Efficient and tunable white-light emission of metal–organic frameworks by iridium-complex encapsulation

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Metal–organic frameworks (MOFs) are well known for their tunable structure and porosity. Many studies have shown they are promising for various important applications, for which their performance can be further enhanced by encapsulating functional species, such as luminescent guest molecules, within the frameworks. Although numerous MOFs are luminescent, very few emit white light and their quantum yield is usually low. Here we report a strategy to achieve efficient white-light emission by encapsulating an iridium complex in the MOF cavity. A mesoporous blue-emitting MOF is prepared as host to encapsulate a yellow-emitting iridium complex, \([\text{Ir}(ppy)_2(bpy)]^+\). The resultant composites emit bright white light with good colour quality (for example, Commission International de l’Eclairage coordinates, colour-rendering index and correlated colour temperature of (0.31, 0.33), 84.5 and 5409 K, respectively), and high quantum yield up to 115\%/C¹²⁶\/C. This strategy may open new perspectives for developing high-performance energy-saving solid-state lighting materials.

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Solid-state light-emitting-diode (LED) materials have been extensively investigated in the recent years because of their potential applications in lighting and displays. Currently, mercury-containing fluorescent lighting is one of the most widely used white-light sources, which relies on the emission of mercury vapour to excite semiconductor phosphors and to achieve white composite photoluminescence (PL). However, the extensive use of mercury varies various environmental concerns. Thus tremendous efforts have been dedicated to search for environmentally more friendly, safer and more energy efficient white phosphor materials for use in the white LEDs (WLEDs) and, including hybrid inorganic materials, rare-earth metal-doped zeolites, organic compounds, and metal complexes. Three types of white phosphor materials are commonly used in phosphor-based methods to generate white light, including (i) monochromatic emitters that emit in the entire visible spectrum, (ii) dichromatic emitters that blend blue and yellow light and (iii) trichromatic emitters that combine red, green and blue lights. Among them, dichromatic and trichromatic approaches have been the main focus because of their finer color rendering properties and higher luminescence efficiency.

Metal–organic frameworks (MOFs) composed of metal ions and multiligand organic ligands are a new family of hybrid inorganic–organic porous materials, and have received tremendous attention in the past two decades. Benefiting from uniform but tunable cavities, tailorability chemistry and high porosity, MOFs have become promising candidates for many important applications such as chemical separation, gas storage, catalysis, drug delivery and optical sensing/detection. MOF materials possess unique advantages for luminescence-based applications primarily because of their capability of incorporating light-emissive building blocks at both metal centres and organic ligands. This allows efficient modulation of luminescent properties. In addition, permanent porosity in these structures permits the accommodation of guest molecules within their frameworks, offering another degree of tunability in their emission properties. Through judicious choice of metal centres and organic linkers, a large number of luminescent MOFs have been synthesized (accounting for > 10% of the total number of reported MOFs) and their possible applications in fluorescent sensors, nonlinear optics, photocatalysis and biomedical imaging have been evaluated. On the other hand, it remains a great challenge to produce high-performance white-emitting MOF materials suitable for solid-state lighting applications. To date, only a few examples of direct white-light-emitting MOFs are realized and are at low quantum yield. Thus, it is essential to develop an effective method to obtain highly efficient, white-light-emitting MOF materials.

Herein, we introduce a new strategy to achieve high quantum yield white light by encapsulating a yellow-emitting Ir(III) complex in the cavity of a blue-emitting MOF. Ir(III) complexes are well known for their high PL efficiency, relatively short lifetimes and emissive light variability. Large-pore MOF structures with tunable pore sizes (up to 9.8 nm (ref. 31)) may be constructed by suitable choice of organic ligands of various length which will ensure the entrapment of Ir(III) complexes in large quantity. Thus, it may be anticipated that a successful encapsulation of yellow-emitting Ir(III) complex in a blue-emitting MOF will not only produce white light, but also generate high quantum yield, because the aggregation of Ir(III) complexes can be effectively prevented and their oscillation may also be effectively constrained when confined into the MOF pores. A cationic Ir(III) complex, [Ir(ppy)2(bpy)]+ ([ppy = 2-phenylpyridine, bpy = 2,2’-bipyridine]), was selected in this study as an encapsulate for its relatively small size which allows easy access to the MOF pores. Hexadentate carboxylate triazine ligand, 2,4,6-tris(2,5-dicarboxyphenylamino)-1,3,5-triazine (H₃TATPT, Supplementary Fig. S1) was chosen as the organic building block to construct highly porous blue-light-emitting MOF, based on the following considerations: (i) it has a suitable length for building MOF structures with desired pore diameters, (ii) it may be multiple metal binding modes and (iii) it emits at 490 nm which will likely result in a blue-emitting MOF material. Cadmium ion was selected as metal centre because of its ability to form a stable, fluorescent coordination polymer and a number of coordination geometries and angles, but also exhibit photostability due to the high thermal stability of its crystals (Supplementary Fig. S4).

