K on a SuperNova, Dual, Cu at zero, Atlas diffractometer. Using Olex2, the structure was solved with the SHELXS-2016 structure solution program using Direct Methods and refined with the SHELXL-2016 refinement package using the least squares

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"Free water molecules are not taken into account. $R₁ = \frac{\sum |F₁| - |F₀|}{\sum |F₀|}$, $wR₂ = \frac{\sum (|F₀|² - |F₁|²)²}{\sum |F₀|²}$."
The formulas of the three compounds are [MgL2(H2O)2] calculated as 3.5, 3.5, and 3 respectively. The molecular spectra which show the disappearance of the absorption peak at 1707 cm−1 confirm the coordination of the Mg(II) ion of three compounds was verified by IR spectroscopy which show the disappearance of the absorption peak at 1707 cm−1 compared to L-H (Figure S1). The guest H2O molecules cannot be totally orientated by SuperNova due to weak intensity or randomness of dissociative H2O in frameworks.

**RESULTS AND DISCUSSION**

**Synthesis.** The magnesium CPs were obtained via solvothermal synthesis in different alkaline environment. The pH values of heterogenous solution of 1, 2, 3 were adjusted by addition of NaOH, DMF/HClO4, DEF/HClO4. The compounds were characterized by IR. The coordination of carboxyl group with Mg(II) ion of three compounds was verified by IR spectra which show the disappearance of the absorption peak at 1707 cm−1 compared to L-H (Figure S1). The guest H2O molecules cannot be totally orientated by SuperNova due to weak intensity or randomness of dissociative H2O in frameworks. Assisted by elemental analysis (CHN), found: 1 (C:50.66%, H:3.51%, N:6.92%), 2 (C:51.3%, H:3.81%, N:8.02%), 3 (C:51.8%, H:3.65%, N:7.57%) and TGA, the number of the guest water molecules for 1, 2, and 3 are calculated as 3.5, 3.5, and 3 respectively. The molecular formulas of the three compounds are [MgL2(H2O)2]·3.5H2O [1], [MgL2(DMF)2]·3.5H2O [2], [MgL2(DEF)(H2O)]·3H2O [3].

**Structural Descriptions.** Crystal Structure of 1. Single crystal X-ray diffraction analysis reveals that three compounds are allomeric, and form a 1D chain structure. Compound 1 crystallizes in monoclinic P21/c space group, and the asymmetric unit contains a half Mg(II) center, one L linker, and one coordinated H2O molecule. As illustrated in Figure 2a, the Mg atom coordinates with four carboxylic oxygen atoms (O17, O17H, O47, O47H) from four L ligands and two oxygen atoms (O20D, O20E) from two H2O molecules. The Mg–O distances range from 2.0370(1) to 2.1001(0) Å for four L ligands and 2.2147(1) Å for H2O. It gives a torsional chain structure (Figure 1a). The torsion angle of O17–Mg–O47H is 87.44°. The distance between the adjacent Mg centers in the chain is 8.6820(2) Å. Associated by supermolecular interactions, the chains pack with each other to give rise to a 3D stacking framework as shown in Figure 1b.

Crystal Structure of 2. The structure of compound 2 is similar to that of 1. The basic difference between 2 and 1 is that coordinated DMF replaces H2O (Figure 2b). The Mg atom is coordinated with four oxygen atoms (O2B, O2C, O4, O4A) from four carboxylate group of L ligands, and two oxygen atoms (O3, O3A) from two DMF molecules. The Mg–O distances range from 2.0597(0) to 2.0689(0) Å for L ligands and 2.1855(0) Å for DMF. It results in a torsional chain structure. The torsion angle of O4–Mg–O2B is 87.776°. The distance between the adjacent Mg centers in the chain is 8.8461(1) Å.

![Figure 1](https://example.com/figure1.png)
Crystal Structure of 3. Compound 3 also exhibits a similar structure to that of 1. As shown in Figure 2c, the Mg atom exhibits coordination with four carboxylate oxygen atoms (O17, O17G, O20D, O20F) from four L ligands, one oxygen (O49) from DEF, and one oxygen (O49G) from H2O. The Mg−O distances range from 2.0331(0) to 2.0463(0) Å for four L ligands, while in the case of DEF as well as H2O, the Mg−O distance is 2.2147(1) Å. This produces a torsional chain structure. The distance between the adjacent Mg centers in the chain is 8.7852(1) Å. Furthermore, among three compounds, compound 3 gives the biggest torsion angle which is 88.108° of O17−Mg−O20F, while 1 has the smallest one. Thus, in order to accommodate larger sized coordinated solvents, the torsion angle of O−Mg−O is as big as possible and the organic−inorganic frameworks adjust themselves owing to the steric hindrance of different solvents of various sizes.

