Electrically Driven White Light Emission from Intrinsic Metal−Organic Framework

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¶Supporting Information

ABSTRACT: Light-emitting diodes (LEDs) have drawn tremendous potential as a replacement of traditional lighting due to its low-power consumption and longer lifetime. Nowadays, the practical white LEDs (WLED) are contingent on the photon down-conversion of phosphors containing rare-earth elements, which limits its utility, energy, and cost efficiency. In order to resolve the energy crisis and to address the environmental concerns, designing a direct WLED is highly desirable and remains a challenging issue. To circumvent the existing difficulties, in this report, we have designed and demonstrated a direct WLED consisting of a strontium-based metal−organic framework (MOF), \([\text{Sr(ntca)}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\) \(_n\) (1), graphene, and inorganic semiconductors, which can generate a bright white light emission. In addition to the suitable design of a MOF structure, the demonstration of electrically driven white light emission based on a MOF is made possible by the combination of several factors including the unique properties of graphene and the appropriate band alignment between the MOF and semi-conductor layer. Because electroluminescence using a MOF as an active material is very rare and intriguing and a direct WLED is also not commonly seen, our work here therefore represents a major discovery which should be very useful and timely for the development of solid-state lighting.

KEYWORDS: light-emitting diode, metal−organic frameworks, graphene, electroluminescence, photoluminescence, natural white light
doped phosphors. It is known that rare-earth mining can cause huge environmental problems.

In stark contrast, using intrinsic white light-emitting materials as an active material could resolve all the shortcomings described above and could result in a high-quality white light source. A non-rare-earth, electrically driven direct white light luminescence would thus be more desirable over all the current commercially available methods. Indeed, several studies have specifically concentrated along this guideline, but reports on the successful demonstration of electrically driven direct white light are few in number and are associated with a complex design. As of this writing, there are only a few reports of direct white light-emitting intrinsic MOFs, which have obvious interest. Hence, more efforts are still needed to design a direct WLED device, which is of obvious interest and importance.

Metal–organic frameworks (MOFs) are a promising new class of hybrid materials that are composed of metallic ions and organic ligands and have attracted tremendous attention due to their unique and tunable properties. Such frameworks have been extensively studied during the past two decades since they have potential applications as chemical separators, in gas storage, drug delivery, and catalysis. Using MOFs in optoelectronic devices, particularly as an electroluminescent (EL) material, is not common and challenging due to their poor electrical conductivity and high porosity. Using a high conducting component element, the electrical conductivity can be enhanced.

Similarly, taking advantage of different efficient emissive building blocks, the resulting emission from the supermolecules can be modulated to achieve a broad band emission, which may lead to the production of white light. Designing an intrinsic white light-emitting MOF is rare and intriguing. A white light-emitting MOF is commonly achieved by doping or encapsulating the frameworks with rare-earth or transition metals with different colors, such as Eu, Tb, Dy, etc. As of this writing, there are only a few reports of direct white light-emitting intrinsic MOFs, which have obvious interest. Then again, strontium has rarely been used to design a MOF complex and even as a luminescent material. Indeed, strontium contributes several electronic transitions which correspond to distinct visible emissions. Because of this unique feature, strontium was studied extensively as a high-frequency optical clock. However, less attention was paid in designing strontium-based optoelectronic devices. Taking advantage of a semiconductor organic ligand, 1,4,5,8-naphthalenetetracarboxylic acid hydrate (H$_4$ntc) and a luminescent metal, in this study, a unique Sr-based MOF, compound 1 was used as an electroluminescent material which is capable of emitting a bright white light.

On the other hand, graphene is an excellent candidate for a transparent electrode due to its high optical transparency and carrier mobility. Based on its unique properties, it was extensively used in optoelectronic devices for different applications. In addition, a composite of graphene, compound 1, and ZnO in this device possesses a unique band alignment to produce electrically driven white light emission. To the best of our knowledge, electrically driven white light emission using a MOF material has not been reported previously. Thus, the proof-of-concept demonstration of electrically driven continuous white light emission provides an alternative way for the development of optoelectronic devices that are made with this unique substance. It worth mentioning that the device was designed and characterized under ambient conditions.

