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Covalent organic polyrotaxanes based on β -cyclodextrin for iodine capture†

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Herein, covalent organic polyrotaxanes (COPRs) were integrated with supermolecule self-assembly and dynamic imine bond formation to act as absorbents that captured radioactive iodine from water. The aromatic building blocks were initially complexed with β -cyclodextrin (β -CD) to form pseudorotaxanes, which were then condensed with aromatic tri-aldehyde *via* mechanical grinding and solvothermal synthesis in sequence. The threading of β -CD throughout the polymer skeleton effectively reduced the usage of expensive building blocks and significantly lowered the cost, while also remarkably enhancing the skeleton polarity, which is closely related to many special applications. Impressively, the threading of CD improved the water dispersibility of COPRs, which displayed an abnormally high iodine adsorption capacity. This novel synthetic strategy allows the incorporation of mechanically interlocked CDs into porous polymeric materials, which provides access to low-cost preparations of COPRs with a brand new structure for specific applications.

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Introduction

Similar to the biological polymer, covalent organic polymers (COPs) enable the precise integration of individual small molecules into open networks with two-dimensional (2D) and three-dimensional (3D) topological structure programmatically through the combined action of covalent bonds and non-covalent interactions.^{1–5} With years of development, there has been substantial achievement in the reaction types and methods for the specific synthesis of COPs. Hitherto, thousands of COPs with sequential connections of various building blocks have been prepared through coded reaction systems.^{6–8} However, to obtain COPs with brand new skeletons or topological structures, which has always served as the driving force for further advancement of COPs, most research is currently focused on tedious monomer design and low-efficiency post-modification of as-synthesized polymer skeletons, as well as novel reaction screening.^{9–11} To realize rapid progress, is it highly desired to devise efficient strategies that use existing monomers and methods to produce novel structures and functions.

As ‘chemistry beyond the molecules’, supramolecular chemistry, with its unique structures and properties, has produced intensive research interests due to the innovative architectures and various biomedical applications.¹² Interlocked molecules such as the rotaxanes, which are formed *via* the host–guest assembly technique, have been widely studied.¹³ There has been frequent investigation of numerous polyrotaxanes formed *via* the covalent polymerization of rotaxanes with other building blocks to construct new materials with novel structures and functions.¹⁴

Most reports describe linear polymers, and to date, only a handful of polyrotaxanes with a spatial multidimensional structure have been synthesized.^{15,16} The vast majority of pseudorotaxanes employed as building blocks are formed through electrostatic interaction.¹⁷ Unfortunately, the vast majority of natural or synthetic molecules are uncharged, which severely hinders the development and application potential of these series of materials.¹⁸

Nuclear waste contains radioactive pollutants widely generated during the nuclear fission process. One example is radioactive iodine, which poses a great threat to ecological systems due to its ultra-long half-lives, and can lead to severe environmental pollution.¹⁹ The development of high-efficiency stable materials and techniques for the capture and storage of radioactive iodine is vital, but remains challenging.²⁰ It is of primary importance to use eco-friendly materials that can promptly absorb waste iodine, and also avoid secondary pollution of the ecological environment caused by waste materials.^{21,22}

Herein, covalent organic polyrotaxanes (COPRs) named COPR-1 and COPR-2, which integrate the advantages of COPs

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and supramolecular polymer, were well designed and facily prepared as solid absorbents to remove iodine pollutants from water. COPR-1 and COPR-2, with the inclusion of β -cyclodextrin (β -CD) as a building block, were able to remarkably accelerate the development of multifunctional materials while avoiding the sophisticated design of building blocks or tedious but low-yield post-modification. At the same product mass, the integration of CD significantly reduced the usage amount of real building blocks, thereby significantly lowering the cost. COPRs combine dynamic imine bonds and supramolecular interactions so that brand new structures can be grown, in which the primary-order skeletal structure is determined by the covalent bonds, and the high-order morphology is precisely shaped by supramolecular forces. The brand new structure endowed great application potential with polyrotaxane-covalent organic frameworks (PR-COF) for the capture and separation of radioactive iodine from the environment.

