

Earth and Environmental Sciences

Special Topic: Nuclear Environment Advances

One step synthesis of nitrogen-rich covalent organic frameworks with flexible secondary amine bonds for efficient iodide capture in aqueous solutions

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Abstract: As the radioactive iodine possessed volatility and diffusibility, it needed to be properly disposed in order to prevent environmental and health risks. Recently, nitrogen-rich covalent organic frameworks (COFs) were found to have high iodine adsorption capacity, but the unstable linkages limited their application. In this work, we synthesized an amine-linked COFs with nitrogen-rich melamine unit named TABN-COF. TABN-COF exhibited a strong affinity for iodine, with an adsorption capacity of up to 365 mg/g for I_3^- in aqueous phase. The ultra-strong stability of TABN-COF enabled it to maintain its crystallinity structure even after treatment with acids, bases, simulated seawater, reducing agents, and oxidizing agents, without compromising the removal rate of I_3^- . These characteristics made TABN-COF promising for the adsorption of I_3^- in complex marine systems.

Keywords: covalent organic frameworks, melamine, amine-linked, iodine adsorption, marine system

INTRODUCTION

Radioactive iodine is one of the most important radioactive pollutants, with common isotopes including ^{129}I and ^{131}I [1,2]. The former possesses a long half-life (1.57×10^7 years), thereby potentially posing a persistent environmental threat [3]. The latter one is a short-lived iodine isotope, which shows high specific activity and good biocompatibility, and easily induces diseases such as thyroid cancer [4,5]. Considering the volatility and diffusibility of iodine, the radioactive iodine needs to be properly disposed in order to prevent environmental and health risks [6,7]. Radioactive iodine, often produced in nuclear waste disposal or accidents, can easily contaminate marine environments due to the proximity of many nuclear power plants to the coast [8]. Solid phase extraction is one of the methods to remove radioactive iodine from water. The marine environment poses a unique challenge for iodine adsorption due to its high salinity, the presence of competing ions, and biological contaminants [9]. Consequently, developing effective adsorbents capable of removing iodine in such complicated environments poses considerable challenges.

Covalent organic frameworks (COFs) are a new class of crystalline organic porous materials, which were

first reported and successfully synthesized by Yaghi in 2005 [10]. With the advancement of research, COFs are attracting widespread attention because the demonstrated exceptional performance and broad prospects in gas separation [11,12], energy storage [13], ion exchange [14], catalysis [15,16], and adsorption [17,18]. As for iodine adsorption, COFs possess unique advantages such as large specific surface area, stable properties, adjustable structure, easy introduction of functional groups [19]. Nitrogen-rich COFs demonstrate excellent performance in iodine adsorption due to their abundance of adsorption sites. For example, Han *et al.* synthesized two structurally similar COFs, namely COF-TAPT and COF-TAPB, in 2022 [20]. These materials were employed for the adsorption of I_2 and CH_3I , revealing that the more nitrogen sites in COF-TAPT played a crucial role in enhancing iodine adsorption performance. In a separate study, Ma *et al.* in 2018 presented a series of nitrogen-rich flexible COFs featuring numerous nitrogen atoms and electron-rich π -conjugated systems, thereby bolstering iodine affinity and offering enhanced adsorption sites [21]. Notably, TPT-BD COF within this series exhibited an impressive iodine uptake capacity of up to 5.43 g/g. Another example is the SCU-COF-2 synthesized by Wang *et al.* in 2021, using the nitrogen-rich monomer 2,2'-bipyridine-5,5'-dicarboxaldehyde [22]. The incorporation of phenyl groups facilitated an electron-rich aromatic framework, while bipyridine units provided nitrogen-rich sites, collectively enhancing the iodine adsorption capacity of SCU-COF-2 to a maximum of 6.0 g/g in the gaseous phase. Melamine is an important nitrogen-rich building blocks with a certain affinity for iodine. So far, it has been reported that polymers containing melamine structural units were designed to absorb iodine. For instance, a polymer with melamine units named H_COF-1 were synthesized through thiol-yne click reaction from hydrogen-bonded single crystals, which could adsorb iodine and I_3^- in water, methanol and cyclohexane [23]. Notably, the iodine adsorption capacity of H_COF-1 in the water phase can reach 2.1 g/g, only slightly lower than the adsorption capacity under gaseous conditions, showcasing its excellent potential for treating iodine-contaminated water. However, due to the low reactivity of melamine, the synthesis of melamine-based COFs remains challenging, with only a limited number of publications on melamine COFs [24–26], such as the TpTt reported by Banerjee *et al.* in 2019, which was synthesized from melamine and 2,4,6-triformylphloroglucinol for heterogeneous photocatalysis [27]. Moreover, the application of melamine-based frameworks in iodine removal is still unclear; further investigation to the iodine removal performance of this class of nitrogen-rich materials is necessary. On the other hand, in the realm of radioactive iodine removal, the complexity of the environment necessitates a high degree of stability in the adsorbent material [28]. However, existing COFs linkages such as boron-oxygen and imine bonds have poor stability and are prone to decomposition under harsh adsorption conditions, which limits the adsorption performance of the material [29]. In contrast, amine-linked COFs consistently demonstrate impressive stability characteristics, exemplified by the rPI-3-COF synthesized through the Leuckart-Wallach reduction reaction reported by Lotsch *et al.* in 2021 [30]. Compared to imine-linked PI-3-COF, this material exhibited enhanced hydrolytic stability. Since the poor reversibility of amine-linkage, currently reported amine-linked COFs are obtained through the reduction of imine bonds or synthesized by using some specific monomers (Figure 1) [31]. For example, Chen *et al.* synthesized an aromatic amine-linked COF using a special monomer dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (DMSS), which could condense to form aromatic secondary amine bond with amine monomer under the catalysis of p-toluenesulfonic acid [32]. But none of these methods can be used to synthesize amine-linked COFs containing melamine units, as melamine has low reactivity and is difficult to directly react to form well-crystallized imine-linked COFs. In addition, the reduction reaction may also have certain

