

Flexible Units in Covalent Organic Frameworks Promote Photocatalytic Uranium Extraction from Wastewater

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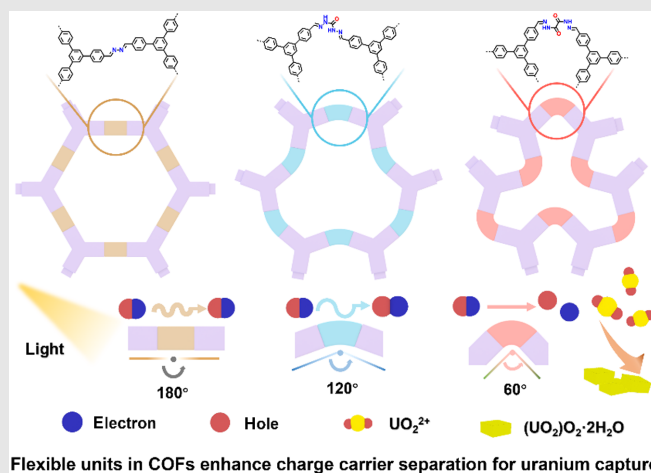
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Covalent organic frameworks (COFs) are increasingly being utilized in photocatalysis due to their programmable band gaps and pore geometries. Flexible COFs are currently of interest for selective sorption, though their use in photocatalysis has received little attention to date. Herein, we propose a strategy for modulating the flexible units of COFs to facilitate efficient charge carrier separation and transfer during photocatalysis. Rotational freedom of flexible linkers in our COFs led to controllable local pore curvature, thereby optimizing optoelectronic properties and boosting photocatalytic activity. One of our developed COFs (COF-3) showed excellent photocatalytic performance for uranium removal from contaminated groundwater and contaminated tap water. Mechanistic studies revealed that COF-3 photocatalytically generated H_2O_2 under visible light irradiation in water, which transformed the UO_2^{2+} to a solid $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ through a redox pathway. The results demonstrate an effective design strategy

towards flexible COF photocatalysts for uranium removal from water and potentially many other applications.



Keywords: covalent organic frameworks, flexible, photocatalysis, uranium removal, $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$

Introduction

Covalent organic frameworks (COFs), as crystalline porous polymeric materials, receive a lot of attention due to their ordered structure, abundant tunable units, high specific surface area and porosity, and good chemical stability.^{1–8} These materials are finding increasing applications in adsorption and separation,^{9,10} gas storage,¹¹

energy storage,¹² sensing,¹³ biomedicine,¹⁴ and photocatalysis,^{15–18} taking advantage of their regular topology and diverse precursor combinations. The performance of COF-based photocatalysts is often limited by fast recombination of photogenerated charge carriers, incomplete electron-hole separation, and low electron transport efficiencies.^{19–23} Therefore, controlling the band gap and energy band positions of COFs, together with enhancing

the separation and transport of photogenerated charges, are vital to the design of high-performance COF photocatalysts.^{21,24}

Recently, researchers have shown that the photogenerated charge separation capability of COFs could be improved for enhancing photocatalytic performance by building donor-acceptor (D-A) structures,²⁵⁻²⁷ doping heteroatoms,²⁸⁻³⁰ constructing heterojunctions,³¹⁻³⁴ and so on. Yang et al.²⁵ reported a series of COFs with intramolecular D-A systems with good charge separation efficiencies by using linkers with electron-withdrawing or electron-donating groups and also constructing π conjugated networks. Moreover, the electronic distribution in the COFs could be tuned by controlling the number and position of heterocyclic nitrogen atoms, thereby promoting photogenerated electron production and enhancing the photocatalytic performance.³⁵ Zhao et al.³⁶ proposed a COF-based material with a S-type heterojunction, where the generation of an internal electric field promotes the rapid transfer of photogenerated electrons and enhances the efficiency of charge transfer and utilization in photocatalysis. However, most of these COF photocatalysts have rigid structures, regular pore arrangements, few structural defects, and stable spatial conformation (consistent with most reported COFs generally having a “regular hexagonal” structure). However, COFs of these types with rigid structures may not be ideal for achieving optimal photocatalytic performance. Compared to rigid units, flexible monomers have a higher degree of rotational freedom, allowing the construction of COFs with more flexible structures.³⁷⁻⁴⁵ By combining both rigid and flexible monomers, it should be possible to prepare COFs with complementary advantages, including a high degree of crystallinity yet a degree of spatial flexibility. Based on the concept that “structure determines nature,” such unique spatial configurations may change the physicochemical properties of COF-based photocatalysts, allowing fine-tuning of electronic, photoinduced electron-hole separation and electron transport properties for better overall performance.

To date, flexible COFs have received little attention in the field of photocatalysis, with relationships between their physical structure, electronic structure, and photocatalytic activity being poorly understood and deserving of further exploration.^{46,47} Herein, we report the successful design and synthesis of crystalline flexible COF photocatalysts in which local pore characteristics and optoelectronic properties are optimized using flexible linker units. The electron-hole distributions and charge transport pathways in the COFs under visible light irradiation were probed using a host of experimental methods and theoretical calculations, thus revealing the relationship between structure and properties at the molecule level. A COF (denoted as COF-3) with the largest pore curvature (dihedral angle of $\sim 60^\circ$ between two opposite terminal groups) exhibited exceptional

charge transfer properties, resulting in a high photocatalytic uranium extraction efficiency and selectivity (removal efficiency $>96\%$ in contaminated groundwater and $>96\%$ in contaminated tap water). COF-3 further showed excellent selectivity for uranium removal (efficiency $>90\%$) in the presence of other metal ions under high ionic strength conditions (e.g., 10-fold excess of Na^+ , Mg^{2+} , K^+ , etc.). COF-1 (dihedral angle of $\sim 180^\circ$) and COF-2 (dihedral angle of $\sim 120^\circ$) with smaller pore curvature showed poor photocatalytic activity under similar conditions. The results provide new insights for the rational design and performance optimization of flexible COF-based photocatalysts.

Experimental Methods

Synthesis of COF-1

In a 5 mL glass ampule, 1,3,5-tris(4-formylphenyl)benzene (TFPB, 50.0 mg) and hydrazine hydrate (N_2H_4 , 0.1 mL) were dissolved in 2.1 mL of a mixed solvent solution consisting of mesitylene (Mes)/1,4-dioxane (Dox)/acetic acid (AcOH, 6 M) with a volume ratio of 1/1/0.1. The mixture was frozen in a liquid nitrogen bath and ampule sealed with a gas torch. The ampule was then heated in an oven at 120°C for 72 h, after which the solid product was collected by vacuum filtration, washed several times with methanol and *n*-hexane, and finally dried under vacuum at 60°C overnight to obtain COF-1.

Synthesis of COF-2

In a 5 mL glass ampule, TFPB (39.0 mg) and carbohydrazide (CHYD, 13.3 mg) were dissolved in 1.1 mL of a mixed solvent solution consisting of *o*-dichlorobenzene (*o*-DCB)/*n*-butanol (*n*-BuOH)/AcOH (6 M) with a volume ratio of 8/2/1. The mixture was frozen in a liquid nitrogen bath and ampule sealed with a gas torch. The ampule was then heated in an oven at 120°C for 72 h, after which the solid product was collected by vacuum filtration, washed several times with methanol and *n*-hexane, and finally dried under vacuum at 60°C overnight to obtain COF-2.

