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

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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, 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. 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, MOFs that integrate both inorganic and organic components are considered emerging RTP materials. 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. 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. Currently, RTP MOFs are mainly focused on rare earth and transition metal centers. Considering the low cost and toxicity, the development of alkaline-earth metal-based materials is of special significance. Unfortunately, the research in this field is still rare due to their poor stability.

RESULTS AND DISCUSSION

Ca-MOF-1 was synthesized according to our former report. 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 lifetime. 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) (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.
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$$^{2-}$ ligand and six O atoms from three IDC$_2$$^{2-}$ ligand and two coordinated water molecules (Figure 2a). The Ca–O 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$$^{2-}$ ligand connects three Ca$^{2+}$ ions in Ca-MOF-2 (Figure 2a). Fewer coordination numbers of IDC$_2$$^{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 (O⋯H–O) with two IDC$_2$$^{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 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.

![Figure 1. Scheme diagram of the Ca-MOF-1 produced Ca-MOF-2 with long afterglow.](https://doi.org/10.1021/acsomega.2c02658)

![Figure 2. (a) Coordination environment of one IDC$_2$$^{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.](https://doi.org/10.1021/acsomega.2c02658)

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 3. PXRD of Ca-MOF-1 produced Ca-MOF-2 in H$_2$O and the water stability of Ca-MOF-2.](https://doi.org/10.1021/acsomega.2c02658)
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 H2IDC enhances the spin–orbit coupling via EI-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. Noteworthily, 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 Kα radiation (λ = 1.54056 Å) 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 Kα radiation (λ = 1.3405 Å) using a HyPix CCD detector.

[Ca(IDC) (H2O)₂]·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-imidazoledicarboxylic acid (30 mg, 0.19 mmol) and formic acid (50 μL) 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 Ca₇N₂C₅O₇H₈ (FW = 248.21): N, 11.28; C, 24.19; H, 3.24. Found: N, 11.68; C, 24.19; 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).

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) Photorecence emission spectra of Ca-MOF-2 in the solid state at 77 K (black) and 298 K (red). (c) Photorecence decay curves of Ca-MOF-2 at 77 K (black) and 298 K (red), τ = 0.967 and 0.643 s.
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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**REFERENCES**

