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## Robust covalent organic frameworks with tailormade chelating sites for synergistic capture of U(vı) ions from highly acidic radioactive waste†

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A synergistic strategy for enhancing  $U(v_1)$  capture under highly acidic conditions (2 M HNO<sub>3</sub>) by radiation resistant phosphonatefunctionalized two-dimensional covalent organic frameworks with tailor-made binding sites bearing a strong affinity was described. The combination of the radiation resistant characteristic with a strong acid-resistant property endows COFs with practical capabilities for actinide capture from real radioactive liquid waste.

The environmental issues arising from the development of nuclear energy have attracted wide attention due to the high radioactivity of nuclear waste.<sup>1</sup> Uranium (U), as the main fuel for nuclear reactors and the predominant radiotoxic element in the spent fuel, possesses a long-term threat to the environment.<sup>2</sup> Conventional separation processes, based on liquid-liquid extraction, possess common disadvantages in several aspects such as large amounts of toxic and/or flammable organic solvent consumption, formation of emulsions, and production of large volumes of radioactive organic wastes. For this reason, designing of tailor-made adsorption materials as an alternative technique has been at the frontier of this field to overcome these severe shortcomings while holding the advantages in U separation from high level liquid waste (HLLW).

Varieties of solid adsorption materials, including functionalized MOFs,<sup>3</sup> mesoporous carbon,<sup>4</sup> graphene oxide (GO),<sup>1,5</sup> and porous aromatic frameworks (PAFs),<sup>6</sup> have been reported to show a high affinity toward uranium. However, these sorbents exhibit very poor uptakes in highly acidic medium (pH < 1). For instance, Wang *et al.*<sup>5</sup> reported GOs for the extraction of

U(vi) from aqueous solution. With increasing pH from 2 to 6, the adsorption ability toward U(vi) improved from 60 to 100 mg g<sup>-1</sup>, whereas the adsorption value fell to only 30 mg g<sup>-1</sup> at pH 1.0. Ion-imprinted PAF<sup>6</sup> could achieve nearly complete removal of U(vi) at pH 6 while reducing the uranyl ion concentration from the ppm to the ppb level, but because of protonation, the uptake decreases considerably at lower pHs. However, the one thing we should always bear in mind is that most of the HLLW is a highly acidic atmosphere throughout. Thus, seeking stable materials with high adsorption capacities, outstanding selectivity, excellent repeatability, and radiation stability toward actinides in a highly acidic environment remains a huge challenge.

Covalent organic frameworks (COFs) are an emerging class of crystalline porous polymers with periodic structures based on the precise integration of organic building blocks.<sup>7</sup> Because of their regular pore structure, high surface area and tunable chemistry, the COF materials are explored in various fields such as energy storage,<sup>8</sup> optoelectronics,<sup>9</sup> catalysis,<sup>10</sup> and a number of others.<sup>11</sup> Compared with MOFs, the important characteristics that COFs possess are because they are ingeniously constructed using organic building blocks containing light-weight elements via strong covalent bonds, allowing them to be excellent candidates for enhancing the sorption capacities when facing harsher conditions. Over the past decade, a large number of functionalized COFs with structural diversity of skeletons and pore walls have been synthesized. However, few COFs have been obtained for addressing radioactive waste issues. Recently, several groups<sup>12-19</sup> have made outstanding contributions to the removal of UO<sub>2</sub><sup>2+</sup> or TcO<sub>4</sub><sup>-</sup> by COFs, respectively. In 2019, our group<sup>20</sup> had designed functionalized COFs with phosphonate as the side arms located in the channel for adsorption of  $UO_2^{2+}$  and  $Pu^{4+}$  under strong acid conditions. Even so, irradiation resistant COFs with strong acid resistance for the removal of actinide ions still remains a largely unexplored virgin territory.

As our interest in this field increases,<sup>20,21</sup> in response to the demanding requirements for U(vi) removal from highly acidic



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Scheme 1 Synthesis of COF-JLU4, COF-IHEP10 and COF-IHEP11 by condensation reaction.

