

Facile Synthesis of a Long Afterglow Calcium–Organic Framework in Water

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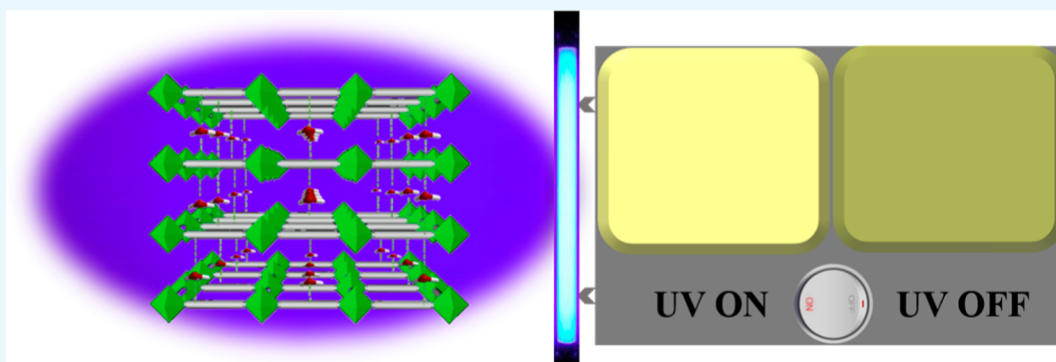
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ABSTRACT: Presented here is a water-stable Ca-MOF that has been facilely synthesized from the metastable 3D framework in water and exhibits room-temperature phosphorescence with second scale long afterglow.

INTRODUCTION

Afterglow appears after removing the excitation light source,^{1,2} which makes afterglow materials have potential applications in many fields, such as organic light-emitting diodes, optical storage, information security, biosensors/imaging, and environmental oxygen content/humidity detection.^{3–13} Long-life room-temperature phosphorescent materials are also known as long afterglow materials. Metal–organic frameworks (MOFs) are one kind of crystalline materials that consist of metal ions or clusters and organic ligands. Compared with inorganics and organic room-temperature phosphorescence (RTP) materials,^{14–19} MOFs that integrate both inorganic and organic components are considered emerging RTP materials.^{20–22} In theory, the strategies explored in other systems such as host–guest doping, halogen bonding, crystallization, and H-aggregation are also applicable in MOFs to achieve RTP.^{3,23} Furthermore, MOFs as RTP materials also own unique merits, for example, both inorganic and organic counterparts as luminescent centers, effective charge transfer between metal and organic ligands, and host–guest interactions.^{24–27} Currently, RTP MOFs are mainly focused on rare earth and transition metal centers.³ Considering the low cost and toxicity, the development of alkaline-earth metal-based materials is of special significance.^{28,29} Unfortunately, the research in this field is still rare due to their poor stability.

Recently, we have reported one RTP Ca-MOF [Ca₃(IDC)₂(DMF)₂(HCOO)₂] (Ca-MOF-1) (H₂IDC = 4,5-imidazoledicarboxylic acid; DMF = *N,N*-dimethylformamide), which exhibited strong RTP with long phosphorescence

lifetime.²⁸ Its long afterglow lasted as long as ca. 4 s. Interestingly, Ca-MOF-1 can be transformed into another RTP compound Ca-MOF-2 in our subsequent research. As a continuous work, we report here the facile synthesis of Ca-MOF-2 [Ca(IDC)₂(H₂O)₂·H₂O] from metastable Ca-MOF-1 in water. Unsurprisingly, Ca-MOF-2 exhibits good water stability. Ca-MOF-2 can be put into water for at least half a year, and it can still be determined by X-ray single crystal diffractometer. More importantly, Ca-MOF-2 inherits remarkable RTP with similar maximum emission peak (ca. 555 nm) and phosphorescence lifetime (ca. 967 and 643 ms at 77 and 298 K). Moreover, the long afterglow can also be observed by the naked eye and lasts about 3 s (Figure 1). This result not only enriches the types of long afterglow MOFs but also provides a new method for the development of stable long afterglow materials.

RESULTS AND DISCUSSION

Ca-MOF-1 was synthesized according to our former report.²⁸ The plate crystals of Ca-MOF-2 can be easily obtained by soaking block crystals of Ca-MOF-1 in water for one day (see

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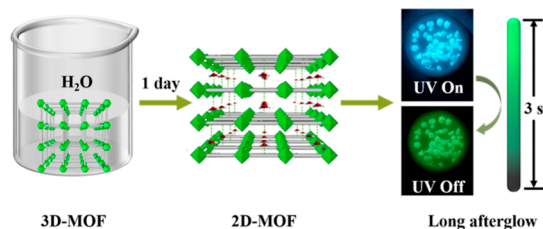


