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Potassium lons Induced Framework Interpenetration for Enhancing the Stability of Uranium-Based Porphyrin MOF with Visible-Light-**Driven Photocatalytic Activity**

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IHEP-9 has good thermal stability up to 400 °C and can maintain its crystalline state in the aqueous solution with pH ranging from 2 to 11. The catalytic activity of IHEP-9 as a heterogeneous photocatalyst for Non-interpenetrated MOF CO₂ cycloaddition under the driving of visible light at room temperature is also demonstrated. This induced interpenetration and fixation method

may be promising for the fabrication of more functional MOFs with improved structural stability.

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of crystalline materials formed by self-assembly of metal ions and organic ligands through coordination.^{1–3} By adjusting metal nodes and organic ligands, a MOF can serve as an ideal carrier, enabling it to have a huge application potential in many fields.⁴⁰11 However, due to the relatively weak coordination bonds, the poor stability (including chemical, thermal, and mechanical stability) of some MOF materials greatly hinders their practical application.¹² Therefore, because of its sufficient urgency and significance, the synthesis and application of stable MOFs have captured ample attention. $^{13-16}$

It is generally believed that the stability of MOF materials is mainly determined by structural features of both the building units of the metal node and the organic linking group, and the strength of the coordination bonds between them.^{9,17,18} For the metal node, the stability of MOF materials synthesized by metal ions with high coordination numbers and high valence electron numbers is usually better. The actinides generally have a larger ionic radius and higher coordination numbers, and their chemical valence states also present multivalent states. The strength of the coordination bond between the metal ion and the organic ligand can be predicted by Pearson's hard soft acid base theory, which is beneficial for guiding the synthesis of highly stable MOFs.¹⁹⁻²¹ Therefore, MOF materials constructed by actinides and oxygen-containing carboxylic acid ligands can be expected to have promising stability.

The frameworks interpenetration is often found in MOF construction, especially when semi-rigid ligands are used. The occurrence of an interpenetrating structure usually reduces the pore volume and size, but this may improve the stability of a MOF to a certain extent.^{13,30} However, it is difficult to accurately improve the stability of a MOF through interpenetration, because the intermolecular forces between the networks are not strong enough, and the structure may undergo deformation or slip in response to the removal of guest molecules. It should be noted that the distance between adjacent metal ions in the interpenetration structure will be greatly shortened. If the metal ions can be connected and fixed in a certain way, the interpenetrating structure can be connected as a whole, which may further improve the stability of the MOF.³¹ In the recent work, we have reported a uranium-based porphyrin MOF IHEP-4 ([(CH₃)₂NH₂]₄- $[(UO_2)_4(Co-TCPP)_3] \cdot 6DMF \cdot 33H_2O)$, which has certain chemical stability and can be applied in organic systems, but it cannot be stable in aqueous solutions.³² At the same time, by changing the synthesis conditions, MOF TCPP-U1 ($[(CH_3)_4$ - $N]_4[(UO_2)_4(TCPP)_3])$ with a similar coordination mode but interpenetrated structure can also be obtained, while its stability has not been significantly improved.³³ The distance

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between the coordination sphere of the adjacent uranyl ions is greatly shortened, nearly 6.88 Å, and the distance between the carboxyl oxygen coordinate with uranyl is even shorter. The coordination connection can be achieved by introducing a simple metal atom or organic linker. Alkali metals have abundant coordination modes, which can effectively connect a variety of components, including ligands, clusters, and macromolecular compounds, and may be used to connect adjacent uranyl ions.^{34–37} The alkali metal is connected to the oxygen of the carboxyl groups and can form a multi-metal oxygen cluster with uranyl. In the MOF structure, there is no longer a single metal atom as a metal node connecting framework, but the metal oxygen cluster bridges the organic ligands to form the framework. Therefore, the stability of the structure may be further improved.

In this work, we have proposed a feasible strategy to improve the stability of a MOF via inducing an interpenetrated structure to be fixed together. As a proof-of-concept case, a new uranium-based porphyrin MOF IHEP-9 $[(UO_2)_4K_2]$ (MnTCPP)₃(H₂O)₁₀]·5DMF·5H₂O with enhanced stability has been successfully prepared by adding alkali metal potassium ions (K⁺) into the reaction system. It is revealed that the presence of K⁺ ions induces the formation of a doubly interpenetrated framework in IHEP-9 that is coordinatively linked by K⁺ ions through two adjacent uranyl ions. The special structural architecture is helpful to improving the framework stability of IHEP-9 as evidenced by its good thermal stability up to 400 °C, and high hydrolytic stability, maintaining the intact crystalline state in the pH range of 2-11. Moreover, IHEP-9 has been applied to the photocatalytic conversion of CO₂ and is of potential as a promising visiblelight-driven photocatalyst.

MATERIALS AND METHODS

Caution! The uranyl nitrate hexahydrate $(UO_2(NO_3)_2 \cdot 6H_2O)$ is a radioactive and chemically toxic compound; strict preventive and protective measures should be taken, albeit a natural low radionuclide. The dust or solution of uranyl nitrate entering the body can cause heavy metal poisoning and internal exposure.

 $UO_2(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water (50 mL) to obtain a uranyl nitrate stock solution (0.50 M). The tetrakis(4-carboxyphenyl) porphyrin (H₄TCPP) and metalloporphyrins MnTCPP were prepared by a modified method.^{38,39} All chemicals and solvents are commercially available and can be used directly without further purification.