Synthesis of COF-3

In a 5 mL glass ampule, TFPB (39.0 mg) and oxalyl dihydrazide (ODH, 17.7 mg) were dissolved in 1.1 mL of a mixed solvent solution consisting of *o*-DCB/*N,N*-dimethylformamide (DMF)/AcOH (6 M) with a volume ratio of 5/5/1. The mixture was frozen in a liquid nitrogen bath and ampule sealed with a gas torch. The ampule was then heated in an oven at 120°C for 72 h, after which the solid product was collected by vacuum filtration, washed several times with methanol and *n*-hexane, and finally dried under vacuum at 60°C overnight to obtain COF-3.

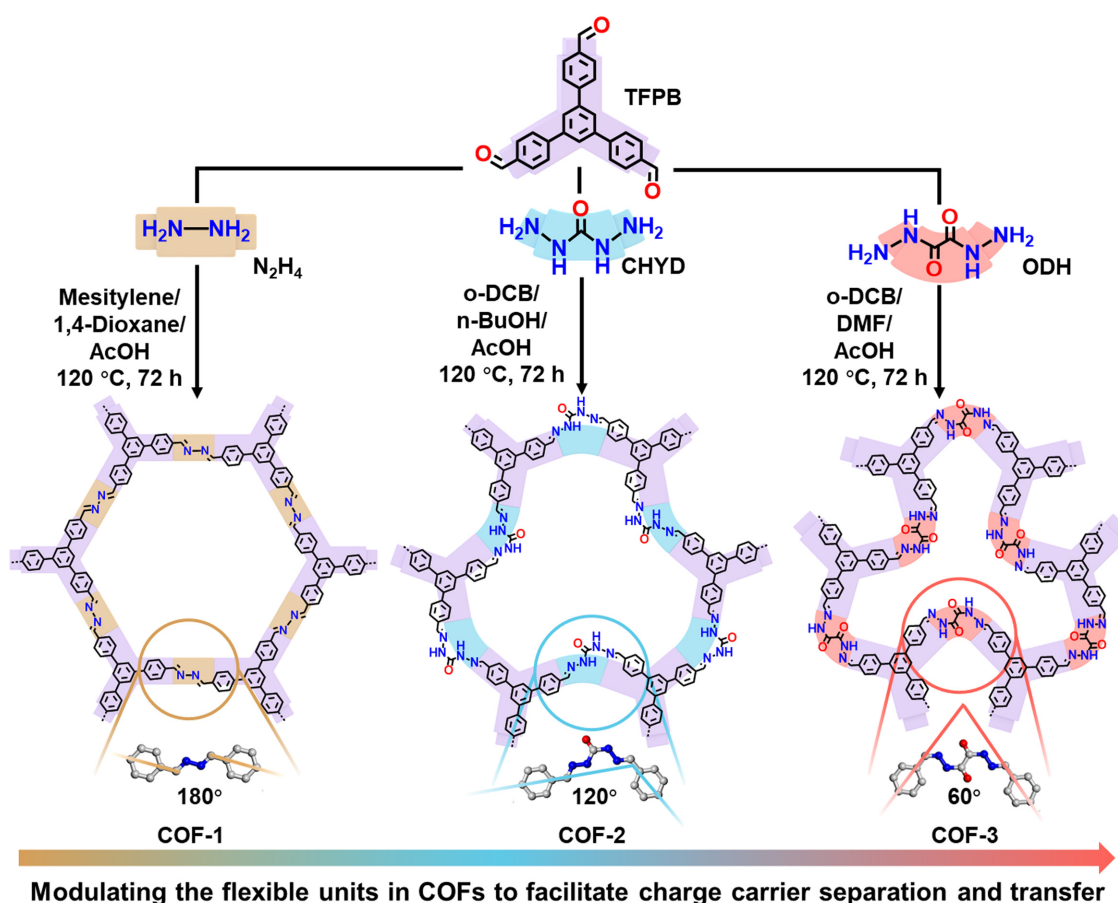


Figure 1 | Schematic illustration of the synthesis of COF-1, COF-2, and COF-3, demonstrating that charge carrier separation and transfer in COFs can be programmed by modulating the flexible units.

Results and Discussion

Design and synthesis of flexible COFs

Figure 1 shows the general synthetic route adopted in this work for the preparation of flexible COFs. The approach relies on the tuning of flexible units. All designed COFs are hydrazone-linked and formed either 2D hexagonal or clover-shaped microporous frameworks. COF-1 was synthesized by the Schiff base condensation reaction of TFPB and N_2H_4 at 120 °C in a mixed solution of mesitylene/1,4-dioxane with 6 M AcOH as a catalyst. COF-2 was synthesized through the reaction of TFPB with CHYD at 120 °C in a mixed solution of *o*-DCB/*n*-BuOH/6 M AcOH. COF-3 was synthesized through the reaction of TFPB and ODH at 120 °C in a mixture of DMF/*o*-DCB/AcOH. The N_2H_4 , CHYD, and ODH linkers exhibited progressively increasing bendability, allowing for different degrees of flexibility in the COF frameworks. The bent geometry of COF-1 approaches 180° in the window edge, which exhibits the relative rigidity of a hexagonal structure. The dihedral angles of ~120° and 60° between two opposite terminal groups of TFPB in COF-2 and COF-3 are varied

to stabilize the frameworks, enhancing the in-plane flexibility. The chemical structures of COF-1, COF-2, and COF-3 with varying flexibility were determined by Fourier transform infrared (FT-IR) spectroscopy, solid-state cross-polarization magic angle spinning ^{13}C NMR (^{13}C CP/MAS NMR), and powder X-ray diffraction (PXRD). FT-IR spectra for COF-1, COF-2, and COF-3 showed the disappearance of the C=O stretch for TFPB (1691 cm^{-1}) and $-\text{NH}_2$ stretches (3345–3176 cm^{-1}) for N_2H_4 , CHYD and ODH, together with the appearance of C=N peaks at 1620 cm^{-1} (for all three COFs), indicating successful hydrazone condensation reactions had occurred (Figure 2a and Supporting Information Figure S1).⁴⁸ For COF-2 and COF-3, new C=O peaks were seen at 1682 cm^{-1} associated with O=C–NH groups. The FT-IR data suggested that the molecular structure of the building blocks remained largely intact during COF formation. The solid-state ^{13}C CP/MAS NMR spectra showed signals at 158, 146, and 149 ppm, further confirming the formation of hydrazone C=N (for all three COFs) and O=C–NH bonds at 154 and 155 ppm (COF-2 and COF-3) (Figure 2b).^{43,49} The peripheral phenyl and central aryl rings of the three COFs showed characteristic peaks between 110 and