Figure 1. Sr-MOF structure and stability. (a) 3D MOF structure composed of an AAA arrangement, where A represents the 2D sheet along the $ab$-axis. The ligand forms a bridge between two metallic layers to form a 2D network. The inset circle shows the stacking of the 2D layers to form a 3D MOF composite which causes a $\pi-\pi^*$ stacking interaction and induces a blue emission. (b) TGA of compound 1. (c) Simulated and experimental PXRD data for compound 1 under different conditions.
RESULTS AND DISCUSSION

An intrinsic luminescent rectangular single-crystalline MOF, compound 1, as shown in Figure 1a, was assembled by the chemical reaction of Sr(NO$_3$)$_2$ and 1,4,5,8-naphthalenetetracarboxylic acid hydrate (H$_4$ntc). A semiconducting ligand, H$_4$ntc was used in order to improve the optoelectronic properties of the compound. A detailed analysis of the synthesis of compound 1 is provided in the Methods section. An elemental analysis of compound 1 is as follows: calcd (%) for C$_{28}$H$_{20}$O$_{20}$Sr$_2$: C, 39.64; H, 2.33; O, 37.55; found (%) C, 39.49; H, 2.37; O, 37.43. The single-crystal X-ray diffraction of compound 1 in Figure 1a reveals a highly pure 2D network crystallized in monoclinic $P2_1/c$ space group. The composite 2D sheets stacked in AAA order along the $c$-axis form a bulk crystal, as shown in Figure 1a. The ligand bridge between the metallic chains, which are stacked up one above the other, as shown in the inset of Figure 1a, forms a hydrogen-bonded vertical $\pi$ stack which has promising optoelectronic properties. The thermal stability of compound 1 was evaluated by conducting thermogravimetric analysis (TGA). The measured weight loss of 4.7% in the range of 70–88 °C corresponds to the dehydration of free guest H$_2$O molecules from the compound. The second step weight loss is associated with the loss of coordinated H$_2$O molecules in the temperature range of 88–192 °C. These results were further confirmed by a simulated and experimentally achieved powder X-ray diffraction (PXRD) study at different temperatures, as shown in Figure 1c.

The electrochemical stability of compound 1 was evaluated by performing current–voltage ($I$–$V$) measurements of a single-crystalline sample with Au electrodes separated by a distance of $\sim$200 $\mu$m, as shown in Figure 2a, where the $I$–$V$ data were collected before and after the application a constant voltage of 15 V for 6 h under ambient conditions. The consistent $I$–$V$ curve indicates the electrochemical stability of compound 1. A series of photoluminescence and Raman scattering spectra were collected before and after the application of electrical signals, as shown in Figure 2b,c, respectively. No significant change in the scattering and emission spectra is indicative of the stable optical properties of compound 1.

The large single-crystalline compound 1 was grained to nanoparticles, which were used to form a thin film. A electroluminescent device was designed to coat the thin film of compound 1 on a 140 nm thick precoated ZnO film on top of a Si/SiO$_2$/Ag substrate, as shown in Figure 3a,b. Single-layer graphene (SLG) was used as a top electrode, which not only provides a suitable band alignment (as discussed below) for carrier injection but also prevents the device from developing a short circuit with any metal-deposited electrodes since MOFs are porous materials. The top poly(methyl methacrylate) (PMMA) layer in Figure 3b protects the graphene film from the atmospheric effect. The optical transparency of the graphene/PMMA layer is given in Figure S1. The device is highly stable against an applied injection voltage of 10 V in ambient conditions. The $J$–$V$ characteristics in Figure 3c depict the formation of a pn junction diode with an ideality factor of 1.76. The estimated conductivity of the compound is found to be $\sim$10$^{-4}$ S/cm, which is relatively high compared to that in many reports on conductivity of the MOF materials, which is due to the semiconducting ligand in the MOF. The organic linker forms a bridge for the mobile charge carriers inside the device, contributing to the essential role in carrier conduction.
applying a constant voltage for 6 h at 10 V, as shown in Figure S6.

