

## RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2024, **11**, 6493Engineering uranyl sites into MOFs for efficient and highly selective photocatalytic CO<sub>2</sub> reduction†Zhi-Heng Zhou,<sup>‡a,b</sup> Xiao-Bo Li,<sup>‡a</sup> Zhi-Wei Huang,<sup>a</sup> Qun-Yan Wu,<sup>id a</sup> Jun-Xi Wang,<sup>a,b</sup> Zhi-Hui Zhang,<sup>id c</sup> Ji-Pan Yu,<sup>a</sup> Lei Mei,<sup>id a</sup> Fu-Qiu Ma,<sup>\*b</sup> Kong-Qiu Hu<sup>\*a</sup> and Wei-Qun Shi<sup>id \*a</sup>

Utilizing sunlight for the photocatalytic reduction of CO<sub>2</sub> to CO and other high value-added products represents a pivotal strategy for environment protection and mitigation of the energy crisis. Herein, we have designed and prepared a uranium-based organic-framework (MOF), IHEP-101, featuring a uranyl photocatalytic active center, engineered for the efficient photocatalytic reduction of CO<sub>2</sub>. Demonstrating exceptional activity, IHEP-101 achieves a CO production rate of up to 458 μmol g<sup>-1</sup> h<sup>-1</sup>. The mechanism underlying IHEP-101's photocatalytic CO<sub>2</sub> reduction is thoroughly detailed through *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and theoretical calculations. This study underscores the effectiveness of UO<sub>2</sub><sup>2+</sup> cations as active sites for the photocatalytic reduction of CO<sub>2</sub>, introducing an innovative method for designing and synthesizing highly efficient photocatalysts aimed at CO<sub>2</sub> reduction.

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## Introduction

In recent decades, with the massive consumption of fossil fuels, the concentration of CO<sub>2</sub> in the atmosphere has gradually increased, leading to significant environmental problems such as global warming and the energy crisis.<sup>1–5</sup> At present, numerous methods for CO<sub>2</sub> conversion exist, including photocatalytic reduction,<sup>6</sup> electrochemical reduction,<sup>7,8</sup> thermochemical conversion,<sup>9,10</sup> adsorption,<sup>11</sup> and biological conversion.<sup>12,13</sup> Among these, the photocatalytic reduction of CO<sub>2</sub> into high value-added products using sunlight is considered one of the most promising solutions due to its cleanliness and environmental friendliness. However, CO<sub>2</sub> is extremely stable, presenting a challenge of overcoming the high dissociation energy of the C=O bond to achieve efficient

conversion.<sup>14–18</sup> Synthesizing efficient and highly selective photocatalysts to reduce the thermodynamic energy barrier is an urgent problem that needs to be addressed.<sup>15,19,20</sup>

Metal-organic frameworks (MOFs) have broad applications in the field of photocatalysis, offering well-defined coordination environments, unique functional ligands, high specific surface areas, and unsaturated metal sites for excellent catalytic performances.<sup>21–39</sup> Furthermore, as heterogeneous catalysts, MOFs can be easily separated from the reaction system for recycling, thus extending the catalyst's service life and preventing pollution. The introduction of different metal ions into MOFs directly affects their structures, physical and chemical properties, and, consequently, their photocatalytic CO<sub>2</sub> reduction performance. Currently, most MOF materials used for the photocatalytic CO<sub>2</sub>RR are based on transition metal elements, with fewer examples of actinide-based MOFs and even rarer use of actinides as catalytic active centers. In recent years, the field of carbon dioxide fixation has increasingly adopted actinide functional materials, notably actinide-based MOFs. For example, Huang *et al.* prepared a supported poly-metallic oxygen cluster mesoporous/microporous porphyrin metal-organic framework POMs@IHEP-20, which achieved a CO yield of 970 μmol g<sup>-1</sup> h<sup>-1</sup>.<sup>19</sup> In addition, Huang *et al.* utilized thorium ions, known for their large ionic radius and high coordination numbers, as metal nodes to precisely regulate the rapid electron transport pathway that forms between the photoactive motifs of porphyrin MOFs, thereby influencing the photocatalytic CO<sub>2</sub>RR performance.<sup>40</sup> It is important to

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note, however, that in these MOFs, actinides serve as the structural components of the metal nodes rather than directly acting as catalytic centers.