Figure 1. Scheme diagram of the Ca-MOF-1 produced Ca-MOF-2 with long afterglow.

the Supporting Information in detail). The crystal structure of Ca-MOF-2 is the same as that previously reported.^{30,31} In Ca-MOF-2, there is one Ca^{2+} ion metal, two coordinate water molecules, and one lattice water molecule in an asymmetric unit. Each Ca^{2+} is seven-coordinated by one N atom from one IDC^{2-} ligand and six O atoms from three IDC^{2-} ligand and two coordinated water molecules (Figure 2a). The Ca–O

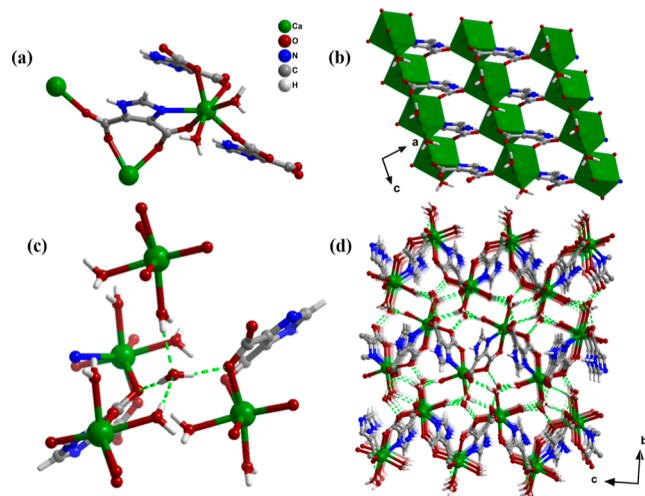


Figure 2. (a) Coordination environment of one IDC^{2-} ion and Ca^{2+} cation in Ca-MOF-2. (b) View of the 2D framework through the *b*-axis. (c) Hydrogen bond environment of each lattice water molecule. (d) Formation of three-dimensional framework of Ca-MOF-2 by the hydrogen bond.

bond distances are in the range of 2.328(2)–2.418(2) Å, and Ca–N bond distance is 2.518(2) Å. Each IDC^{2-} ligand connects three Ca^{2+} ions in Ca-MOF-2 (Figure 2a). Fewer coordination numbers of IDC^{2-} ligands and more monodentate coordination water molecules hinder the extension of structures of Ca-MOF-2 to form a two-dimensional layered structure (Figure 2b). As shown in Figure 2c,d, each lattice water molecule is located in the interlayer and forms four hydrogen bonds ($\text{O}\cdots\text{H}\cdots\text{O}$) with two IDC^{2-} ligands and two coordination water molecules, and then the formation of three-dimensional framework by the hydrogen bond happens. The lattice water molecules can act as both hydrogen bond acceptors and donors, and the hydrogen bonding information on Ca-MOF-2 can be clearly observed (Figure 2d). Detailed hydrogen bond lengths and bond angles are shown in Table S2.

Though Ca-MOF-1 is a three-dimensional calcium–organic framework, its solvent stability in water is not good. The Ca-MOF-1, immersed in water for 1 day, works as a precursor to synthesize another two-dimensional layered structure Ca-

MOF-2. The synthetic method of Ca-MOF-2 is obviously better than that of a previous report,³⁰ because hydrazine hydrate was used in the original synthesis scheme of Ca-MOF-2. As illustrated in Figure 3, metastable Ca-MOF-1 turned into

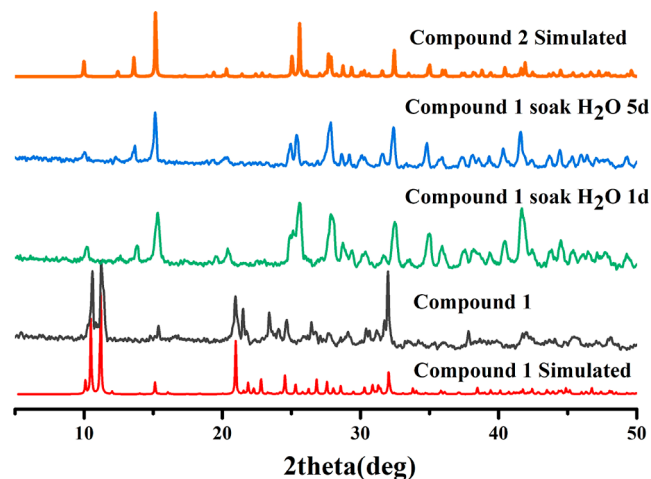


Figure 3. PXRD of Ca-MOF-1 produced Ca-MOF-2 in H_2O and the water stability of Ca-MOF-2.

water-stable Ca-MOF-2 after 1 day in water. The experimental PXRD result matched well with that of Ca-MOF-2 simulated pattern from single-crystal XRD structure. Also, Ca-MOF-2 had good solvent stability in water for 5 days. Moreover, Ca-MOF-2 can still obtain accurate single crystal structure after soaking in water for more than half a year. It may even be stable in water all the time.