1. Duan, L. Creating Schrödinger-cat states. Nat. Photonics 2019, 13, 73–74.
2. Miao, Q.; Xie, C.; Zhen, X.; Lu, Y.; Duan, H.; Liu, X.; Jokerst, J. V.; Pu, K. Molecular afterglow imaging with bright, biodegradable polymer nanoparticles. Nat. Biotechnol. 2017, 35, 1102–1110.
3. Gao, R.; Kodaitami, M. S.; Yan, D. Recent advances in persistent luminescence based on molecular hybrid materials. Chem. Soc. Rev. 2021, 50, 5564–5589.
4. Feng, L.; Day, G. S.; Wang, K.-Y.; Yuan, S.; Zhou, H.-C. Strategies for Pore Engineering in Zirconium Metal-Organic Frameworks. Chem. 2020, 6, 2902–2923.
5. Yuan, S.; Qin, J. S.; Lollar, C. T.; Zhou, H. -C. Stable Metal-Organic Frameworks with Group 4 Metals: Current Status and Trends. ACS Cent. Sci. 2018, 4, 440–450.
6. Yuan, J.; Dong, J.; Lei, S.; Hu, W. Long afterglow MOFs: a frontier study on synthesis and applications. Mater. Chem. Front. 2021, 5, 6824–6849.
7. Yang, X.; Yan, D. Long-afterglow metal-organic frameworks: reversible guest-induced phosphorescence tunability. Chem. Sci. 2016, 7, 4519–4526.
8. An, Z.; Zheng, C.; Tao, Y.; Chen, R.; Shi, H.; Chen, T.; Wang, Z.; Li, H.; Deng, R.; Liu, X.; Huang, W. Stabilizing triplet excited states for ultralong organic phosphorescence. Nat. Mater. 2015, 14, 685–690.
9. Wang, Z.; Zhu, C.-Y.; Wei, Z.-W.; Fan, Y.-N.; Pan, M. Breathing-Ignited Long Persistent Luminescence in a Resilient Metal–Organic Framework. Chem. Mater. 2019, 32, 841–848.
10. He, S.; Xie, C.; Jiang, Y.; Pu, K. An Organic Afterglow Protheranostic Nanoassembly. Adv. Mater. 2019, 31, No. e1902672.
11. Wang, Z.; Zhu, C.-Y.; Fu, P. Y.; Mo, J. T.; Ruan, J.; Pan, M.; Su, C. Y. Enhanced Long Persistent Luminescence by Multifold Intercalation in Metal-Organic Frameworks. Chemistry 2020, 26, 7458–7462.
12. Tao, Y.; Chen, R.; Li, H.; Yuan, J.; Wan, Y.; Jiang, H.; Chen, C.; Si, Y.; Zheng, C.; Yang, B.; Xing, G.; Huang, W. Resonance-Activated Spin-Flipping for Efficient Organic Ultralong Room-Temperature Phosphorescence. Adv. Mater. 2018, 30, No. e1803856.
13. Pan, M.; Liao, W.-M.; Yin, S.-Y.; Sun, S.-S.; Su, C.-Y. Single-Phase White-Light-Emitting and Photoluminescent Color-Tuning Coordination Assemblies. Chem. Rev. 2018, 118, 8889–8935.
14. Yuan, J.; Chen, R.; Tang, X.; Tao, Y.; Xu, S.; Jin, L.; Chen, C.; Zhou, X.; Zheng, C.; Huang, W. Direct population of triplet excited states through singlet-triplet transition for visible-light excitible organic afterglow. Chem. Sci. 2019, 10, 5031–5038.
15. Li, F.; Li, Z.; Cai, Y.; Zhang, M.; Shen, Y.; Wang, W. Afterglow photocatalysis of Ag,PO, through different afterglow coatings and photocatalysis mechanism. Mater. Lett. 2017, 208, 111–114.
16. Jin, Y.; Hu, Y.; Chen, L.; Wang, X.; Ju, G.; Mou, Z.; Ballato, J. Luminescence Properties of Dual-Emission (UV/Visible) Long Afterglow Phosphor SrZrO3: Pr3+. J. Am. Ceram. Soc. 2013, 96, 3821–3827.
17. Xu, S.; Chen, R.; Zheng, C.; Huang, W. Excited State Modulation for Organic Afterglow: Materials and Applications. Adv. Mater. 2016, 28, 9920–9940.
18. Hirata, S. Recent Advances in Materials with Room-Temperature Phosphorescence: Photophysics for Triplet Emission Stabilization. Adv. Opt. Mater. 2017, 5, 1700116.
19. Hayduk, M.; Riebe, S.; Voskuhl, J. Photoluminescence Through Hindered Motion of Pure Organic Emitters. Chem.—Eur. J. 2018, 24, 12221–12230.
20. Zhao, Y.; Yang, X.-G.; Lu, X.-M.; Yang, C.-D.; Fan, N.-N.; Yang, Z.-T.; Wang, L.-Y.; Ma, L.-F. {Zn} Cluster-Based Metal-Organic Framework with Enhanced Room-Temperature Phosphorescence and Optoelectronic Performances. Inorg. Chem. 2019, 58, 6215–6221.
21. Yang, X.; Yan, D. Strongly Enhanced Long-Lived Persistent Room Temperature Phosphorescence Based on the Formation of Metal-Organic Hybrids. Adv. Opt. Mater. 2016, 4, 897–905.
(22) Du, X.-S.; Yan, B.-J.; Wang, J.-Y.; Xi, X.-J.; Wang, Z.-Y.; Zang, S.-Q. Layer-sliding-driven crystal size and photoluminescence change in a novel SCC-MOF. Chem. Commun. 2018, 54, 5361–5364.

(23) Wang, Z.; Zhu, C. Y.; Yin, S. Y.; Wei, Z. W.; Zhang, J. H.; Fan, Y. N.; Jiang, J. J.; Pan, M.; Su, C. Y. A Metal-Organic Supramolecular Box as a Universal Reservoir of UV, WL, and NIR Light for Long-Persistent Luminescence. Angew. Chem., Int. Ed. 2019, 58, 3481–3485.

