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Photoisomerization-mediated tunable pore size in metal organic frameworks for U(VI)/V(V) selective separation

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PAPER PRESENTATION

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Background

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A Bio-inspired Nano-pocket Spatial Structure for Targeting Uranyl Capture

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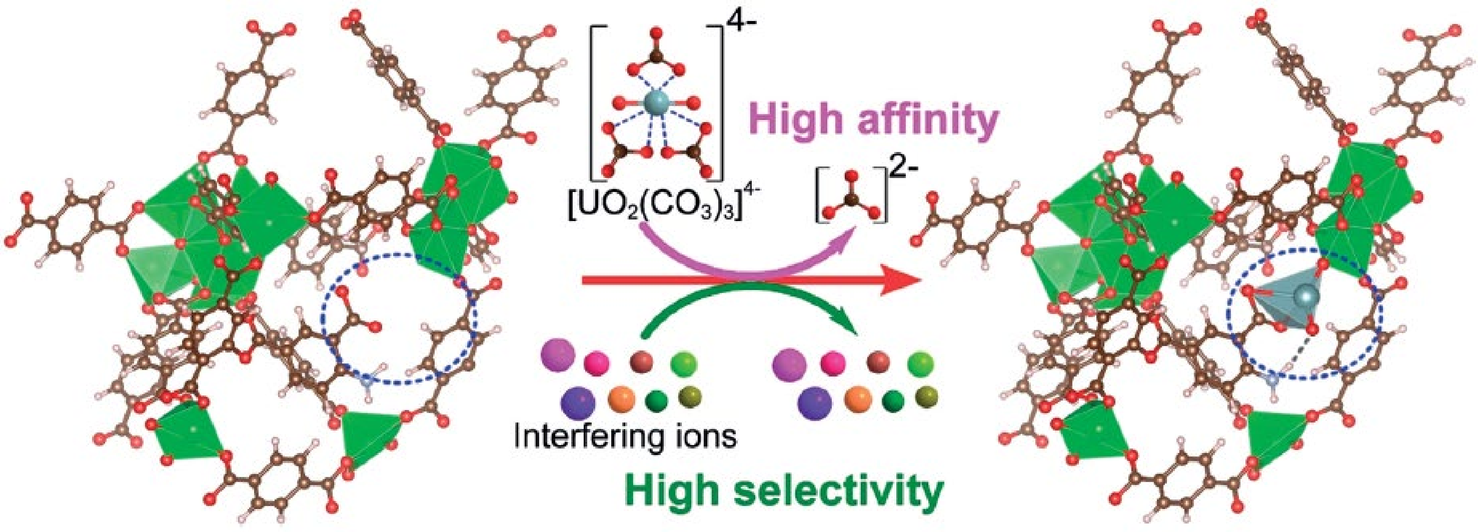

Figure 1. Scheme for targeting uranyl capture by nano-pocket in MOF.

UiO-66-3C4N - 393.97 mg·g^{-1}

Introduction

- This study proposes a light-responsive, dynamically tunable pore system that enables precise spatial coordination and size-matching for the selective capture of uranyl species.

- In the visible-light-induced open state, the flexible pore architecture enhances ion transport and improves the accessibility of $[UO_2(CO_3)_3]^{4-}$ complexes to active binding sites, thereby resulting in increased adsorption capacity.

- Under UV-induced closed-state conditions, the MOF adopts a more rigid and contracted pore structure that offers both a precisely size-matched cavity and a favorable coordination environment for $[UO_2(CO_3)_3]^{4-}$ rather than $[H_2VO_4]^{-}$.

- This strategy demonstrated remarkable efficacy, achieving a high uranium adsorption capacity of 588.24 mg· g^{-1} and an exceptional U(VI)/V(V) separation factor of 215.

- In this study, a light-responsive framework was constructed by incorporating photoactive diarylethene (DAE) isomer units into two structurally stable zeolitic imidazolate frameworks (ZIF-70 and ZIF-60), which possess similar chemical compositions but distinct pore sizes.

Why this paper?

- The light-controlled switching gives a unique ability to tune the material in real time, solving the trade-off between capacity and selectivity.
- This is a first-of-its-kind approach for the highest uranium-vanadium separation using photo-responsive MOFs.

