RESEARCH ARTICLE

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Nanotrap Grafted Anionic MOF for Superior Uranium Extraction from Seawater

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Dedicated to Prof. Satishchandra Ogale on the occasion of his 70th birthday

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PAPER PRESENTATION
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Introduction

- Here they have reported a novel anionic metal-organic framework (iMOF-1A), which features unique pyrazinic sites with strong Lewis basic properties. This framework serves as an effective nanomaterial for selectively extracting uranium through ion exchange, showcasing its capability to retain uranium ions securely and prevent undesirable leaching due to its inherent ionic properties.

- This ionic MOF captures 99.8% of uranium within 120 minutes, reducing its concentration from 20,000 parts per billion (ppb) to 24 ppb. Moreover, they exhibit high adsorption capacities of 1336.8 mg/g and 625.6 mg/g when exposed to uranium-spiked deionized water and artificial seawater, respectively.

- The material provides an exceptionally high enrichment index of approximately 5754. It meets the UES standard of 6.0 mg/g within a span of 16 days and yields 9.42 mg/g after 30 days of exposure to natural seawater.

Why this paper?

- In this paper, they have done Isothermal titration calorimetry (ITC) experiments, which provide a detailed quantification of the thermodynamics of adsorption processes in aqueous media, which was unexplored in the literature for the uranium adsorption process.

- They have also explored techniques such as Nano FTIR and TFM which show that the sequestration process is associated with both ion exchange and supramolecular interactions throughout the single crystals of iMOF-1A.

Background

ACS central science

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Nanotrap Grafted Anion Exchangeable Hybrid Materials for Efficient Removal of Toxic Oxoanions from Water

Samraj Mollick, Sahel Fajal, Satyam Saurabh, Debanjan Mahato, and Sujit K. Ghosh*

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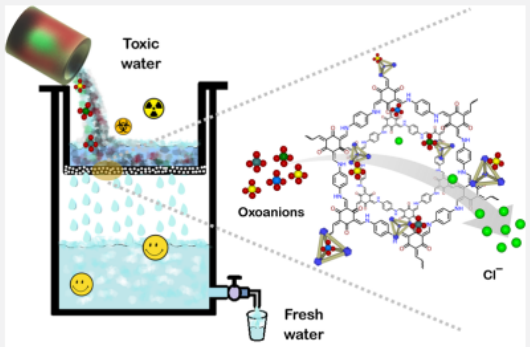

Toxic oxoanions capture by IPcomp-3(200) hybrid material

ACS APPLIED OPTICAL MATERIALS

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Hydrolytically Stable Luminescent Cationic MOF for Selective Detection of Toxic Organic Arsenic in Water

Gourab K. Dam, Sahel Fajal, Subhajit Dutta, Sumanta Let, Aamod V. Desai, and Sujit K. Ghosh*

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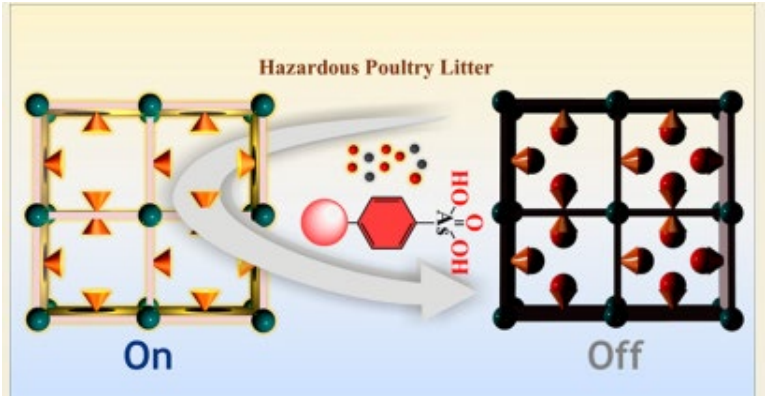
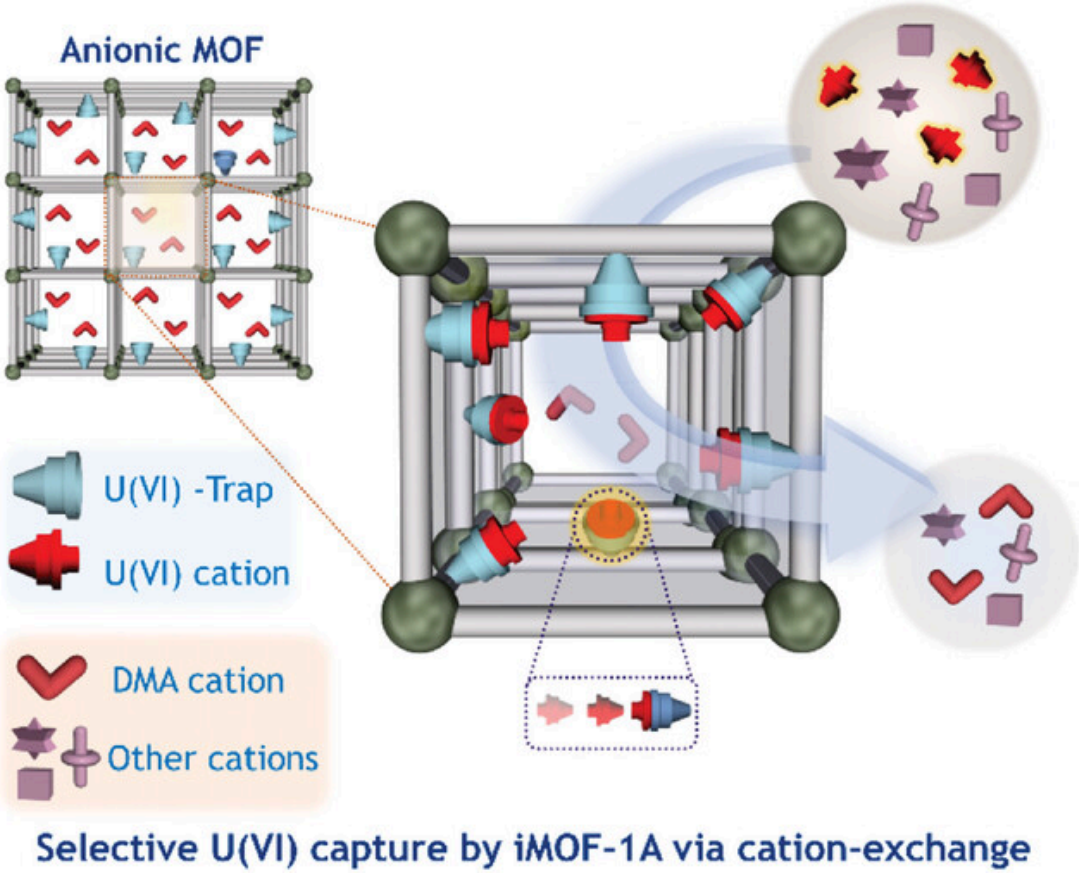