Results and discussion

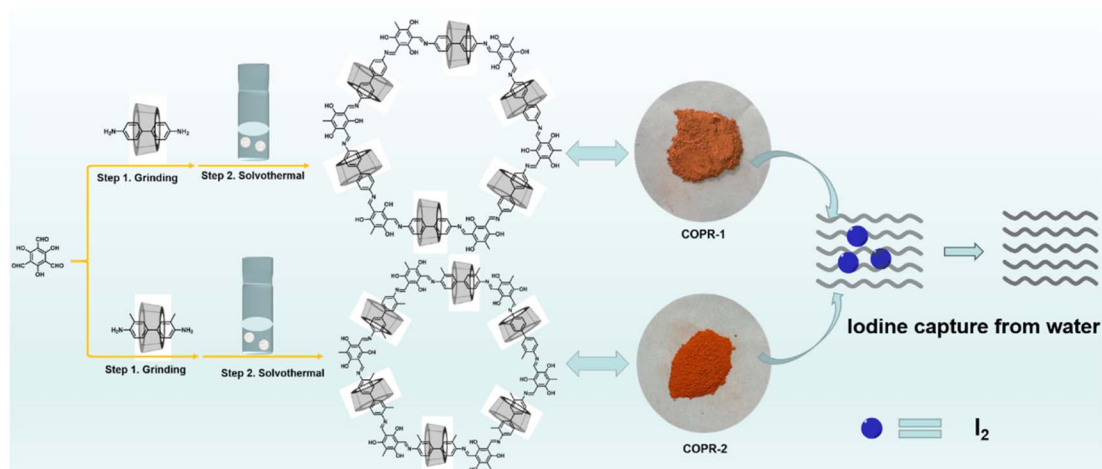
Scheme 1 presents the typical design and synthesis strategy for COPRs. Two typical COPRs, denoted as COPR-1 and COPR-2, were quantitatively prepared *via* a two-step sequential synthesis through the acid-catalyzed Schiff-base condensation reaction. Briefly, the C2-symmetric CD inclusions (bearing two amino groups) were pre-polymerized with C3-symmetric 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde *via* mechanical grinding for 30 min under the catalysis of *p*-methylbenzene sulfonic acid (TMSA).²³ Afterwards, the reaction mixture was transferred to a sealed Pyrex tube containing the mixed solvent of alcohol (EtOH) and orthodichlorobenzene (*o*-DCB) at 120 °C, which was maintained at that temperature for 3 days to synthesize the final COPRs.²⁴ Because of the prepolymerization, uniform introduction of CD into the porous skeleton occurred. The details for the synthesis are given in the ESI.†

The chemical compositions and bond linking of COPR-1 and COPR-2 were characterized by Fourier transform infrared (FT-IR) spectroscopy (Fig. 1a) and solid-state ^{13}C cross-

polarization magic angle spinning nuclear magnetic resonance (^{13}C CP/MAS NMR, Fig. 1b) spectroscopy. The FT-IR spectroscopy of COPR-1 and COPR-2 simultaneously shows all the amalgamated features of the CD inclusions and 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde. Specifically, both COPRs displayed an evident peak at 1622 cm^{-1} that corresponded to the newly formed $\text{C}=\text{N}$ bonds.²⁴ Typical stretching vibrations of the CD rings located at approximately 3368 cm^{-1} (V_{OH}) and 1031 cm^{-1} ($\text{V}_{\text{C-O-C}}$) were also clearly detected.²⁵ The characteristic vibration bands associated with the CHO groups (1690 cm^{-1}) of 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde and NH_2 groups (3384 , 3322 , and 3208 cm^{-1}) of CD inclusion disappeared, further demonstrating the occurrence of aldehyde ammonia Schiff base condensation.^{26–28} Similarly, apart from the feature signals of aromatic carbon (106 and 141 ppm), the solid-state ^{13}C NMR of COPRs also produced the characteristic resonance of the carbon signal from CD at approximately 72 and 54 ppm .²⁹ These results demonstrated the formation of a CD-threaded porous skeleton.