The fluorescence emission and excitation spectra measured at room temperature in solid Ca-MOF-2 are displayed in the Supporting Information. As shown in Figure S2, Ca-MOF-2 exhibits the characteristic transitions at 470 nm. The fluorescence lifetime (τ) of Ca-MOF-2 is 3.63 ns at room temperature, as shown in Figure S3 and Table S4. Comparing the results of the literature,²⁸ one can know that the fluorescence properties belong to Ca-MOF-2 itself, not to the ligand. The quantum yield was measured in solid at room temperature. As shown in Figure S4, the quantum yield of Ca-MOF-2 in solid is 4.02%. Moreover, the quantum yield of Ca-MOF-2 is smaller than that of Ca-MOF-1. It may be attributed to the different geometrical structures of the MOFs.

According to our prior work, the three-dimensional MOF displayed fascinatingly phosphorescence properties and long afterglow at room and low temperatures. When using water as a medium, metastable Ca-MOF-1 became a raw material to produce water-stable Ca-MOF-2. Interestingly, for Ca-MOF-2, phosphorescence properties and long afterglow at room and low temperatures were also discovered. The phosphorescence properties and the lifetimes in solid were measured at room and low temperatures (Figure 4 and Table S4). Whether it was 77 K or 298 K, the remarkable phosphorescent phenomenon was observed, and the peak position (about 555 nm) of the phosphorescent emissive peak showed no change (Figure 4b). The phosphorescence lifetime was estimated as 0.643 and 0.967 s for Ca-MOF-2 at 298 and 77 K (Figure 4c). Obviously, the lifetime at 298 K was shorter than that at 77 K. Significantly, after removal of the UV light, yellow emission could be recognized easily by naked eye and also captured by a digital camera in the time range of 0–3 s, confirming the long

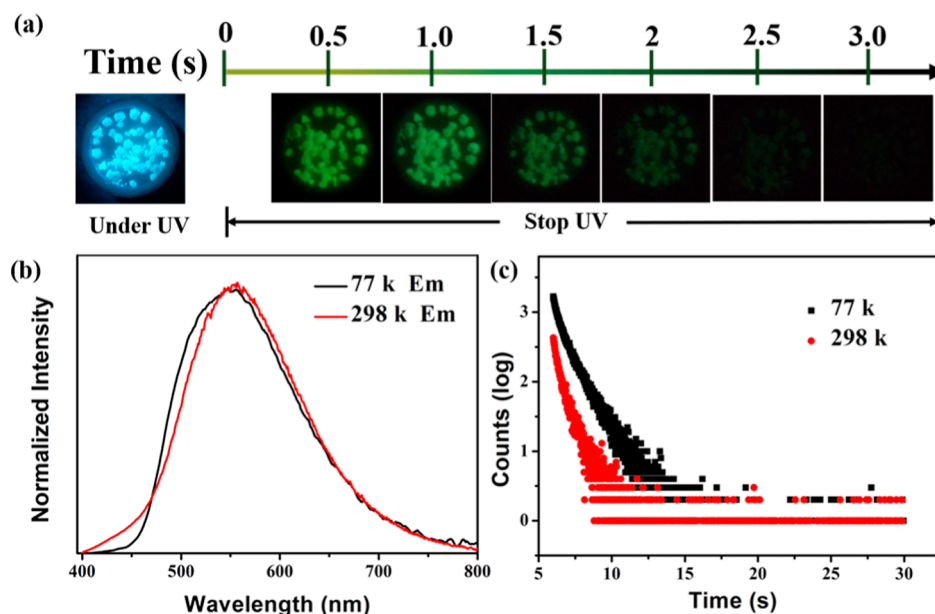


Figure 4. (a) Photographs of the afterglow for Ca-MOF-2 taken at different time intervals before and after turning off the UV excitation (365 nm) under ambient conditions in the night at room temperature. (b) Phosphorescence emission spectra of Ca-MOF-2 in the solid state at 77 K (black) and 298 K (red). (c) Phosphorescence decay curves of Ca-MOF-2 at 77 K (black) and 298 K (red), $\tau = 0.967$ and 0.643 s.

afterglow characteristics for Ca-MOF-2 (Figure 4a). The room temperature phosphorescence (RTP) afterglow may be attributed to the following aspects: (1) the presence of atoms O and N with lone-pair electrons in the ligand H₃IDC enhances the spin-orbit coupling via El-Sayed's rule.^{32,33} (2) Based on strong coordination and hydrogen bonding interaction, the 2D Ca-MOF forms a three-dimensional supramolecular structure through strong hydrogen bonding interaction in crystal building in order to trap, stabilize, and protect the generated triplet excitons.^{3,32,34–36} Molecular motions/vibrations might be confined and non-radiative loss of excitons reduced. Thus, the phosphorescence emission was promoted.^{15,22,23} The little difference in the phosphorescent lifetime between Ca-MOF-1 and Ca-MOF-2 was due to the same ligand and the formation of a three-dimensional structure. Only Ca-MOF-1 is a three-dimensional MOF, and the other is a three-dimensional framework formed by a two-dimensional MOF to hydrogen bond.