The device possesses a broad and continuous electroluminescent spectrum covering the visible range, as shown in Figure 4a. The calculated chromaticity of the EL emission has a value close to the point (0.333, 0.333), showing white light color temperature of ∼5400 K, as shown in Figure 4b. Again, the value of $\lambda_{EL_{\text{max}}}$ was found to be close to 555 nm, the maximum sensibility wavelength of the human eye. Quite interestingly, compared with the emission spectrum of AM0, as shown in Figure 4c, our device is capable of producing natural white light. The emitted EL spectrum was further compared with commercially available WLEDs of the same color temperature, as shown in Figure S2. It reveals the important fact that our design is capable of reducing the strong blue emission peak of current commercial WLEDs. It is noteworthy that the strong blue emission may induce a significant health risk.14 Notably, the demonstration of EL using a MOF as an active material in the solid-state lighting is rare and intriguing, and a direct white light EL emission is also not commonly seen. Therefore, the results reported here comprise a significant discovery, which has remarkable potential for practical applications.

Let us now underpin the working principle responsible for the white light emission arising from our designed device. MOF supermolecules have a well-defined porous geometry consisting of metal ions and organic ligands.25,61 Concerning emission, both the metal and ligand both take part in the emission process. Thus, MOFs can cover a wide range of emissions due to their multifaceted structure which cannot be found in a single material.26,62 Several possibilities have been proposed in the literature concerning the origin of the emission. In particular, the major contribution in emission originates from (i) linker-based emission, (ii) ligand to metal charge transfer and/or metal to ligand charge transfer (MLCT), (iii) metal-based emission, and (iv) adsorbate-based emission.62 The emission spectra of the as-designed MOF was studied under different excitation powers by excitation of a 266 nm pulsed laser at room temperature, as shown in Figure 5a. It produces a bright white light emission with a quantum yield of ∼10%. The corresponding CIE chromaticity diagram is given in Figure 5b. With a pumping power of around 42 $\mu$W, the resulting spectrum has a CIE coordinate of (0.327, 0.367), which is very close to the value of white color (0.333, 0.333). The inset in Figure 5b is the image taken by a mobile camera under the 266 nm exposure, which shows a bright white light.

In Figure 5c, a quantitative analysis of the contributions of different transition mechanisms involved in the supermolecule are shown. The temperature-dependent PL spectrum at 90 °C shown in Figure S3 reveals that free H₂O molecules in compound 1 do not play any role in the emission process. Thus, the bright white light arises from the superimposition of the first three types of possible mechanisms, as discussed above. The appearance of sharp peaks can be found in literature as the...
intermetallic electronic transitions of strontium, which become more prominent at higher excitation, as shown in Supporting Information Figure S4. Again, under excitation by a 266 nm laser in a powdered sample of the free organic ligand, a broad blue line was observed, as shown in Figure 5d, which is due to the presence of \( \pi^* \) interligand transitions. Hence, the presence of the broad blue line in the emission spectra of compound 1 is associated with the hydrogen-bonded vertical \( \pi \) stacks, as shown in the inset of Figure 1a. The broad peaks centered at 507 and 642 nm could be assigned to the broadened intermetallic energy states in the solid, which are circled in Figure S4. The appearance of the peak centered at 568 nm can be attributed to the transition of metal to ligand (M–L) charge transfer, which can be further confirmed by electroluminescent results discussed below. Interestingly, the MLCT-related peak is absent in the PL emission spectrum at 250 °C in Figure S3. At 250 °C, the PXRD spectrum and TGA data reveal a water-free compound 1. Thus, this result implies that coordinated water molecules can assist the MLCT emission in the supermolecule.

In order to further confirm our interpretation of the origin of the PL spectra, time-resolved photoluminescence measurements were carried out at the maxima of the different transitions associated with PL, as shown in Figure 5e. The peak centered at 435 nm shows a decay time \( \sim 0.60 \pm 0.20 \) ns, which is close to the decay time of \( \sim 0.98 \pm 0.20 \) ns for the emission of the free H4ntc ligand, as shown in Figure 5f. The peaks centered at 507, 568, and 640 nm have dual lifetimes with shorter and longer lifetimes corresponding to a metal-based emission and an emission due to MLCT, respectively. The
experimentally achieved lifetime of the emission was tabulated, and the results are shown in Table S1. Similar to the PL spectra, the emission peaks can also be categorized into different origins on the basis of their decay lifetime, as shown in the Supporting Information Table S1, which provides excellent evidence to support our proposed mechanism. Note that the measured values of the PL lifetimes are in good agreement with the published reports for linker-based emissions, metal-based emission, and emission due to MLCT.\textsuperscript{62,64–66}