solutions, we developed a three-component reaction system consisting of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (TBTA) with a mixture of tetraethyl (((2,5-di(hydrazinecarbonyl)-1,4-phenylene)bis(oxy))-bis(ethane-2,1-diyl))bis(phosphonate) (TBBP) and 2,5-dimethoxyterephthalohydrazide (DMPA) at various molar ratios  $(X = [TBBP]/([TBBP] + [DMPA]) \times 100 =$ 0, 50, and 100) for the synthesis of three COFs with different phosphonate contents on their edges (Scheme 1). Herein, the non-phosphonate substituted COF, named COF-JLU4, was prepared by TBTA and DMPA using mesitylene/dioxane as the solvent in the presence of 6 M acetic acid with subsequent heating at 120 °C for 7 days according to the literature report.<sup>22</sup> COF-IHPE10 (partially anchoring phosphonates) and COF-IHEP11 (fully chelating phosphonates) were constructed by a similar operating procedure. The Fourier transform infrared (FT-IR) spectrum of COFs exhibited a peak at ~1628 cm<sup>-1</sup> corresponding to a lower energy characteristic of the carbonyl stretching vibration in the  $\beta$ -keto-enamine bond, which is attributed to the 2D  $\pi$ -conjugated sheet and intramolecular hydrogen bonding. The characteristic stretching vibration peaks for C=C (1591 cm<sup>-1</sup>) and N-H (3293 cm<sup>-1</sup>) confirmed the occurrence of a condensation reaction (Fig. S1-S3, ESI<sup>+</sup>). The high throughput of the phosphonate transformation was determined by the gradual disappearance of the peaks assigned to the methyl groups at around 57 ppm in the solidstate <sup>13</sup>C cross-polarization magic-angle spinning (CP/MAS) NMR spectrum of COF-IHEP10 and COF-IHEP11 (Fig. S4-S7, ESI<sup>†</sup>). Meanwhile, the concomitant emergence of strong peaks at 64.4, 27.2, and 17.1 ppm was ascribed to the phosphonate species. These results confirm the successful construction of COF-IHEP10 and COF-IHEP11.



**Fig. 1** Experimental (red), simulated (blue) and difference plot (black) PXRD patterns of COF-IHEP10 (a) and COF-IHEP11 (b). Simulated PXRD patterns with an eclipsed structure (AA stacking mode) for COF-IHEP10 (c) and COF-IHEP11 (d). (C, gray; N, blue; P, purple; O, red. H atoms are omitted for clarity).

The crystalline structures of COF-IHEP10 and COF-IHEP11 were determined by powder X-ray diffraction (PXRD) analysis with Cu K $\alpha$  radiation in conjunction with the Pawley refinement and computational approaches. COF-IHEP10 exhibits a strong PXRD peak at 3.60°, a weaker peak at 6.81°, and low-intensity broad features around 15.0° and 26.2°, corres-

ponding to the (100), (220), (600) and (001) facets, respectively (Fig. 1a). To elucidate the atomic information of this framework, Pawley refinements of the PXRD patterns were performed in combination with the initially built unit cell from molecular mechanics calculations. The details are provided in Fig. S35 and 36.<sup>†</sup> The simulated structure of COF-IHEP10 exhibits a PXRD pattern fitting well with the experimentally measured one (Fig. 1c). A hexagonal primitive unit cell (P1) with the lattice parameters of a = b = 50.03 Å, c = 3.60 Å,  $\alpha = \beta =$ 90°, and  $\gamma = 120^\circ$  was deduced with residuals of  $R_{\rm p} = 1.35\%$ and  $R_{wp}$  = 1.86%. COF-IHEP11 has a strong PXRD peak at 3.53°, some weaker peaks at 5.83°, 6.93°, 9.24°, and 12.10° and low-intensity broad features around 26.6°, corresponding to the (100), (200), (210), (220) and (001) facets, respectively (Fig. 1b). The simulated PXRD pattern fits relatively well with the experimental one compared to COF-IHEP10. The hexagonal primitive unit cell (P6) with the lattice parameters of a = b= 28.47 Å, c = 3.60 Å,  $\alpha = \beta = 90^{\circ}$ , and  $\gamma = 120^{\circ}$  was obtained with residuals of  $R_p$  = 4.42% and  $R_{wp}$  = 3.44%. The complete structures are given in Fig. S35 and S36† for clarity. The Brunauer-Emmett-Teller (BET) surface areas of COF-IHEP10 and COF-IHEP11 were calculated as 386 and 167 m<sup>2</sup> g<sup>-1</sup>, respectively (Fig. 2a and b). The nonlocal density functional theory (NLDFT) gave rise to a pore size distribution with an average pore width of ~2.0 Å and 1.3 Å for COF-IHEP10 and COF-IHEP11, respectively (Fig. S8-S10, ESI<sup>†</sup>), which agrees well with the calculated values based on the eclipsed structure (Fig. 1d; Table S1<sup>†</sup>).