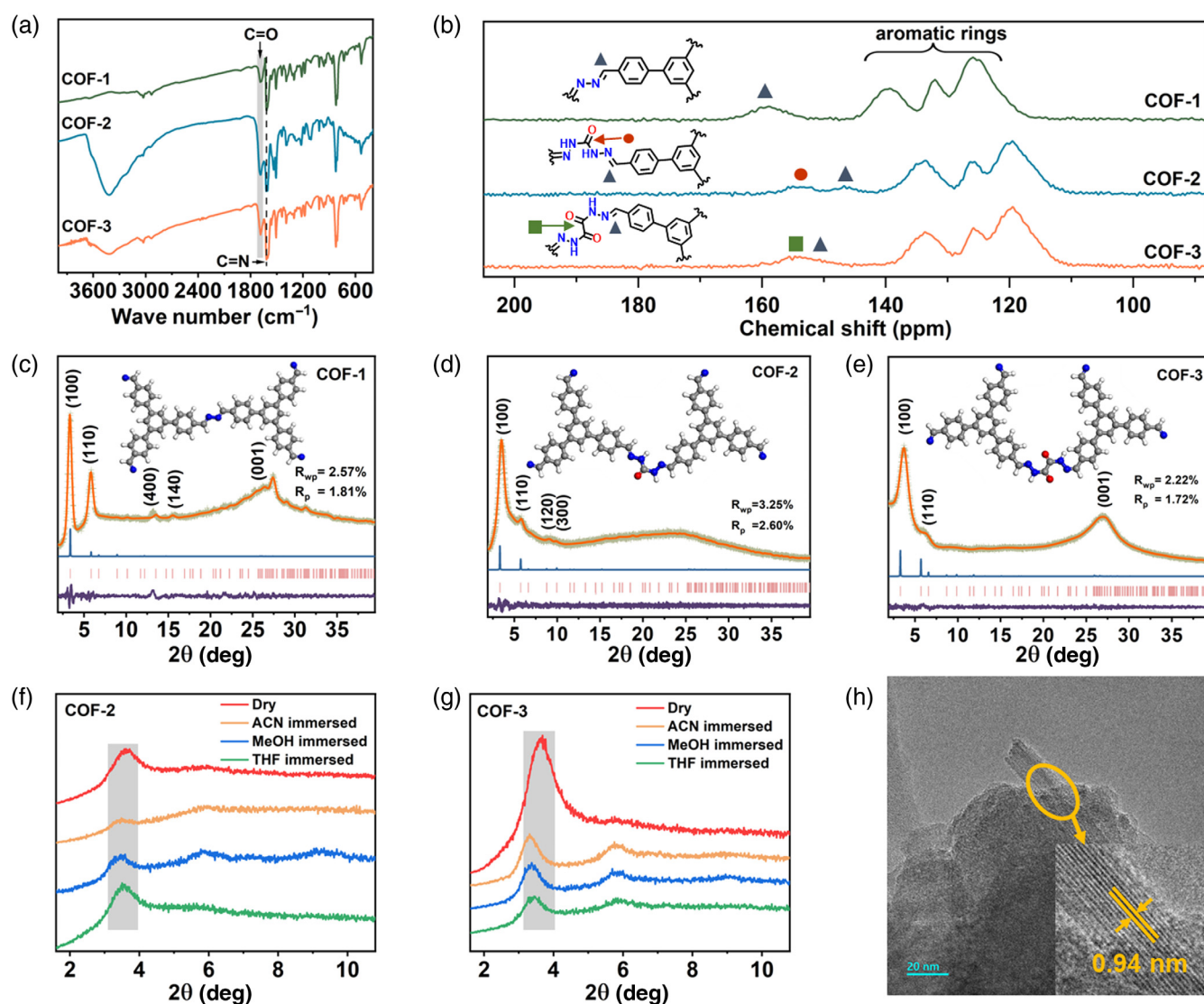


Figure 2 | (a) FT-IR spectra of COF-1, COF-2, and COF-3. (b) Solid-state ^{13}C CP/MAS NMR spectra of COF-1, COF-2, and COF-3. (c-e) Experimental PXRD patterns of COF-1, COF-2, and COF-3 with corresponding Pawley refinement (orange), simulated results (blue), and Bragg positions (brick red) showing good fit to the experimental data (khaki) with minimal differences (violet). The insets show the localized structural models of each COF. (f, g) PXRD patterns of COF-2 and COF-3 in various solvents. (h) HR-TEM image of COF-3, highlighting the pore spacing.

140 ppm. The flexibility of interligand linkages is one of the challenges in synthesizing COFs containing flexible monomers and resolving their crystal structure.⁵⁰ PXRD (small angle X-ray scattering analysis used for zero-shift correction) with Pawley refinement analysis was next used to determine the crystal structures of COF-1, COF-2, and COF-3. The PXRD pattern of COF-1 exhibited intense peaks at $2\theta = 3.4^\circ, 5.8^\circ, 13.2^\circ, 15.5^\circ$, and 26.5° (Figure 2c), which could readily be assigned to diffraction on (100), (110), (400), (140), and (001) planes, respectively. Pawley refinement revealed COF-1 to crystallize in the P6₃/m space group with lattice parameters of $a = b = 30.06 \text{ \AA}$, $c = 3.48 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, together with the negligible profile

differences ($R_{\text{wp}} = 2.57\%$, $R_p = 1.81\%$) (Supporting Information Table S1). The structural simulation matched an eclipsed AA stacking structural model well, with the layer distance and pore diameter in COF-1 calculated to be $\sim 3.48 \text{ \AA}$ and $\sim 1.9 \text{ nm}$, respectively (Figure 2c and Supporting Information Figure S2). The high degree of freedom for chemical bond rotation created a variety of possible spatial configurations for COF-2 and COF-3. We predicted and modeled various possible structural types based on the different connection orientations resulting from the different angles of bond rotation (Supporting Information Figures S3 and S4). The experimental PXRD pattern of COF-2 showed diffraction peaks at $3.5^\circ, 5.7^\circ, 8.9^\circ$, and 9.9° , which could be

assigned to (100), (110), (120), and (300) crystal reflections, respectively (Figure 2d). The experimental PXRD diffraction peaks for COF-3 showed peaks at 3.6°, 6.0°, and 26.6°, which were assigned to the (100), (110), and (001) crystal reflections, respectively (Figure 2e). A reasonable theoretical crystal structure for the AA stacking model was established by simulating the experimental PXRD patterns with the Materials Studio software, with one set of simulated data closely matching the experimental PXRD results (Supporting Information Figures S5 and S6). Pawley fitting was used to refine the unit cell parameters, revealing that COF-2 crystalized in a hexagonal P-6 space group with unit cell parameters of $a = b = 30.82 \text{ \AA}$, $c = 3.51 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ with $R_{wp} = 3.25\%$ and $R_p = 2.60\%$ (Supporting Information Table S2). Similarly, the refined unit cell parameters for COF-3 were determined as $a = b = 28.35 \text{ \AA}$, $c = 3.50 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$, with agreement factors of $R_{wp} = 2.22\%$ and $R_p = 1.72\%$ (Supporting Information Table S3). The low R_{wp} and R_p values in the refinements pointed to a high degree of fitting, confirming the controllable local pore curvature (dihedral angle of $\sim 120^\circ$ and 60° between two opposite terminal groups, respectively) of COF-2 and COF-3 (Supporting Information Figures S7 and S8). The contents of C, N, and H in the COFs determined by elemental analysis were close to the theoretical values for the designed structures, confirming the successful synthesis of flexible COFs rather than cluttered polymers (Supporting Information Table S4). For flexible COFs, crystal structural change can be induced by immersing the COFs in various solvents under measurement conditions. Following immersion in acetonitrile (ACN), methanol (MeOH), and tetrahydrofuran (THF), the peaks at 3.4°, 3.5°, and 3.6° for COF-1, COF-2, and COF-3 shifted to 3.35°, 3.3°, and 3.3°, respectively. COF-1 with relatively poor flexibility showed almost no change in crystal structure, whereas the more flexible COF-2 and COF-3 showed progressively larger peak shifts. It is apparent that flexible COFs exhibit more structurally alterability when their pores are filled by guest molecules (Figure 2f,g and Supporting Information Figure S9). The structural analysis revealed that COF-2 and COF-3 have similar pore diameters, but COF-3 showed a more squeezed pore structure.