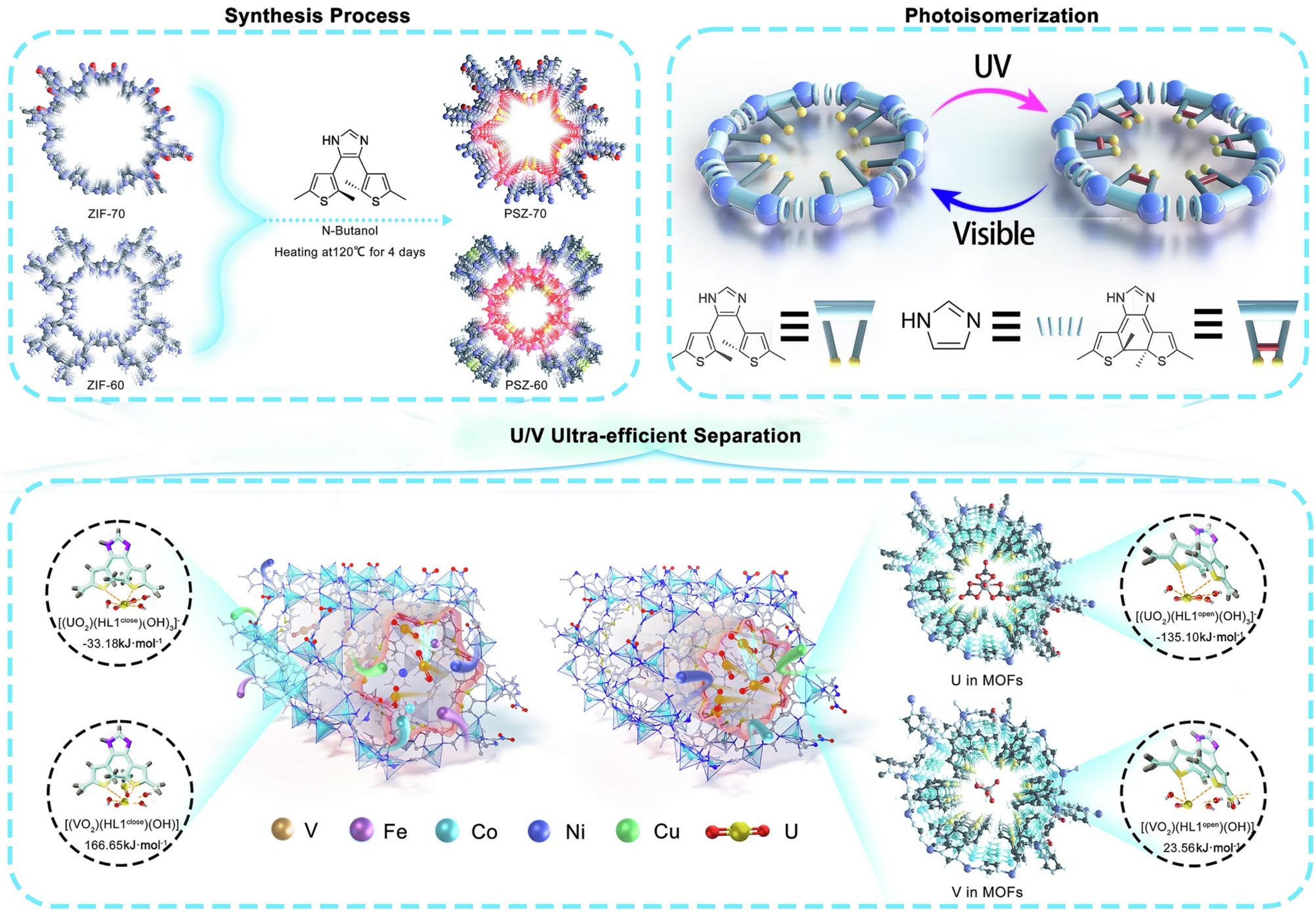

Fig. 1. Construction of a composite photoisomeric material framework and illustration of the selective uranium extraction process. Synthesis process: section grafting of photoisomerization monomers in ZIF-60 and ZIF-70. Photoisomerization Section: Photo-responsive isomerization of composite photoisomerized MOFs. U/V Ultra-efficient Separation Section: Differential recognition and separation of U(VI) and V(V) by composite photoisomerized MOFs in a polymetallic ion interference system.