With TATPT and Cd²⁺, we successfully prepared a three-dimensional (3D) mesoporous blue-emitting anionic MOF, [(CH₃)₂NH₂][Cd₂Cl₃(TATPT)₄]·12DMF·18H₂O (1) which contains two types of cages with the dimensions of approximate 2 and 3 nm. Compound 1 emits bright blue light (λem = 425 nm) and is photoactive when bound to functional ligands. The [(CH₃)₂NH₂][Cd₂Cl₃(TATPT)₄]·12DMF·18H₂O (1) sample at 3.8 wt% of Ir-complex yield (0.30, 0.35), 84.5 and 5409 K for CIE, CCT, and CRI, respectively.

Results

X-ray diffraction analysis of compound 1. Compound 1 was synthesized by reacting H₃TATPT and CdCl₂·2.5H₂O (1:1 molar ratio) in a N,N-dimethylformamide (DMF)/MeOH solvent mixture heated at 120°C for 2 days. The reaction produced colourless crystals with polyhedral morphology (Supplementary Fig. S2). The phase purity of 1 was confirmed by powder X-ray diffraction (PXRD) analysis. The formula of 1 was obtained by single-crystal X-ray diffraction, elemental analysis (EA), thermogravimetric analysis (TGA) and by taking into account charge balance considerations. The protonated [(CH₃)₂NH₂][Cd₂Cl₃(TATPT)₄]·12DMF·18H₂O (1) is a result of decomposition of DMF.

Single-crystal X-ray diffraction analysis reveals that 1 is a 3D non-interpenetrated framework. It crystallizes in cubic space group Fmm-3m (Supplementary Table S1). The asymmetric unit of 1 contains one crystallographically independent cadmium ion, one chlorine ion and one-sixth of TATPT ligand. Other disordered cations and guest molecules are not crystallographically well defined. Compound 1 is built on a cuboid Cd₂(Cl₂(CO₃)₂ secondary building unit (SBU). In this SBU, the two Cd atoms are nine-coordinated by a μ₂-Cl and eight carboxylate oxygen atoms from four TATPT ligands in enneahedral geometry (Supplementary Fig. S3a). The μ₂-Cl atom connects the two Cd atoms lying at the centre of the rectangular parallelepiped. The bond lengths of Cd–O carboxylate (2.285–2.646 Å) are the highest among all white-light-emitting MOF materials reported to date. The phase purity of 1 was confirmed by powder X-ray diffraction (PXRD) analysis. The formula of 1 was obtained by single-crystal X-ray diffraction, elemental analysis (EA), thermogravimetric analysis (TGA) and by taking into account charge balance considerations. The protonated [(CH₃)₂NH₂][Cd₂Cl₃(TATPT)₄]·12DMF·18H₂O (1) is a result of decomposition of DMF.

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residue is CdO (observed 16.0%, calculated 15.1%). Furthermore, the framework began to take place at this temperature. The final size of windows is about 11 Å2. Eight such truncated tetrahedrons occupy the eight vertices of a cube, resulting in a mesoporous truncated octahedron through corner sharing. The dimensions of this truncated octahedron are 27.2 × 23.1 × 27.2 Å3 with a window size of ~15.5 × 15.5 Å2. The truncated octahedra propagate to form a three-dimensional non-interpenetrated extended open network (Fig. 1c and Supplementary Fig. S3). The pore structure can also be viewed as three intersecting1D channels with a window size of 15.5 × 15.5 Å2. From the topological point of view, each of the Cd4(j2−Cl)(CO2)3h SBU acts as a four-connected node and every TATPT ligand serves as a three-connected node, thus the framework can be described as a binodal (3,4)-connected 3D network with topology (Schläfi symbol (6^2.8.10^2.16^3)h) (Fig. 1d). The solvent molecules and [(CH3)2NH2] cations reside in the channels. The effective free volume of 1, calculated by PLATON software, is 67.8% of the crystal volume (38,769.5 Å3 of the 57,186.8 Å unit cell volumes), upon removal of the guest molecules.