The powder X-ray diffraction (PXRD, Fig. 1c) pattern for COPR-1 and COPR-2 only presented strong broad diffraction peaks at $2\theta = 25.5^\circ$, demonstrating the amorphous structure of the as-synthesized samples.³⁰ The thermogravimetric analysis (TGA) of COPR-1 and COPR-2 displayed a stepwise weight loss. The rapid weight loss occurring below 100°C was attributed to the evaporation of water strongly absorbed in the O-rich porous networks.³¹ Afterwards, a relatively flat weight loss at temperatures ranging from 100 to 300°C was attributed to the decomposition of CD rings threaded in the porous skeleton. Weight loss that occurred at $>300^\circ\text{C}$ was attributed to the thermal decomposition of the conjugated skeleton (Fig. 1d).

The surface and inner micromorphology of COPR-1 and COPR-2 were investigated *via* transmission electron microscopy (TEM). The TEM images (Fig. 2) revealed that COPR-1 (Fig. 2a–d) and COPR-2 (Fig. 2f–h) were composed of bulk fused by a layered sheet. Specifically, as presented in Fig. 2a–d, COPR-1 displayed a uniformly distributed fringe structure, assignable to the wide threading of CD units into the porous skeleton. As



Scheme 1 Typical route and strategy for the synthesis of covalent organic polyrotaxanes (COPRs).