Scheme 1. A schematic representation of nanotrap grafted cation exchangeable MOF selectively capturing Uranyl ions from a mixture of other interfering cations.

Synthesis

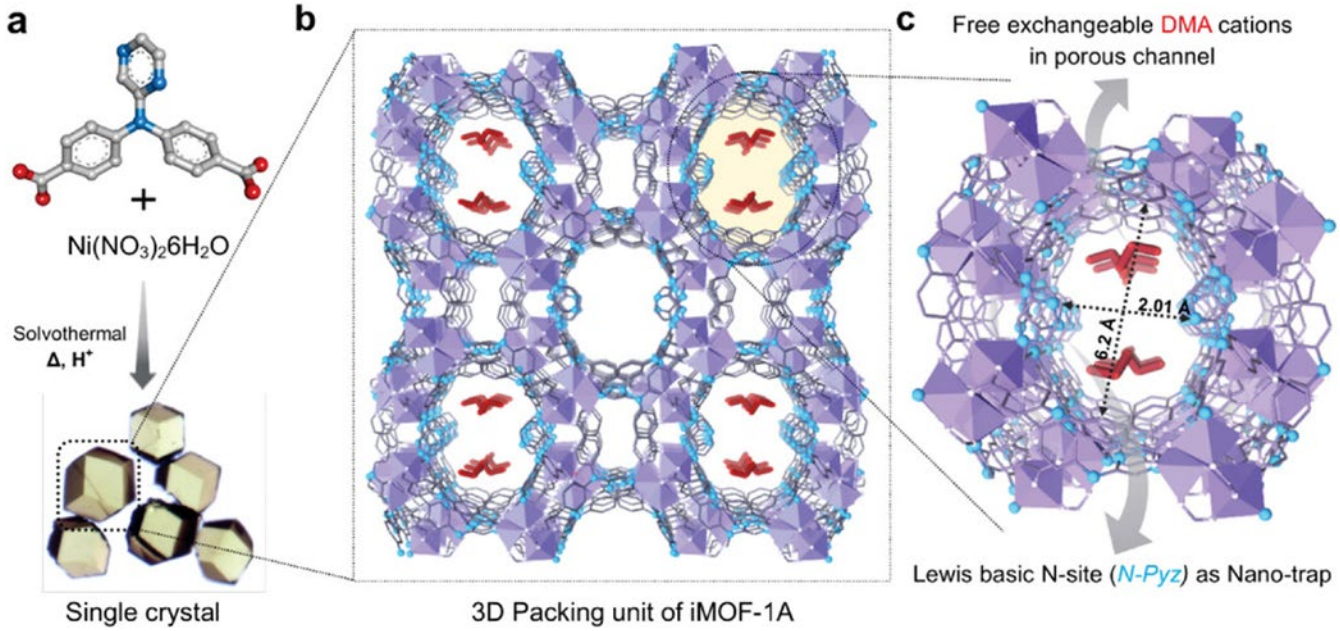


Figure 1. a) Representation of the synthetic protocol leading to iMOF-1A, by varying the uncoordinated anions within its pores; b) perspective view of iMOF-1A revealing its bi-porous nature with two types of Ultramicroporous channels sustaining the framework; c) orderly arrangement of DMA cations within pore; (colour codes: grey—C, cyan-blue—N, white—O, purple—Ni, guest—scarlet red (DMA cations), solvent molecules and H atoms are omitted for clarity).

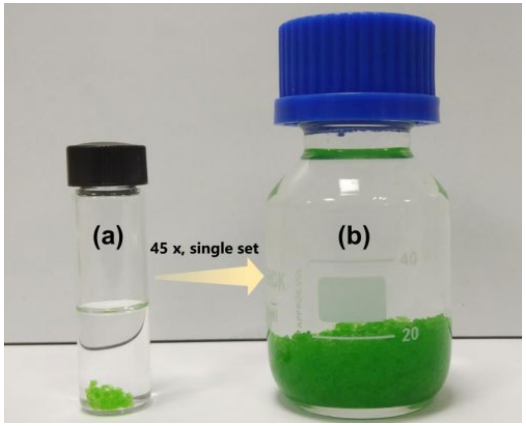


Fig. S7. Scale up; (a) milligram scale (~490±20 mg/batch) to (b) gram scale synthesis (~20.9 g/ batch) of iMOF-1A in unit batch. Scale up ratio; 45x, x: minimum scale up size.