To confirm the chemical stability, we dispersed COF-IHEP11 in aqueous solution with different acidities adjusted by HNO3 for 24 h. As shown in Fig. 3a, the PXRD patterns of the immersed materials at the pH range 1-14 and 1 M HNO<sub>3</sub> are almost the same as that of the pristine COF sample, which indicates that COF-IHEP11 could hold its original crystal structure over this acidity range. At 3 M HNO<sub>3</sub>, the proton starts to enter into the interlayer, and the layered structure became swollen. Despite this, the COF-IHEP11 still retained its original crystallinity partly. In addition, a key consideration is that, facing high intensity irradiation of the highly acidic radioactive waste, the COFs should be robust to high radiation doses. To further evaluate the irradiation stability of the COFs, dry COF-IHEP11 samples as well as the samples soaked in water were exposed to a y-irradiation environment using a 60Co source, followed by PXRD and FT-IR



Fig. 2 (a)  $N_2$  adsorption and desorption isotherms of COF-IHEP10 at 77 K. (b)  $N_2$  adsorption and desorption isotherms of COF-IHEP11 at 77 K.



Fig. 3 (a) Stability of COF-IHEP11 after being immersed in an aqueous solution with different acidic environments (pH 1 to 14 and 1 to 3 M HNO<sub>3</sub>) for 24 h as demonstrated by PXRD patterns. (b) Radiation stability of COF-IHEP11 after different doses of gamma irradiation.

characterizations. The PXRD patterns confirmed that COF-IHEP11 retained its original crystallinity (Fig. 3b). Undoubtedly, the excellent irradiation stability of COFs has two key factors that must be considered to overcome the challenges of the intense irradiation environment: the first is the intra-layer infinitely extended  $\pi$ -conjugated system and the second is the adjacent interlayer  $\pi$ - $\pi$  stacking. This assembling architecture could effectively transfer and dissipate the radiation energy between the intra-layer and interlayer of COFs, thus avoiding the breaking of the covalent bonds of COFs. Meanwhile, FT-IR results also suggested an unchanged structure, which further confirms the excellent radiation stability (Fig. S17, ESI<sup>†</sup>). COF-JLU4 and COF-IHEP10 show similar chemical stability and radiation stability to COF-IHEP11 since no discriminable changes of their conjugated structure were observed following irradiation and strong acid treatment (Fig. S11-16, ESI<sup>†</sup>). Thermogravimetric analysis indicates that our COFs are thermally stable up to 250 °C (Fig. S18-20, ESI<sup>+</sup>). In all, these COFs maintain reliable chemical stability and excellent radiation resistance, which are the prerequisite for the real-time application potential as the trap material for actinide capture from highly acidic radioactive waste.

After confirming the conjugated structure, porosity with a high density of phosphonate groups as the side arm of COF-IHEP10 and COF-IHEP11, U(vI) capture by these COFs was performed in detail to evaluate their capture ability toward U(vi) and their potential for HLLW treatment and environmental remediation. The U(vi) adsorption kinetics of COFs was studied with an initial concentration of 100 ppm at pH 1.0. As shown in Fig. 4a, the concentration of U(v1) in the aqueous solution decreases rapidly as the contact proceeded. In the initial 20 min, the uptake of U(vi) is 75 mg  $g^{-1}$  for COF-IHEP10 and 80 mg  $g^{-1}$  for COF-IHEP11. After about 3 h, the adsorption process reaches an equilibrium with an adsorption capacity of ~110 mg  $g^{-1}$  for the two COFs. Although the COF-JLU4 shows a similar kinetic process, the adsorption capacity is less than 70 mg  $g^{-1}$  because of the lack of a chelating site in the skeleton of the COFs. In order to clarify the adsorption process of U(vi), pseudo-first-order and pseudo-second-order models were applied to analyse the kinetic data (Table S2, ESI<sup>†</sup>). It is found that the pseudo-second-order model fits well the experimental kinetic data with a much better correlation coefficient, and the



Fig. 4 (a)  $U(v_1)$  adsorption kinetics of COFs at pH 1.0. (b)  $U(v_1)$  adsorption kinetics of COFs (pH 1.0, contact time = 4 h). (c)  $U(v_1)$  adsorption onto COFs at a wide range of acidity. (d) Recycle use of COFs for  $U(v_1)$  uptake at pH 1.0.

result obviously indicates that the  $U(v_1)$  adsorption by the COFs is dominated by chemical adsorption. These results show that COFs could capture  $U(v_1)$  from lower acidic solution rapidly, and the relatively fast kinetics can meet the requirement of spent fuel reprocessing.

