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# Three Mechanisms in One Material: Uranium Capture by a Polyoxometalate–Organic Framework through Combined Complexation, Chemical Reduction, and Photocatalytic Reduction

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Abstract: The design and synthesis of uranium sorbent materials with high uptake efficiency, capacity and selectivity, as well as excellent hydrolytic stability and radiation resistance remains a challenge. Herein, a polyoxometalate (POM)organic framework material (SCU-19) with a rare inclined polycatenation structure was designed, synthesized through a solvothermal method, and tested for uranium separation. Under dark conditions, SCU-19 can efficiently capture uranium through ligand complexation using its exposed oxo atoms and partial chemical reduction from  $U^{VI}$  to  $U^{IV}$  by the lowvalent Mo atoms in the POM. An additional U<sup>VI</sup> photocatalytic reduction mechanism can occur under visible light irradiation, leading to a higher uranium removal without saturation and faster sorption kinetics. SCU-19 is the only uranium sorbent material with three distinct sorption mechanisms, as further demonstrated by X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) analysis.

t is desirable and important to develop enrichment technologies of uranium for both sustainable development of nuclear power and environmental protection, as uranium is a key resource in the nuclear fuel cycle and also a global environmental contaminant with combined radio- and chemo toxicity.<sup>[1]</sup> A series of solid adsorbent materials has been developed for uranium capture, including inorganic minerals, mesoporous silica, carbon-based materials, and advanced porous materials.<sup>[2]</sup> However, these materials are still severely limited by lacking a combined performance of stability, removal kinetics, sorption capacity, selectivity, and reusability. Reducing the soluble and environmentally mobile U<sup>VI</sup> to the less soluble and relatively immobile U<sup>IV</sup> species for uranium immobilization is considered as a promising strategy for achieving these goals. In fact, U<sup>VI</sup> can be reduced to U<sup>IV</sup> by

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biologically, chemically, and photocatalytic processes.<sup>[3]</sup> Ironbased materials, such as  $Fe^{II}/Fe^{III}$  hydroxide, FeS, zerovalent iron, have been intensively studied for the removal of uranium from contaminated water.<sup>[4]</sup> The removal of U<sup>VI</sup> by iron-based materials is attributed to combined adsorption and reduction procedure. However,  $Fe^{II}$  or  $Fe^{0}$ , the active component in the material, is easily oxidized and deactivated in the air. On the other hand, poor reusability becomes the critical defect of such materials.

Polyoxometalates (POMs) are a class of inorganic metaloxygen clusters built from the connection of  $\{MO_x\}$  polyhedra (M = V, Nb, Mo, or W, etc., x = 5, 6).<sup>[5]</sup> Besides multiple applications in catalysis, medicine, and materials science,<sup>[6]</sup> POMs have been studied for separation and immobilization of radioactive wastes since early 1990s. Pope et al. developed a strategy of binding uranyl to vacant POMs, and then thermally decomposed to inert tungsten bronze materials, which may serve as a possible waste form of actinides.<sup>[7]</sup> In addition, POMs are good electron reservoirs that exhibit rich redox properties without structural degradation. Moisy et al. found heteropolyblue  $[P_2W_{17-n}^{VI}W_n^VO_{61}]^{(10+n)-}$  could reduce  $U^{VI}$  to  $U^{IV}$  and stabilize  $U^{IV}$  in the complex  $[U(P_2W_{17}O_{61})_2]^{16-1}$ in aqueous solution.<sup>[8]</sup> However, the use of bare POMs as adsorbent is limited because of their high solubility, easy aggregation nature, and small surface area. Therefore, introducing POMs into a suitable solid matrix should be viewed as an alternative strategy to overcome these drawbacks.