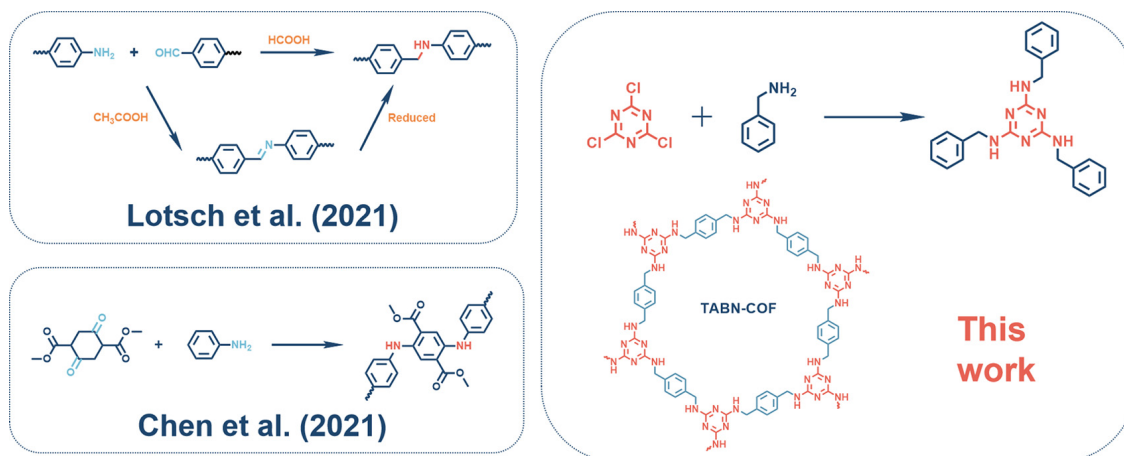


Figure 1 Current methods for the synthesis of amine-linked COFs and the method used in this paper for synthesizing melamine-based COFs containing amine linkage.

effects on the material structure and crystallinity. To conveniently obtain amine-linked COFs containing melamine units, it might be necessary to introduce new monomers and novel reactions.

Herein, cyanuric chloride and p-xylylenediamine were selected to form an amine-linked COFs named TABN-COF with melamine unit. The presence of melamine structure and amine linkage in the framework collectively created a nitrogen-rich environment, enhancing the affinity for iodine and demonstrating significant potential for iodine removal from seawater. TABN-COF exhibited exceptional stability, maintaining its crystallinity structure even after being soaked in high concentrations of acids, bases, and simulated seawater for an extended period of five days. When applied to aqueous phase iodine adsorption, the I_3^- adsorption capacity of TABN-COF could achieve up to 365 mg/g. Moreover, it retained sustained high removal rates even in the presence of competing ions, simulated seawater, as well as acid, base and redox agents, indicating the remarkable potential of this novel adsorbent for iodine removal application in seawater.

RESULTS AND DISCUSSION

Synthesis and structural analysis

The model compound TABN was synthesized and analyzed by ^1H nuclear magnetic resonance (NMR) spectroscopy [33]. The characteristic peaks of hydrogen atoms at benzyl and aromatic rings were identified, which corresponded to literature. This observation suggests that cyanuric chloride can react with benzylamine structure within the realm of small molecules to yield an amine-linked compound. The successful realization of this reaction has laid the foundation for the synthesis of COF.