More details about the internal structure of the COF-2 and COF-3 were elucidated from high-resolution transmission electron microscopy (HR-TEM) images. The HR-TEM images of COF-2 exhibited regular lattice fringes with spacings of 3.5 Å, corresponding to the interlayer distance in the simulated structure (Supporting Information Figure S10). For COF-3, lattice fringes with a spacing of 0.94 nm were observed corresponding to (100) planes, with this spacing being similar to the average pore size of $\sim 1.18 \text{ nm}$ for COF-3 (Figure 2h). Furthermore, COF-3 exhibited additional lattice fringes with a spacing of 3.6 Å, which can be attributed to the interlayer

stacking distance (Supporting Information Figure S11). These findings further validated the well-ordered porous structures of COF-2 and COF-3. The specific surface area and void fraction of COF-1, COF-2, and COF-3 were probed using N₂ adsorption-desorption data collected at 77 K, with all samples showing type II sorption isotherms (Figure 3a). Substantial adsorption-desorption hysteresis over a wide P/P₀ range was observed for all COFs, reflecting their structural flexibility. The N₂ uptake logarithmic plots for COF-2 and COF-3 showed higher N₂ uptake than COF-1 at low relative pressures (P/P₀, ranging from 0.001 to 0.01), suggesting that COF-2 and COF-3 with controllable local pore curvature possessed a greater volume of smaller pores (Supporting Information Figure S12). The calculated Brunauer-Emmett-Teller surface areas of COF-1, COF-2, and COF-3 were 534.9, 601.4, and 671.9 m²/g, respectively. The pore sizes calculated by the density-functional theory (DFT) method for COF-1, COF-2, and COF-3 were 1.94, 1.18, and 1.18 nm, respectively, closely matching the structural simulation results (Figure 3b). Scanning electron microscopy (SEM) revealed COF-1, COF-2, and COF-3 to form wire-like structures through particle aggregation (Supporting Information Figure S13). Thermogravimetric analysis (TGA) showed that all COFs possessed good thermal stability under a nitrogen atmosphere, with decomposition not starting until $\sim 300^\circ \text{C}$ (Supporting Information Figure S14). All three samples showed small weight losses below 100 °C, corresponding to the loss of low-boiling guest molecules (e.g., methanol). The contact angles of deionized water on the surfaces of COF-1, COF-2, and COF-3 were determined to be 55.2°, 60.9°, and 72.0°, respectively (Supporting Information Figure S15). Differing from polar units (C=O), which induce hydrophilicity, the local pore curvature of COF-2 (dihedral angle of $\sim 120^\circ$) and COF-3 (dihedral angle of $\sim 60^\circ$) prevents the exposure of polar groups and increases local capillary pressure, impeding water from entering the pores. The obtained weakly hydrophilic surfaces were expected to facilitate the diffusion and adsorption of uranyl ions on the COF surfaces.

Photoelectronic properties of the flexible COFs

The optical, electrochemical, and photoelectrochemical properties of the synthesized COFs were investigated using steady-state photoluminescence (PL) spectra, time-resolved fluorescence spectroscopy, electrochemical impedance spectroscopy (EIS), photocurrent measurements, Mott-Schottky diagrams, and ultraviolet/visible diffuse reflectance spectroscopy (UV/vis DRS). Upon excitation, COF-1 presented a characteristic emission band centered at 581 nm, while COF-2 and COF-3 displayed redshifted emissions at 592 nm, signaling the highly planarity and more conjugated nature of the