Recently, POMs have been intensively employed as building units with diverse coordination modes for the designing of POM-based metal-organic frameworks (MOFs), finding applications in many fields including but not limited to catalysts, photochromics, and magnetic materials.<sup>[9,10]</sup> Although POM-based MOFs exhibit foreseeable performance in sequestration of uranium by a combined advantage of both POMs and MOFs, the elimination of U<sup>VI</sup> from aqueous solutions by such materials remains unexplored. Among the numerous reported POM-based MOFs, the materials derived from mixed valent  $\epsilon$ -Keggin polyoxomolybdate  $\{\epsilon\text{-PMo}^V_8Mo^{VI}_4O_{40}Zn_4\}$  (Zn- $\epsilon\text{-Keggin}) units are$ taken into consideration because of their inherent reducing capability, multiple connected mode and excellent stability.<sup>[10]</sup> In this family, most of the materials were constructed from Zn-E-Keggin nodes with bi-/tri-dentate carboxylate linkers. Hence, there are always large unexchangeable charge-balancing cations such as tetrabutylammonium cation jammed in the framework, generating a major barrier for achieving high

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adsorption efficiency. To address this problem, in this work, a neutral POM-based MOF, [ $\epsilon$ -PMo<sup>V</sup><sub>8</sub>Mo<sup>VI</sup><sub>4</sub>O<sub>37</sub>(OH)<sub>3</sub>Zn<sub>4</sub>]-(TPB)<sub>3/2</sub>·6H<sub>2</sub>O (**SCU-19**, TPB = 1,2,4,5-tetra (4-pyridyl) benzene), was successfully designed and synthesized.

Single-crystal X-ray diffraction analysis reveals that SCU-19 crystallizes in the orthorhombic space group Pcca. The asymmetric unit consists of one  $\varepsilon$ -Keggin POM [ $\varepsilon$ - $PMo_{8}^{V}Mo_{4}^{VI}O_{37}(OH)_{3}Zn_{4}]$ , one and a half coordinated TPB ligands, and other guest molecules (Figure S1 in the Supporting Information; the CCDC number is given in the Supporting Information). The bond valence sum calculation and Xray photoelectron spectroscopy (XPS) analysis demonstrate the existence of eight  $Mo^V$  and four  $Mo^{VI}$  ions in the  $\epsilon$ -Keggin POM. The E-Keggin polyoxoanion is linked to four TPB ligands via coordination with four  $Zn^{II}$  ions, while each  $Zn^{II}$ ion is 4-coordinated by three O atoms from the POM and one N donor from the TPB ligands (Figure 1a). The TPB ligands can be categorized into two different types including TPB1 and TPB2. As expected, TPB1 linkers acting as fourconnecting nodes, are connected by four adjacent Zn-E-Keggin subunits through the four N atoms, forming a linear chain along the caxis (Figure S2a). Every TPB2 ligand employs two meta-oriented pyridine N atoms to connect these adjacent 1D chains by coordinating to other two Zn<sup>II</sup> ions, resulting in a 2D network (Figure 1b, Figure S2b). To simplify the structure of the 2D layer, the TPB1 can be regarded as a planar 4-connected node, and the Zn-E-Keggin



**Figure 1.** Crystal structure of **SCU-19**: a) connection mode between Znε-Keggin and TPB ligands, b) view of the 2D layer from [210], Keggin anions highlighted in polyhedral representation. C dark gray; N blue; O red; Zn turquoise; H atoms are omitted for clarity. c) 3D polycatenation framework. (d) and (e) arrays by inclined polycatenation of 2D simplified layers viewed from different directions.

unit can be viewed as a 3-connected node by omitting the unexpanded TPB2 ligands. Therefore, the 2D structure can be reduced to a rare  $(4.6^2)^2(4.6.4.6)$  topological network (Figure S2 c).

The void space in the four-membered and six-membered rings of the 2D layer is large enough for these 2D nets to be mutually entangled into a layer-packing structure. Each individual layer is catenated with an infinite number of other inclined layers leading to a rare inclined polycatenation  $2D+2D\rightarrow 3D$  framework (Figure 1c, Figure S3 and S4). There are two types of catenations in the polycatenation structure of SCU-19: four-membered rings interlock with four-membered rings and six-membered rings interlock with six-membered rings (Figure 1 d,e). In most inclined polycatenation systems, two or three identical sets of 2D parallel motifs interlock in different stacking directions, resulting in an increase of dimensionality  $(2D \rightarrow 3D)$  which is beneficial on improving the stability of the overall structure.<sup>[11]</sup> Interestingly, four sets of 2D motifs are mutually catenated through two different patterns in the polycatenation system of SCU-19. To our knowledge, POM-based MOFs exhibiting inclined polycatenation of 2D layer have never been reported. Based on such a polycatenation, the 3D architecture of SCU-19 exhibits a series of 1D channels with the window of approximately  $7 \times 7$  Å along the c axis. The large void volume (21.9%, calculated by PLATON) is occupied by solvent molecules.