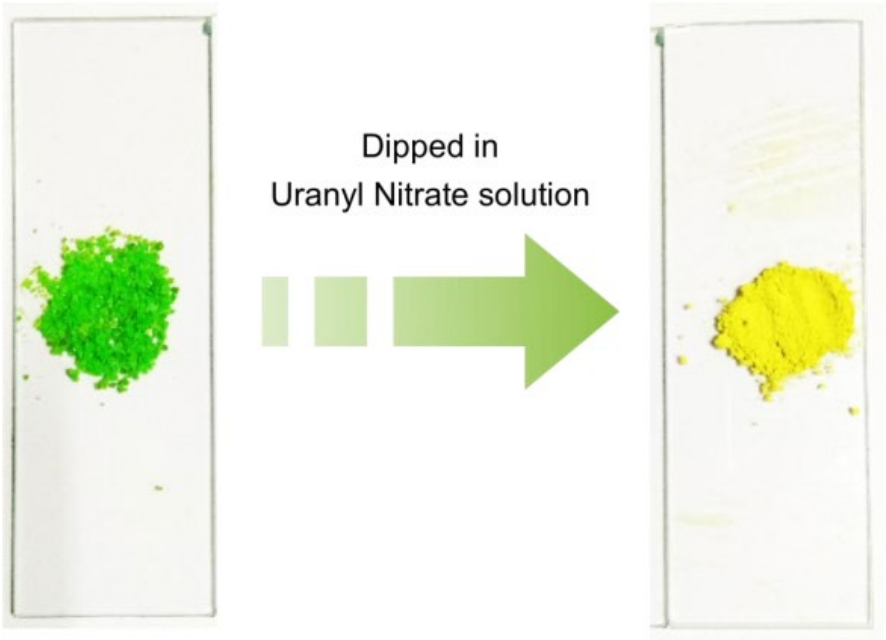


Fig. S13. Visual imaging of iMOF-1A before and after U capture studies; dry form.

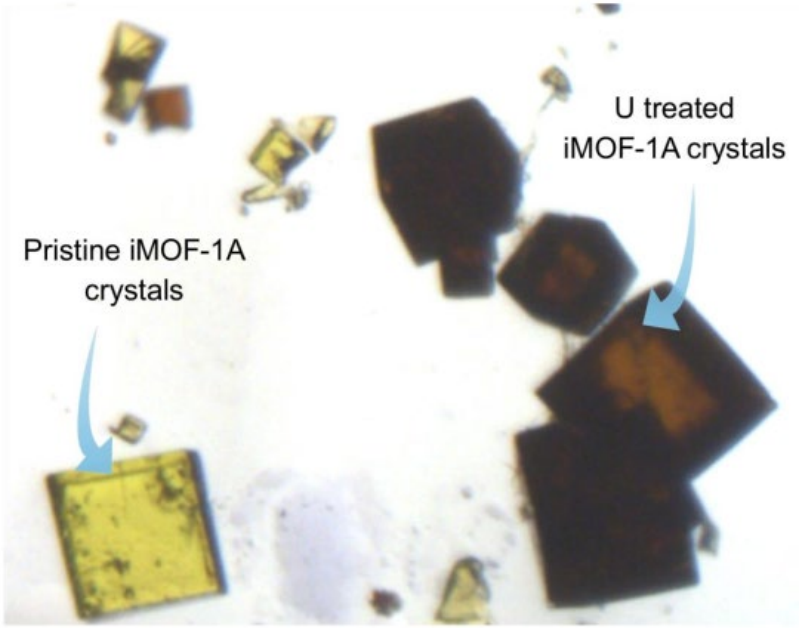


Fig. S14. Zoomed view visualization of iMOF-1A single crystals after several days of saturated U solution treatment: wet form (local contrast in single view).