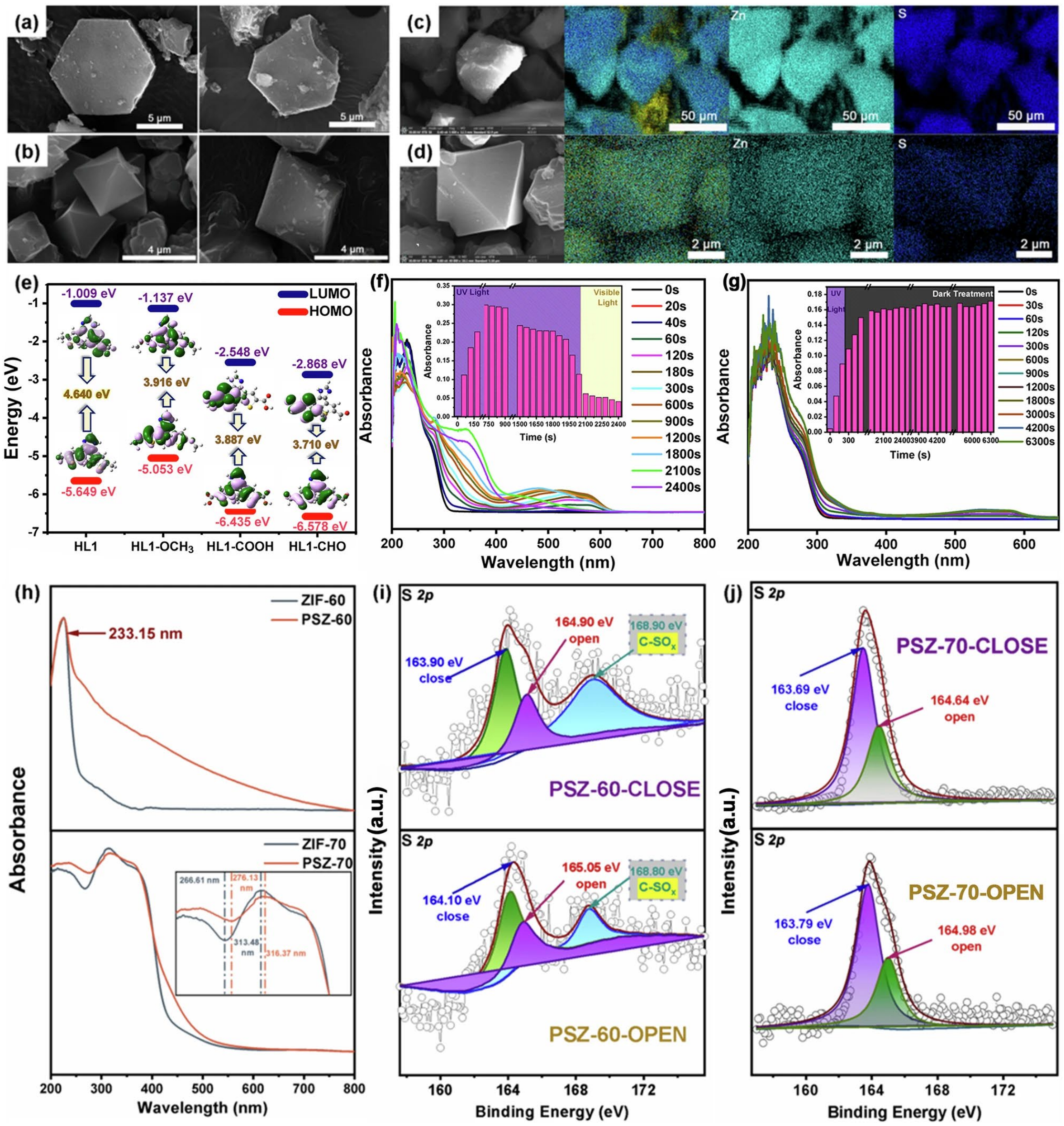

Fig. 2. Characterization of physical and chemical properties of materials. a. SEM images of ZIF-70 (left) and PSZ-70 (right). b. ZIF-60 (left) and PSZ-60 (right). c, d. SEM images and EDX analysis (C(yellow), N(green), O(red), Zn(turquoise), S(dark blue), subgraphs from left to right are the composition of all elements, Zn and S, respectively) of PSZ-70 (up) and PSZ-60 (down). e. Molecular orbital diagram of HL1 and corresponding partial derivatives. f, g. Absorbance of HL1 in a methanol solution in the wavelength range of λ=200–800 nm under UV-visible switching light source conditions (left) and UV-dark conditions (right) (the inset figures in both 2f and 2g show the absorbance change of the solution anchored at 545 nm, respectively). h. DRS analysis of ZIF-70, ZIF-60, PSZ-70, and PSZ-60 (The top and bottom graphs show the change of absorbance in the range of 200–800 nm before and after grafting the photoswitch with ZIF-60 and ZIF-70, respectively; the inset figure of bottom graph is an enlarged display of the spectrum in the range of 200–400 nm). i. XPS analysis of the open/closed conformational transition process of PSZ-60 (The top and bottom graphs show the binding energy changes of the splitting peaks in the S 2p spectra of PSZ-60 in the photoisomerized open-state and closed-state). j. XPS analysis of the open/closed conformational transition process of PSZ-70 (The top and bottom graphs show the binding energy changes of the splitting peaks in the S 2p spectra of PSZ-70 in the photoisomerized open-state and closed-state).