The phase purity was confirmed by the powder X-ray diffraction (PXRD) patterns (Figure S5). Based on the N<sub>2</sub> adsorption isotherm at 77 K (Figure S10), the Brunauer-Emmett-Teller (BET) and Langmuir surface area of **SCU-19** is 32.6 and 100.8 m<sup>2</sup>g<sup>-1</sup>, respectively. As shown in Figure S6a, **SCU-19** shows thermal stability up to 380 °C. Based on the X-ray diffraction experiments under elevated temperatures (Figure S6b), the crystalline structure of **SCU-19** is maintained up to 300 °C. Importantly, **SCU-19** is stable in water solutions in the pH range from 2 to 12 (Figure S7). Besides, **SCU-19** also exhibits excellent radiation resistance, where no structural and crystal degradation was observed after large dose  $\beta$  irradiation or  $\gamma$  irradiation (Figure S8).

To evaluate the removal performance of **SCU-19** towards  $U^{VI}$ , batch experiments were systematically performed. The pH value of the solutions greatly affects the surface charge of the material, which directly leads to the variation of binding sites. Based on the initial pH dependent sorption study shown in Figure S13, detailed sorption experiments were carried out under pH 4.0. As shown in Figure 2a, the adsorption kinetics of **SCU-19** toward  $U^{VI}$  indicates a fast adsorption process. The sorption of uranium could remove 80% of  $U^{VI}$  at about 90 min. As shown in Table S3, the adsorption of uranyl ions onto **SCU-19** can be fitted by pseudo-second-order model, suggesting that the interaction between  $U^{VI}$  and **SCU-19** is controlled by chemical sorption.

The sorption isotherm was measured at 300 K (pH 4.0). As depicted in Figure 2 b, the isotherm curve can be fitted by Langmuir model ( $R^2 > 0.99$ ).<sup>[12]</sup> The maximum sorption capacity ( $q_{\rm max}$ ) value of U<sup>VI</sup> on **SCU-19** was determined to be 557.56 mg g<sup>-1</sup> (Table S4), higher than those of the majority of previously reported MOF materials (Table S5).<sup>[2]</sup> In

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**Figure 2.** a) Adsorption kinetics of U<sup>VI</sup> by **SCU-19**. Experimental conditions: material dosage = 0.5 gL<sup>-1</sup>, pH 4.0, initial U<sup>VI</sup>  $\approx$  10 mgL<sup>-1</sup>. b) Adsorption isotherms of U<sup>VI</sup> by **SCU-19**. c) Competitive sorption of coexistent ions by **SCU-19** with molar ratio of metal ions to U<sup>VI</sup> of about 10 times. Experimental conditions: material dosage = 0.5 gL<sup>-1</sup>, pH 4.0, initial U<sup>VI</sup>  $\approx$  10 mgL<sup>-1</sup>, and the concentration of the competing ions is around 100 mgL<sup>-1</sup>. d) Uptake of uranium by **SCU-19** under dark and visible light with initial uranium concentrations of approximately 400 ppm, material dosage = 0.5 gL<sup>-1</sup>, pH 4.0.

addition, the presented material is of high selectivity. When ten times excess of competing cations are present including monovalent (Na<sup>+</sup>, K<sup>+</sup>), divalent (Ca<sup>2+</sup>, Mg<sup>2+</sup> and Pb<sup>2+</sup>), approximately 10 ppm of U<sup>VI</sup> can be still completely removed (Figure 2 c). Even in the presence of high concentration Eu<sup>3+</sup>, the removal percentage toward UO<sub>2</sub><sup>2+</sup> is still as high as 90.02 %.