Spectroscopic Studies. As illustrated in our previous work, Ir(III) units were proven to exhibit interesting photo−physical properties derived from metal-to-ligand charge-transfer (3MLCT) transitions and ligand-to-ligand charge-transfer (LLCT) transition.17 Verified by UV−vis absorption measurements, Ir(III) unit exhibits a strong absorption band ranging from 200 to 500 nm, and all three complexes have a broad absorption similar to Ir(III) unit. Further research on the photoluminescent properties of 1−3, as well as the Ir(III) unit, was performed in the solid state at room temperature. The emission bands are similar to that of free Ir(III) unit, suggesting that the fluorescent emissions of 1−3 arise from the Ir(III) unit. Compared to the free Ir(III) unit, which displays a strong emission band at 575 nm with orange luminescence upon excitation at 468 nm, the emissions of three compounds all show a blue shift (Figure 4a). Interestingly, three compounds show different fluorescence which can be identified by the naked eye under the illumination of a UV lamp (Figure 4b). Compounds 1 and 2 exhibit strong yellow photoluminescence with an emission maximum at 544 and 554 nm upon excitation at 468 nm. However, for 3, the emission maximum is 570 nm, which is very adjacent to that of Ir(III) unit. The different emission maxima of three compounds are possibly induced by solvents of various electron-donating abilities. The electron-donating ability of O is stronger than N and that of −CH2−CH3 is stronger than −CH3, so the electron-donating ability of solvents increases from H2O < DMF < DEF, and the emission maximum of corresponding compounds shifts to higher wavelengths.28

Further research on time−resolved fluorescence decay of Ir(III) unit and 1−3 was carried out, and the luminescence decay is fitted by a biexponential curve, as shown in Figures S2−S5. The fluorescence lifetime of the Ir(III) unit is determined to be 7.6 µs, and the three CPs maintain a long fluorescence lifetime of the Ir(III) unit, which is 7.7 µs, 11.3 µs, and 7.7 µs for 1, 2, and 3, respectively (Table S2). It is observed that the fluorescence lifetimes of 1 and 3 are appropriate to that of the Ir(III) unit, while the lifetime of 2 is effectively increased. Moreover, the quantum yields (the ratio of a phosphor giving photons to absorption photons) increase largely from 6.8% of the Ir(III) unit to 14.6% (1) and 18.1% (2), but decreases obviously to 2.4% (3) (Table S2). Photoluminescent
efficiencies of 1 and 2 are enhanced owing to the construction of the organic–inorganic framework, which strengthened the rigidity of Ir(III) unit and decreased the self-quenching; however, the quantum yield of 3 obviously decreases. It is speculated that the terminal –CH₂–CH₃ of DEF in 3 is flexible, and drastic vibrations of –CH₂–CH₃ increase the nonradiative decay rate and decrease the quantum yield. Compounds 1–3 appear to be good candidates for fluorescent materials due to their advantageous photophysical properties.29

**Thermal and Moisture Stability.** PXRD was used to verify the phase purity of all three compounds. The peaks of synthesized compounds correspond well with the simulated patterns from single crystal structures (Figures S6–S8). The thermal stability can be assessed by TGA, PXRD, and emission spectra. As shown in Figures S9–S11, the TG analysis of three compounds gives similar curves. For three compounds, weight loss was observed from about 60 °C upon which loss of guest water molecules occurs (1: 3.8%, 2: 3.56%, 3: 3.16%). Among 190–330 °C, there are no obvious mass changes of three compounds. After all the guest water molecules were removed by being heated at 200 °C in oven for 6 h, the structural integrity of the frameworks are indicated by XRD. The PXRD patterns of the water-removed samples are coincident with the previous ones except for some small orientation changes due to the loss of guest water molecules. To further test the thermal stability, we adopted a novel strategy, put forward by Li.30 The thermal stability can be evaluated by the change in emission intensity after thermal treatment. The decrease in emission intensity is 12.5%, 9.3%, and 9.6% for 1, 2, and 3 after being heated at 200 °C in oven for 6 h (Figures S12–S14 and Table S1). Then the water-removed samples are placed in an ambient environment for 2 days, and the rehydrated samples show PXRD patterns consistent with the synthesized ones, which indicates no framework collapse or phase transition. As Li demonstrated, the moisture stability of materials can be evaluated by testing the changes of PXRD (Figures S15–S17) and quantum yields after placing the materials in air for a period of time.31 After being exposed to air for >1 month, three compounds show scarcely any changes in PXRD patterns. Upon excitation at 468 nm, the quantum yields of 1, 2, and 3 become 14.1%, 17.5%, and 2.2% (Table S2). The decreases of three compounds in quantum yield are <1%. Thus, the three compounds all show excellent stability of moisture and heat.

## CONCLUSION

In summary, we have successfully synthesized three allomeric CPs with the Ir(III) unit and Mg(II) ion in different solvents via solvothermal reactions. The three compounds exhibit advantageous photophysical properties, including intense emissions, long fluorescence lifetimes, and high quantum yields, which stem from the Ir(III) unit based on the metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT). In addition, the solvents exert a profound influence on photophysical properties. This interesting phenomenon provides a new strategy to tune the photophysical properties of coordination polymers without altering the structure or the chromophore linker.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b01391.

## REFERENCES