Synthesis. The synthesis of **IHEP-9** is detailed, introduced as a representative: $UO_2(NO_3)_2$ (0.03 mmol), MnTCPP (0.02 mmol), KCl (0.1 mmol), DMF (4.0 mL), and acetic acid (0.08 mL) were loaded into a 10 mL autoclave. The autoclave was sealed and heated to 150 °C in an oven for 2 days, then cooled to room temperature naturally. A brown positive tetragonal double cone crystal of **IHEP-9** was produced and washed three times with DMF (Figure 1a). Yield: 79.4% based on MnTCPP. The actinides metalloporphyrin MOFs with other transition metals were synthesized by similar methods.

Actinide porphyrin MOFs with different metal loadings were synthesized via a post-synthesis strategy. The uranyl and H_4 TCPP were constructed into the actinide porphyrin MOF in advance, which is washed with DMF to obtain pure samples of **IHEP-9** (H_2). The resulting crystal sample was immersed in a DMF solution containing MnCl₂ (0.05 mmol) and 2,6-lutidine, and heated at 120 °C for 1 day. The obtained crystal sample was washed three times with DMF.

Characterization. Powder X-ray diffraction measurements (PXRD) were obtained with a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) in the range of $3.5-50^{\circ}$ (step size: 0.02°). Simulated PXRD patterns were obtained from SCXA data using Mercury 3.3 software from the Cambridge Crystal Data



Figure 1. (a) Optical images of IHEP-9. (b) The asymmetric unit of IHEP-9. Color scheme: U (yellow), K (purple), Mn (pink), C (gray), O (red), N (blue). H atoms were omitted for clarity. (c) Two adjacent uranyl groups are connected via the K atom. (d) The metal node U-K-U cluster is connected by a metalloporphyrin ligand.

Center (CCDC). Thermogravimetric analysis (TGA) was recorded from a TA Q500 analyzer over the temperature range of 25-800 °C in an air atmosphere with a heating rate of 5 $^\circ\text{C/min}.$ The Fourier transform infrared (FT-IR) spectra were performed on KBr pellets in the range of 4000-400 cm⁻¹ on a Bruker Tensor 27 spectrometer. The XPS spectra were recorded on a Thermo ESCALAB 250 electron spectrometer with a multi-detection analyzer using an Al K α X-ray source (1486.6 eV). Surface charging effect was corrected with the C 1s peak at 284.6 eV as a reference. High resolution Mn 2p and U 4f peaks were fitted by using the CasaXPS program after subtraction of the background (Shirley baseline correction). The N2 adsorption experiments were measured on a micromeritics ASAP 2020 HD88 instrument at liquid nitrogen temperature (-196 °C). The samples were degassed under vacuum at 60 °C before measurements. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distributions were derived using the nonlocal density functional theory model. ¹H NMR spectra were performed on a Bruker Avance III analyzer in chloroform-d (CDCl₃) using TMS as an internal standard.

Single crystal X-ray data were collected on a Bruker APEXII X-ray diffractometer equipped with a CMOS PHOTON 100 detector with a Cu K α X-ray source (K α = 1.54178 Å). Data were indexed, integrated, and scaled using DENZO and SCALEPACK from the HKL program suite (Otwinowski and Minor, 1997).⁴⁰ The structures were solved by the direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-2014) on F^2 . Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. The SQUEEZE routine of PLATON was used to remove the diffraction contribution from disordered solvents of compound IHEP-9.⁴¹

Theoretical Methods. The structures of the model fragments of IHEP-4 and IHEP-9 were optimized by the PBE0 method with the Gaussian 09 program.⁴² The quasi-relativistic effective core potentials (RECPs) and ECP60MWB-SEG were applied to the U atom,^{43–45} while the 6-31G(d) basis sets were used for H, C, O, and K atoms.



Figure 2. (a) Single-layer planar structure of the interpenetrated MOF. (b) Single-layer channel structure of the interpenetrated MOF. (c) Single-layer channel structure of **IHEP-9** viewed along the *b* axis. (d) The 3D structure of **IHEP-9**. (e) Double-layered interpenetrated MOF connected by K atom. Color scheme: U (yellow), K (purple), Mn (pink), O (red).

Solvation effect was considered in DMF ($\varepsilon = 36.7$) using the conductor-like polarizable continuum model (CPCM) with Klamt atomic radii.^{46,47} At the PBE0/RECP/6-31G(d) level of theory, the fragments have no imaginary frequencies in DMF. To gain more accurate energies, single-point calculations were performed at the PBE0/RECP/6-311+G(d) level of theory.

RESULTS AND DISCUSSION

Structure Description and Characterization of IHEP-9. The single crystal X-ray diffraction (SCXRD) analysis indicates that IHEP-9 crystallizes in the tetragonal I41/amd space group. Pertinent crystal parameters and structure refinement are summarized in Table S1 (Supporting Information). There are two fully deprotonated metalloporphyrin ring ligands, one UO_2^{2+} ion, one K^+ ion, and five water ligands in the asymmetric unit of IHEP-9 (Figure 1b). The dimethylamine molecules present in the MOF cavity for charge balancing are generated *in situ* by the decomposition of DMF.48 The Mn1 porphyrin ring in the two metalloporphyrin rings is slightly bent, while the Mn2 porphyrin ring is an almost perfect plane (Figure S1). The uranyl ion achieves eight-coordination, including two oxygen atoms in the axial direction and six oxygen atoms derived from the carboxyl group of the porphyrin derivative. The distance of U-O bonds in the equatorial plane is in the range of 2.42–2.47 Å, and the axial U-O bond length is between 1.77 and 1.75 Å, which is similar to those reported in the literatures.⁴⁹ Two adjacent U···· U distances are 6.69 Å. O4 and O5 of the uranyl equatorial plane is bridged through a K atom, which gave rise to the oxygen in the equatorial plane to be slightly twisted and not on a plane. The K atom is also coordinated with the water molecule, and the lengths of the K-O bonds range from 2.64 to 2.71 Å. It is precisely because potassium ions participate in the coordination, which makes the two isolated uranyl groups connected to each other, further increasing the compact degrees of the MOF and making the pores' size more diversified. Structure simplification and calculations by the TOPOS40 program showed that IHEP-9 exhibits a 4,4,4-c 3nodal net (Figure S2) with a topology point symbol of $\{6^3.8^3\}_4\{6^4.8^2\}_3$. The distance between the Mn(II) in the center of the porphyrin and the N atom on the porphyrin ring is approximately 2.02 Å, and the distances between Mn and the O atoms of the coordination water molecule are 2.19–2.28 Å.