(24) Li, D.; Yang, X.; Yan, D. Cluster-Based Metal-Organic Frameworks: Modulated Singlet-Triplet Excited States and Temperature-Responsive Phosphorescent Switch. ACS Appl. Mater. Interfaces 2018, 10, 34377–34384.

(25) Zhu, L.-L.; Huang, Y.-E.; Gong, L.-K.; Huang, X.-Y.; Qi, X.-H.; Wu, X.-H.; Du, K.-Z. Ligand Control of Room-Temperature Phosphorescence Violating Kasha’s Rule in Hybrid Organic–Inorganic Metal Halides. Chem. Mater. 2020, 32, 1454–1460.

(26) Mieno, H.; Kabe, R.; Notsuka, N.; Allendorf, M. D.; Adachi, C. Long-Lived Room-Temperature Phosphorescence of Coronene in Zeolitic Imidazolate Framework ZIF-8. Adv. Opt. Mater. 2016, 4, 1015–1021.

(27) Yang, Y.; Wang, K.-Z.; Yan, D. Ultralong Persistent Room Temperature Phosphorescence of Metal Coordination Polymers Exhibiting Reversible pH-Responsive Emission. ACS Appl. Mater. Interfaces 2016, 8, 15489–15496.

(28) Lu, D.-F.; Wang, Z.-W.; Wang, F.; Zhang, J. Phosphorescent Calcium-Based Metal-Organic Framework with Second-Scale Long Afterglow. Inorg. Chem. 2021, 60, 10075–10078.

(29) Zhai, L.; Yang, Z.-X.; Zhang, W.-W.; Zuo, J.-L.; Ren, X.-M. Dual-emission and thermochromic luminescence alkaline earth metal coordination polymers and their blend films with polyvinylidene fluoride for detecting nitrobenzene vapor. J. Mater. Chem. C 2018, 6, 7030–7041.

(30) Starosta, W.; Leciejewicz, J.; Premkumar, T.; Govindarajan, S. Crystal structures of two Ca(II) complexes with imidazole-4,5-dicarboxylate and water ligands. J. Coord. Chem. 2006, 59, 557–564.

(31) Wang, D.-E.; Wang, F.; Meng, X.-G.; Ding, Y.; Wen, L.-L.; Li, D.-F.; Lan, S.-M. Syntheses, Crystal Structures and Luminescent Properties of Three Inorganic-Organic Hybrid Frameworks Constructed from 4,5-Imidazoledicarboxylate. Z. Anorg. Allg. Chem. 2008, 634, 2643–2648.

(32) Wu, S. L.; Pan, Z. F.; Chen, R. F.; Liu, X. G. Long Afterglow Phosphorescent Materials; Springer: Switzerland, 2017.

(33) Sebastian, E. S.; Rodríguez-Diéguez, A.; Seco, J. M.; Cepeda, J. Coordination Polymers with Intriguing Photoluminescence Behavior: The Promising Avenue for Greatest Long-Lasting Phosphors. Eur. J. Inorg. Chem. 2018, 2018, 2155–2174.

(34) Yang, X.-G.; Lu, X.-M.; Zhai, Z.-M.; Qin, J.-H.; Chang, X.-H.; Han, M.-L.; Li, F.-F.; Ma, L.-F. π-Type halogen bonding enhanced the long-lasting room temperature phosphorescence of Zn(II) coordination polymers for photoelectron response applications. Inorg. Chem. Front. 2020, 7, 2224–2230.

(35) Yang, X.-G.; Zhai, Z.-M.; Lu, X.-M.; Qin, J.-H.; Li, F.-F.; Ma, L.-F. Hexanuclear Zn(II)-Induced Dense π-Stacking in a Metal-Organic Framework Featuring Long-Lasting Room Temperature Phosphorescence. Inorg. Chem. 2020, 59, 10395–10399.

(36) Yang, X.-G.; Lu, X.-M.; Zhai, Z.-M.; Zhao, Y.; Liu, X.-Y.; Ma, L.-F.; Zang, S.-Q. Facile synthesis of a micro-scale MOF host-guest with long-lasting phosphorescence and enhanced optoelectronic performance. Chem. Commun. 2019, 55, 11099–11102.