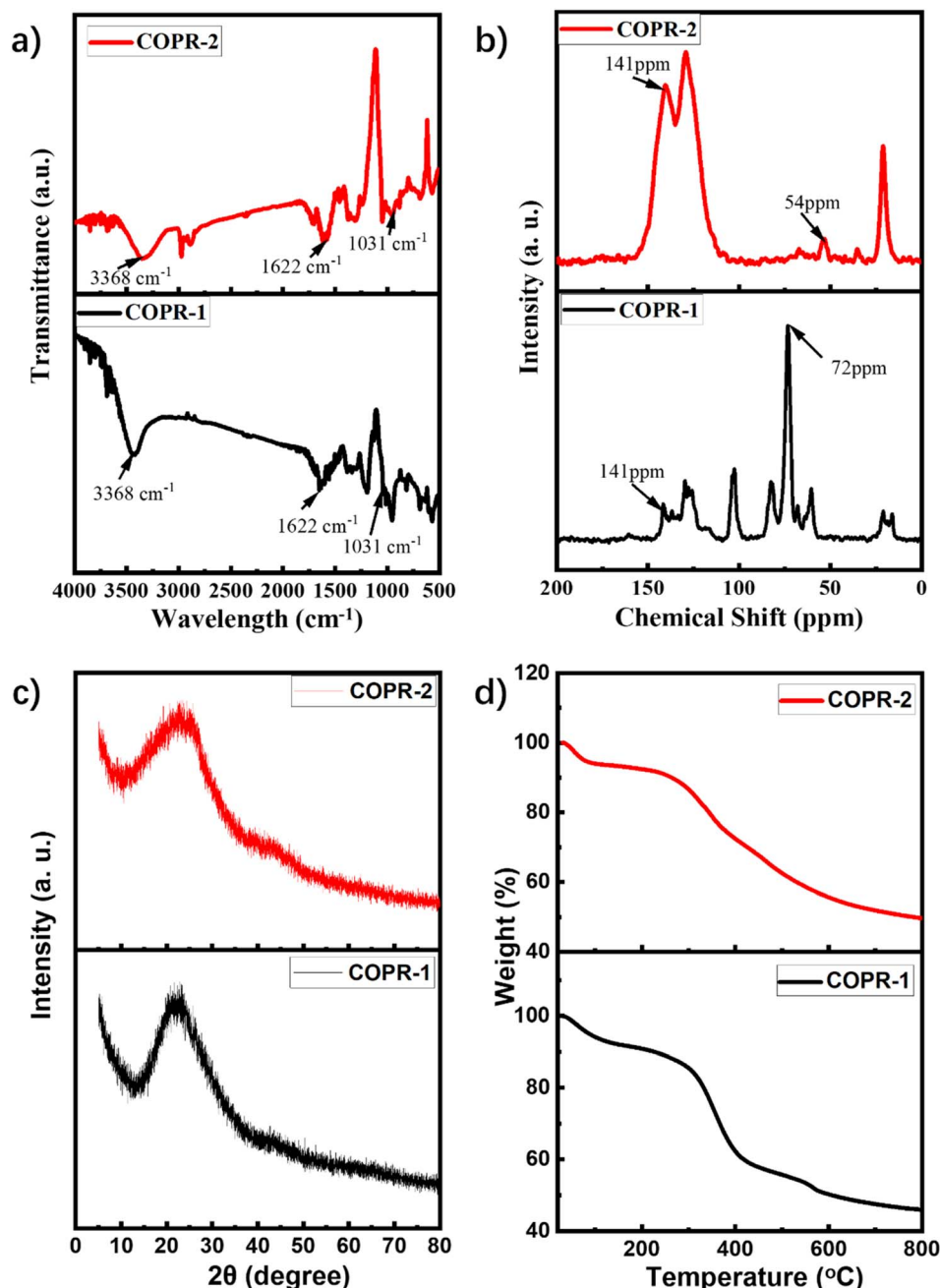


Fig. 1 Physical characterization of COPR-1 and COPR-2: (a) FTIR of COPR-1 and COPR-2. (b) Solid state ^{13}C NMR of COPR-1 and COPR-2. (c) PXRD of COPR-1 and COPR-2. (d) TGA of COPR-1 and COPR-2.

expected, the elemental mapping and corresponding energy dispersive X-ray spectroscopy (EDS) results for COPR-1 (Fig. 2e) and COPR-2 (Fig. 2j) confirmed the homogeneous distribution of C, N, and O over the CD-threaded polymer skeleton. The oxygen content in COPR-1 and COPR-2 was among the highest level in as-reported polymer-based networks.³² The high heteroatom content enabled facile encapsulation of iodine from water (Fig. 3).

Based on the aforementioned results, the capacity of COPR-1 and COPR-2 to absorb iodine from water was examined using β -CD as a control. Fig. 3 shows that because of the unique O-rich

structure, COPR-1 and COPR-2 possessed excellent capacity to absorb saturated I_2 solutions, as verified by the obvious color change over the duration of time, which faded from orange to almost colorless within 80 min (insets in Fig. 3a and c). The rate of iodine removal from water significantly increased over time for COPR-1 and COPR-2. Notably, COPR-1 and COPR-2 presented a hierarchical absorption process with a rapid uptake during the initial 20 min, and then a relatively slow increase. Compared with β -CD (Fig. S1†), there was a much faster iodine adsorption rate for COPR-1 and COPR-2. Specifically, the most prominent iodine removal capacity was demonstrated by COPR-