The original double-penetrating structure is woven into a MOF containing dense channels by the connection of K atoms (Figure 2d,e), which greatly reinforces its stability. Due to the coordination of the potassium atoms, the plane oxygen of the uranyl group is twisted, not in a plane, which results in the MOF material to be irregularly cubic in space. Two porphyrin rings with different torsional degrees make the structure more complicated. In terms of a single layer of the interpenetrated structure, the uranyl ion as a metal node coordinated with the carboxyl group of the porphyrin derivative, the MOF forms a three-level pore structure in the space (Figure 2b,c). The potassium atom is like a steel nail that connects two separate interpenetrating structures together, turning the original single metal node into a U-K-U metal oxygen cluster (Figure 1c,d), which will inevitably lead to increased stability of the MOF at the metal node.

Enhanced Stability of the Interpenetrated Framework. Compared to our previously reported actinide porphyrin MOF IHEP-4,³² IHEP-9 has a much richer pore structure. The pore shape of IHEP-9 is a slender row of channels, and its pore sizes range from 7 to 15 Å (Figure 3). IHEP-4 has a more uniform aperture distribution, with channel diameters as high as 23 Å. Despite that the pore size of IHEP-9 is slightly reduced, a reasonable explanation is that the connected double-layer interpenetrating structure sacrifices a part of the hole space, but its stability is consolidated greatly compared with IHEP-4. In order to verify the stability of IHEP-4 and IHEP-9, we optimized the structures of the model fragments of IHEP-4 and IHEP-9 in DMF (Figure S3). The parameters of bond lengths calculated at the PBE0/RECP/6-31G(d) level of theory are very close to the corresponding experimental values (Tables S2 and S3), which suggests that the theoretical method is suitable for calculating these systems.



Figure 3. (a, b) The planar structure of IHEP-4 and **IHEP-9.** (c, d) The channel structure of IHEP-4 and **IHEP-9.** (e, f) The channel structure of IHEP-4 and **IHEP-9** viewed along the *c* axis. Color scheme: U (yellow), K (purple), Mn (pink), C (gray), O (red), N (blue).

Thermodynamic analysis was estimated by the reaction of $2[UO_2TCPP_3]^- + K^+ + 2H_2O \rightarrow [(UO_2TCPP_3)_2K(H_2O)_2]^-.$ At a higher level of theory (PBE0/RECP/6-311+G(d)), the calculated reaction energy ΔE is -23.4 kcal/mol, indicating that this reaction is an exothermic reaction; i.e., IHEP-9 is more stable compared to IHEP-4. Therefore, the uranyl ions in IHEP-9 are bridged by potassium ions to from U-K-U metal clusters, which greatly improves the stability of IHEP-9. As expected, the consequences of the stability test demonstrated that IHEP-9 remained exceedingly stable after soaking and shaking for 24 h in an aqueous solution of pH 2-11 (Figure 4d). The FT-IR spectra of IHEP-9 (Figure 4a) show the U= O absorption band in the region of 920 cm^{-1, 50,51} The typical vibrations corresponding to carboxylate groups and B_{3u} vibration of porphyrin correspond to 1660 and 1388 cm⁻¹, respectively.⁵² The BET surface area is 121 m³/g for IHEP-9, and the pore size distribution also reveals that the crystal presents multi-level mesoporous channels, which is consistent with the crystal structure (Figure 4c). The pore volume ratio calculated by PLATON reaches 71.9%. The results of TGA (Figure 4b) prove that the thermal stability of IHEP-9 reached 400 °C, and there was about 14.1% weight loss before thermal decomposition, which can be attributed to disordered water molecules and DMF solvents. The weight loss did not further increase until 500 °C, which indicates the complete decomposition of IHEP-9, and the remaining 34.8% mass residue can be regarded as a mixture of U₃O₈, Mn₂O₃, and K_2O_2 . S^{3,54} On the basis of the mass loss of IHEP-9 during heating, we estimate that the molar mass of the compound should be 4467 g/mol. Therefore, the number of H₂O and DMF molecules can be reckoned by the equations, $(4467 \times$ $(0.062)/18 \approx 15; (4467 \times 0.079)/73 \approx 5, and the molecular$



Figure 4. (a) The FT-IR spectrum of **IHEP-9**. (b) TGA of **IHEP-9** measured under an air atmosphere. (c) N_2 sorption/desorption isotherm and pore-size distribution of **IHEP-9**. (d) The PXRD patterns of **IHEP-9** after soaking in an aqueous solution of pH 2–11 for 24 h.

formula of **IHEP-9** is $[(UO_2)_4K_2(MnTCPP)_3(H_2O)_{10}]$ · 5DMF·5H₂O.