CONCLUSIONS

In conclusion, the RTP Ca-MOF-2 has been synthesized from 3D Ca-MOF-1 precursors, which exhibited high water stability. The phosphorescence lifetimes of Ca-MOF-2 are 0.967 and 0.643 s at 77 and 298 K, respectively. Noteworthy, long afterglow of Ca-MOF-2 reached second scale and maintained for about 3 s at room temperature. The supramolecular framework includes a large amount of coordinated water and exhibits intramolecular and intermolecular interactions (coordination and hydrogen bond). The presence of rich interactions may enhance rigidity of molecular conformations and restrict molecular motions/vibrations, which improves RTP efficiency and water stability.

EXPERIMENTAL SECTION

Materials and Methods. All reagents were of commercial origin and were used as received. The C, H, and N microanalyses were carried out with a CE instruments EA

1110 elemental analyzer. Fourier transform infrared (FTIR) spectra were recorded with a Spectrum One FTIR Spectrometer in the 400–4000 cm⁻¹ range. Photoluminescence spectra (PL), fluorescence spectra (FL), and the luminescence decay curves were performed on an Edinburgh FLS1000 fluorescence spectrometer. Powder X-ray diffraction data were collected on a Rigaku Mini Flex II diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range of 5–50° with a scanning rate of 10° min⁻¹. Thermogravimetric analysis data were carried out in an N₂ atmosphere with a heating rate of 10 °C/min on an STA 449F3 integration thermal analyzer. Data of Ca-MOF-2 (the first time) were collected on MarCCD mx300 at the National Center for Protein Sciences Shanghai at the Shanghai Synchrotron Radiation Facility. Data of Ca-MOF-2 (half a year) were collected at 100.00 K on an ROD, Synergy Custom system, HyPix diffractometer equipped with Ga K α radiation ($\lambda = 1.3405 \text{ \AA}$) using a HyPix CCD detector.

[Ca(IDC)(H₂O)₂] \cdot H₂O: for the synthetic method of Ca-MOF-1 ([Ca₃(IDC)₂(DMF)₂(HCOO)₂]), we referred to the literature reported previously.²⁸ CaCl₂ (80 mg, 0.72 mmol) was added to a 3.0 mL DMF solution containing 4,5-imidazolecarboxylic acid (30 mg, 0.19 mmol) and formic acid (50 μ L) in a glass vial. The resulting solution was stirred for 40 min and then heated to 120 °C for 5 days. Clusters of pale-yellow and rod-shaped crystals were obtained. The yield of Ca-MOF-1 was low and needed to be picked out because the yield in each glass vial was inconsistent.

Ca-MOF-1 (0.120 g, 0.18 mmol) was immersed in 18 mL H₂O for about 1 day. The colorless flake crystals of Ca-MOF-2 (0.067 g, 0.27 mmol) suitable for X-ray diffraction were obtained. The yields were 56% based on Ca-MOF-1. Anal. Calcd for CaN₂C₅O₇H₈ (FW = 248.21): N, 11.28; C, 24.19; H, 3.24. Found: N, 11.68; C, 24.09; H, 2.63. IR (KBr, cm⁻¹): 3340 (s), 3047 (s), 2981 (s), 2866 (s), 2775 (s), 2635 (s), 1681 (s), 1600 (s), 1500 (s), 1377 (s), 1180 (s), 1079 (s), 949 (s), 800 (s), 523 (s).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c02658>.

Crystal data and structure refinement for Ca-MOF-2; hydrogen bonds for Ca-MOF-2; selected bond lengths for Ca-MOF-2; TGA curve of Ca-MOF-2; fluorescence excitation and emission spectra of Ca-MOF-2; fluorescence decay curve of Ca-MOF-2 at room temperature; luminescence quantum yield of Ca-MOF-2 at room temperature; fluorescence excitation and emission spectra of ligand, Ca-MOF-1, and Ca-MOF-2 at room temperature; and fluorescence lifetime and quantum efficiency as well as a phosphorescence lifetime of Ca-MOF-2 in the solid state (PDF)

Synthesis and characterization details and CIF files for Ca-MOF-2 (CIF)

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Notes

The authors declare no competing financial interest.

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