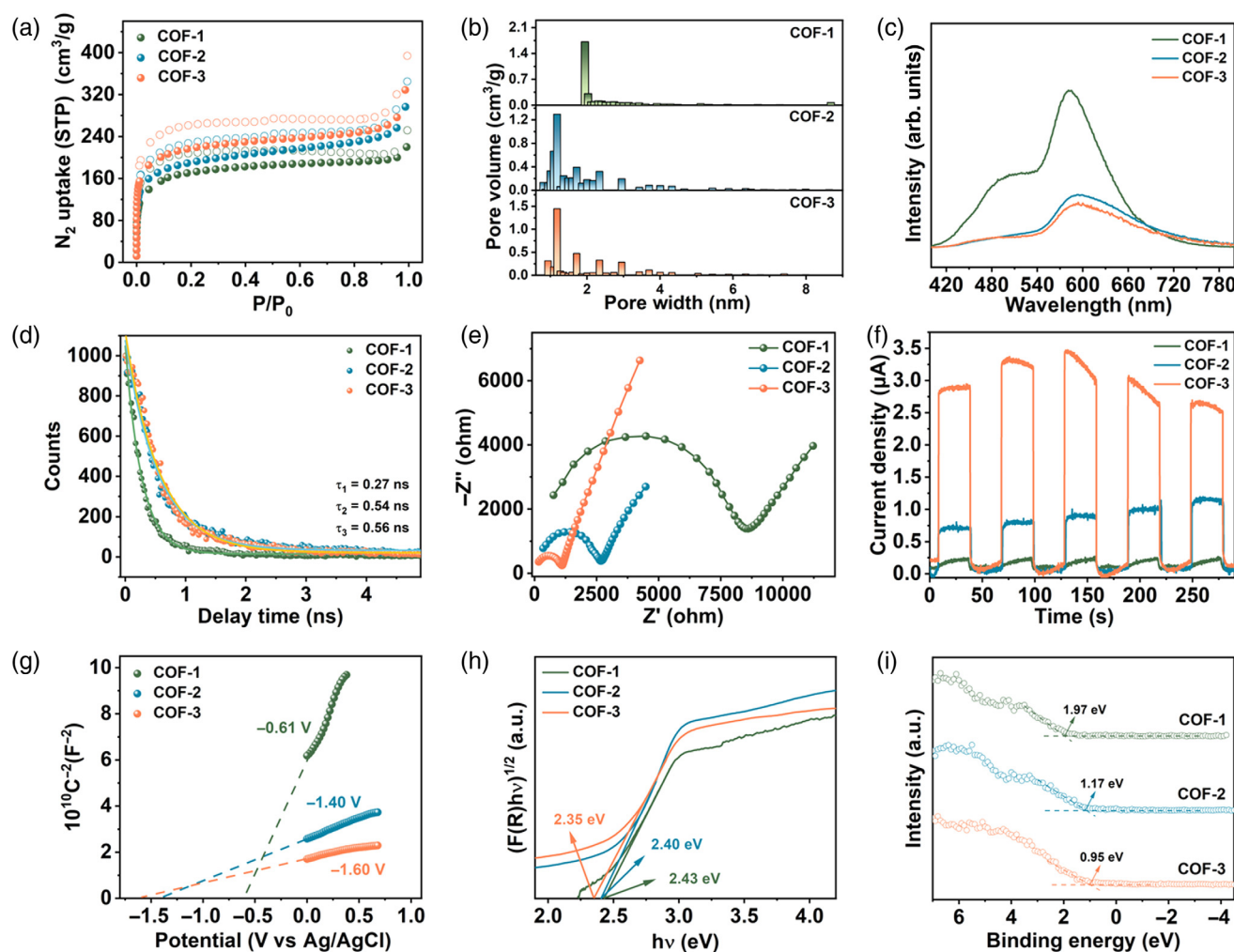


Figure 3 | (a) N_2 sorption isotherms measured at 77 K for COF-1, COF-2, and COF-3. (b) Pore size distributions of COFs determined by N_2 physisorption at 77 K. (c) Steady-state PL spectra under 375 nm excitation. (d) TRPL spectra of COF-1, COF-2, and COF-3 (excitation at 375 nm). (e) EIS spectra of COF-1, COF-2, and COF-3. (f) Photocurrent responses of COF-1, COF-2, and COF-3 under visible light. (g) Mott-Schottky plots for COF-1, COF-2, and COF-3. (h) UV-visible diffuse reflectance spectra for COF-1, COF-2, and COF-3. (i) VB-XPS spectra for COF-1, COF-2, and COF-3.

COF-2 and COF-3 frameworks (Figure 3c). Moreover, COF-3 demonstrated superior fluorescence quenching efficiency compared to COF-1 and COF-2, indicating inhibited carrier recombination. Time-resolved photoluminescence emission decay spectra (TRPL) showed that the average fluorescence lifetimes of COF-2 and COF-3 (0.54 and 0.56 ns) were longer than those of COF-1 (0.27 ns) (Figure 3d). This suggests that the recombination of photogenerated electron-hole pairs in COF-2 and COF-3 were suppressed compared to COF-1, which was expected to facilitate charge separation and transfer during photocatalysis. EIS was used to visualize the differences in the internal resistance of the different COFs. COF-3 showed a lower electron transfer resistance than COF-1 and COF-2, as evidenced by a smaller semicircle diameter at low frequencies in the EIS Nyquist curves

(Figure 3e). The photoelectric properties of COF-1, COF-2, and COF-3 were evaluated by photocurrent response tests. COF-3 demonstrated the largest transient-photocurrent response across multiple cycles of on-off photocurrent testing (Figure 3f), suggesting that it was the most effective in capturing photons to produce excited-state charge carriers. Next, the flat band potential (E_{fb}) obtained by the Mott-Schottky method was used to determine the conduction band (CB) position of each sample. The positive slope of the Mott-Schottky plots in Figure 3g implied that COF-1, COF-2, and COF-3 were n-type semiconductors with the CB (E_{CB}) numerically equal to the flat band potential (E_{fb}). The CB versus Ag/AgCl values of COF-1, COF-2, and COF-3 were determined to be -0.61 , -1.40 , and -1.60 eV, respectively. The UV/vis DRS spectra of COF-1, COF-2, and COF-3 showed that

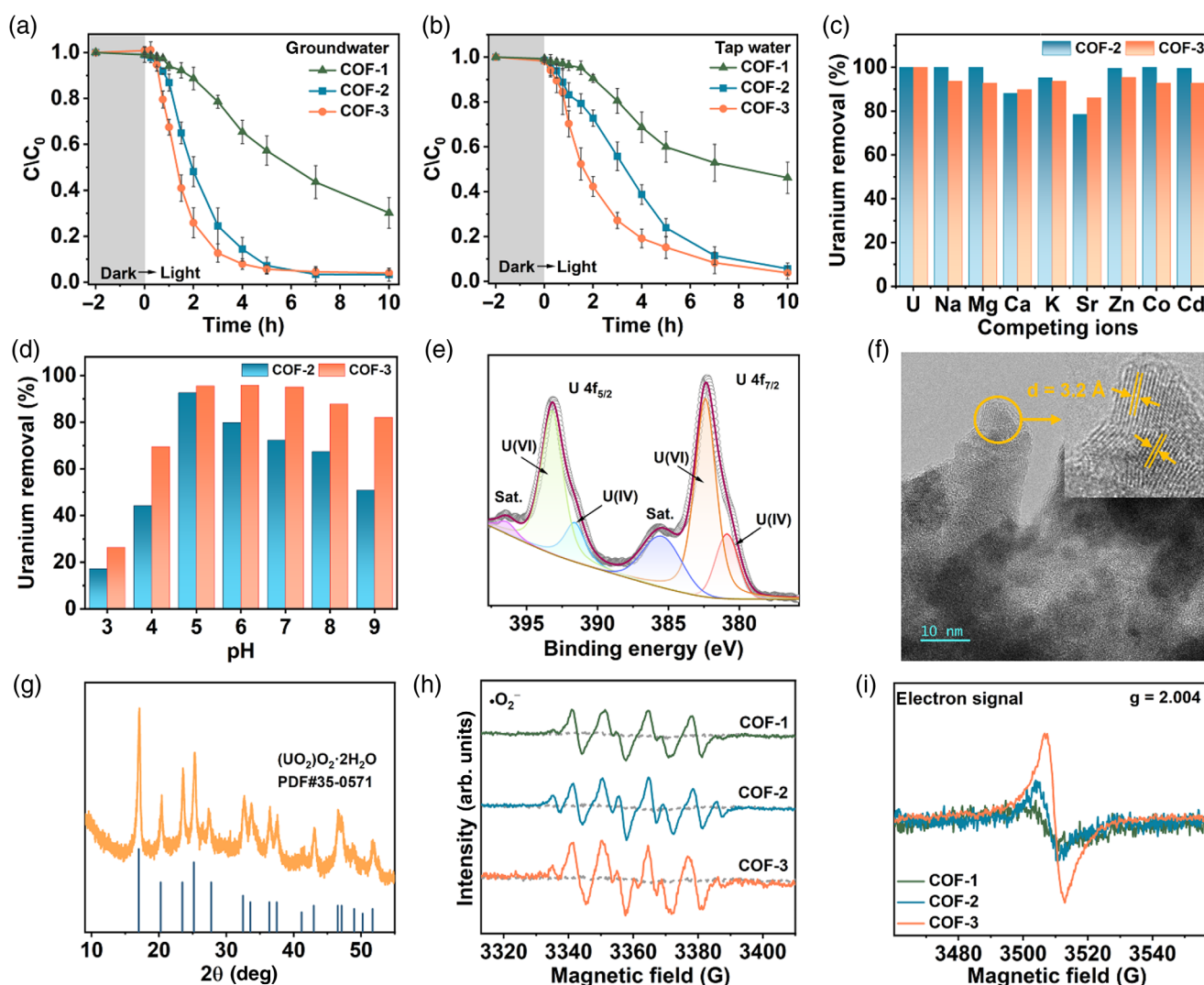


Figure 4 | (a, b) Uranium extraction from spiked groundwater or tap water with initial uranium concentrations of ~ 20 ppm, using COF-1, COF-2, and COF-3 as photocatalysts. (c) Effect of possible competing ions on uranium removal by COF-2 and COF-3. (d) Effect of initial pH on the removal of uranium by COF-2 and COF-3. (e) U 4f XPS spectrum of COF-3 after photocatalysis. (f) HR-TEM image of COF-3 after photocatalysis. (g) PXRD pattern of COF-3 after photocatalysis. (h) EPR spectra for $\cdot\text{O}_2^-$ -DMPO complexes formed under visible light irradiation of COFs. The gray spectra were collected from samples kept in the dark, whilst the colored curves were collected for samples exposed to visible light. (i) EPR spectra showing CB electron-signals for each COF.