Uranium is widely recognized for its pivotal role in nuclear power generation. However, the focus also extends to the recycling of depleted uranium, the principal component of spent fuel, which has attracted much attention.<sup>41–44</sup> The uranyl ion exhibits exceptional photochemical properties, notably a peak absorption wavelength near 470 nm, allowing it to be excited by blue light ranging from 450 to 495 nm.<sup>45–50</sup> In addition, the excited states of uranyl showcase a fluorescence lifetime in the microsecond range, and complexes containing uranyl enable efficient electron transfer from the photoexcited  $^*UO_2^{2+}$  to organic molecules.<sup>51–55</sup> These distinctive photochemical properties, combined with varied structural configurations, establish uranyl complexes as exemplary candidates for the development of new photocatalysts. Acting as a photocatalyst, the uranyl ions can be activated through the ligand-to-metal charge transfer (LMCT) process. Within this process, electrons within the  $O=U=O$  unit are transferred from the O 2p orbital to the U 5f orbital, effectively leading to electron promotion from the highest occupied molecular orbital (HOMO) to the non-bonded orbital. This induces the formation of a U(v) center and an oxygen radical, thereby facilitating direct catalysis of the conversion and synthesis of a diverse array of compounds.<sup>54,56,57</sup> By integrating the uranyl cation within a MOF as a catalytic active site, its catalytic functionality is further refined, offering a more controllable approach to catalysis.

The development of salen ligands and their metal complexes has been rapid due to their simple synthesis methods and their structures, which are both diverse and easily modifiable.<sup>58</sup> Salen ligands, featuring an  $[N_2O_2]$  coordination cavity, can coordinate with various metal ions to form  $M(\text{Salen})$  ( $M = \text{Cu}, \text{Co}, \text{Zn}, \text{etc.}$ ) complexes, exhibiting excellent charge transfer capabilities and abundant catalytic active sites. Consequently, they have been widely used in photocatalysis.<sup>59–63</sup> For example, Su and coworkers synthesized two coordinatively unsaturated Co–Salen complexes that demonstrated high activity and CO selectivity for visible-light-driven  $\text{CO}_2$  reduction in a water-containing system.<sup>64</sup> Azam and collaborators found that a uranyl salen coordination complex could capture visible light and selectively photocatalytically reduce  $\text{CO}_2$  to MeOH.<sup>65</sup>

In this work, two novel uranium-based MOFs,  $[(\text{CH}_3)_2\text{NH}_2][UO_2][UO_2(\text{L1})(\text{DMF})][UO_2(\text{L1})(\text{H}_2\text{O})]_{0.5}(\text{DMF})_{1.5}$  (IHEP-101,  $H_4L1 = 5,5'-((1E,1'E)-((2,2\text{-dimethylpropane-1,3-diyl})\text{bis(azaneylylidene)})\text{bis(methaneylylidene)})\text{bis(4-hydroxy-3-methoxybenzoic acid)})$  and  $[UO_2(\text{DMF})][UO_2(\text{L2})(\text{DMF})]$  (IHEP-102,  $H_4L2 = 5,5'-((1E,1'E)-(\text{ethane-1,2-diylbis(azaneylylidene)})\text{bis(methaneylylidene)})\text{bis(4-hydroxy-3-methoxybenzoic acid)})$ , were synthesized by the solvothermal reaction of the uranyl cation and the two previously mentioned salen ligands. IHEP-101 features a three-dimensional (3D) framework composed of adjacent two-dimensional (2D) cellular networks that are stacked through  $\pi$ – $\pi$  interactions. IHEP-102 possesses a compact three-dimensional (3D) structure formed from adja-

cent one-dimensional (1D) chains stacked by  $\pi$ – $\pi$  interactions. The photocatalytic  $\text{CO}_2$ RR results revealed that IHEP-101 could achieve a CO yield of  $458 \mu\text{mol g}^{-1} \text{h}^{-1}$  without requiring the addition of a sacrificial agent. Moreover, the mechanism underlying the photocatalytic  $\text{CO}_2$ RR facilitated by IHEP-101 was comprehensively elucidated through *in situ* Diffuse Reflectance Infrared Fourier Transform (DRIFTS) spectroscopy and theoretical analyses.