To understand the nature of the emitted EL spectrum, we deconvoluted the spectrum into different areas corresponding to different transitions that are involved in the EL emission, as shown in Figure 6a. It was found that the EL spectrum also consists of four major peaks which can be described as being similar to the transitions in the PL spectrum, as shown in Figure 6b. A corresponding schematic illustration of the energy band diagram is given in Figure 6c,d based on the published literature data related to the band structures of the constituent elements.\textsuperscript{17,53,56} The interligand (L–L) transition at 410 nm
was confirmed by measuring the PL of the free ligand. Similar to the PL spectra, the EL emission peaks centered at 506.5 and 644.0 nm are due to the relaxation of electrons at broadened intermetallic (M−M) low-lying energy levels.47 The emission intensity of the M−M transitions are dominant over the L−L transition due to the fact that the LUMO energy level of the M−M is lower than that of the LUMO level of the L−L transition. Hence, the appearance of the peak centered at 560 nm can be attributed to charge transfer from the M−M LUMO level to the L−L HOMO level, as shown in Figure 6d, which is referred to as the MLCT in the literature.62 It should be noted that the quantum efficiency (QE) of the current EL device has a value of 1.2%, which is relatively low compared to that of commercially available bright white LEDs with a QE of around 40%. The findings reported herein serve a proof-of-concept demonstration that MOFs can provide an excellent material for electrically driven white light emission. Further studies with more advanced EL cells and MOF structures can greatly enhance the intensity of white light emission for realizing practical applications.

The thickness dependence of the electroluminescence spectrum was studied. It was found that the emission from the device decreases drastically at higher thicknesses. The quantum efficiency corresponding to the emission is shown in Figure 7a. Thus, an optimum thickness of the active MOF layer can greatly improve the emission efficiency. When the thickness is too small, there exists not enough MOF material to emit light, while a too thick MOF layer will cause a very large resistance and induce a poor luminescence efficiency. The stability of the device performance was estimated by measuring the luminescence efficiency multiple times over a long period of time, and the results are shown in Figure 7b. The device performance was consistent under ambient conditions for a period of more than 2 months. This high stability of the device efficiency can be correlated to the several factors involved in our design. In addition to the fact that the stable MOF compound 1 was synthesized, the top graphene/PMMA layer serves as an excellent passivation layer70 on the MOF, which significantly enhances the electrochemical stability of the device. This result can be attributed to the outstanding behavior of the very small lattice constant of the graphene layer, which can prevent external molecules from penetrating into the porous structure of the MOF. Notably, MOF is unstable due to its porous structure. Furthermore, the excellent thermal conductivity of the graphene layer68 induces superior heat transport throughout the device which can prevent the effect of heating on the emission of our device under a high injection current.

CONCLUSIONS

In conclusion, we have demonstrated a different type of environmentally friendly MOF-based WLED, which is capable of producing a natural white light emission centered at around 555 nm, the maximum sensibility for the human eye. Because of multifunctional and tunable properties, MOFs were extensively used during the past few years in different applications, including storage, separation, sensing, guest capture, and release. However, even though the tunable optoelectronic properties of MOFs have great promise for designing high-performance optoelectronic devices, the related studies are rather limited. Our demonstration of an electrically driven white light emission from MOF material was made possible through the design of a suitable MOF structure and a combination of the unique properties of graphene and band alignment between the MOF and a semiconducting material. In view of the increasing consciousness of the energy crisis on our planet, our result of using a MOF as a white light electroluminescent material should be very useful and timely for the future development of solid-state lighting.

METHODS

Synthesis of Compound 1. The single-crystalline compound 1, ((Sr(ntca)(H2O)2)H2O)n, was assembled by the chemical reaction of Sr(NO3)2 and 1,4,5,8-naphthalenetetracarboxylic acid hydrate (H4ntc) in an EtOH/H2O solution under hydrothermal conditions at 120 °C for 3 days through a single-step self-assembly process (Scheme 1).66

Scheme 1. Synthesis of Compound 1 via a Single-Step Self-Assembly Method

The elemental analysis of compound 1 was performed using a PerkinElmer 2400 CHN elemental analyzer. The analysis revealed the following data: calc (%) for C19H14O6Sr: C, 39.64; H, 2.33; O, 37.55; found (%) C, 39.49; H, 2.37; O, 37.43.