the samples have strong absorption bands in the wavelength range of 400–500 nm (visible range) (Supporting Information Figure S16). From the Kubelka-Munk function transformed spectra, the optical band gaps (E_g) for COF-1, COF-2, and COF-3 were calculated to be 2.43, 2.40, and 2.35 eV, respectively (Figure 3h). The band gap energies of COF-2 and COF-3 were slightly lower than that of COF-1, suggesting that less energy is needed to create charge carriers in COF-2 and COF-3. Based on the experimentally determined band gaps and CB levels (using the empirical equation $E_{\text{CB}} = E_{\text{VB}} - E_g$), the valence band (E_{VB}) levels were calculated to be 2.02, 1.20, and 0.95 eV for COF-1, COF-2, and COF-3, respectively

(Supporting Information Figure S17). The E_{VB} values, measured directly from valence band X-ray photoelectron spectroscopy (VB-XPS) data, were determined to be 1.97, 1.17, and 0.95 eV, respectively (Figure 3i). These values were consistent with calculated values. The band alignment of COF-1, COF-2, and COF-3 indicated a thermodynamic feasibility for photocatalytic uranyl reduction (Supporting Information Figure S17). Notably, the CB positions for all the COFs were all more negative than the potential for the $\text{O}_2/\text{H}_2\text{O}_2$ redox couple (0.68 V vs normal hydrogen electrode), suggesting that the COFs were capable of reducing oxygen dissolved in water to H_2O_2 under visible light irradiation. These results indicate that

the developed COFs could be utilized as an effective photocatalyst platform for uranium removal from aqueous solutions due to their well-defined structures, high porosity, and excellent charge separation and transport properties under visible light conditions, which satisfy the requirement for transform UO_2^{2+} in solution to UO_2 , UO_3 , and $[(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}]$ solids.^{51–53} Thus, we next carried out a series of photocatalytic experiments to assess the viability of the flexible COFs for the removal of uranium from contaminated aqueous solutions.

Photocatalytic uranium extraction studies

Nuclear energy, as a high-energy-density and low- CO_2 emission technology, is recognized as a promising alternative to conventional fossil fuel-based energy sources.⁵⁴ Uranium (as ^{235}U) is the main fuel essential to the operation of nuclear fission reactors.⁵⁵ Traditionally, ^{235}U is obtained from uranium ore and spent fuel recycling.⁵⁶ However, leakage of uranium-containing substances into water caused by nuclear accidents or uranium mining can be highly hazardous to human health, leading to kidney failure, leukemia, cancer, and other diseases.^{57–59} These risks motivate the development of high-performance adsorbents and catalytic technologies which can efficiently and safely remove uranium from mining waste, contaminated water, and seawater (the latter is now being pursued as a route for mining uranium).

Encouraged by their flexible structures and good optoelectronic properties, the photocatalytic activities of COF-1, COF-2, and COF-3 for uranium removal from contaminated groundwater and tap water were investigated. The COFs were immersed in uranyl-spiked (~ 20 ppm) groundwater or tap water for 2 h to achieve adsorption equilibrium before irradiation with a Xenon lamp. As shown in Figure 4a, COF-3 quickly removed uranium from spiked groundwater, with removal efficiencies of 59% and 92% achieved after 1.5 and 4 h, respectively, without requiring any additional sacrificial agents. A removal capacity of 403.6 mg/g was obtained after 7 h (removal efficiency $>96\%$). COF-2 showed slightly lower uranium removal efficiencies (with removal efficiencies of $\sim 52\%$ and 93% achieved after 2 and 5 h, respectively; 396.3 mg/g uranium after 7 h) under similar conditions (Figure 4a). By comparison, COF-1 possessed a much lower uranium removal efficiency ($\sim 70\%$ removal efficiency after 10 h), which confirmed the key role of the flexible units in COF-2 and COF-3 in boosting photocatalytic uranium removal performance. Furthermore, we evaluated the photocatalytic performance of COF-1, COF-2, and COF-3 in ~ 20 ppm uranyl-spiked tap water (Figure 4b). As expected, the photocatalytic efficiency for uranium removal followed the order COF-3 ($>85\%$ removal efficiency after 5 h) $>$ COF-2 ($>76\%$ removal efficiency after 5 h) $>$ COF-1 ($>40\%$ removal efficiency after 5 h). The photocatalytic removal of COF-1, COF-2,

and COF-3 in ~ 20 ppm uranyl-spiked seawater was further evaluated to verify the relationship between the flexible structures of the COFs and performance (Supporting Information Figure S18). COF-2 and COF-3 demonstrated removal efficiencies of $\sim 80\%$ and 88%, higher than that of COF-1 ($\sim 46\%$), proving the superior photocatalytic performance of flexible COFs in seawater. These results demonstrate that COF-3 exhibited the highest photocatalytic activity, evidence for very efficient charge carrier generation and utilization under visible light irradiation. The presence of competing ions can potentially hinder the photocatalytic capture of uranium. Encouraged by the above results, we then evaluated the photocatalytic performance of COF-2 and COF-3 in the presence of various competing ions. As shown in Figure 4c, both COF-2 and COF-3 showed excellent selectivity for uranium against other metal ions under high ionic strength conditions (e.g., Na^+ , Mg^{2+} , K^+ , etc.). COFs could remove over 90% of uranium in a tenfold excess of other competing ions, demonstrating potential to address the traditional limitations of COFs in practical photocatalytic applications. Another key factor affecting uranium photocatalytic extraction is the different pH values in natural water systems, which in turn can affect the surface charge of COF materials and also uranium speciation. We evaluated the photocatalytic performance of COF-2 and COF-3 in ~ 20 ppm uranyl-spiked solutions with pH ranging from 3 to 9. COF-3 showed higher activity than COF-2 at all pH values whilst maintaining excellent photocatalytic performance, with $>95\%$ uranium removal in the pH range of 5 to 7, and $>87\%$ at pH 8 (Figure 4d). These results highlight the outstanding properties of COF-3 as a photocatalyst for the efficient and highly selective removal of uranium from contaminated water.