Visible-Light-Driven Photocatalytic Cycloaddition Reaction of CO₂. The presence of easily substituted sites in metalloporphyrins indicates the availability of Lewis acidity, and both uranyl and porphyrin rings can act as photosensitizers.^{31,55} More importantly, by utilizing the characteristics of a highly ordered structure and uniform pore sizes and environments of MOF, a metal-porphyrin ligand with catalytic activity can be used as secondary building units (SBUs) to synthesize a single-atom catalyst, which can be predicted to have good catalytic activity.56,57 Therefore, we explored the utilization of IHEP-9 as a heterogeneous catalyst for photocatalytic CO₂ cycloaddition. Under typical reaction conditions, 1 mmol of epoxides catalyzed by 0.01 mmol of catalysts under 0.1 MPa CO₂ and room temperature for 12 h. A 45 W, 6500 K compact fluorescent lamp was applied as the visible light source. 16.2 mg (5 mol %) of tetrabutylammonium bromide (TBAB) was used as a cocatalyst, and 1 mL of acetonitrile was added as a diluent to the system. The photocatalytic reaction was performed in a high-pressure glass reactor, and the catalyst was separated by centrifugation. The product was eventually separated by column chromatography and weighed to determine the catalytic yield. The recovered solid catalyst was washed three times with fresh methanol and dried under vacuum before use in a catalytic cycle experiment.

Styrene oxide was first selected as a quintessential substrate for studying CO_2 cycloaddition reactions. As display in Table 1, in the presence of the cocatalyst TBAB, **IHEP-9** has high

Table 1. Synthesis of Styrene Carbonate from CO_2 and Epoxy Styrene with Photocatalyst IHEP-9



photocatalytic activity for CO_2 fixation. For the single component in the catalyst, whether it is $UO_2(NO_3)_2$, $MnCl_2$, or porphyrin ligand, the catalytic effect on CO_2 cycloaddition is very poor or even ineffective. We mixed the inorganic salts and organic ligands by physical doping, and the catalytic efficiency was still unsatisfactory, roughly equal to the sum of the catalytic efficiency of each catalyst component. Apparently, the catalytic efficiency has been greatly improved by constructing ligands and metals into a metal–organic framework.

In order to investigate the role of transition metals in the catalytic process, we prepared a series of actinide porphyrin MOFs by a solvothermal method based on different metal-loporphyrin ligands and used these materials in CO_2 photocatalytic cycloaddition experiments. With the gradual

increase of the atomic number, it shows a trend of decreasing first and then increasing, which is consistent with experimental and theoretical calculation results reported in the literature.^{58,59} Among them, **IHEP-9** (**Mn**) has the highest catalytic efficiency (Table 2). On the basis of previous reports, the CO₂

 Table 2. Photocatalytic Efficiency of IHEP-9 with Different

 Transition Metals

entry	IHEP-9 (M)	TBAB (mg)	$T(^{\circ}C)$	yield (%)
1	Mn ²⁺	16.2	RT	>99
2	Fe ³⁺	16.2	RT	95
3	Co ²⁺	16.2	RT	47
4	Cu ²⁺	16.2	RT	67
5	Zn^{2+}	16.2	RT	85

cycloaddition reaction usually requires coordination of transition metals with epoxy compounds, and MOFs constructed based on different metalloporphyrin ligands will exhibit greatly different catalytic activities.^{60–62} Furthermore, we adjusted the content of manganese in the center of the porphyrin plane by a postsynthetic method. As visible in Table S4, the catalytic efficiency of **IHEP-9** (**Mn**) gradually increased from the lowest 48% to 99% with the increase of the ratio of metal ion Mn. Therefore, in this system, transition metals as a single-atom catalyst in the framework will greatly affect the photocatalytic efficiency of CO₂ cycloaddition.

Under the same reaction conditions, we applied the catalyst system to a broad variety of epoxides, providing the respective cyclic carbonates. As appears in Table 3, a series of epoxides successfully undergo cycloaddition with CO₂, and corresponding carbonate compounds have been prepared, with satisfactory yields (78-99%). After the catalysis was completed, the catalyst was collected by centrifugation, and then rinsed with methanol three times and then dried under vacuum. Two more times, catalysis experiments were performed; despite that the catalytic effect is slightly reduced, the high catalytic efficiency is still maintained (Figure S8). The PXRD of IHEP-9 after three cycles of catalysis points out that the MOF shows excellent stability (Figure S9). According to the results of XPS, as illustrated in Figure S10, the valence state of manganese at the center of the porphyrin plane did not change significantly after catalysis, and remained stable Mn²⁺, which again verified the stability of IHEP-9.63,64 The valence state of uranium has also not converted.⁵¹

Taking into consideration our data and previous reports, a feasible mechanism for this photocatalytic reaction is proposed (Figure 5). First, under the excitation of visible light, the photogenerated electrons of the porphyrin derivative can activate CO_2 into free radical CO_2^- , and the corresponding photogenerated hole can convert the epoxide into a betatopic epoxide radical cation (Figure S11).^{65–68} Second, after the epoxide radical cation coordinated with the metal ion at the center of the porphyrin, a ring-opening reaction occurred under the attack of nucleophilic Br^{-.69,70} Third, the CO_2^- can quickly react with ring-opened epoxy compounds, and further convert it into the cyclic carbonate through the intramolecular ring closure.^{71,72}

CONCLUSIONS

In summary, we present a method to enhance the stability of a MOF through introducing K⁺ to improve the stability of metal nodes via coordinatively linked framework interpenetration.

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Table 3. Substrate Scope for the Conversion of Epoxides

Entry ^[a]	Epoxides	Products	Yield (%) ^[b]	TON ^[c]	TOF (h ⁻¹) ^[d]
1	\checkmark		>99%	200	16.67
2	CI CI	ci	>99%	200	16.67
3			78%	156	13
4		and	92%	184	15.3

^{*a*}Reaction conditions: epoxide (1 mmol), CO₂ (0.1 MPa), 12 h, RT, catalyst/TBAB (0.5/5 mol %). ^{*b*}Total yield determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*}TON: moles of cyclic carbonate per mole of catalyst used. ^{*d*}TOF: moles of cyclic carbonate per mole of catalyst used per hour.



Figure 5. Schematic mechanism of the photocatalytic reactions by IHEP-9.