Graphene Growth. A SLG of high-quality was grown on copper foil by the standard chemical vapor deposition (CVD) method.69 The purity and the surface roughness of the copper foil play an important role in determining the quality of the CVD graphene. Thus, a 99.98% pure copper foil from Sigma-Aldrich was used. In order to reduce the surface roughness of the copper foil, it was polished by electrolysis of 85% H3PO4 at 1.7 V for 15 min. We used the same quality Cu as the anode and cathode in order to maintain the purity of the polished Cu. Finally, we used the Cu that was initially at the anode electrode for growing the graphene in a CVD furnace. In the graphene growth process, 60 sccm H2 was first allowed to flow for 60 min at a temperature of 1000 °C, followed by addition of CH4 at 3.4 sccm for the next 30 min while keeping the previous parameters the same.70 Finally, the furnace was cooled to room temperature. Due to the chemical reaction of CH4 and H2 at the high temperature in the CVD, a uniform, high-quality SLG was deposited on the Cu. The quality of the graphene was analyzed by obtaining the Raman scattering spectrum, as shown in Figure S7.

ZnO Nanoparticle Synthesis. ZnO nanoparticles were synthesized by a standard hydrothermal method.71 First, 0.44 g of Zn(CH3COO)n was dissolved in 20 mL of ethanol under magnetic stirring. Next, 0.116 g of LiOH was added to the ethanol solution over a period of 30 min, after which 0.4 mL of deionized water was added with continuous stirring. The resulting solution was then placed in a 60 °C water bath for 30 min. Under these conditions, the ZnO nanoparticles began to nucleate and the resulting turbid solution was centrifuged at 3000 rpm for 2 min. A white precipitate was deposited at the bottom of the reaction tube. To remove unreacted elements and acetate salt, the suspension was separated from the white precipitate. Finally, isopropl alcohol was mixed with ethanolamine (0.2 wt %) and was then added to the precipitate to prepare a solution with suspended n-type ZnO nanoparticles.

Device Fabrication. The single-crystal MOF with a cubic millimeter size was ground to form MOF nanoparticles. Then, a solution of MOF nanoparticles was prepared with water or alcohol. Finally, it was spin-coated in the desired substrate to make a film. To design the device, a 140 nm film of ZnO nanoparticles was prepared as the n-type layer on top of 100 nm pre-Ag-coated Si/SiO2 substrate. Thereby, the MOF solution was coated (Figure 3a). Finally, SLG was used as the top electrode (Figure 3b). The graphene carrier film,
PMMA, was kept as it avoids the atmospheric effects on the graphene and provides a mechanical strength to the graphene layer.

Optoelectronic Characterization of the Device. The electronic characterizations of the device were accomplished using a Keithley 2400 electrometer and a standard probe station. The optical measurements were performed using a Horiba Jobin Yvon iHR 550 spectrometer. The carrier lifetime was measured using a Keithley 2520 high-speed electrometer and a Horiba Jobin Yvon TRIAX 320 spectrometer.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.6b03030. X-ray data for Sr-MOF (CIF)
Table S1, Figures S1–S8, and references (PDF)

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Author Contributions
Y.-F.C. and G.H. conceived the idea of device fabrication and wrote the manuscript. G.H. designed the devices and carried out the experiments for both the optical and electrical properties of the materials and devices. K.-L.L. and M.U. designed the MOF crystal and analyzed its crystal structure. T.-P.C. and G.H. measured the EL spectrum with commercial equipment. T.-Y.W. and C.-Y.L. performed the experiments. G.H. designed the MOF crystal and analyzed its crystal structure. T.-Y.W. and C.-Y.L. measured the EL spectrum with commercial equipment. All authors discussed the results and edited the manuscript. Y.-F.C. and K.-L.L. supervised and coordinated all the work.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Ministry of Science and Technology of the Republic of China under Contract No. NSC102-2112-M-002-008-MY3 and Ministry of Education of the Republic of China under Contract No. 104R890932. G.H. thanks the support of Taiwan International Graduate Program, the Republic of China under Contract No. NSC102-2112-M-002-008-MY3 and Ministry of Education of the Republic of China under Contract No. 104R890932. G.H. thanks the support of Taiwan International Graduate Program.

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