TGA and transition metal ion exchange experiments. Overall, the framework structure is anionic with H2O molecule, (CH3)2NH2 cations as well as DMF residing in the channels, as determined by EA, TGA and by the consideration of charge balance. The TGA data (Supplementary Fig. S4) reveal that the first weight loss corresponds to the loss of solvent and water molecules (20.3 wt%). The desolvated framework remains stable until ~210°C (Supplementary Fig. S4). The decomposition of the framework began to take place at this temperature. The final residue is CdO (observed 16.0%, calculated 15.1%). Furthermore, transition metal cation exchange experiments were performed by soaking samples of 1 in solutions of Cu(NO3)2·3H2O, Co(NO3)2·6H2O, Ni(NO3)2·6H2O and Zn(NO3)2·6H2O in DMF solvent, respectively. After a few days the colour of the solid changed from colourless to teal, red and light green, for Cu2+, Co2+ and Ni2+, respectively (Supplementary Fig. S5). For Zn(NO3)2, no colour change was observed. A PXRD comparison of 1 before and after exchange experiments indicates that the integrity of 1 is retained after transition metal cation exchange uptake (Supplementary Fig. S6). The successful exchange of (CH3)2NH2 with transition metal cations was confirmed by 1H NMR spectroscopic studies after cation exchange experiments (Supplementary Fig. S7). The products were characterized by Inductively coupled plasma (ICP) spectroscopy (Supplementary Table S2) and the results show that approximately 0.46 CuII, 0.37 CoII, 0.26 NiII and 0.28 ZnII per formula was impregnated into the framework.

**Figure 1 | Structure of 1 determined by single-crystal XRD. (a) Ball and stick representations of the truncated tetrahedral and truncated octahedral cages, the yellow spheres represent the void inside the cages. (b) Polyhedral presentation of a. (c) The 3D polyhedral structure of 1. (d) The (3,4)-connected augmented net (top) as a natural tiling.**

**PL. measurements of H6TATPT and compound 1.** The emission spectra of the H6TATPT ligand, and compound 1 in powder form were measured at room temperature and displayed in Supplementary Fig. S8. The free H6TATPT ligand exhibits a weak emission at 490 nm under the excitation at 370 nm, which is due presumably to the π→π* transition of the intraligands. Upon excitation at the same wavelength, compound 1 shows significantly enhanced bright blue light emission with an emission maximum at 425 nm (Supplementary Fig. S9). Compared with the free organic linker, the large enhancement of emission intensity and strong blue shift (about 65 nm) of the emission in 1 may be attributed to metal-to-ligand charge transfer (MLCT) and the coordination effects of the ligand to Cd (II) cations, which increases the ligand conformational rigidity and reduces the non-radiative decay. The CIE coordinates for the blue emission of compound 1 was calculated to be (0.175, 0.145), close to that of saturated blue emitter with CIE coordinates of (0.14, 0.08)44. The quantum yield of compound 1 was measured under λex = 370 nm at room temperature and a value of 15.1% was obtained. These data demonstrate that compound 1 is an efficient blue-light emitter.

Encapsulating [Ir(ppy)2(bpy)]³⁺ in compound 1. Primary Ir³⁺ complex, [Ir(ppy)2(bpy)]³⁺ (with a counter ion [PF6]⁻), was selected as the encapsulant45. With a molecular size of ~10 × 11 Å2 which is smaller than the aperture of the pore windows of compound 1, the complex can enter the pores readily. The [Ir(ppy)2(bpy)][PF6] complex was synthesized according to the reported procedure46 and its structure is shown in Fig. 2. The emission spectrum of [Ir(ppy)2(bpy)][PF6] was measured in DMF solution at room temperature and plotted in Supplementary Fig. S10. From the emission spectrum it is clear that when excited at 370 nm, [Ir(ppy)2(bpy)][PF6] emits yellow light with broad and structureless emission at 570 nm, indicating a predominant MLCT or LLCT character.