Specifically, the K⁺ induces the formation of doubly interpenetrating frameworks, participates in metal coordination, and connects two uranyl ions together to realize a novel U-K-U metal oxygen cluster. The actinide porphyrin MOF **IHEP-9** can be thermally stable up to 400 °C and still maintain a crystalline state in an aqueous solution of pH 2–11. This method is valuable for improving the stability of MOF materials. Owing to the large conjugate system of the porphyrin and exposed Mn^{2+} Lewis acid sites, **IHEP-9** can be very efficient in visible-light-driven photocatalytic CO₂ conversion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02473.

The synthesis and characterization methods of materials, crystal data and structure refinement, typical figures including PXRD, cycle experiments, stability test, XPS, photoelectric test, and NMR spectra (PDF)

Accession Codes

CCDC 1993868 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276–279.

(2) Jiao, L.; Seow, J. Y. R.; Skinner, W. S.; Wang, Z. U.; Jiang, H. L. Metal-organic frameworks: Structures and functional applications. *Mater. Today* **2019**, *27*, 43–68.

(3) Xu, C. P.; Fang, R. Q.; Luque, R.; Chen, L. Y.; Li, Y. W. Functional metal-organic frameworks for catalytic applications. *Coord. Chem. Rev.* **2019**, 388, 268–292.

(4) Li, J.; Wang, X. X.; Zhao, G. X.; Chen, C. L.; Chai, Z. F.; Alsaedi, A.; Hayat, T.; Wang, X. K. Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chem. Soc. Rev.* **2018**, *47*, 2322–2356.

(5) Gao, Q.; Xu, J.; Bu, X. H. Recent advances about metal-organic frameworks in the removal of pollutants from wastewater. *Coord. Chem. Rev.* **2019**, 378, 17–31.

(6) Huang, Y. B.; Liang, J.; Wang, X. S.; Cao, R. Multifunctional metal-organic framework catalysts: synergistic catalysis and tandem reactions. *Chem. Soc. Rev.* **2017**, *46*, 126–157.

(7) Wang, L.; Han, Y. Z.; Feng, X.; Zhou, J. W.; Qi, P. F.; Wang, B. Metal-organic frameworks for energy storage: Batteries and super-capacitors. *Coord. Chem. Rev.* **2016**, *307*, 361–381.

(8) Yang, F.; Xu, G.; Dou, Y. B.; Wang, B.; Zhang, H.; Wu, H.; Zhou, W.; Li, J. R.; Chen, B. L. A flexible metal-organic framework with a high density of sulfonic acid sites for proton conduction. *Nat. Energy* **2017**, *2*, 877–883.

(9) Yin, Z.; Wan, S.; Yang, J.; Kurmoo, M.; Zeng, M. H. Recent advances in post-synthetic modification of metal-organic frameworks: New types and tandem reactions. *Coord. Chem. Rev.* **2019**, 378, 500–512.

(10) Yin, Z.; Wang, Q. X.; Zeng, M. H. Iodine Release and Recovery, Influence of Polyiodide Anions on Electrical Conductivity and Nonlinear Optical Activity in an Interdigitated and Interpenetrated Bipillared-Bilayer Metal-Organic Framework. J. Am. Chem. Soc. 2012, 134, 4857–4863.

(11) Zeng, M. H.; Tan, Y. X.; He, Y. P.; Yin, Z.; Chen, Q.; Kurmoo, M. A Porous 4-Fold-Interpenetrated Chiral Framework Exhibiting Vapochromism, Single-Crystal-to-Single-Crystal Solvent Exchange, Gas Sorption, and a Poisoning Effect. *Inorg. Chem.* **2013**, *52*, 2353–2360.

(12) Ding, M. L.; Cai, X. C.; Jiang, H. L. Improving MOF stability: approaches and applications. *Chem. Sci.* **2019**, *10*, 10209–10230.

(13) Feng, R.; Jia, Y. Y.; Li, Z. Y.; Chang, Z.; Bu, X. H. Enhancing the stability and porosity of penetrated metal-organic frameworks through the insertion of coordination sites. *Chem. Sci.* **2018**, *9*, 950–955.

(14) Zhu, X. W.; Zhou, X. P.; Li, D. Exceptionally water stable heterometallic gyroidal MOFs: tuning the porosity and hydro-

phobicity by doping metal ions. Chem. Commun. 2016, 52, 6513-6516.

(15) He, H. M.; Sun, Q.; Gao, W. Y.; Perman, J. A.; Sun, F. X.; Zhu, G. S.; Aguila, B.; Forrest, K.; Space, B.; Ma, S. Q. A Stable Metal-Organic Framework Featuring a Local Buffer Environment for Carbon Dioxide Fixation. *Angew. Chem., Int. Ed.* **2018**, *57*, 4657–4662.

(16) McHugh, L. N.; McPherson, M. J.; McCormick, L. J.; Morris, S. A.; Wheatley, P. S.; Teat, S. J.; McKay, D.; Dawson, D. M.; Sansome, C. E. F.; Ashbrook, S. E.; Stone, C. A.; Smith, M. W.; Morris, R. E. Hydrolytic stability in hemilabile metal-organic frameworks. *Nat. Chem.* **2018**, *10*, 1096–1102.

(17) Li, N.; Xu, J.; Feng, R.; Hu, T. L.; Bu, X. H. Governing metalorganic frameworks towards high stability. *Chem. Commun.* **2016**, *52*, 8501–8513.

(18) Howarth, A. J.; Liu, Y. Y.; Li, P.; Li, Z. Y.; Wang, T. C.; Hupp, J.; Farha, O. K. Chemical, thermal and mechanical stabilities of metalorganic frameworks. *Nat. Rev. Mater.* **2016**, *1*, 15018.