## Experimental

**Caution!** Uranyl nitrate hexahydrate  $UO_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is a radioactive and chemically toxic reactant, and precautions with suitable care and protection for handling such substances should be followed although it was used in the experiment.  $UO_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in ultra-pure water (50 mL) to obtain a uranyl nitrate stock solution (0.50 M).

3-Formyl-4-hydroxy-5-methoxybenzoic acid was synthesized according to a published procedure.<sup>66</sup>  $H_4L1$  and  $H_4L2$  were synthesized according to a modified version of a published procedure.<sup>67</sup> Other required chemicals are derived from commercial products and can be used directly without further purification.

### Synthesis

**The synthesis of IHEP-101.**  $H_4L1$  (18.34 mg, 0.04 mmol),  $UO_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (25.10 mg, 0.05 mmol) and DMF (2 mL) were sealed in a 10 mL Teflon-lined autoclave, heated to 120 °C and kept at a constant temperature for 3 days. After cooling to room temperature, the red single crystals of IHEP-101 were filtered and washed with DMF. Yield: 60% based on  $H_4L1$ .

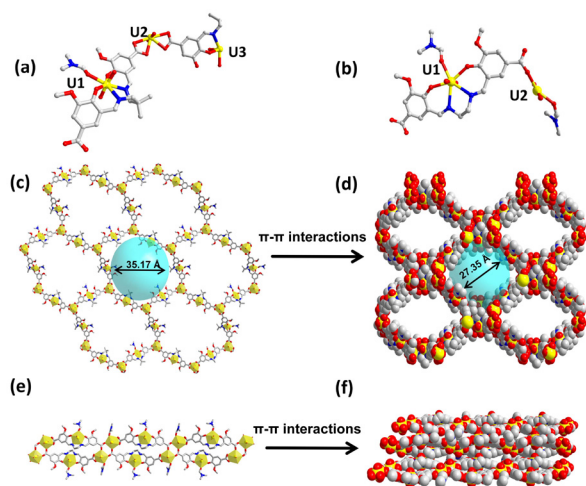
**The synthesis of IHEP-102.**  $H_4L2$  (16.66 mg, 0.04 mmol),  $UO_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (25.10 mg, 0.05 mmol) and DMF (2 mL) were sealed in a 10 mL Teflon-lined autoclave, heated to 120 °C and kept at a constant temperature for 3 days. After cooling to room temperature, the red single crystals of IHEP-102 were filtered and washed with DMF. Yield: 65% based on  $H_4L2$ .

## Results and discussion

### Structural description of IHEP-101

The single crystal X-ray diffraction study of IHEP-101 reveals that it crystallizes in the monoclinic space group  $C2/c$  (Table S1†). The asymmetric unit of the framework structure contains three  $UO_2^{2+}$  cations,  $3/2$   $L1^{4-}$  ligands, one DMF molecule, and one  $\text{H}_2\text{O}$  molecule as shown in Fig. 1a. The lengths of the U–O bonds on the equatorial plane are in the range of 2.229(12)–2.509(10) Å, and the lengths of the axial U–O bonds are in the range of 1.737(13)–1.774(8) Å, which are similar to the literature reports (Table S2†).<sup>68–70</sup> U1 and U3 adopt a similar pentagonal bipyramidal geometry, bound to two phenoxy atoms and two imine nitrogen atoms of  $L1^{4-}$  ligands and one oxygen atom of DMF or  $\text{H}_2\text{O}$ , respectively, on the equatorial plane. Each U2 atom coordinates to six oxygen





**Fig. 1** (a) Asymmetric unit of IHEP-101. (b) Asymmetric unit of IHEP-102. (c) Single layer of IHEP-101. (d) Complete structure of IHEP-101. (e) Single strand of IHEP-102. (f) Complete structure of IHEP-102. Color scheme: U, yellow; C, gray; O, red; N, blue. Hydrogen atoms were omitted for clarity.