In an initial attempt, powder samples of 1 were immersed into DMF solutions of [Ir(ppy)2(bpy)]³⁺ (10⁻⁴ mol l⁻¹) in duplicate. After 7 and 10 days, both soaked samples were removed from the solution. An obvious colour change from colourless to light yellow was observed, indicative of a successful encapsulation of [Ir(ppy)2(bpy)]³⁺ into the framework of compound 1. As evidenced by the PXRD data, the [Ir(ppy)2(bpy)]³⁺@1 samples maintain their crystallinity (Supplementary Fig. S11). The concentrations of encapsulated [Ir(ppy)2(bpy)]³⁺ were measured by ICP experiment. The results show that ~7.5 wt% and ~8.8 wt% [Ir(ppy)2(bpy)]³⁺ were embedded, respectively, with respect to Cd. PL spectra were collected on both
The orange and dark cyan spheres represent the void inside the cages. Compound 1 emits bright blue light. (c,d) [Ir(ppy)2(bpy)]+ encapsulated samples [Ir(ppy)2(bpy)]+@1 emit white (3.5 wt%) and yellow (8.8 wt%) light, respectively, using the same 365 nm ultraviolet lamp.

Figure 3 | PL spectra of 1 and [Ir(ppy)2(bpy)]+ encapsulated 1. Room temperature emission spectra of 1 and [Ir(ppy)2(bpy)]+@1 with different concentration of [Ir(ppy)2(bpy)]+; black, emission spectrum of 1; red, 0.52 wt%; [Ir(ppy)2(bpy)]+ at 1; green, 1.04 wt%; blue, 3.5 wt%; cyan, 3.7 wt%; pink, 4.5 wt%; yellow, 7.5 wt%; orange, 8.8 wt%. All measurements were performed on solid samples at an excitation wavelength (λex) of 370 nm.

[Ir(ppy)2(bpy)]+@1 samples. As shown in Fig. 3 (yellow and orange curves), the PL spectra of both samples exhibit two emission maxima at ~425 and ~530 nm, respectively, when irradiated at 370 nm. The emission at 425 nm is attributed to MLCT in 1 whereas the emission at 530 nm presumably originates from [Ir(ppy)2(bpy)]+. However, in comparison with the emission of free [Ir(ppy)2(bpy)]+, there is an obvious blue shift (about 40 nm) in the emission spectra of the [Ir(ppy)2(bpy)]+@1 composite. A possible explanation for such large blue shift is that the confinement of [Ir(ppy)2(bpy)]+ within the pores of 1 leads to a phenomenon very similar to a 'rigidochromic effect' reported and explained previously on similar metal complexes. The corresponding CIE coordinates were calculated and the values are (0.37, 0.47) and (0.40, 0.50) for 7.5 wt% and 8.8 wt% encapsulated samples, respectively, at an excitation wavelength (λex) of 370 nm. The quantum yield of the 8.8 wt% [Ir(ppy)2(bpy)]+@1 sample was measured at room temperature. A value of 28.7% was achieved at λex = 370 nm. The photograph of its emission is shown in Fig. 2d, Supplementary Fig. S12c and Supplementary Fig. S13, excited at 365 nm using an ultraviolet lamp. Another interesting phenomenon observed in the PL spectra is that the intensity of the 530 nm emission is higher for the 8.8 wt% than for the 7.5 wt% encapsulated sample, whereas the intensity of 425 nm emission is similar for the two samples. This is another evidence that the 530 nm emission is due to [Ir(ppy)2(bpy)]+.

Fabrication of WLEDs of [Ir(ppy)2(bpy)]+@1 composite. To obtain white-light emission, a more balanced distribution of the two emissions is needed. This can be accomplished by reducing the amount of [Ir(ppy)2(bpy)]+ in compound 1. The corresponding PL spectra of [Ir(ppy)2(bpy)]+ encapsulated samples at different concentrations were collected and plotted in Fig. 3. The PL spectra show that the intensity of the emission at 530 nm decreases monotonically as the [Ir(ppy)2(bpy)]+ amount decreases. White-light emission was achieved as the concentration of Ir complex was adjusted from 1.04 wt% to 3.7 wt% (see Fig. 4, and Supplementary Table S3). The optimal concentration for the white light was found to be 3.5 wt%, with CIE coordinates of (0.31, 0.33). This is very close to those of the pure white light (0.33, 0.33). Other related colour parameters, including the CCT and CRI, were also estimated. At this concentration, these values...
are \( \sim 80 \) and \( \sim 5,900 \) K, respectively. The quantum yield was measured and a value up to 20.4% was obtained \((\lambda_{\text{ex}} = 370 \text{ nm})\) for this sample. This value is highest among all reported white-light-emitting MOFs\(^{12,23-29}\) to this date (Supplementary Table S4), and is approaching that of the best inorganic–organic hybrid semiconductor white-light emitters\(^{36}\). Photographs showing white-light emission of a 3.5 wt% \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) sample under radiation at 365 nm (ultraviolet lamp) are given in Fig. 2b and Supplementary Fig. S12.