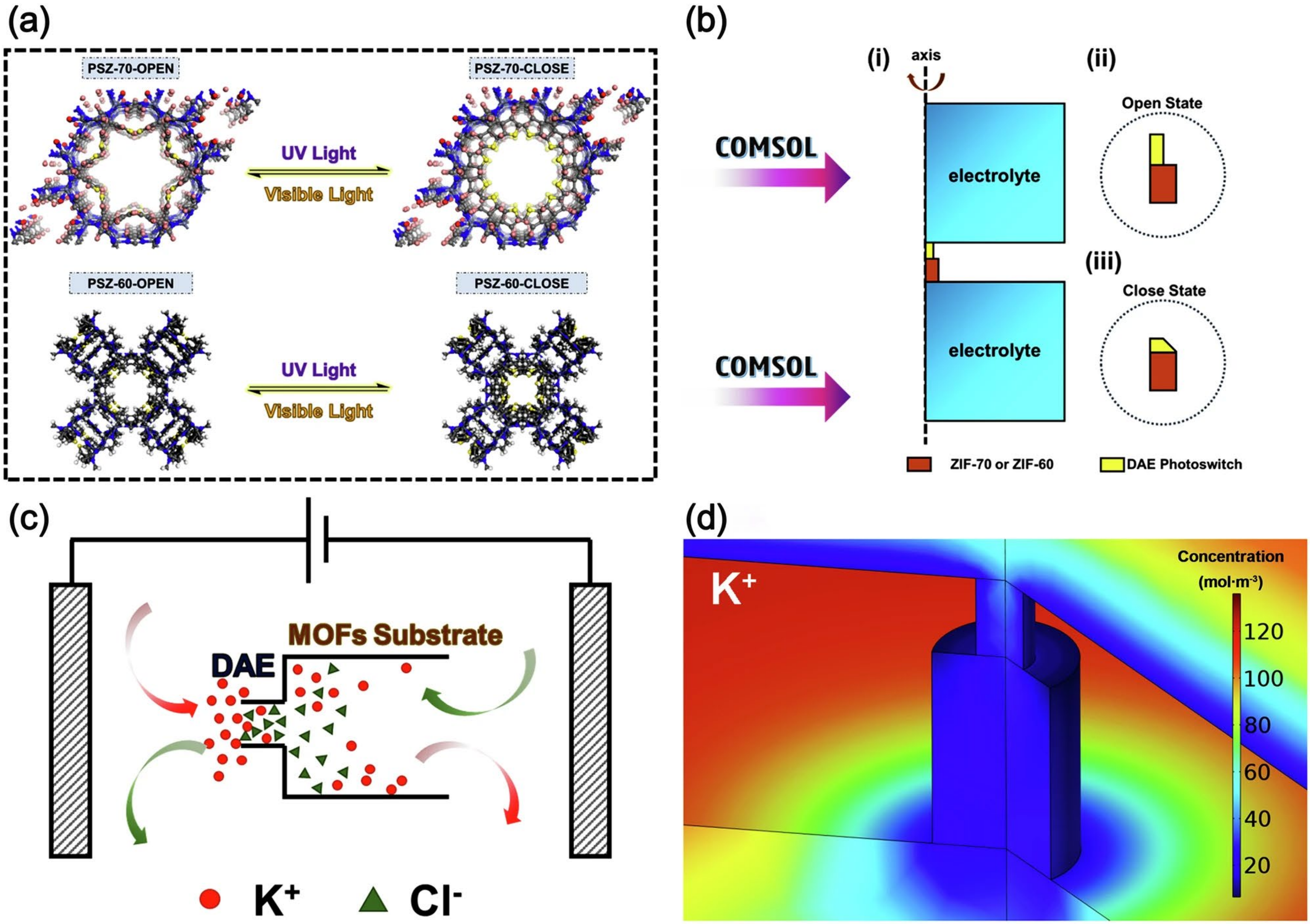

Fig. 3. Finite element modeling and mass transfer simulation of the photoisomerized MOFs. a Diagram of the theoretical open/closed conformational transition of PSZ-70 and PSZ-60. b Simulation of the structure of the composite material in COMSOL software in the open and closed states of the photoswitch ((i) Construction of axisymmetric model; (ii) the two-dimensional geometric model of the pore structure when the photoswitch is under the open-state; (iii) the two-dimensional geometric model of the pore structure when the photoswitch is under the closed-state). c Illustration of the swimming behavior of ions in photoisomeric composites driven by an electric field (with K+ and Cl− as examples). d Heatmap of the concentration flux of K+ in the experimentally simulated system in the photoswitch open state.