Photocatalytic uranium extraction studies

Next, we conducted detailed experimental studies and theoretical calculations on the COFs to obtain deeper insights into their photocatalytic uranium removal mechanism and to explore the charge carrier separation and transfer pathways under visible light irradiation. The FT-IR spectrum showed a new FT-IR peak at 933 cm^{-1} for the uranium-containing product after the photocatalytic reaction (Supporting Information Figure S19). XPS was first employed to determine the surface valence state of generated products after photocatalysis. U 4f XPS data for the used COFs showed two sets of signals, each with a 4:3 area ratio. Peaks at 382.4 and 393.2 eV were readily assigned to the $\text{U } 4f_{7/2}$ and $\text{U } 4f_{5/2}$ signals, respectively, of a U(IV) species, while a more intense set of peaks at 380.9 and 391.6 eV were due to a U(VI) species (Figure 4e).⁶⁰ A further set of peaks at even higher binding energy was assigned to “shake-up” satellites. HR-TEM images showed lattice fringes with

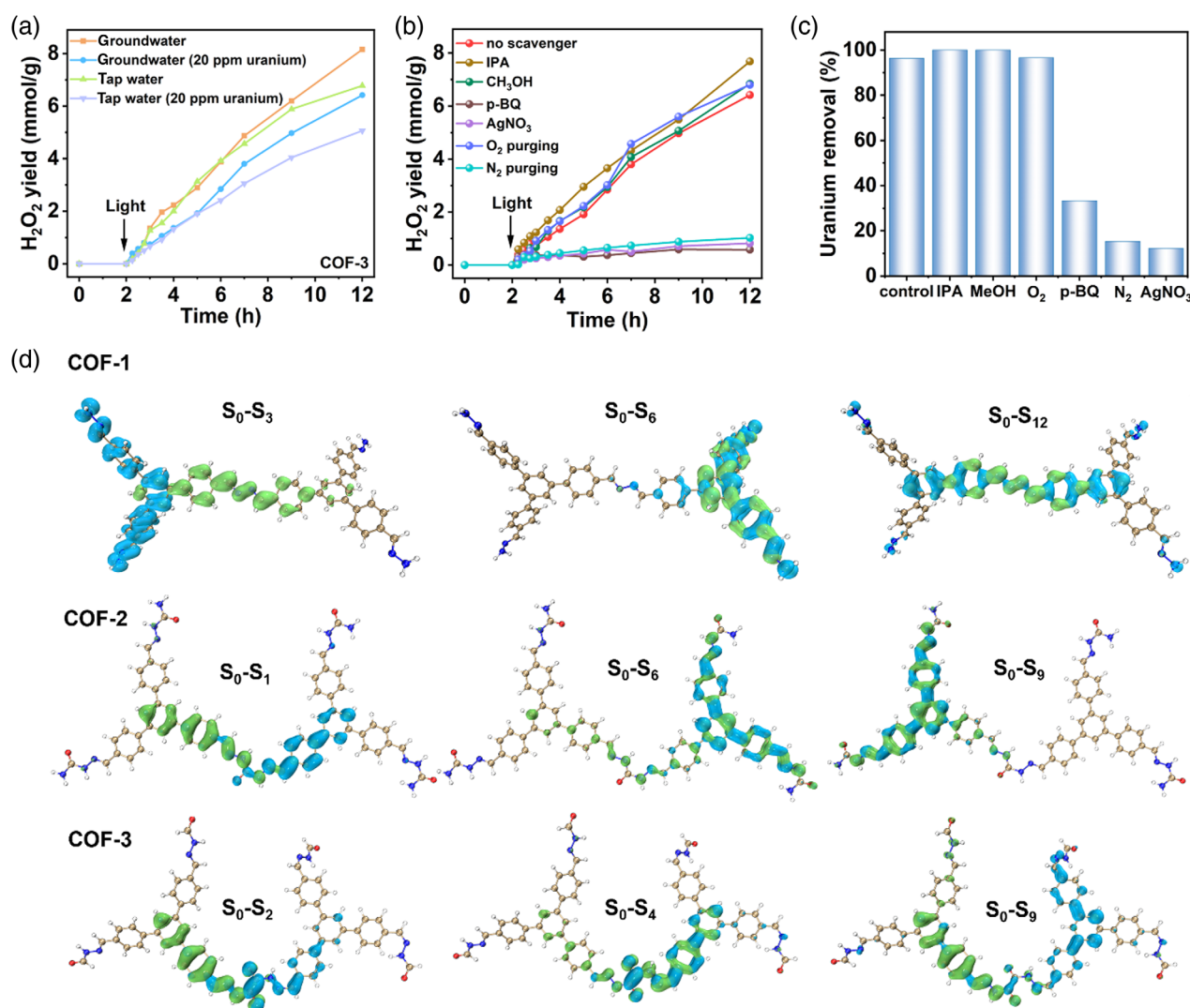


Figure 5 | (a) Photocatalytic H_2O_2 production performance of COF-3 in groundwater or tap water. (b) Quenching experiments for photocatalytic H_2O_2 production. (c) Quenching experiments for photocatalytic uranium removal. (d) The hole-electron excitation analysis for COF-1, COF-2, and COF-3 (blue regions represent electrons and green regions represent holes).

interplanar distances of around 3.2 Å, which could be assigned to the (111) plane of UO_2 or (200) plane of $(UO_2) \cdot 2H_2O$ (Figure 4f).⁶¹ We next carried out uranium removal experiments in ~50 ppm uranyl-spiked groundwater and obtained a pale-yellow product, which allowed us to run PXRD measurements to identify the uranium-containing solid products. PXRD pattern collected for COF-3 after the photocatalytic uranium capture tests revealed that the dominant product was $(UO_2)O_2 \cdot 2H_2O$ (PDF#35-0571) (Figure 4g). Electron paramagnetic resonance (EPR) spectroscopy was employed to investigate the formation of oxygen radicals ($\cdot O_2^-$ and 1O_2) during the photocatalytic process of the COFs. The EPR spectra in Figure 4h display the consecutive characteristic peaks corresponding to $\cdot O_2^-$ -DMPO, under visible

light irradiation, COF-3 exhibits a significantly stronger signal, indicating that COF-3 has a greater photoexcited electron reduction ability compared to COF-1 and COF-2. No signals for spin-trapped O_2^- were detected in the absence of light, further confirming the photoinduced activity of COFs. Further experiments using 2,2,6,6-tetramethyl-4-piperidone as a spin-trapping agent, revealed that all three COFs generated 1O_2 under visible light irradiation, reflecting the π -conjugation of COFs in the energy transfer process (Supporting Information Figure S20).⁶² EPR spectroscopy was employed to examine light-induced charge carrier generation. COF-1, COF-2, and COF-3 exhibited new EPR signals around $g = 2.004$, under visible light excitation, indicating the formation of CB electrons. Among the COFs,

COF-3 showed the strongest EPR signal, indicating better hole-electron separations and transfer capabilities compared to the other COFs (Figure 4i).