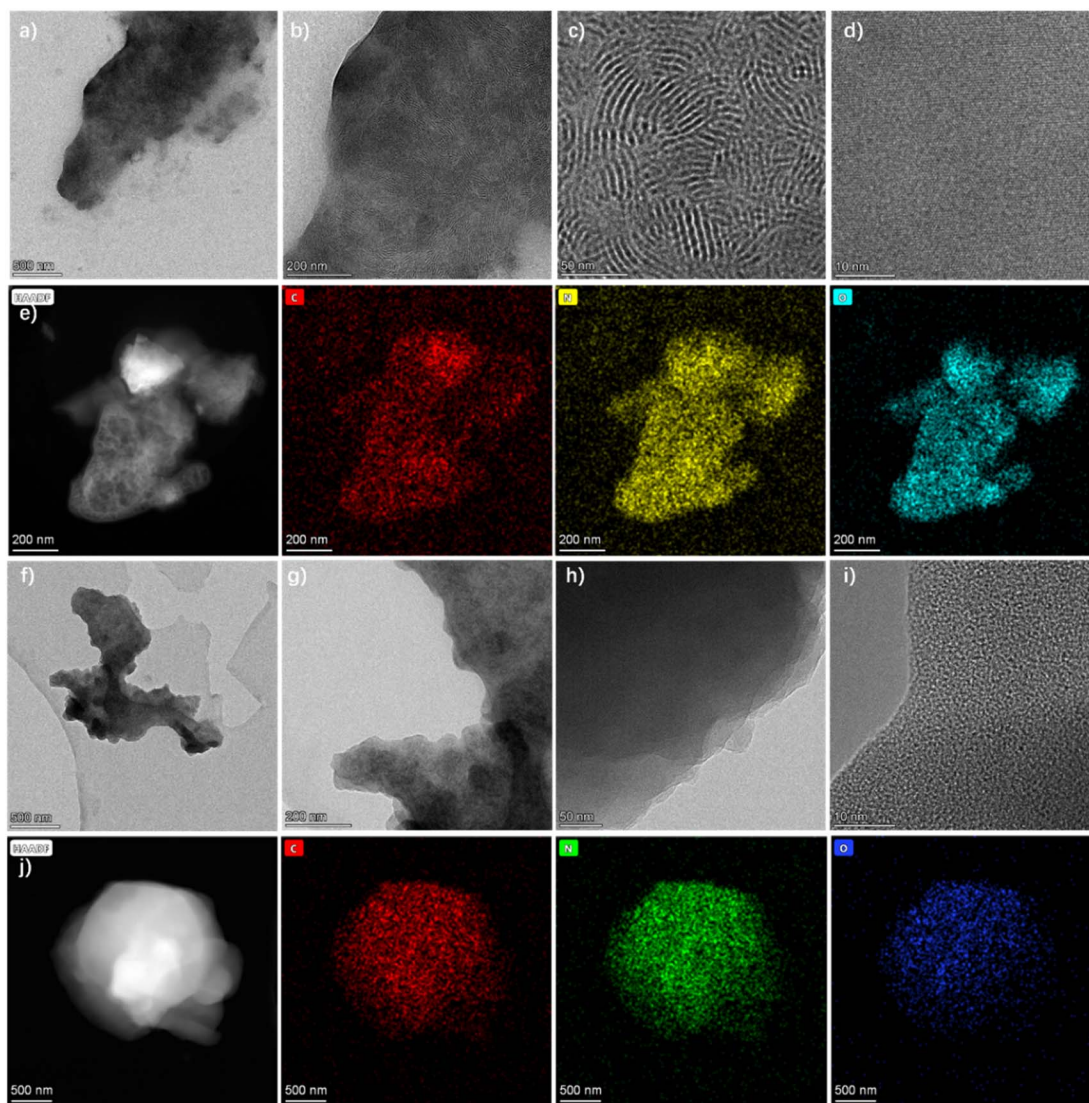


Fig. 2 Electron microscopy characterization of COPR-1 and COPR-2: (a–d) TEM of COPR-1 at different scale bars of 500, 200, 50, and 10 nm, respectively. (e) HAADF elemental mapping of COPR-1. (f–i) TEM of COPR-2 at different scale bars of 500, 200, 50, and 10 nm, respectively. (j) HAADF elemental mapping of COPR-2.

2, which rapidly captured over 91% of the iodine from water within 80 min, and was faster than the COPR-1 (85%) and β -CD (74%) samples. All these results revealed that the threading of high-polarity CDs was effective in altering the material properties. Additionally, the efficiency of the COPRs in capturing radioactive iodine was comparable to previously reported efficiencies for various absorbents.^{33,34}

The capacity of the two as-synthesized adsorbents to capture iodine in hexane was evaluated *via* recording the change in the UV-visible absorption over time. The iodine solution (500 mg L^{-1}) was prepared *via* dissolving 3 mg of iodine in 3 mL of hexane solution. As the adsorption time progressed, the color of the hexane solution containing iodine gradually faded (Fig. S2†). Notably, the COPRs exhibited rapid adsorption of iodine within the first 20 h, ultimately reaching adsorption equilibrium after 60 h (Fig. S3†). Both COPRs showcased remarkable capabilities for trapping iodine in *n*-hexane, which

approached 400 mg g^{-1} for COPR-1 and COPR-2, simultaneously.