(19) Tan, Y. X.; Yang, X.; Li, B. B.; Yuan, D. Q. Rational design of a flu-type heterometallic cluster-based Zr-MOF. *Chem. Commun.* **2016**, *52*, 13671–13674.

(20) Yuan, S.; Feng, L.; Wang, K. C.; Pang, J. D.; Bosch, M.; Lollar, C.; Sun, Y. J.; Qin, J. S.; Yang, X. Y.; Zhang, P.; Wang, Q.; Zou, L. F.; Zhang, Y. M.; Zhang, L. L.; Fang, Y.; Li, J. L.; Zhou, H. C. Stable Metal-Organic Frameworks: Design, Synthesis, and Applications. *Adv. Mater.* **2018**, *30*, 1704303.

(21) Li, X. Y.; Li, Y. Z.; Yang, Y.; Hou, L.; Wang, Y. Y.; Zhu, Z. H. Efficient light hydrocarbon separation and CO_2 capture and conversion in a stable MOF with oxalamide-decorated polar tubes. *Chem. Commun.* **2017**, *53*, 12970–12973.

(22) Dolgopolova, E. A.; Rice, A. M.; Shustova, N. B. Actinide-based MOFs: a middle ground in solution and solid-state structural motifs. *Chem. Commun.* **2018**, *54*, 6472–6483.

(23) Carter, K. P.; Ridenour, J. A.; Kalaj, M.; Cahill, C. L. A Thorium Metal-Organic Framework with Outstanding Thermal and Chemical Stability. *Chem. - Eur. J.* 2019, *25*, 7114–7118.

(24) Dolgopolova, E. A.; Ejegbavwo, O. A.; Martin, C. R.; Smith, M. D.; Setyawan, W.; Karakalos, S. G.; Henager, C. H.; Zur Loye, H. C.; Shustova, N. B. Multifaceted Modularity: A Key for Stepwise Building of Hierarchical Complexity in Actinide Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2017**, *139*, 16852–16861.

(25) Liu, W.; Xie, J.; Zhang, L. M.; Silver, M. A.; Wang, S. A hydrolytically stable uranyl organic framework for highly sensitive and selective detection of Fe^{3+} in aqueous media. *Dalton T.* **2018**, 47, 649–653.

(26) Li, P.; Vermeulen, N. A.; Malliakas, C. D.; Gomez-Gualdron, D. A.; Howarth, A. J.; Mehdi, B. L.; Dohnalkova, A.; Browning, N. D.; O'Keeffe, M.; Farha, O. K. Bottom-up construction of a superstructure in a porous uranium-organic crystal. *Science* **2017**, *356*, 624–627.

(27) Li, P.; Vermeulen, N. A.; Gong, X. R.; Malliakas, C. D.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. Design and Synthesis of a Water-Stable Anionic Uranium-Based Metal-Organic Framework (MOF) with Ultra Large Pores. *Angew. Chem., Int. Ed.* **2016**, *55*, 10358–10362.

(28) Li, Y. X.; Yang, Z. X.; Wang, Y. L.; Bai, Z. L.; Zheng, T.; Dai, X.; Liu, S. T.; Gui, D. X.; Liu, W.; Chen, M.; Chen, L. H.; Diwu, J.; Zhu, L. Y.; Zhou, R. H.; Chai, Z. F.; Albrecht-Schmitt, T. E.; Wang, S. A mesoporous cationic thorium-organic framework that rapidly traps anionic persistent organic pollutants. *Nat. Commun.* **2017**, *8*, 1354.

(29) Zhang, Z. H.; Senchyk, G. A.; Liu, Y.; Spano-Franco, T.; Szymanowski, J. E. S.; Burns, P. C. Porous Uranium Diphosphonate Frameworks with Trinuclear Units Templated by Organic Ammonium Hydrolyzed from Amine Solvents. *Inorg. Chem.* **2017**, *56*, 13249–13256.

(30) Ma, S. Q.; Wang, X. S.; Yuan, D. Q.; Zhou, H. C. A coordinatively linked Yb metal-organic framework demonstrates high thermal stability and uncommon gas-adsorption selectivity. *Angew. Chem., Int. Ed.* **2008**, *47*, 4130–4133.

(31) Huang, Z. W.; Hu, K. Q.; Mei, L.; Kong, X. H.; Yu, J. P.; Liu, K.; Zeng, L. W.; Chai, Z. F.; Shi, W. Q. Mixed-Ligands Strategy Regulates Thorium-based MOFs. *Dalton T.* **2020**, *49*, 983–987.

(32) Hu, K. Q.; Huang, Z. W.; Zhang, Z. H.; Mei, L.; Qian, B. B.; Yu, J. P.; Chai, Z. F.; Shi, W. Q. Actinide-Based Porphyrinic MOF as a Dehydrogenation Catalyst. *Chem. - Eur. J.* **2018**, *24*, 16766–16769.

(33) Shao, L.; Zhai, F. W.; Wang, Y. L.; Yue, G. Z.; Li, Y. R.; Chu, M. F.; Wang, S. A. Assembly of porphyrin-based uranium organic frameworks with (3,4)-connected pto and tbo topologies. *Dalton T.* **2019**, *48*, 1595–1598.

(34) Chen, G. H.; He, Y. P.; Zhang, S. H.; Zhang, J. Tuning a layer to a three-dimensional cobalt-tris(4 '-carboxybiphenyl)amine frame-work by introducing potassium ions. *Inorg. Chem. Commun.* **2018**, *90*, 65–68.

(35) He, Y. P.; Yuan, L. B.; Zhang, J. Polycatenation tuned microporosity of two metal-tris(4 '-carboxybiphenyl)amine frame-works with multilayer structures. *Dalton T.* **201**7, *46*, 13352–13355.