Clearly, the observed broad emission of \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) is simply a combination of the two independent emissive components, \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) and \(1\). Such an additive behaviour is possible when there is essentially no energy and electron/charge transfer between the two species. This is evident from the absorption and emission spectra of the individual components\(^{52}\) (Supplementary Figs S14 and S15) and the fact that the second emission peak \((\lambda_{\text{em}} = 425 \text{ nm})\) is independent from the first and is a monotonic function of Ir concentration (Fig. 3).

To further verify this, we have carried out lifetime measurements on \(1\) and \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) at \(\lambda_{\text{ex}} = 370 \text{ nm}\) and \(\lambda_{\text{em}} = 425 \text{ nm}\) by time-correlated single photon counting. The results show that compound \(1\) exhibits single-exponential decay behaviour with a lifetime of \(\sim 0.84 \text{ ns}\) (Supplementary Fig. S16). The lifetime is 0.77 and 0.75 ns for the 3.5 and 8.8 wt% of \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\), respectively. These data indicate that the lifetimes of \(1\) and \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) encapsulated samples remain little affected, and thus, confirming that there is no energy transfer between the two components (\([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(+ 1\))\(^{53}\).

To evaluate the temperature effect on the emission, PL spectra (Supplementary Fig. S17) and quantum yield (Supplementary Table S5) of \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) were collected at various temperatures. As shown in Supplementary Fig. S17, the intensity of the yellow emission \((530 \text{ nm})\) is essentially unaffected over the entire temperature range investigated. For blue emission \((425 \text{ nm})\), a very small change is observed below 115 °C. Above this temperature, the emission intensity and consequently, quantum yield, are reduced considerably. At 150 °C, a \(\sim 40\%\) loss is observed (Supplementary Fig. S17). This is due to the partial degradation of the MOF framework upon heating at high temperatures. Thus, \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) is relatively stable only below 115 °C.

WLED assemblies using this material were fabricated by two methods. The first one employed a commercially available ultraviolet LED (similar to the reported procedure\(^{36}\)) and an \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) sample \(\text{Ir}^3\text{doped}\) as phosphor. The resultant WLED exhibits bright white light at an applied voltage of 3.8 V (see Fig. 5). The second WLED was made by an InGaAsN chip \((370 \text{ nm})\) and an \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) sample at \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) concentration of 3.8 wt% (Supplementary Fig. S18). The latter yielded a CIE, CCT and CRI values of \((0.30, 0.35), 84.5\) and 5409 K (Supplementary Table S6), respectively. On the basis of these results, it is clear that the \([\text{Ir}(\text{ppy})_{2}(\text{bpy})]^{+}\) \(@1\) materials not only have potential for practical lighting applications, but more importantly, this method of encapsulation of a luminescence-active molecular complex into a luminescent MOF to generate white light and to systemically tune the emission quality also represents a new approach to fabricate WLEDs with superior performance.

**PL of Eu\(^{3+}\) and Tb\(^{3+}\) co-doped emitters.** Rare-earth ions (for example, Eu\(^{3+}\), Tb\(^{3+}\) and Dy\(^{3+}\)) have been commonly used as dopants to obtain white-light emission. To evaluate their effect in \(1\), the samples of white-emitting Eu\(^{3+}\) and Tb\(^{3+}\) co-doped \(1\) were prepared (Supplementary Fig. S19) and their luminescent properties were studied. Under the excitation at 370 nm, the MOF emission colour was fine-tuned to white by soaking \(1\) in DMF solutions containing nitrate salts of Eu\(^{3+}\) and Tb\(^{3+}\) in a molar ratio of 1:2. The corresponding CIE coordinates for this sample is \((0.36, 0.32)\), approaching the coordinates of pure white light. Figure 6 shows photographs of the co-doped samples excited by a standard laboratory ultraviolet lamp (365 nm). The PL spectra of the co-doped samples were also collected under excitation at 370 nm (Fig. 6). These spectra feature a broad emission peak centred at 425 nm and several narrow-band emission peaks at 492, 545, 594 and 618 nm. The broad emission at 425 nm can be attributed to MLCT in \(1\). The peaks at 492 and 545 nm are characteristic emissions of Tb cation. The maximal intensities at 594 and 618 nm are corresponding to the emissions of Eu cation. The white-light-emission quantum yield of this sample was measured at room temperature under \(\lambda_{\text{ex}} = 370 \text{ nm}\). A value of 11.3% was obtained which is significantly lower than that of Ir\(^{3+}\) encapsulated \(1\), assuming that the energy migrates through the same electronic levels located in the MOF structure to the doped lanthanide ions\(^{34}\). This result indicates that Ir\(^{3+}\)-complex encapsulating method is likely a more effective approach to obtain high-efficient white-light-emitting MOF materials. On the other hand, introduction of Eu\(^{3+}\) or Tb\(^{3+}\) ions into \(1\) can lead to
red and green light emissions. The corresponding PL spectra and the corresponding optical photographs are also given in Fig. 6.