atoms from three carboxylic groups on the equatorial plane. Two adjacent U2 atoms are bridged together by one assembled  $[\text{UO}_2(\text{L1})]^{2-}$  ligand to generate a twisted two-dimensional (2D) honeycomb-like network (Fig. 1c). Then adjacent layers are stacked into a three-dimensional (3D) framework through  $\pi$ - $\pi$  interactions (Fig. 1d). In addition, the single layer of IHEP-101 has a 35.17 Å diameter pore which is partially obscured by interlamellar stacking, but IHEP-101 has formed a pore with a diameter of approximately 27.35 Å along the *c*-axis (Fig. S5†). The PLATON calculation result indicates that the pore volume ratio of IHEP-101 reached 46.4%.

### Structural description of IHEP-102

Single crystal X-ray diffraction reveals that IHEP-102 crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit contains two  $\text{UO}_2^{2+}$  cations, one  $\text{L2}^{4-}$  anion, and two DMF molecules, as shown in Fig. 1b. U1 locates in the  $\text{L2}^{4-} [\text{N}_2\text{O}_2]$  cavity and coordinates to two phenoxy atoms and two imine nitrogen atoms of an  $\text{L2}^{4-}$  ligand, as well as one oxygen atom of DMF, thus forming a metallized ligand  $[\text{UO}_2(\text{L2})]^{2-}$ . Each U2 atom coordinates to four oxygen atoms from three carboxyl groups and one oxygen atom of DMF on the equatorial plane. Therefore, each  $[\text{UO}_2(\text{L2})]^{2-}$  ligand bridges three U2 atoms and two adjacent U2 atoms are bridged together by two  $[\text{UO}_2(\text{L2})]^{2-}$  ligands to form a regular one-dimensional (1D) chain structure (Fig. 1e). Then, adjacent chains are stacked into a dense three-dimensional (3D) structure through  $\pi$ - $\pi$  interactions (Fig. 1f).

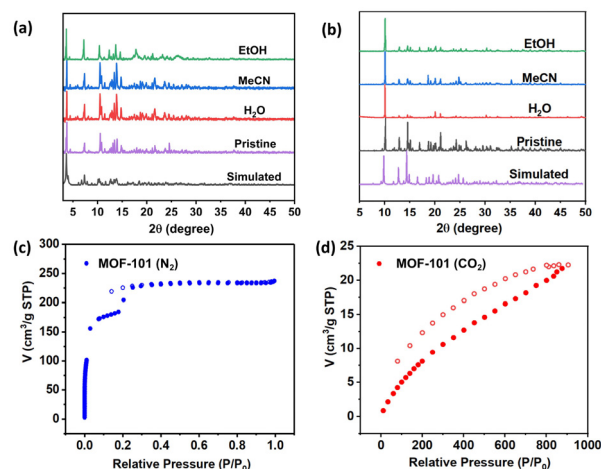
### Characterization of coordination compounds

The phase purity and structural stability of IHEP-101 and IHEP-102 were assessed through powder X-ray diffraction (PXRD) analysis. The PXRD patterns of IHEP-101 and IHEP-102 were found to be consistent with the patterns simu-

lated from their CIF files, indicating that both materials exhibit high phase purity (Fig. S7†). In addition, PXRD analyses confirmed that IHEP-101 and IHEP-102 display stability in conventional solvents (Fig. 2a and b).

The thermal stability of IHEP-101 and IHEP-102 was evaluated through thermogravimetric analysis (TGA), as shown in Fig. S8.† IHEP-101 exhibits a loss of dimethylamine molecules and  $\text{H}_2\text{O}$  molecules, as well as some solvent molecules, within the temperature range of 30–250 °C. Loss of DMF molecules occurred between 250 and 373 °C. Subsequently, the framework began to decompose, with the weight decreasing continuously until complete decomposition noted at 630 °C, leaving behind 52.8%  $\text{U}_3\text{O}_8$  in the product. IHEP-102 shows a 5% weight loss before 230 °C, attributed to the release of solvent molecules. The loss of the coordinated DMF molecule was noted from 230 to 405 °C. The framework then commenced disassembly after 405 °C, with the weight further decreasing until stabilization, with the remaining  $\text{U}_3\text{O}_8$  fragment stable upon further heating until 800 °C. As shown in Fig. 2c, the  $\text{N}_2$  adsorption-desorption isotherm reveals that the Brunauer-Emmett-Teller (BET) specific surface area of IHEP-101 reaches  $681.79 \text{ cm}^2 \text{ g}^{-1}$ , and the corresponding pore size distribution also indicates the presence of several uniform mesoporous/microporous channel structures (Fig. S10†). Furthermore, the  $\text{CO}_2$  adsorption-desorption isotherm of IHEP-101 reveals that it possesses a high  $\text{CO}_2$  adsorption capacity of  $40.28 \text{ cm}^3 \text{ g}^{-1}$  (Fig. 2d).