Then, the recyclability of COPR-1 and COPR-2 was also investigated in detail. The results, illustrated in Fig. S4,† demonstrated that after undergoing three adsorption–elution cycles, both adsorbents exhibited remarkable regenerability, with only a minimal decrease in their adsorption capacities. This finding suggested that these specially designed adsorbents featured excellent recyclability, and were suitable for repeated use. Additionally, the desorption process of both adsorbents in methanol were evaluated (Fig. S5†). The corresponding results indicated that both adsorbents were capable of effectively eluting the adsorbed iodine into a methanol solution within 60 min.

Subsequently, X-ray photoelectron spectroscopy (XPS) was conducted to estimate the capacity to adsorb iodine by the as-synthesized COPRs. As shown in Fig. 4a and c, characteristic



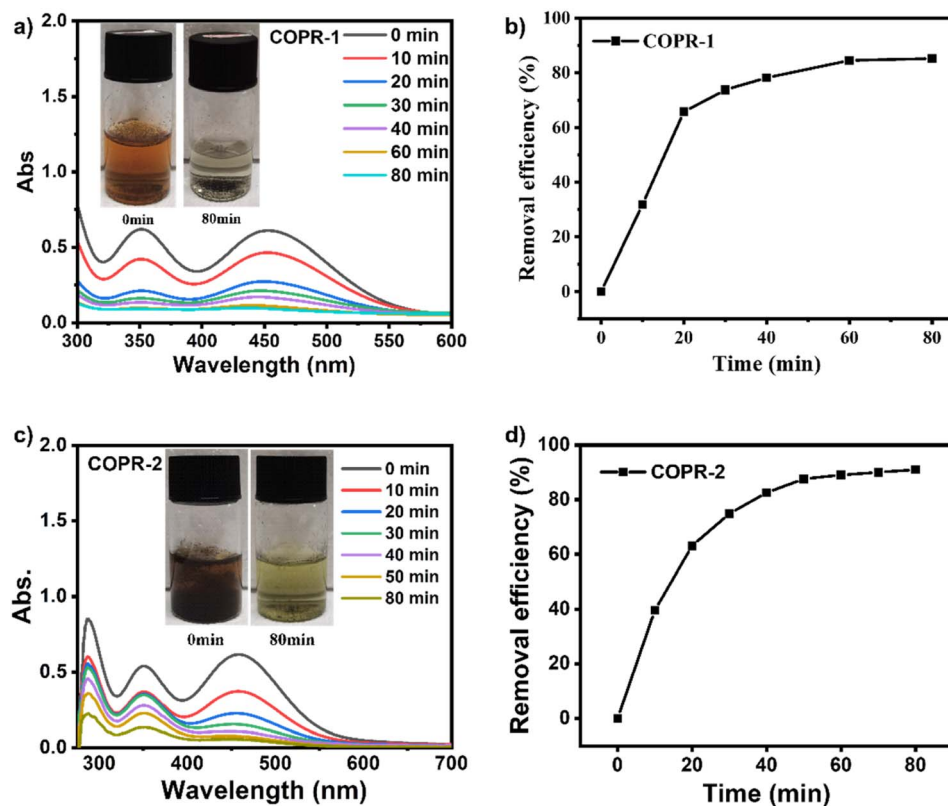


Fig. 3 (a) UV-vis spectra of aqueous iodine solutions before and after the addition of COPR-1. (b) The removal efficiency for COPR-1. (c) UV-vis spectra of aqueous iodine solutions before and after the addition of COPR-2. (d) The removal efficiency for COPR-2.