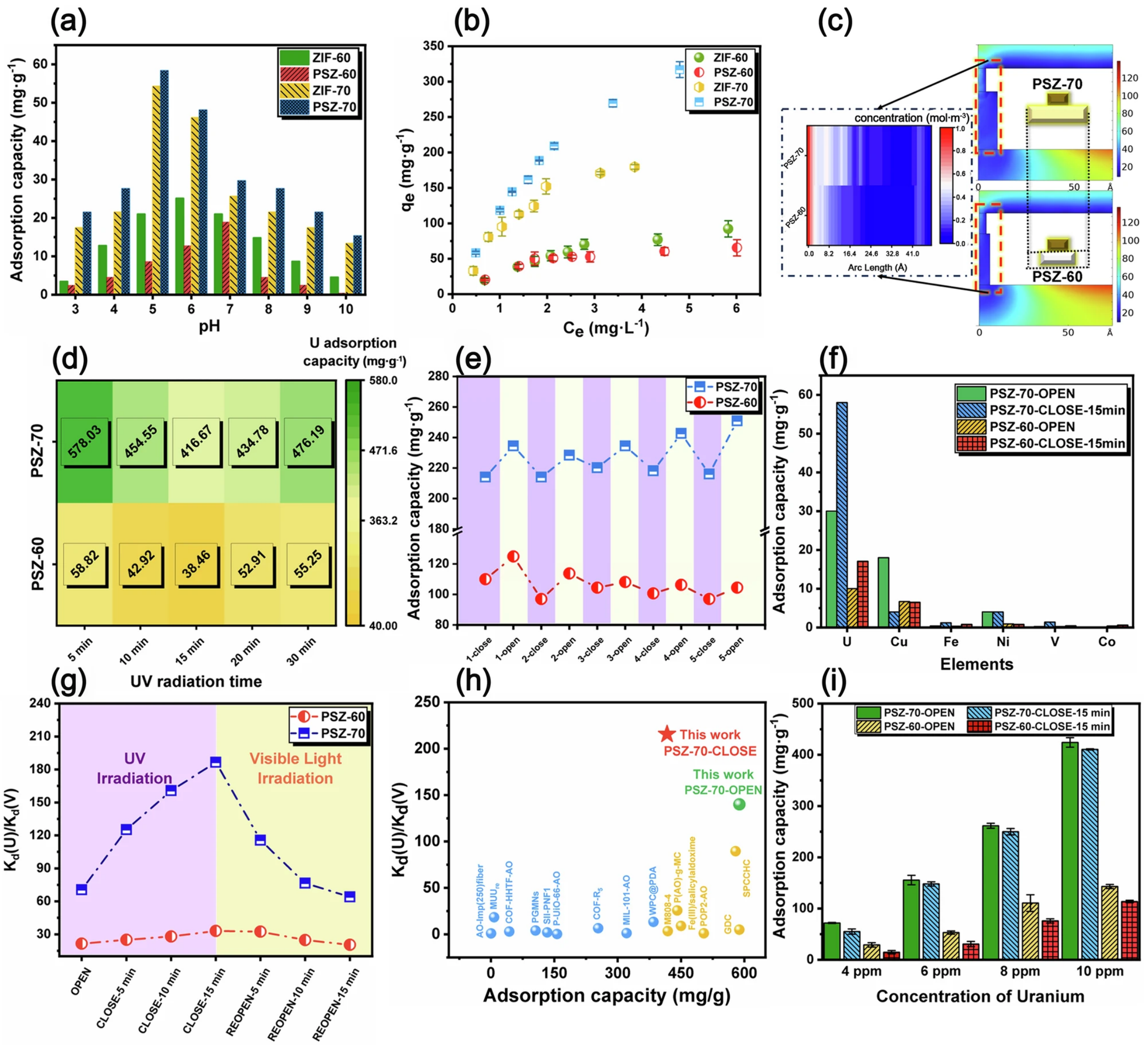

Fig. 4. Adsorption and separation of uranium by the composite Photoisomerized MOFs. a. Variation in the maximum adsorption capacity with pH for ZIF-70, PSZ-70, ZIF-60, and PSZ-60. b. Adsorption isotherms of two substrates MOFs and their corresponding photoisomeric composites at 298 K. c. Visualization of ion swimming by different substrate pore sizes of MOFs. d Comparison of the maximum adsorption capacity of uranium by the photoisomerization process of PSZ-70 and PSZ-60. e Photoisomerization fatigue test under alternate UV-Vis exposure cycles (Purple color indicates the absorbance measurements under UV irradiation, yellow color indicates the absorbance measurements under visible light irradiation, and the bar widths do not correlate with the measurement duration. Number-close indicates the number of times the photoswitch was in the closed state during the five-cycle test (i.e., the photoswitch was in the closed state for the nth time (n = 1, 2, 3, 4, 5)), and this description also applies to the open state). f. Adsorption selectivity of PSZ-70 and PSZ-60 with their corresponding open/closed isomeric states for some metal cations in simulated seawater systems. g. Test of the separability of uranium and vanadium by in situ photo-controlled reversible isomerization. h. Comparison of the maximum adsorption capacities and U(VI)/V(V) separation ratios of photoisomerized MOFs with adsorbent materials in some of similar experimental systems. i. PSZ-70 and PSZ-60's adsorption abilities in fully open and closed conformations in natural seawater with uranium spikes. Error bars in Fig. 4b and i represent standard deviations (SD) calculated from three independent replicate experiments for each data point; the SD was computed to reflect the variability of the measurements.