The UV-vis absorption spectra of IHEP-101 and IHEP-102 were examined to evaluate their capacity for absorbing visible light. As shown in Fig. S11a and S12a,† IHEP-101 and IHEP-102 exhibit similar UV-vis absorption spectra, with strong absorption in both the ultraviolet and visible regions. Based on the Tauc plots, the band gap of IHEP-101 was determined to be 2.10 eV, and for IHEP-102, it is 2.09 eV (Fig. S11b and S12b,† respectively). The Mott-Schottky plots were utilized



**Fig. 2** (a) PXRD patterns of IHEP-101 after soaking in multiple solvents. (b) PXRD patterns of IHEP-102 after soaking in multiple solvents. (c)  $\text{N}_2$  adsorption-desorption isotherms of IHEP-101. (d)  $\text{CO}_2$  adsorption-desorption isotherms of IHEP-101.





to ascertain the conduction band (CB) potentials of IHEP-101 and IHEP-102 (Fig. S11c and S12c†). The results of Mott-Schottky analyses conducted at frequencies of 1200, 1400 and 1600 Hz reveal that both materials are typical n-type semiconductors.<sup>30,71</sup> Consequently, the LUMO levels were determined to be  $-0.60$  V for IHEP-101 and  $-0.553$  V for IHEP-102 (vs. NHE). From the band gaps and conduction band (CB) potential data, the valence band (VB) potentials of IHEP-101 and IHEP-102 were calculated as  $1.50$  V and  $1.537$  V (vs. NHE), respectively. These findings underscore the potential of both IHEP-101 and IHEP-102 as promising photocatalysts (Fig. S11d and S12d†). As depicted in Fig. S13,† under full-spectrum irradiation, IHEP-101 rapidly achieved a stable photocurrent density of  $0.38 \mu\text{A cm}^{-2}$  with a reversible response during on-off cycling, whereas IHEP-102 exhibited a photocurrent density of  $0.36 \mu\text{A cm}^{-2}$ . The similar photocurrent responses suggest comparable charge separation efficiencies in both materials.

### Performance of photocatalytic CO<sub>2</sub> reduction

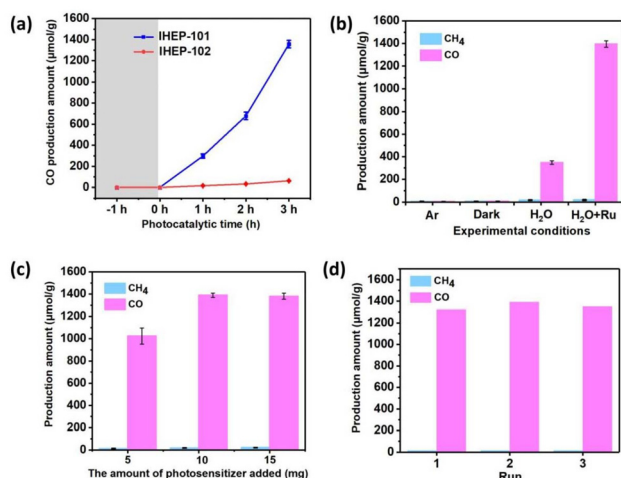
The CO<sub>2</sub>RR experiments were carried out under visible-light irradiation ( $\lambda > 420$  nm) in a CH<sub>3</sub>CN/H<sub>2</sub>O mixture (4/1, volume ratio), with IHEP-101 or IHEP-102 prepared as the catalyst, and [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (bpy = 2,2'-bipyridine) as the photosensitizer without an additional sacrificial agent. As shown in Fig. 3a, the CO<sub>2</sub>RR result of IHEP-101 shows a nearly linear increase in CO production over 3 h corresponding to a rate of  $458 \mu\text{mol g}^{-1} \text{h}^{-1}$ . The photocatalytic selectivity for CO production was 98.6%, with CH<sub>4</sub> the only other gaseous product identified (Fig. 3b). In addition, the <sup>1</sup>H NMR results indicate that no liquid products (HCOOH, CH<sub>3</sub>OH, etc.) produced from the photocatalytic reduction of CO<sub>2</sub> were detected (Fig. S15†). When substituting CO<sub>2</sub> with Ar or conducting the reaction