Photocatalytic reduction was recently demonstrated to be an efficient and green route for UVI uptake.<sup>[13]</sup> The estimated band gap of SCU-19 based on Kubelka-Munk Function is 2.71 eV (Figure S19), indicating that SCU-19 can be photo-excited by visible light.<sup>[14]</sup> According to the Mott-Schottky plot (Figure S20), the positive slope suggests that SCU-19 is a n-type semiconductor with a flat-band potential of -0.58 V. The conduction band (CB) and valence band (VB) energy levels were calculated to be -0.68 V and 2.03 V (vs. saturated calomel electrode (SCE)), indicating that photo-reduction of  $U^{VI}$  to  $U^{IV}$  is thermodynamically feasible.<sup>[13]</sup> To evaluate the photo assisted uranium removal performance of SCU-19, the batch experiments were studied under visible light irradiation with methanol as the sacrificial agent. Obvious differences on the sorption capacity and kinetics were observed between the experiments performed under dark and light irradiation conditions, respectively (Figure 2d, and Figure S14, S15). Specifically, the mass of removed uranium under light irradiation is significantly larger than that under dark condition, resulting in a removal capacity of 728.34 mgg<sup>-1</sup> and an extraction percentage of 91.04%. Note the first number is not a saturated value from the view of a catalytic uptake process, which can be further elevated when the initial uranium concentration is higher or increasing the reaction time. Additionally, uranium-loaded **SCU-19** samples could be regenerated by elution with 0.01M HNO<sub>3</sub> aqueous solution with a uranium desorption rate of 91.57% (Figures S16,S17).

The notably high removal efficiency and capacity of SCU-19 toward uranium could be achieved by three possible mechanisms. The first is the adsorption process, which greatly benefits from the unique hydrophilic channels, and the ligand complexation using the exposed terminal oxygen atoms of POMs in the structure. The second is the chemical reduction process, in which the Mo<sup>V</sup> of the POM units in SCU-19 may reduce parts of the adsorbed  $U^{VI}$  to  $U^{IV}$ . The third is the photocatalytic reduction process, in which photo-reduction of uranium could occur due to the suitable photoelectric characteristics of SCU-19. To better understand the interaction mechanism between SCU-19 and UVI, elemental mapping, XPS and X-ray absorption near edge structure (XANES) analysis were further performed. Elemental distribution mapping of the U<sup>VI</sup>-loaded samples shows the presence and uniform distribution of uranium on the surface of SCU-19 (Figure S21). In the XPS curve fitting results, the peaks for  $U 4f_{7/2}$  (380.99 and 382.20 eV) in the high-resolution U 4f spectrum suggest the coexistence of U<sup>VI</sup> and U<sup>IV</sup> after the sorption (Figure 3a).<sup>[15]</sup>

The relative ratio of  $U^{IV}$  was calculated to be 11.7% in samples under dark while the relative ratio of  $U^{IV}$  increases to 37.5% for the light-irradiated sample (Figure 3a). The



*Figure 3.* a) U 4f XPS spectra of **SCU-19** samples loaded with uranium under dark and light conditions. b) Mo 3d XPS spectra of **SCU-19** and uranium-loaded samples under dark and light conditions. c) U L<sub>3</sub>-edge XANES spectra of the U<sup>IV</sup> and U<sup>VI</sup> references and the samples loaded with uranium under dark and light conditions. d) Mo K-edge XANES spectra for H<sub>3</sub>PMo<sub>12</sub> (Mo(VI)), **SCU-19**, and of the uranium-loaded sample under dark and light conditions. The initial uranium concentration is around 400 ppm, material dosage = 0.5 gL<sup>-1</sup>, pH 4.0.