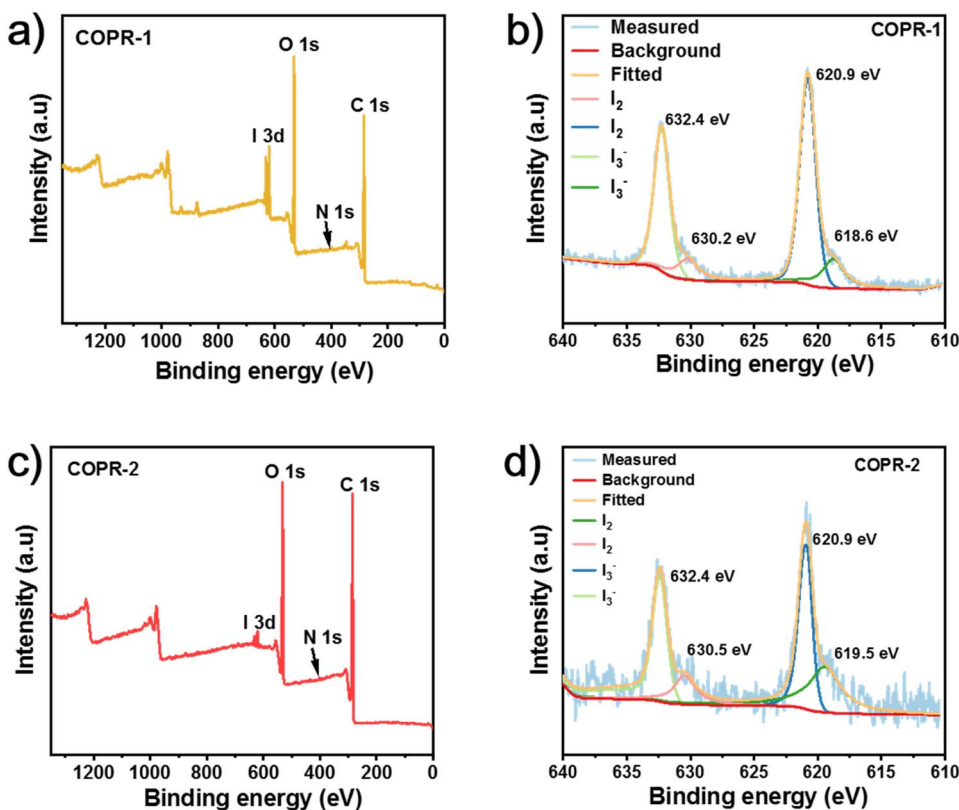


Fig. 4 (a) XPS survey spectra of COPR-1 after iodine adsorption. (b) XPS I3d spectra of COPR-1 after iodine adsorption. (c) XPS survey spectra of COPR-2 after iodine adsorption. (d) XPS I3d spectra of COPR-2 after iodine adsorption.

signals belonging to I3d were clearly detected from the XPS survey spectrum of COPR-1 and COPR-2, concurrently, demonstrating the capture of iodine from water. The high resolution I3d spectra of COPR-1 (Fig. 4b) and COPR-2 (Fig. 4d) showed obvious I3d3/2 and I3d5/2 splitting peaks located at approximately 632.4 and 620.9 eV, respectively, which revealed that the iodine dissolved in the aqueous solution was strongly adsorbed on the polyrotaxane skeleton.³⁵ Furthermore, the binding energy belonging to I_3^- (619.4 and 630.1 eV) and I_2 (620.6 and 632.1 eV) was also clearly detected, concurrently.³⁶ All our data revealed that the iodine absorbed in the as-synthesized COPRs was mainly in the form of polyiodide anions and iodine monomers, which demonstrated a hybrid iodine capture process for COPR-1 and COPR-2 dominated by physical and chemical adsorption.

Conclusion

A novel but facile strategy for the concurrent design and synthesis of COPRs with brand new structures and functions was realized by the rational integration of CD-based pseudorotaxane moieties into a COF backbone. COPRs were prepared *via* a stepwise Schiff base reaction through the integration of mechanical grinding and solvothermal synthesis. Compared with traditional methods, this strategy not only enables the scalable preparation of polyrotaxanes with controllable structure and function, but it also presents a highly effective procedure for controlling the polarity of a porous skeleton for specific applications. This work bridges the field between mechanically interlocked CDs and polymeric materials, and provides a protocol for the low-cost preparation of polyrotaxanes with targeted functions.

Data availability

The authors declare that all the experimental data are available.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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