under dark conditions, only trace amounts of gaseous products can be detected, suggesting that CO is indeed produced from the photocatalytic reduction of CO<sub>2</sub>, not from the degradation of IHEP-101. Remarkably, even without the introduction of a photosensitizer, IHEP-101 is capable of achieving CO<sub>2</sub> photocatalytic reduction, with a CO production rate of  $115.79 \mu\text{mol g}^{-1} \text{h}^{-1}$  and a selectivity of 95.2%. After three photocatalytic cycles, IHEP-101 retains similar catalytic activity and high crystallinity, demonstrating that the material has excellent stability during the photocatalytic process (Fig. 3d and Fig. S16a†). Fourier transform infrared spectroscopy (FT-IR) analysis further verifies the stability of IHEP-101 post-photocatalysis (Fig. S16b†). Although IHEP-101 and IHEP-102 exhibit similar photoelectrochemical properties, the photocatalytic CO<sub>2</sub>RR performance of the latter significantly lags behind that of the former. This discrepancy can likely be attributed to the low porosity of IHEP-102, which hinders the diffusion of CO<sub>2</sub> to the metal active sites.

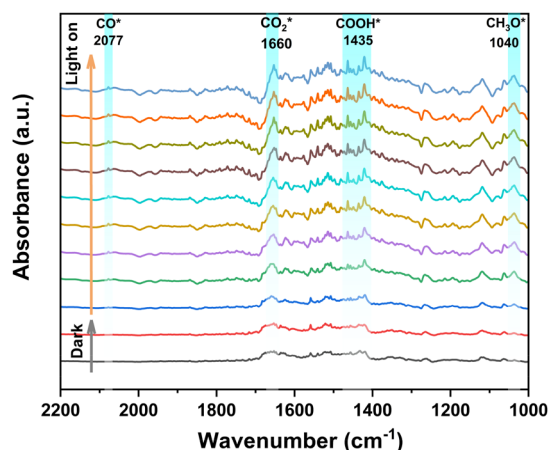
### Mechanisms of photocatalytic CO<sub>2</sub> reduction

The reaction intermediates of the photocatalytic CO<sub>2</sub> reduction process can be determined by *in situ* DRIFTS measurement, as shown in Fig. 4. Under dark conditions, the spectral signals remain inactive. However, upon exposure to light irradiation, several new peaks can be observed, which can be assigned to a variety of intermediate states potentially involved in the CO<sub>2</sub> reduction process. The observed peaks at  $1635 \text{ cm}^{-1}$  (CO<sub>2</sub>\*) and  $1600 \text{ cm}^{-1}$  (\*COOH) are eventually converted to the reduction product CO. Furthermore, the \*CO intermediates are promptly eliminated from the reaction interface, culminating in the formation of CO. Therefore, only a very faint peak corresponding to \*CO can be observed at  $2077 \text{ cm}^{-1}$ .<sup>40,72</sup> The characteristic peak at  $1040 \text{ cm}^{-1}$  is attributed to \*CH<sub>3</sub>O, which is an intermediate product of CH<sub>4</sub>.<sup>40</sup>

DFT calculations were performed to further uncover the CO<sub>2</sub>RR mechanism of IHEP-101, as shown in Fig. 5. First of

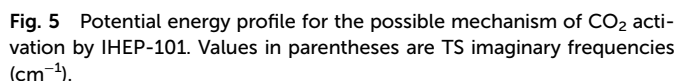


**Fig. 3** (a) Time-dependent evolution of CO<sub>2</sub> reduction products over IHEP-101. (b) Catalytic efficiency of IHEP-101 under different conditions. (c) The effect of additive amount of photosensitizer on photocatalytic performance. (d) The recycling performance of IHEP-101 for the photocatalytic reduction of CO<sub>2</sub>.