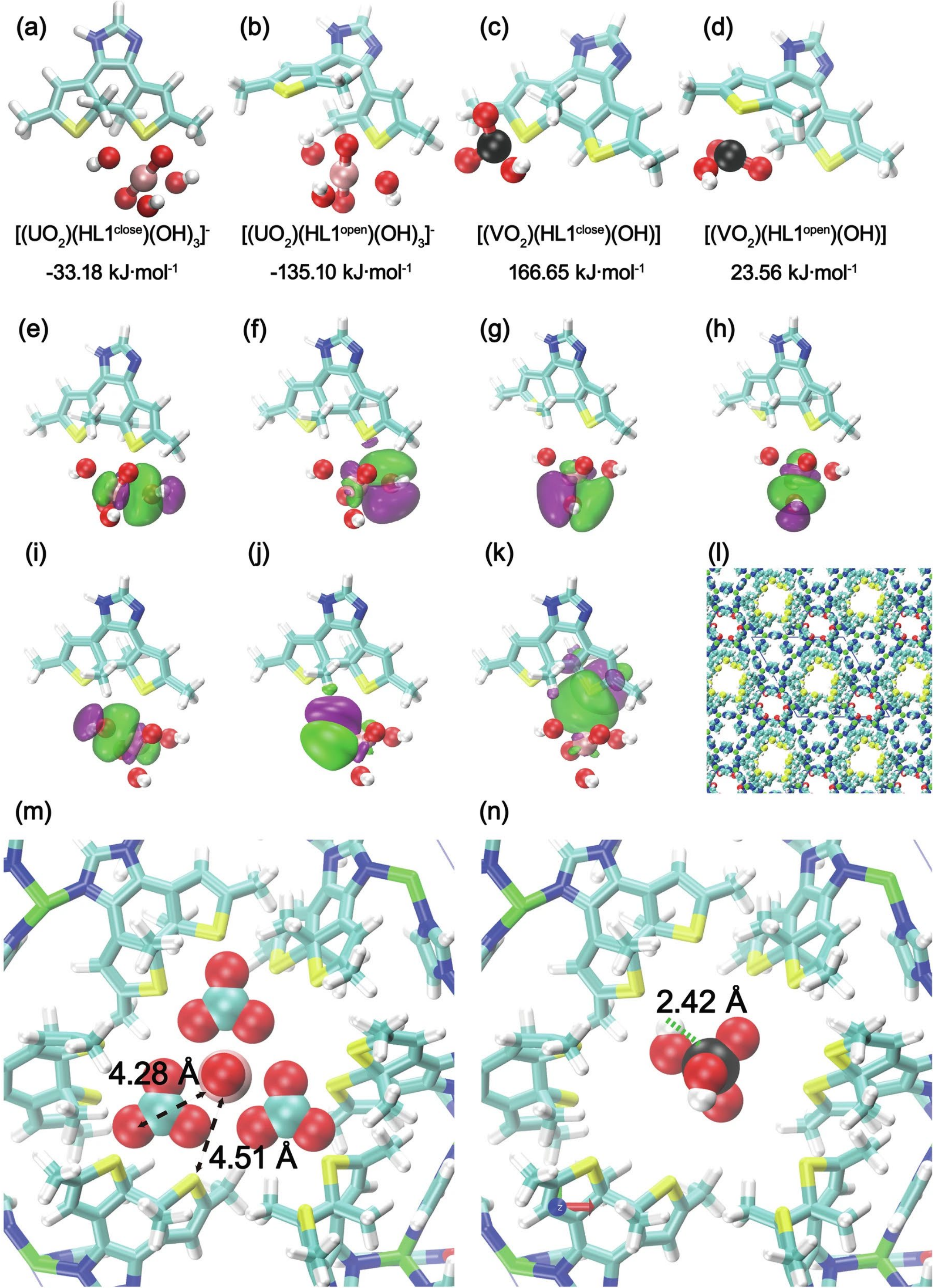

Fig. 5. Separation mechanism of uranium by the photoisomerized MOFs. a–d Optimized complex structures formed by HL1close and UO_2^{2+}, HL1open and UO_2^{2+}, HL1close and VO_2^+, and HL1open and VO_2^+ according to DFT simulations. e–k NBO orbitals between U and O in the hydroxyl group and between U and S in the dimethylthiophene group for the [(UO2)(HL1close)(OH)3]− complex. l Optimized structure of PSZ-70-close from DFT simulations. m, n Overlap of the optimized structure of [UO2(CO3)3]4− with the optimized structure of PSZ-70-close, and overlap of the optimized structure of [H2VO4]− with the optimized structure of PSZ-70-close.H, C, N, O, S, U, V, and Zn atoms are shown in white, cyan, blue, red, yellow, pink, black, and green, respectively. The NBO orbitals are indicated by green and purple isosurfaces.

Conclusion

- A novel photo-switchable MOF was engineered by integrating diarylethene (DAE) photo switches into ZIF-70 and ZIF-60 frameworks, enabling reversible control of pore size and coordination environment using UV and visible light.

- Light-induced pore adjustment allowed precise size- and charge-based discrimination, enabling highly selective uptake of U(VI) species over V(V), even under competing conditions.

- The system demonstrated a record-high uranium adsorption capacity (588.24 $mg \cdot g^{-1}$) and an unprecedented U(VI)/V(V) separation factor (215), surpassing traditional adsorbents.

Thank you