Discussion

In this study, we have demonstrated that encapsulating an Ir(III) complex cation in the pores of an anionic MOF structure represents a convenient and efficient route to achieve white-light emission with high quantum yield and optimized colour quality. H_{6}TATPT was chosen as organic building block in the MOF synthesis, not only for its suitable length, but also for its blue emission which was retained in the resultant framework. A cationic yellow-emitting Ir(III) complex, [Ir(ppy)_{2}(bpy)]^{+}, was selected as the encapsulant based on the consideration of pore size and its complementary yellow emission. [Ir(ppy)_{2}(bpy)]^{+} was successfully introduced in the pore of the MOF host via encapsulating experiments. The encapsulated amount can easily be controlled and fine-tuned by varying exposure time and concentration. At an [Ir(ppy)_{2}(bpy)]^{+} concentration of 3.5 wt%, high-quality white light was obtained and the resultant material possesses CIE coordinates (0.31, 0.33) that are very close to those of pure white light and good colour quality (CRI ~ 80 and CCT ~ 5900 K). In addition, this material also has the highest emission quantum yield (up to 20.4%) of Ir complex. Eu^{3+} and the resultant material possesses CIE coordinates (0.31, 0.33) with high-quality white light was obtained. The WLED also has the highest emission quantum yield (up to 20.4%) of Ir complex. Eu^{3+} and the resultant material possesses CIE coordinates (0.31, 0.33) with high-quality white light was obtained.

Procedure for encapsulating [Ir(ppy)_{2}(bpy)]^{+} in 1. The samples of 1 (40 mg) were doped in 10 ml DMF solutions containing 1 x 10^{-3} mol L^{-1} [Ir(ppy)_{2}(bpy)][PF_{6}] under stirring in 10 ml sealed glass bottles. After 0.5, 1, 2, 3, 4 and 10 days, the immersed samples were taken out and washed with DMF to remove residual Ir complex on the surface. The concentrations of encapsulated [Ir(ppy)_{2}(bpy)]^{+} in [Ir(ppy)_{2}(bpy)]^{+} at I were measured by ICP experiment and the results were shown in Supplementary Table S3. The corresponding CIE coordinates were also calculated and listed in Supplementary Table S3.

Procedure for the preparation of lanthanide-doped compounds. Eu/Tb@1 sample was prepared by immersing freshly prepared compound 1 in DMF solutions of lanthanide nitrates with molar ratios of 1:2 (total amount 0.03 mmol in 5 ml DMF). After 7 days of soaking, the crystals were taken out of solution and washed with DMF to remove residual lanthanide ions on the surface. A similar process was employed to prepare Eu^{3+} or Tb^{3+} doped sample by soaking sample of 1 in DMF solutions of lanthanide nitrates of Eu^{3+} or Tb^{3+} (0.01 mmol in 5 ml DMF). After 7 days of soaking, respectively, the crystals were washed with DMF to remove residual lanthanide ions on the surface.

Fabrication of a simple WLED assembly. A WLED was fabricated by dipping the white phosphor of 3.8 wt% [Ir(ppy)_{2}(bpy)]^{+} @ I on an ultraviolet InGaN LED chip (λ_{em} = 370 nm). The colour parameters of the device including CIE, CCT and CRI were measured by Ocean Optics USB 4000 Spectrometer at a forward current of 150 mA.

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Author contributions
C.-Y.S., Z.-M.S., X.-L.W. and J.L. designed the experiments, interpreted the data and co-wrote the paper. C.-Y.S., X.Z. and D.-X.Z. carried out synthesis, optical measurements and data analysis. C.Q., P.L., G.-G.S., K.-Z.S. and H.W. performed other characterization experiments and related analyses. All authors discussed and commented on the manuscript.

Additional information
Accession codes: The X-ray crystallographic coordinates for complex 1 have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 916964. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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