(36) Shi, D. Y.; Cui, C. J.; Hu, M.; Ren, A. H.; Song, L. B.; Liu, C. S.; Du, M. A microporous mixed-metal (Na/Cu) mixed-ligand (flexible/rigid) metal-organic framework for photocatalytic H-2 generation. *J. Mater. Chem. C* **2019**, *7*, 10211–10217.

(37) Moussawi, M. A.; Leclerc-Laronze, N.; Floquet, S.; Abramov, P. A.; Sokolov, M. N.; Cordier, S.; Ponchel, A.; Monflier, E.; Bricout, H.; Landy, D.; Haouas, M.; Marrot, J.; Cadot, E. Polyoxometalate, Cationic Cluster, and gamma-Cyclodextrin: From Primary Interactions to Supramolecular Hybrid Materials. *J. Am. Chem. Soc.* **2017**, 139, 12793–12803.

(38) Feng, D. W.; Gu, Z. Y.; Li, J. R.; Jiang, H. L.; Wei, Z. W.; Zhou, H. C. Zirconium-Metalloporphyrin PCN-222: Mesoporous Metal-Organic Frameworks with Ultrahigh Stability as Biomimetic Catalysts. *Angew. Chem., Int. Ed.* **2012**, *51*, 10307–10310.

(39) Asano, N.; Uemura, S.; Kinugawa, T.; Akasaka, H.; Mizutani, T. Synthesis of biladienone and bilatrienone by coupled oxidation of tetraarylporphyrins. *J. Org. Chem.* **2007**, *72*, 5320–5326.

(40) Otwinowski, Z.; Minor, W. Processing of X-ray diffraction data collected in oscillation mode. *Methods Enzymol.* **1997**, *276*, 307–326. (41) Spek, A. L. Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **2003**, *36*, 7–13.

(42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J. Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

(43) Kuchle, W.; Dolg, M.; Stoll, H.; Preuss, H. Energy-Adjusted Pseudopotentials for the Actinides-Parameter Sets and Test Calculations for Thorium and Thorium Monoxide. *J. Chem. Phys.* **1994**, *100*, 7535–7542.

(44) Cao, X. Y.; Dolg, M. Segmented contraction scheme for smallcore actinide pseudopotential basis sets. *J. Mol. Struct.: THEOCHEM* **2004**, 673, 203–209.

(45) Cao, X. Y.; Dolg, M. Segmented contraction scheme for smallcore lanthanide pseudopotential basis sets. *J. Mol. Struct.: THEOCHEM* **2002**, 581, 139–147.

(46) Klamt, A.; Jonas, V.; Burger, T.; Lohrenz, J. C. W. Refinement and parametrization of COSMO-RS. J. Phys. Chem. A **1998**, 102, 5074–5085.

(47) Klamt, A.; Schuurmann, G. Cosmo-a New Approach to Dielectric Screening in Solvents with Explicit Expressions for the

Screening Energy and Its Gradient. J. Chem. Soc., Perkin Trans. 2 1993, 799-805.

(48) Delmas, L. C.; White, A. J. P.; Pugh, D.; Horton, P. N.; Coles, S. J.; Lickiss, P. D.; Davies, R. P. Trisiloxane-centred metal-organic frameworks and hydrogen bonded assemblies. *CrystEngComm* **2018**, 20, 4541–4545.

(49) Zeng, L. W.; Hu, K. Q.; Mei, L.; Li, F. Z.; Huang, Z. W.; An, S. W.; Chai, Z. F.; Shi, W. Q. Structural Diversity of Bipyridinium-Based Uranyl Coordination Polymers: Synthesis, Characterization, and Ion-Exchange Application. *Inorg. Chem.* **2019**, *58*, 14075–14084.

(50) Huang, Z. W.; Li, Z. J.; Wu, Q. Y.; Zheng, L. R.; Zhou, L. M.; Chai, Z. F.; Wang, X. L.; Shi, W. Q. Simultaneous elimination of cationic uranium(vi) and anionic rhenium(vii) by graphene oxidepoly(ethyleneimine) macrostructures: a batch, XPS, EXAFS, and DFT combined study. *Environ. Sci.: Nano* **2018**, *5*, 2077–2087.

(51) Huang, Z. W.; Li, Z. J.; Zheng, L. R.; Zhou, L. M.; Chai, Z. F.; Wang, X. L.; Shi, W. Q. Interaction mechanism of uranium(VI) with three-dimensional graphene oxide-chitosan composite: Insights from batch experiments, IR, XPS, and EXAFS spectroscopy. *Chem. Eng. J.* **2017**, 328, 1066–1074.

(52) Tu, W. W.; Lei, J. P.; Wang, P.; Ju, H. X. Photoelectrochemistry of Free-Base-Porphyrin-Functionalized Zinc Oxide Nanoparticles and Their Applications in Biosensing. *Chem. - Eur. J.* **2011**, *17*, 9440–9447.

(53) Wang, L.; Zhao, R.; Gu, Z. J.; Zhao, Y. L.; Chai, Z. F.; Shi, W. Q. Growth of Uranyl Hydroxide Nanowires and Nanotubes by the Electrodeposition Method and Their Transformation to One-Dimensional U_3O_8 Nanostructures. *Eur. J. Inorg. Chem.* 2014, 2014, 1158–1164.

(54) Kraus, C. A.; Parmenter, E. F. Further studies of the oxides of potassium. J. Am. Chem. Soc. 1934, 56, 2384–2388.

(55) Capaldo, L.; Merli, D.; Fagnoni, M.; Ravelli, D. Visible Light Uranyl Photocatalysis: Direct C-H to C-C Bond Conversion. *ACS Catal.* **2019**, *9*, 3054–3058.