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relative ratio of Mo<sup>V</sup> decreases from 66.7% to 43.2% under dark, suggesting that Mo<sup>V</sup> is involved in the chemical reduction of U<sup>VI</sup> to U<sup>IV</sup>. Besides, the relative ratio of Mo<sup>V</sup> decreases from 66.7% to 51.9% under light, indicating that the chemical reduction of U<sup>VI</sup> to U<sup>IV</sup> also occurs under light in addition to the photo-reduction. As shown in Figure 3 c, the absorption edge of the U<sup>VI</sup>-loaded samples is located between those of U<sup>VI</sup> and U<sup>IV</sup> standards in the U L<sub>3</sub>-edge XANES spectrum, further illustrating that parts of U<sup>VI</sup> are reduced into U<sup>IV</sup> under both dark and light irradiation conditions.<sup>[16]</sup> The Mo K-edge XANES spectra (Figure 3d) were also recorded to determine the valence change of molybdenum,<sup>[17]</sup> in agreement with the result of XPS analysis.

The PXRD patterns of uranium-loaded **SCU-19** samples suggest that the material could maintain integrity during the U<sup>VI</sup> removal process (Figure S9). Negligible amounts of Mo are released into the solution detected by inductively coupled plasma-atomic emission spectrometry (ICP-AES) during the sorption process (Table S6), further confirming the stability of **SCU-19**. As illustrated in Figure 4, U<sup>VI</sup> ions are first adsorbed



*Figure 4.* Schematic representation of the proposed mechanism for the removal of  $U^{VI}$  by **SCU-19**.

into the frameworks through ligand complexation, followed by chemical reduction of the adsorbed  $U^{VI}$  to insoluble  $U^{IV}$  by the Mo<sup>V</sup> of the POM units. This process is beneficial on regenerating the active site for further uptake of additional  $U^{VI}$ . Under the light irradiation, the material can be photoexcited, forming pair of the CB and the VB. During this process, the electrons generated on the frameworks are transferred to the oxidized POMs forming the reduced POMs for further reduction of additional  $U^{VI}$  to  $U^{IV}$ .

The foregoing results demonstrate the first example of uranium capture based on a POM-based MOF material. **SCU-19** is featured with a unique  $2D + 2D \rightarrow 3D$  polycatenation structure, resulting in excellent stability toward hydrolysis and ionization irradiation. The combination of advantages including the rich redox activity of POMs and the strong pre-enrichment of MOFs significantly increases the uranium removal efficiency, giving rise to the unique combination of three uranyl uptake mechanisms of complexation, chemical

reduction, and photocatalytic reduction. We believe that more POM-based MOF materials with advanced removal performance toward uranium and other radionuclides (e.g.  $^{99}\text{TcO}_4^{-})^{[18]}$  could rapidly emerge in the near future.

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#### Conflict of interest

The authors declare no conflict of interest.