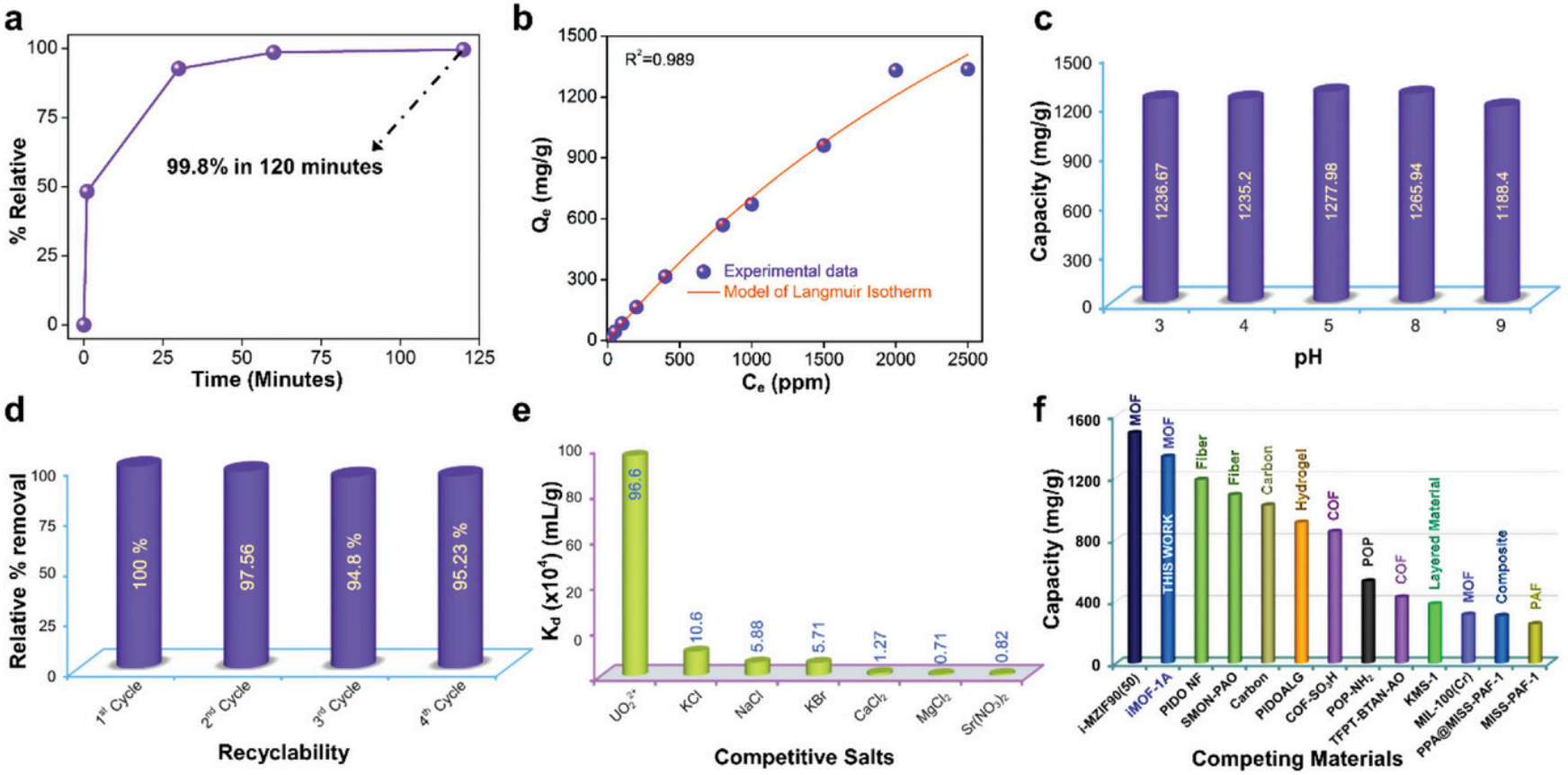


Figure 2. Uranium capture from various uranium-spiked water systems by iMOF-1A. a) Kinetics of uranium removal efficiency from spiked water samples spiked with 20000 ppb uranium at V/m = 2250 mL g-1. b) Langmuir isotherms. c) pH-dependent adsorption capacity tests. d) Recyclability test. e) Distribution coefficient, *K*d value of iMOF-1A for different meddling cations. f) Comparison of uranium adsorption capacities from uranium-spiked water comprising various reported excellent adsorbents (Table S3, Supporting Information).