(56) Fang, X. Z.; Shang, Q. C.; Wang, Y.; Jiao, L.; Yao, T.; Li, Y. F.; Zhang, Q.; Luo, Y.; Jiang, H. L. Single Pt Atoms Confined into a Metal-Organic Framework for Efficient Photocatalysis. *Adv. Mater.* **2018**, *30*, 1705112.

(57) Ding, M. L.; Flaig, R. W.; Jiang, H. L.; Yaghi, O. M. Carbon capture and conversion using metal-organic frameworks and MOF-based materials. *Chem. Soc. Rev.* **2019**, *48*, 2783–2828.

(58) Sirijaraensre, J. Mechanistic insights into CO_2 cycloaddition of styrene oxide on paddle-wheel metal clusters: a theoretical study. *New J. Chem.* **2019**, *43*, 11692–11700.

(59) Ren, Y. W.; Chen, J. G.; Qi, C. R.; Jiang, H. F. A New Type of Lewis Acid-Base Bifunctional M(salphen) (M = Zn, Cu and Ni) Catalysts for CO₂ Fixation. *ChemCatChem* **2015**, 7, 1535–1538.

(60) Xu, H.; Cao, C. S.; Hu, H. S.; Wang, S. B.; Liu, J. C.; Cheng, P.; Kaltsoyannis, N.; Li, J.; Zhao, B. High Uptake of ReO_4^- and CO_2 Conversion by a Radiation-Resistant Thorium-Nickle $[\text{Th}_{48}\text{Ni}_6]$ Nanocage-Based Metal-Organic Framework. *Angew. Chem., Int. Ed.* **2019**, 58, 6022–6027.

(61) Sharma, N.; Dhankhar, S. S.; Kumar, S.; Kumar, T. J. D.; Nagaraja, C. M. Rational Design of a 3D Mn-Metal-Organic Framework Based on a Nonmetallated Porphyrin Linker for Selective Capture of CO_2 and One-Pot Synthesis of Styrene Carbonates. *Chem.* - *Eur. J.* **2018**, 24, 16662–16669.

(62) Lyu, J. F.; Zhang, X.; Li, P.; Wang, X. J.; Buru, C. T.; Bai, P.; Guo, X. H.; Farha, O. K. Exploring the Role of Hexanuclear Clusters as Lewis Acidic Sites in Isostructural Metal-Organic Frameworks. *Chem. Mater.* **2019**, *31*, 4166–4172.

(63) Guan, J. Q.; Duan, Z. Y.; Zhang, F. X.; Kelly, S. D.; Si, R.; Dupuis, M.; Huang, Q. G.; Chen, J. Q.; Tang, C. H.; Li, C. Water oxidation on a mononuclear manganese heterogeneous catalyst. *Nat. Catal.* **2018**, *1*, 870–877.

(64) Bai, L.; Duan, Z. Y.; Wen, X. D.; Si, R.; Guan, J. Q. Atomically dispersed manganese-based catalysts for efficient catalysis of oxygen reduction reaction. *Appl. Catal., B* **2019**, 257, 117930.

(65) Daiyan, R.; Lu, X. Y.; Ng, Y. H.; Amal, R. Liquid Hydrocarbon Production from CO₂: Recent Development in Metal-Based Electrocatalysis. *ChemSusChem* **2017**, *10*, 4342–4358.

(66) Prajapati, P. K.; Kumar, A.; Jain, S. L. First Photocatalytic Synthesis of Cyclic Carbonates from CO_2 and Epoxides Using CoPc/TiO₂ Hybrid under Mild Conditions. *ACS Sustainable Chem. Eng.* **2018**, *6*, 7799–7809.

(67) Raza, F.; Park, J. H.; Lee, H. R.; Kim, H. I.; Jeon, S. J.; Kim, J. H. Visible-Light-Driven Oxidative Coupling Reactions of Amines by Photoactive WS₂ Nanosheets. *ACS Catal.* **2016**, *6*, 2754–2759.

(68) Zhang, Z. J.; Zhu, Y. F.; Chen, X. J.; Zhang, H. J.; Wang, J. A Full-Spectrum Metal-Free Porphyrin Supramolecular Photocatalyst for Dual Functions of Highly Efficient Hydrogen and Oxygen Evolution. *Adv. Mater.* **2019**, *31*, 1806626.

(69) Sharma, N.; Dhankhar, S. S.; Nagaraja, C. M. A Mn(II)porphyrin based metal-organic framework (MOF) for visible-lightassisted cycloaddition of carbon dioxide with epoxides. *Microporous Mesoporous Mater.* **2019**, 280, 372–378.

(70) Gao, W. Y.; Chen, Y.; Niu, Y. H.; Williams, K.; Cash, L.; Perez, P. J.; Wojtas, L.; Cai, J. F.; Chen, Y. S.; Ma, S. Q. Crystal Engineering of an nbo Topology Metal-Organic Framework for Chemical Fixation of CO_2 under Ambient Conditions. *Angew. Chem., Int. Ed.* **2014**, *53*, 2615–2619.

(71) Ugale, B.; Kumar, S.; Dhilip Kumar, T. J.; Nagaraja, C. M. Environmentally Friendly, Co-catalyst-Free Chemical Fixation of CO_2 at Mild Conditions Using Dual-Walled Nitrogen-Rich Three-Dimensional Porous Metal-Organic Frameworks. *Inorg. Chem.* **2019**, *58*, 3925–3936.

(72) Wu, G. P.; Wei, S. H.; Ren, W. M.; Lu, X. B.; Li, B.; Zu, Y. P.; Darensbourg, D. J. Alternating copolymerization of CO_2 and styrene oxide with Co(III)-based catalyst systems: differences between styrene oxide and propylene oxide. *Energy Environ. Sci.* 2011, 4, 5084–5092.