**Keywords:** metal–organic frameworks · photocatalysis · polyoxometalates · reduction · uranium

- a) M. Gavrilescu, L. V. Pavel, I. Cretescu, *J. Hazard. Mater.* 2009, *163*, 475-510; b) X. Wang, X. Dai, C. Shi, J. Wan, M. A. Silver, L. Zhang, L. Chen, X. Yi, B. Chen, D. Zhang, K. Yang, J. Diwu, J. Wang, Y. Xu, R. Zhou, Z. Chai, S. Wang, *Nat. Commun.* 2019, *10*, 2570.
- [2] a) D. Wang, J. Song, J. Wen, Y. Yuan, Z. Liu, S. Lin, H. Wang, H. Wang, S. Zhao, X. Zhao, M. Fang, M. Lei, B. Li, N. Wang, X. Wang, H. Wu, Adv. Energy Mater. 2018, 8, 1802607; b) Q. Sun, B. Aguila, L. D. Earl, C. W. Abney, L. Wojtas, P. K. Thallapally, S. Ma, Adv. Mater. 2018, 30, 1705479; c) Q. Sun, B. Aguila, J. Perman, A. S. Ivanov, V. S. Bryantsev, L. D. Earl, C. W. Abney, L. Wojtas, S. Ma, Nat. Commun. 2018, 9, 1644; d) X. Wang, L. Chen, L. Wang, Q. Fan, D. Pan, J. Li, F. Chi, Y. Xie, S. Yu, C. Xiao, F. Luo, J. Wang, X. Wang, C. Chen, W. Wu, W. Shi, S. Wang, X. Wang, Sci. China Chem. 2019, 62, 933-967; e) Y. Yuan, Y. Yang, X. Ma, Q. Meng, L. Wang, S. Zhao, G. Zhu, Adv. Mater. 2018, 30, 1706507; f) Y. Yuan, Q. Meng, M. Faheem, Y. Yang, Z. Li, Z. Wang, D. Deng, F. Sun, H. He, Y. Huang, H. Sha, G. Zhu, ACS Cent. Sci. 2019, 5, 1432-1439; g) J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, Chem. Soc. Rev. 2018, 47, 2322-2356; h) T. Zheng, Z. Yang, Z. Liu, D. Gui, X. Dai, S. Liu, L. Zhang, Y. Gao, L. Chen, D. Sheng, Y. Wang, J. Diwu, J. Wang, R. Zhou, Z. Chai, T. E. Albrecht-Schmitt, S. Wang, Nat. Commun. 2017, 8, 15369.
- [3] a) J. J. Kiernicki, M. Zeller, S. C. Bart, Angew. Chem. Int. Ed. 2017, 56, 1097–1100; Angew. Chem. 2017, 129, 1117–1120;
  b) S. P. Hyun, J. A. Davis, K. Sun, K. F. Hayes, Environ. Sci. Technol. 2012, 46, 3369–3376; c) X. Rui, M. J. Kwon, E. J. O'Loughlin, S. Dunham-Cheatham, J. B. Fein, B. Bunker, K. M. Kemner, M. I. Boyanov, Environ. Sci. Technol. 2013, 47, 5668–5678; d) X. Liu, P. Du, W. Pan, C. Dang, T. Qian, H. Liu, W. Liu, D. Zhao, Appl. Catal. B 2018, 231, 11–22.

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\* These are not the final page numbers!

- [4] a) S. Yan, B. Hua, Z. Bao, J. Yang, C. Liu, B. Deng, *Environ. Sci. Technol.* 2010, 44, 7783–7789; b) Z. J. Li, Z. W. Huang, W. L. Guo, L. Wang, L. R. Zheng, Z. F. Chai, W. Q. Shi, *Environ. Sci. Technol.* 2017, 51, 5666–5674.
- [5] a) M. T Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) Y. P. Jeannin, *Chem. Rev.* **1998**, 98, 51–76.
- [6] a) S. S. Wang, G. Y. Yang, Chem. Rev. 2015, 115, 4893-4962;
  b) K. Suzuki, F. Tang, Y. Kikukawa, K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 2014, 53, 5356-5360; Angew. Chem.
  2014, 126, 5460-5464; c) X.-J. Kong, Z. Lin, Z.-M. Zhang, T. Zhang, W. Lin, Angew. Chem. Int. Ed. 2016, 55, 6411-6416; Angew. Chem. 2016, 128, 6521-6526.
- [7] a) K.-C. Kim, M. T. Pope, J. Am. Chem. Soc. 1999, 121, 8512– 8517; b) K. Wassermann, M. T. Pope, M. Salmen, J. N. Dann, H.-J. Lunk, J. Solid State Chem. 2000, 149, 378–383.
- [8] a) L. Bion, P. Moisy, C. Madie, *Radiochim. Acta* 1995, 69, 251 257; b) L. Bion, P. Moisy, F. Vaufrey, S. Méot-Reymond, C. Madic, *Radiochim. Acta* 1997, 78, 73–82.
- [9] a) D.-Y. Du, J.-S. Qin, S.-L. Li, Z.-M. Su, Y.-Q. Lan, *Chem. Soc. Rev.* 2014, *43*, 4615–4632; b) C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren, Z.-M. Su, *J. Am. Chem. Soc.* 2009, *131*, 1883–1888; c) X. Kuang, X. Wu, R. Yu, J. P. Donahue, J. Huang, C.-Z. Lu, *Nat. Chem.* 2010, *2*, 461–465.
- [10] a) L. M. Rodriguez-Albelo, A. R. Ruiz-Salvador, A. Sampieri, D. W. Lewis, A. Gomez, B. Nohra, P. Mialane, J. Marrot, F. Secheresse, C. Mellot-Draznieks, R. Ngo Biboum, B. Keita, L. Nadjo, A. Dolbecq, J. Am. Chem. Soc. 2009, 131, 16078–16087; b) B. Nohra, H. El Moll, L. M. Rodriguez Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. Ngo Biboum, J. Lemaire, B. Keita, L. Nadjo, A. Dolbecq, J. Am. Chem. Soc. 2011, 133, 13363–13374; c) J. S. Qin, D. Y. Du, W. Guan, X. J.