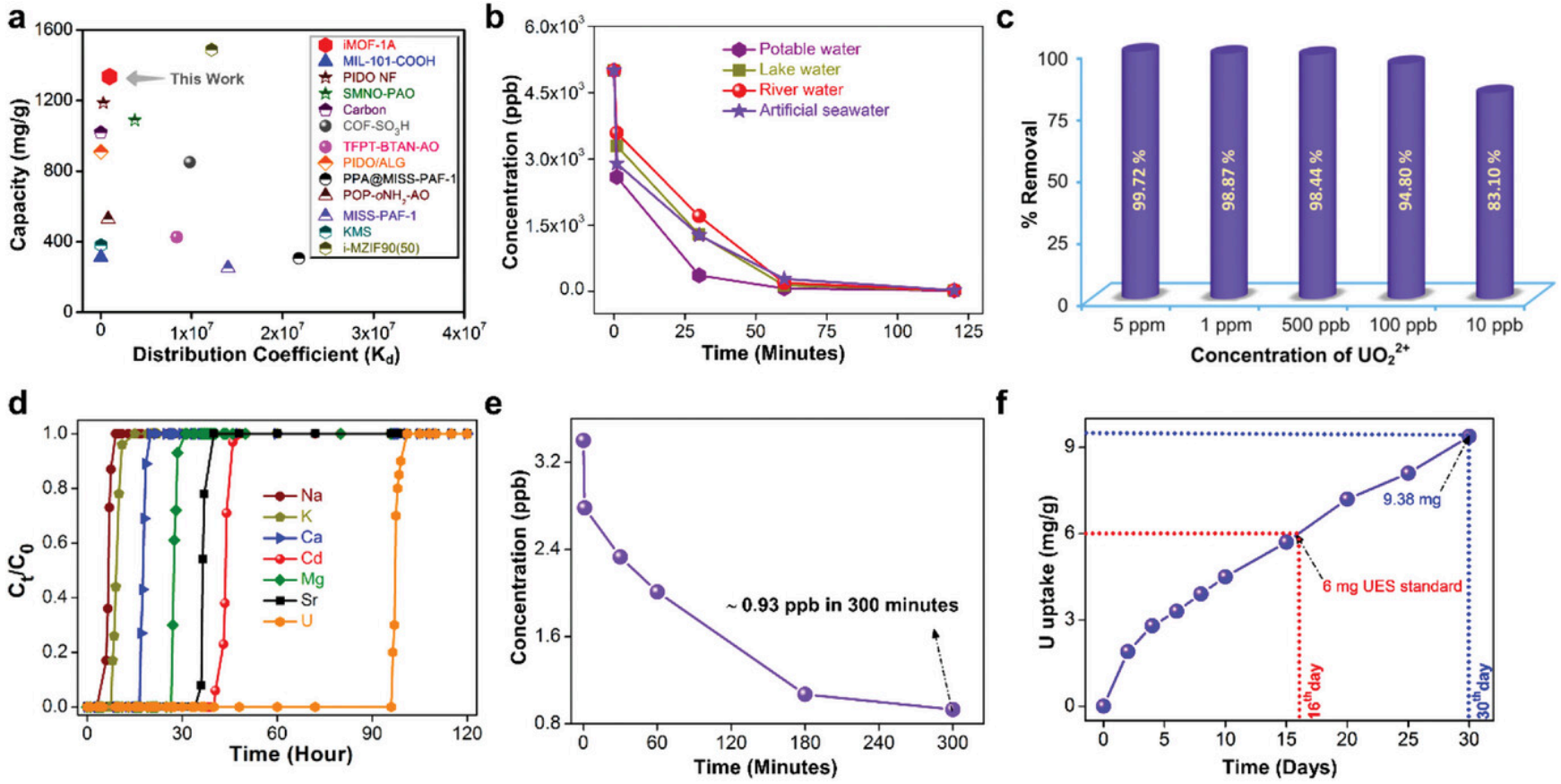


Figure 3. Uranium capture from spiked seawater as well as nonspiked natural seawater by iMOF-1A. a) Comparison of uranium adsorption capacities against distribution coefficient for various excellent adsorbents from water. b) The kinetics of uranium removal efficiency from various water samples spiked with 5000 ppb uranium at V/m = 2666.7 mL g-1. c) Removal % of U from various trace amounts of U spiked artificial seawater by iMOF-1A at V/m = 1000 mL g-1. d) Breakthrough experiments of a mixed solution composed of 3 ppm uranium and 3 ppm other competitive metal cations in water through iMOF-1A packed bed. e) Removal % of U from natural nonspiked seawater (i.e., natural seawater). f) The adsorption performance for uranyl ions during 30 days of close contact with natural seawater (uranyl ion concentration of ≈3.4 ppb) meeting UES standards.

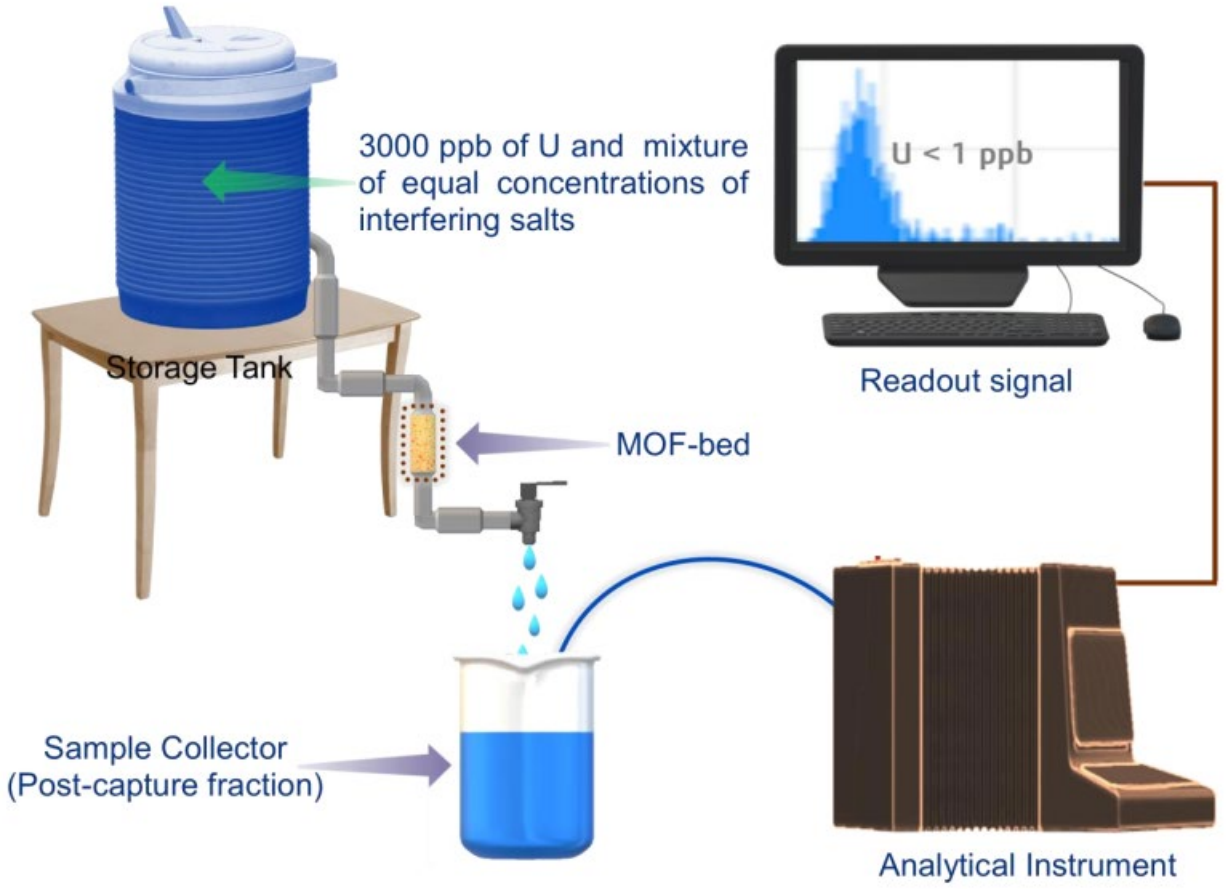


Fig. S30. Schematic representation of the breakthrough experiments of a mixed solution composed of 3 ppm uranium and 3 ppm other competitive metal cations containing water by iMOF-1A packed bed.