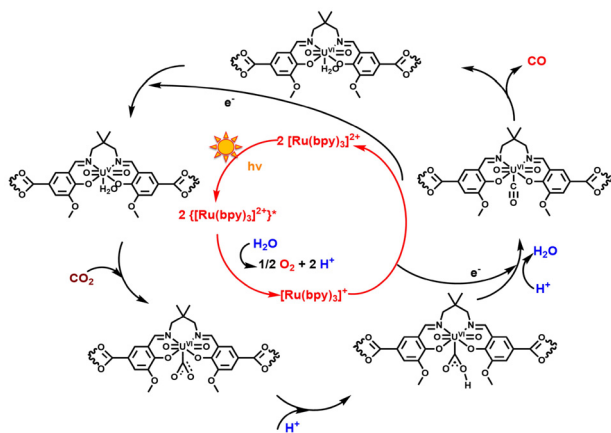


**Fig. 4** *In situ* DRIFTS spectra of IHEP-101 at 1000–2200 cm<sup>-1</sup>. A representative spectrum was selected at 5 min intervals, with the 10th minute being the start time of light irradiation.





Based on existing experimental data and literature reports, a potential reaction pathway for the photocatalytic reduction of CO<sub>2</sub> by IHEP-101 is proposed, as shown in Fig. 6. Initially, the photosensitizer [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O (bpy = 2,2'-bipyridine)



**Fig. 6** Schematic mechanism of the photocatalytic CO<sub>2</sub> reduction by IHEP-101.

and the L1 ligand generate photogenerated electrons and holes upon exposure to visible light. The holes are utilized for the oxidation of H<sub>2</sub>O, and the photogenerated electrons are transferred from both the photosensitizer and the L1 ligand to the uranyl active sites in the unsaturated coordination in the MOF. This transfer reduces the hexavalent uranyl to the pentavalent uranium. Subsequently, through a two-electron transfer process, electrons are transferred to CO<sub>2</sub>, achieving the photocatalytic reduction of CO<sub>2</sub> to CO, while the uranium is re-oxidized from pentavalent back to hexavalent.

## Conclusions

In summary, two novel uranium-based MOFs, IHEP-101 and IHEP-102, have been synthesized using the coordination of salen ligands with UO<sub>2</sub><sup>2+</sup> cations. IHEP-101 exhibits a high specific surface area and demonstrates a remarkable efficiency in the photocatalytic reduction of CO<sub>2</sub>. The mechanism of photocatalytic CO<sub>2</sub> reduction by IHEP-101 is clearly elucidated using *in situ* DRIFTS and theoretical calculations. DFT calculations have confirmed that the activation of CO<sub>2</sub> by IHEP-101 is both thermodynamically and kinetically feasible, accompanied by a cyclic transition in the oxidation state of the U atom. This work highlights the potential of UO<sub>2</sub><sup>2+</sup> cations as active sites in the photocatalytic reduction of CO<sub>2</sub>, which provides valuable insights for further studies on the photocatalytic performance of the uranyl group and the design of new MOFs for photocatalysis.

## Author contributions

Z.H. Zhou conceived all experiments and wrote the manuscript. X.B. Li performed the theoretical calculations. Z.W. Huang, Z.H. Zhang, Q.Y. Wu, J.P. Yu and J.X. Wang assisted in performing the tests. K.Q. Hu, L. Mei and W.Q. Shi provided search ideas, and reviewed and edited the manuscript. F.Q.

Ma, and W.Q. Shi provided revision guidance, suggestions and part of the financial support.

## Data availability

Crystallographic data for IHEP-101 and IHEP-102 have been deposited at CCDC under 2358409 and 2358410† and can be obtained from <https://doi.org/10.1039/d4qi01578a>.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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