Bo, Y. F. Li, L. P. Guo, Z. M. Su, Y. Y. Wang, Y. Q. Lan, H. C. Zhou, J. Am. Chem. Soc. 2015, 137, 7169-7177.

- [11] L. Carlucci, G. Ciani, D. M. Proserpio, T. G. Mitina, V. A. Blatov, *Chem. Rev.* 2014, 114, 7557–7580.
- [12] a) I. Langmuir, J. Am. Chem. Soc. 1918, 40, 1361–1403; b) H.
   Freundlich, Z. Phys. Chem. 1906, 57, 385–470.
- [13] a) E. Selli, V. Eliet, M. R. Spini, G. Bidoglio, *Environ. Sci. Technol.* 2000, *34*, 3742–3748; b) H. Li, F. Zhai, D. Gui, X. Wang, C. Wu, D. Zhang, X. Dai, H. Deng, X. Su, J. Diwu, Z. Lin, Z. Chai, S. Wang, *Appl. Catal. B* 2019, *254*, 47–54.
- [14] a) T. Zhang, W. Lin, Chem. Soc. Rev. 2014, 43, 5982-5993; b) H.
   Liu, C. Xu, D. Li, H.-L. Jiang, Angew. Chem. Int. Ed. 2018, 57, 5379-5383; Angew. Chem. 2018, 130, 5477-5481.
- [15] E. S. Ilton, P. S. Bagus, Surf. Interface Anal. 2011, 43, 1549-1560.
- [16] K. Sanyal, A. Khooha, G. Das, M. K. Tiwari, N. L. Misra, Anal. Chem. 2017, 89, 871–876.
- [17] H. Wang, S. Hamanaka, Y. Nishimoto, S. Irle, T. Yokoyama, H. Yoshikawa, K. Awaga, J. Am. Chem. Soc. 2012, 134, 4918–4924.
- [18] a) D. Sheng, L. Zhu, X. Dai, C. Xu, P. Li, C. I. Pearce, C. Xiao, J. Chen, R. Zhou, T. Duan, O. K. Farha, Z. Chai, S. Wang, *Angew. Chem. Int. Ed.* 2019, *58*, 4968–4972; *Angew. Chem.* 2019, *131*, 5022–5026; b) L. Zhu, D. Sheng, C. Xu, X. Dai, M. A. Silver, J. Li, P. Li, Y. Wang, Y. Wang, C. Xiao, J. Chen, R. Zhou, C. Zhang, O. K. Farha, Z. Chai, T. E. Albrecht-Schmitt, S. Wang, *J. Am. Chem. Soc.* 2017, *139*, 14873–14876.

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## **Communications**



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**P** Uranium Capture

H. Zhang, W. Liu, A. Li, D. Zhang, X. Li, F. Zhai, L. Chen, L. Chen, Y. Wang, S. Wang\* \_\_\_\_\_

Three Mechanisms in One Material: Uranium Capture by a Polyoxometalate– Organic Framework through Combined Complexation, Chemical Reduction, and Photocatalytic Reduction



**Stuck on U**: Uranium capture by a polyoxometalate–organic framework is possible through three different mechanism, these are complexation, chemical reduction, and photocatalytic reduction. The material features a unique  $2D + 2D \rightarrow 3D$ polycatenation structure, resulting in excellent stability toward hydrolysis and ionization irradiation.

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