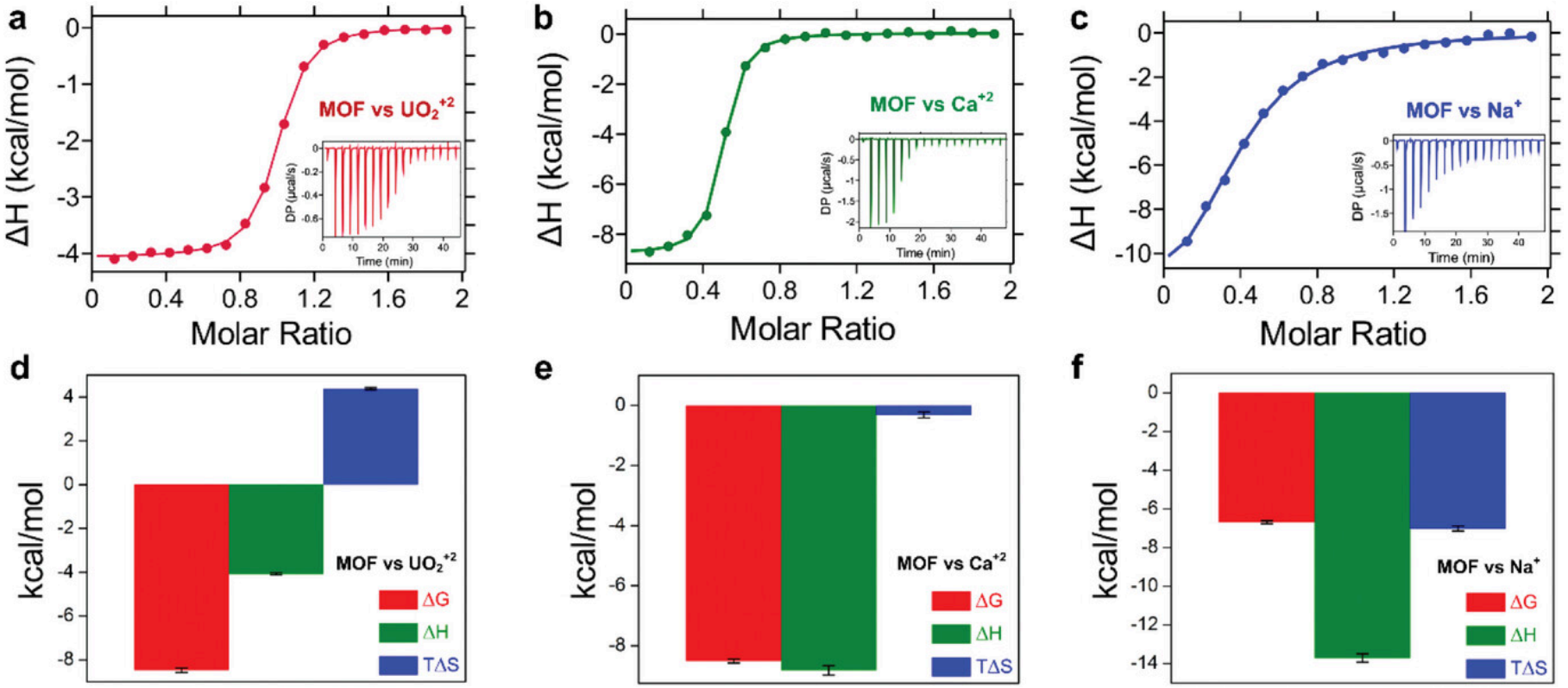
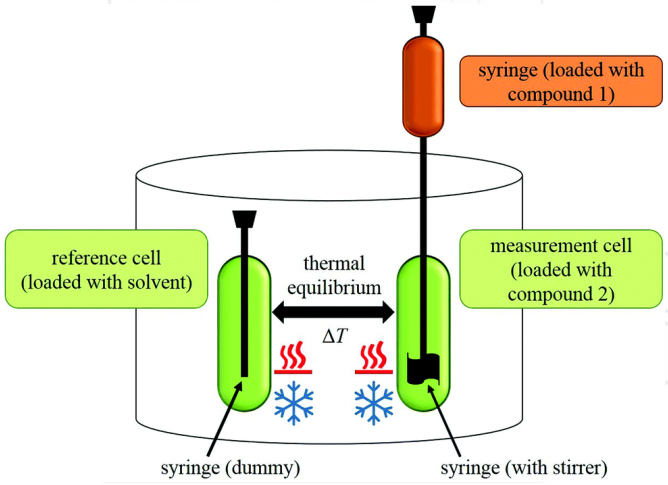


Figure 4. ITC thermograms resulting from injections of a) UO_2^{2+} salts, b) Ca^{2+} salts, and c) Na^{+} salts. The inset depicts the magnitude of the exothermic peaks. The magnitude of thermodynamic parameters of d) UO_2^{2+} salts, e) Ca^{2+} salts, and f) Na^{+} salts; demonstrating uranium chemisorption and entropy relevance in comparison to other cations.