The above results encouraged us to study the photocatalytic formation pathway of $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ on the COFs. The surface affinity of COF-1, COF-2, and COF-3 for positively charged ions was determined by zeta potential measurements (Supporting Information Figure S21). The COFs all demonstrated negative ζ -potentials at pH values >3 or 4 (depending on the COF), which was expected to promote the adsorption of positively charged ions (e.g., H^+ , uranyl ions).^{63,64} The generation of H_2O_2 was expected to play an important role in the photocatalytic removal of uranium and formation of $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. Thus, we monitored the H_2O_2 production performance of COF-3 in groundwater and tap water under visible light irradiation. After 10 h, the H_2O_2 production capacities in groundwater and tap water reached 8.16 and 6.78 mmol/g, respectively (Figure 5a and Supporting Information Table S5). In contrast, the H_2O_2 production capacities were reduced to 6.42 and 5.07 mmol/g in ~20 ppm uranyl-spiked groundwater and tap water, respectively (Figure 5a). The result is explained by the consumption of H_2O_2 by reaction with uranyl ions. Subsequently, we conducted a series of free radical trapping experiments using scavengers.^{65,66} As shown in Figure 5b, the H_2O_2 production capacity decreased from 6.42 to 1.03 mmol/g after purging with N_2 , with similar results also being observed by adding AgNO_3 (air atmosphere, electron scavenger). Further, the H_2O_2 production capacity slightly increased after purging the solution with O_2 . When p-benzoquinone (p-BQ) is used for scavenging $\cdot\text{O}_2^-$, the obtained H_2O_2 production capacity was ~0.58 mmol/g.^{65,66} Moreover, the H_2O_2 production capacity increased to 7.69 mmol/g in the presence of isopropanol, which is used to scavenge $\cdot\text{OH}$.^{65,66} These results suggested that the production of H_2O_2 relied on the reduction of dissolved O_2 by photogenerated electrons, confirming that photocatalytic oxygen reduction reaction was the dominant pathway for photocatalytic H_2O_2 production by COF-3.⁶⁷ Next, we determined the uranium removal efficiency of COF-3 in the presence of various scavengers (Figure 5c), and the results agreed well with a reported photocatalytic $\text{UO}_2^{2+} \rightarrow [(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}]$ pathway (i.e., $\text{UO}_2^{2+} + 2\text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow (\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O} (\text{s}) + 2\text{H}^+$).⁶⁷ In addition, small amounts of UO_2 are formed from the direct reduction of UO_2^{2+} by CB electrons ($\text{UO}_2^{2+} + 2\text{e}^- \rightarrow \text{UO}_2 (\text{s})$).

On the basis of the above experimental results, we next carried out an electrostatic potential (ESP) distribution analysis for COF-1, COF-2, and COF-3 to understand the structure-photocatalytic performance relationship. COF-1, COF-2, and COF-3 all exhibit negative ESP at the bending points, indicating that different functional groups (from N-N to O=C-NH) created electron-rich regions in the fragments, leading to distinct local charges

in the flexible COFs. The local charges of COF-2 and COF-3 were more inhomogeneous compared to COF-1, suggesting more straightforward excitation and transport of charge carriers via induction of local charges (Supporting Information Figure S22).^{25,68-70} The electron localization function was employed to explore the electron delocalization degree in the COFs. Intuitively, it was found that with increasing rotational freedom in the flexible linkers, the electron distribution became more delocalized, which in theory would enable easier electronic excitation with the delocalized π -electrons able to be transferred in the conjugation plane (Supporting Information Figure S23). To further analyze the pore curvature effect on the C=N links and segments around links, Mulliken charge distributions were calculated (Supporting Information Figure S24). Compared to the symmetric charge distribution of linear segments in COF-1 (dihedral angle of ~180°), the charge differences on both sides were greater in the configurations with pore curvature (COF-2 and COF-3 with dihedral angles of ~120° or 60°, respectively), indicating that high pore curvature enhanced intramolecular electron mobility, thereby boosting photogenerated charge transfer.⁷¹ Time-dependent density-functional theory (TD-DFT) and hole-electron excitation analysis were utilized to study the hole-electron distributions of COF-1, COF-2, and COF-3 in their excited states (Figure 5d).^{72,73} The stronger the oscillator strength between the ground state and a certain excited state, the easier it is to absorb electromagnetic waves at the corresponding frequency and transition to that excited state. As a result, the corresponding absorption peak in the absorption spectrum is identified (Figure 5d and Supporting Information Figure S25). For COF-1, the $\text{S}_0\text{-S}_3$, $\text{S}_0\text{-S}_6$, and $\text{S}_0\text{-S}_{12}$ transitions are the three states with the strongest oscillator strength, in which $\text{S}_0\text{-S}_6$ and $\text{S}_0\text{-S}_{12}$ are localized excitations (LE), showing no significant separation in the distribution of holes and electrons. Similarly, the separation of electrons and holes in $\text{S}_0\text{-S}_6$ and $\text{S}_0\text{-S}_9$ transitions of COF-2 is insufficient. Different from the LE state ratio in COF-1 and COF-2, the $\text{S}_0\text{-S}_2$ and $\text{S}_0\text{-S}_9$ transitions in COF-3 exhibit distinct charge-transfer excited (CT) states, characterized by a significant spatial distribution of electrons and holes. Electrons and holes in CT states tend to be distributed on both sides of the bending plane for COF-2 ($\text{S}_0\text{-S}_1$) and COF-3 ($\text{S}_0\text{-S}_2$ and $\text{S}_0\text{-S}_9$), which is different from COF-1. Our findings show that flexible COFs with abundant, well-separated holes and electrons demonstrate improved photocatalytic activity. In addition, as a component of relatively rigid frameworks, the hydrazone connectors of COF-1 are located in the distribution area of holes. For flexible COF-2 and COF-3, there is no significant distinction of electron or hole accumulation in the amide region under CT states, indicating that the functional groups located at the in-plane bend do not act as a photocatalytic electron donor or acceptor. Thus, the rapid

photogenerated charge excitation and transport in COF-2 and especially COF-3 depend on their increased pore curvature, facilitating good electron separation and reduction capability in photocatalytic processes.

Taken together, our experimental results and theoretical calculations verify that flexible COFs (especially COF-3) with tunable local pore curvature demonstrate optimized optoelectronic properties and superior photocatalytic activity toward uranium removal in contaminated water resources compared to more rigid COFs (COF-1 and COF-2). The key design considerations employed here include the introduction of flexible ligands with high rotational freedom, the connection of different bending states to achieve controllable local pore curvature, and the optimization of efficient charge carrier separation and transport. Finally, uranyl ions in solution are transformed into $(\text{UO}_2)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ solids by the COFs to facilitate collection under visible-light excitation.

Conclusion

In summary, we have developed a new design strategy for constructing hydrazone-linked flexible COF photocatalysts. The flexible linkers exhibited progressively increasing bendability, allowing for different degrees of flexibility (dihedral angles of 180° , 120° , and 60°) in the COF frameworks. Experimental and theoretical studies verified that high local pore curvature, as exemplified by COF-3 [possessing the highest flexibility and largest pore curvature (i.e., the lowest dihedral angle) among developed COFs in this work], can facilitate charge carrier separation and reduce electron-hole recombination in photocatalytic processes. COF-3 possessed excellent uranium removal abilities in contaminated groundwater (removal efficiency $>96\%$) and tap water (removal efficiency $>96\%$). Further, COF-3 maintained good photocatalytic activity across a wide range of pH values and at high ionic strengths. This study demonstrates that flexible COF photocatalysts have enormous potential for uranium removal from contaminated water sources and other applications.

Supporting Information

Supporting Information is available and includes additional chemicals, instrumentation, experimental procedures, FT-IR spectra, PXRD patterns, elemental analysis, SEM images, TGA curves, UV-visible diffuse reflectance spectra, EPR spectra, Band alignment, Zeta potentials, contact angles, and DFT calculations.

Conflict of Interest

There is no conflict of interest to report.

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