To further understand the mode of U(vi) adsorption on the COFs, Langmuir and Freundlich models were selected to match the experimental data. The results indicated that the adsorption isotherm fitted well to the Langmuir model compared to the Freundlich model because of a better correlation coefficient for phosphonate-decorated COFs (Table S3, ESI<sup>+</sup>). The saturated adsorption capacities for U(v1) are 102, 127, and 147 mg g<sup>-1</sup> for COF-JLU4, COF-IHEP10 and COF-IHEP11, respectively (Fig. 4b). To further investigate the influence of system acidity on the U(vi) adsorption by the COFs, pH values varying from 1 to 5 and 1 to 3 M HNO3 were tested. As shown in Fig. 4c, the U(vi) uptake was affected by the solution acidity during the adsorption. In particular, the U(vi) uptake of COF-IHEP11 is 203 mg  $g^{-1}$  with a removal percentage of 81.2% at pH 5.0, which is slightly higher than that of COF-IHEP10. When the acidity of the solution was increased from pH 5.0 to 3.0, the U(vi) uptake of COF-IHEP11 decreased to 118 mg  $g^{-1}$ due to competitive protonation. At pH 1.0, COF-IHEP11 achieved a U(vi) removal percentage of 45.2%, corresponding to a capacity of 113 mg  $g^{-1}$ . Such a high adsorption capacity reveals a remarkable attraction of COFs toward U(vi). More significantly, when highly acidic media were used, as is typical for irradiated and high discharge waste liquid treatment and disposal, the U(v1) uptakes of 92 mg  $g^{-1}$  in 1 M HNO<sub>3</sub> and 82 mg  $g^{-1}$  in 2 M HNO<sub>3</sub> were associated with COF-IHEP11. In light of this, the adsorption capability of COF-IHEP11 toward U(vi) from strongly acidic solution is breath-taking and the value clearly meets the demands for spent fuel reprocessing. In the entire acidity range tested, especially in highly acidic medium, what is really worth noting is that the U(vi) uptake onto the three COFs follows the order of COF-IHEP11 > COF-IHEP10 > COF-JLU4.

Cycle performance of COFs is critical for real applications. After the treatment of U/COF-IHEP11 with sodium carbonate aqueous solution, it is obvious that COF-IHEP11 can be fully regenerated. Notably, COF-IHEP11 retained 92% of the original capacity even after four cycles (Fig. 4d). This outcome confirmed the recycle use of COF-IHEP11 for the facile removal of U(vi). Selectivity is another important factor for practical U(vi) removal from water. It is apparent that at pH 1.0, COF-IHEP11 can effectively remove uranyl ions at a capacity of 113 mg g<sup>-1</sup>, but it is not active for other metal ions, such as Zn(n), Co(n), Ni (n), Cd(n), Sr(n), Yb(m), Sm(m), Nd(m) and La(m), while for other metal ions it is less than 6 mg g<sup>-1</sup> (Fig. 5). Therefore, COF-IHEP11 is able to remove toxic and radioactive U(vi) ions in a highly selective manner.

To explore the binding mechanism of uranyl ions, we selected COF-IHEP11 as a representative model and performed density functional theory calculations based on the Born– Oppenheimer approximation. Fig. 6 displays the optimized favorable binding mode of the uranyl ion with COF-IHEP11.







**Fig. 6** The favorable binding mode of uranyl with COF-IHEP11 (left panel) and the charge density distribution within the plane consisting of the uranium atom and two carbonyl oxygen atoms (right panel) in RGB mode. The bond lengths between uranium and its surrounding neighbors are displayed in angstroms. The H-bonds are also shown in dotted blue lines. Gray, blue, red, pink, and yellow spheres represent C, N, O, U, and P atoms, respectively.

We can see that the uranium atom of the uranyl ion prefers to be five-coordinated by four oxygen atoms respectively from the P=O moiety, the backbone, one water molecule, and one nitrogen atom on the backbone. The calculated bond lengths range from 2.267 to 2.830 Å, respectively. The relatively long interaction distance, 2.830 Å, between uranium and water would be attributed to the steric effect, which inhibits the closer approaching of water to uranium. In contrast, the carbonyl oxygen atoms play a more important role in attracting the uranyl ion with much shorter U-O bonds of 2.267 and 2.433 Å. The charge density distribution within the plane consisting of the uranium atom and two carbonyl oxygen atoms is also shown in Fig. 6. Obviously, the electron density overlaps around the U-O and U-N bonds with the O/N atoms from the backbone, which indicates the formation of coordination bonds. Our theoretical calculations suggested that the remarkable performance of COF-IHEP11 can be attributed to the synergistic effect of carbonyl functional groups on the COF skeleton and phosphonate active sites as side arms in the COF channels.

In summary, we herein report an operational strategy for enhancing U(vi) removal from highly acidic radioactive waste by a radiation resistant phosphonate-functionalized COF through the synergistic action of the skeleton and side arm. Considering the acid and radiation-resistant nature of COF-IHEP11, it can be a promising sorbent candidate for intense radiation actinide capture from wastewater. Further work to fabricate more effective COF sorbents by varying the skeleton and lateral side techniques, and also to emerge as an excellent scaffold for applications in the nuclear fuel cycle, is in progress.

### Conflicts of interest

There are no conflicts to declare.

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