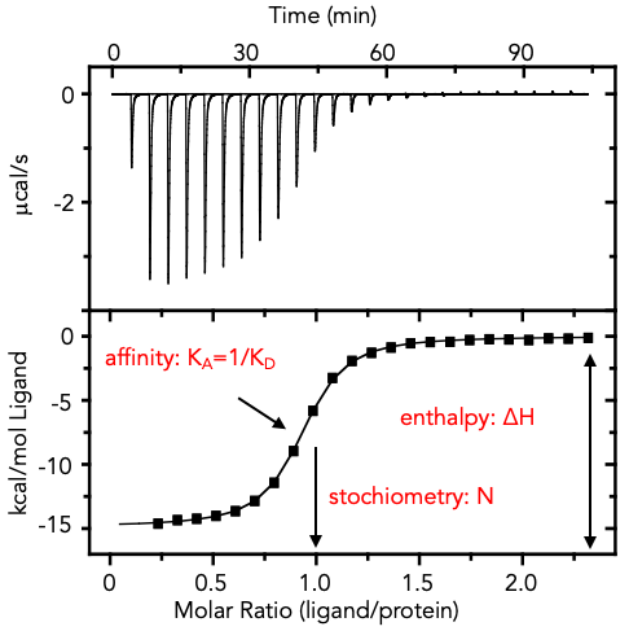


Figure 4. ITC thermograms resulting from injections of a) UO_2^{2+} salts, b ; the magnitude of the exothermic peaks. The magnitude of thermodynamic parameters of d) UO_2^{2+} salts, e) Ca^{2+} salts, and f) Na^+ salts; demonstrating uranium chemisorption and entropy relevance in comparison to other cations.

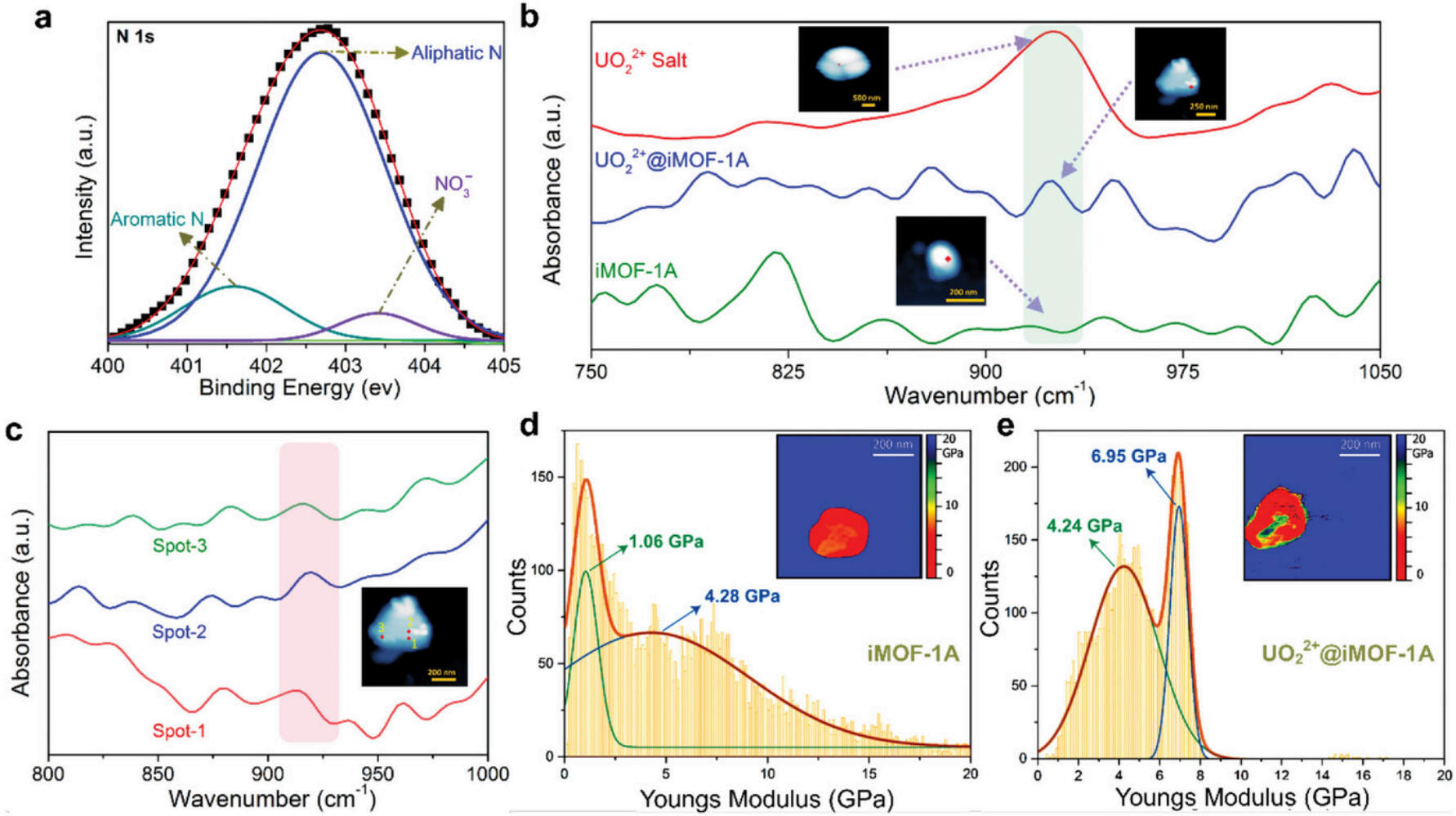


Figure 5. Uranium capture in iMOF-1A single crystals; a) magnified XPS spectra of N 1s for UO_2^{2+}@iMOF-1A; b) nano-FTIR spectra of iMOF-1A, UO_2^{2+}@iMOF-1A, and UO_2^{2+} salt, inset: nanoscopic spots corresponding to a probe size of ≈20 nm; c) local probing spots of UO_2^{2+}@iMOF-1A; d) TFM for iMOF-1A; e) TFM quantification plots for UO_2^{2+}@iMOF-1A, TFM reconstructions corresponding to different pressure points showing local stiffnesses of a single crystal.; insets: the Young's modulus map.

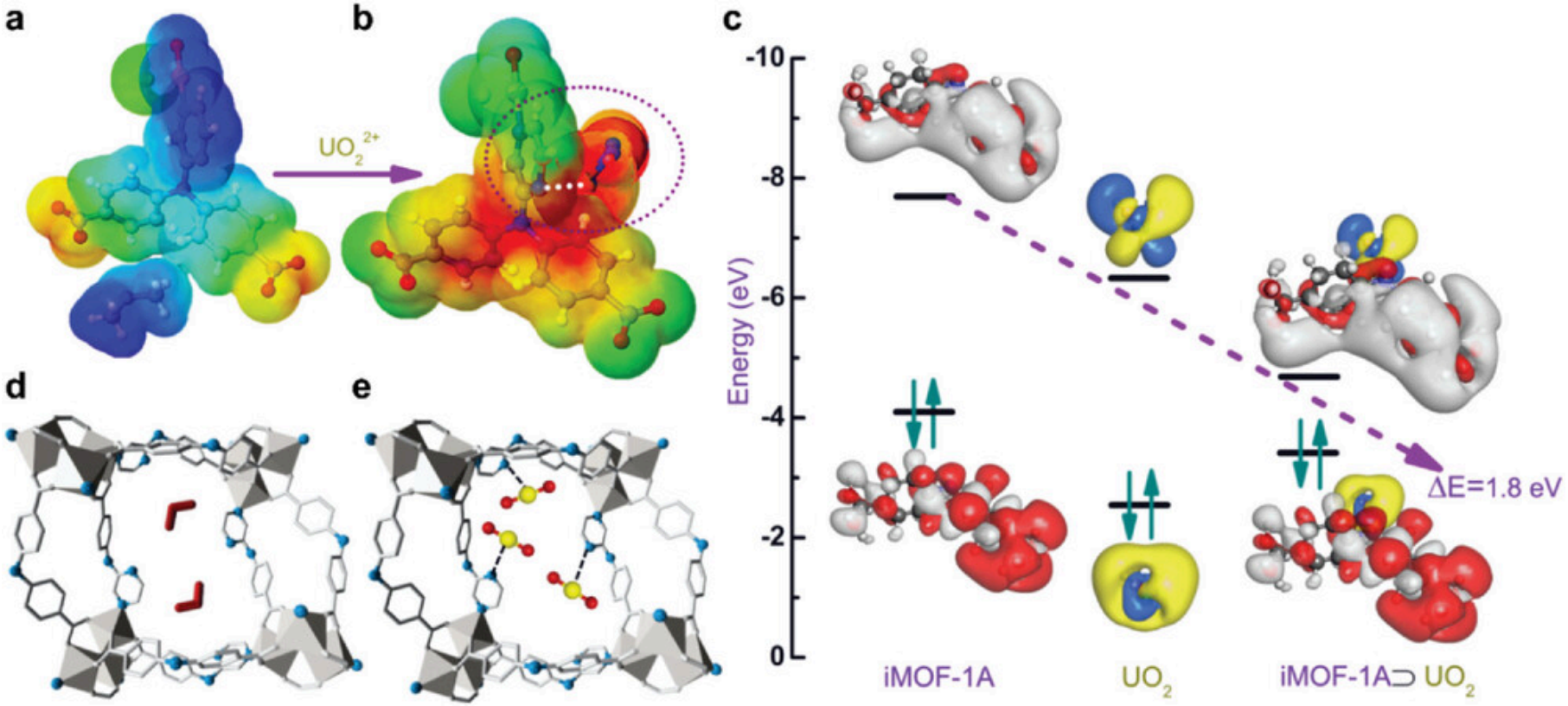


Figure 6. a) ESP of the asymmetric unit of iMOF-1A and b) ESP of iMOF-1A unit after UO2 interactions. c) Distribution of HOMO–LUMO in an iMOF-1A, UO_2^{2+} and after interaction between iMOF-1A and UO_2^{2+}. DFT-optimized guest-interaction sites in iMOF-1A including; d) exchangeable DMA cations and e) UO_2^{2+}, highlights the N···UO_2^{2+} interaction between the framework Pyz-N atoms and UO_2^{2+} molecules.

Conclusion

- Successfully demonstrated uranium extraction by a highly stable and novel anionic MOF (iMOF-1A) through both the ion exchange and interaction processes.
- The framework is capable of the efficient capturing of trace amounts of uranium in a wide range of water systems, including artificial seawater.
- The ionic adsorbent exhibited ultrafast capture kinetics with a remarkably high enrichment index (5754) and high sorption capacity derived dually from both; uranium spiked water and natural seawater, i.e., 1336.8 mg g^{-1} and 9.38 mg g^{-1}, respectively, which are among the highest values reported in the domain of MOFs.
- The nano-FTIR and TFM studies supported the notion of U capture that occurs throughout the MOF crystals, confirming that both ion exchange processes and supramolecular interactions are involved in the uranium sequestration studies.

Thank you