Amine-linked TABN-COF was synthesized in one pot using cyanuric chloride and p-xylylenediamine as monomers with acetonitrile as the solvent and N,N-diisopropylethylamine as the catalyst. The structure and chemical composition of TABN-COF was analyzed by Fourier transform infrared spectroscopy (FT-IR), ^{13}C solid-state nuclear magnetic resonance spectroscopy (^{13}C ssNMR), X-ray photoelectron spectroscopy (XPS). In the FT-IR spectra of TABN-COF and monomers (Figure 2a), the C–Cl peak at 850 cm^{-1} from cyanuric chloride and the N–H stretching vibration peak around 3300 cm^{-1} from p-xylylenediamine disappeared in the

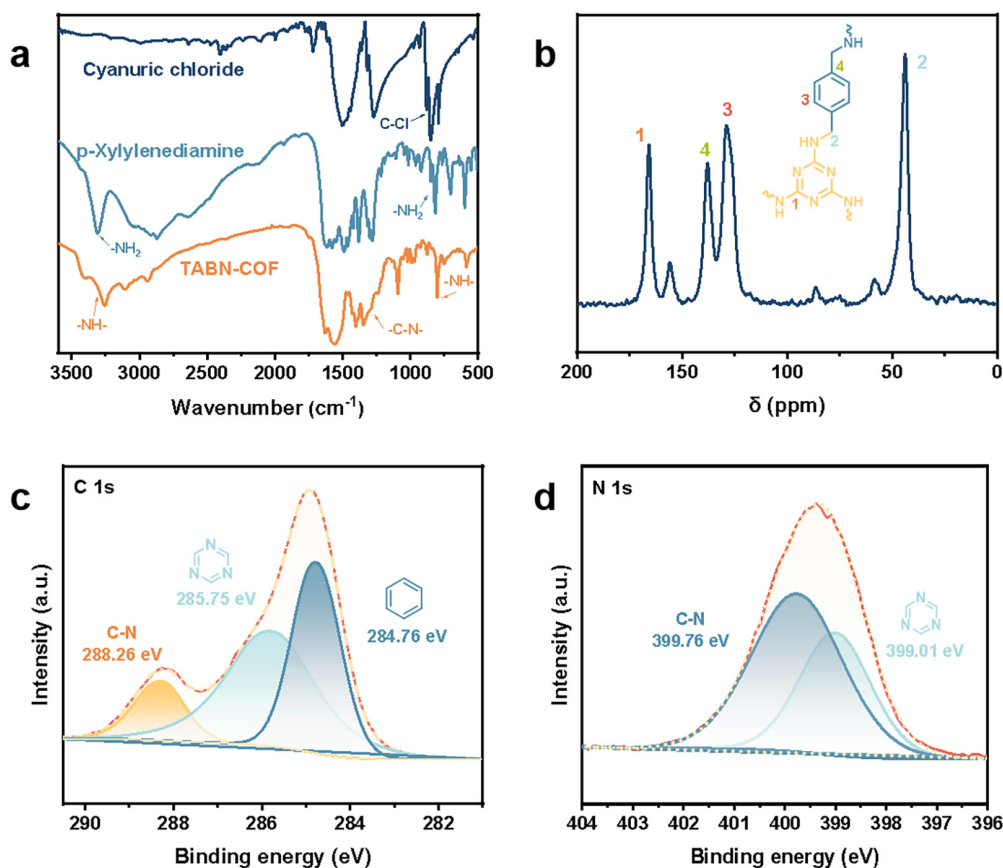


Figure 2 (a) FT-IR spectra of cyanuric chloride, p-xylylenediamine, and TABN-COF; (b) ^{13}C Solid-state NMR of TABN-COF; XPS analysis of TABN-COF, including (c) C 1s spectrum and (d) N 1s spectrum.

TABN-COF, while the -N-H- characteristic peak of secondary amine around 3250 cm^{-1} and the C-N stretching vibration peak emerged around 1230 cm^{-1} appeared, indicating the successful synthesis of TABN-COF. The ^{13}C ssNMR spectrum (Figure 2b) further confirmed the successful synthesis of TABN-COF. The peak around 43 ppm corresponded to the carbon atoms in the amine linkage of TABN-COF, indicating the successful formation of the amine bonds, while peaks around 128 ppm and 137 ppm corresponded to the two types of carbon atoms in the benzene rings, and the peak at 165 ppm corresponded to the carbon atoms in the triazine ring. In addition, characterization of the material was also performed by XPS (Figure 2c, d, Figure S1). The C 1s spectrum showed the binding energy at 288.26 eV, 285.75 eV and 284.76 eV were attributed to C-N, triazine and benzene ring, respectively [34]. Correspondingly, the binding energy at 399.76 eV was attributed to C-N, while the peak at 399.01 eV was for the triazine rings, in the N 1s spectrum.

The spectroscopic experimental results mentioned above essentially confirmed that the polymerization reaction based on cyanuric chloride and p-xylylenediamine monomers can generate a two-dimensional framework layer (Figure 3a). To further investigate the stacking structure between the layers, powder X-ray diffraction (PXRD) was used to investigate the crystal structure of TABN-COF. In the PXRD pattern (Figure 3b), the diffraction peak at 8.6° for TABN-COF indicates its crystallinity. The structure of TABN-COF was simulated and refined in Materials Studio, which corresponded well with the ABC stacking simulation

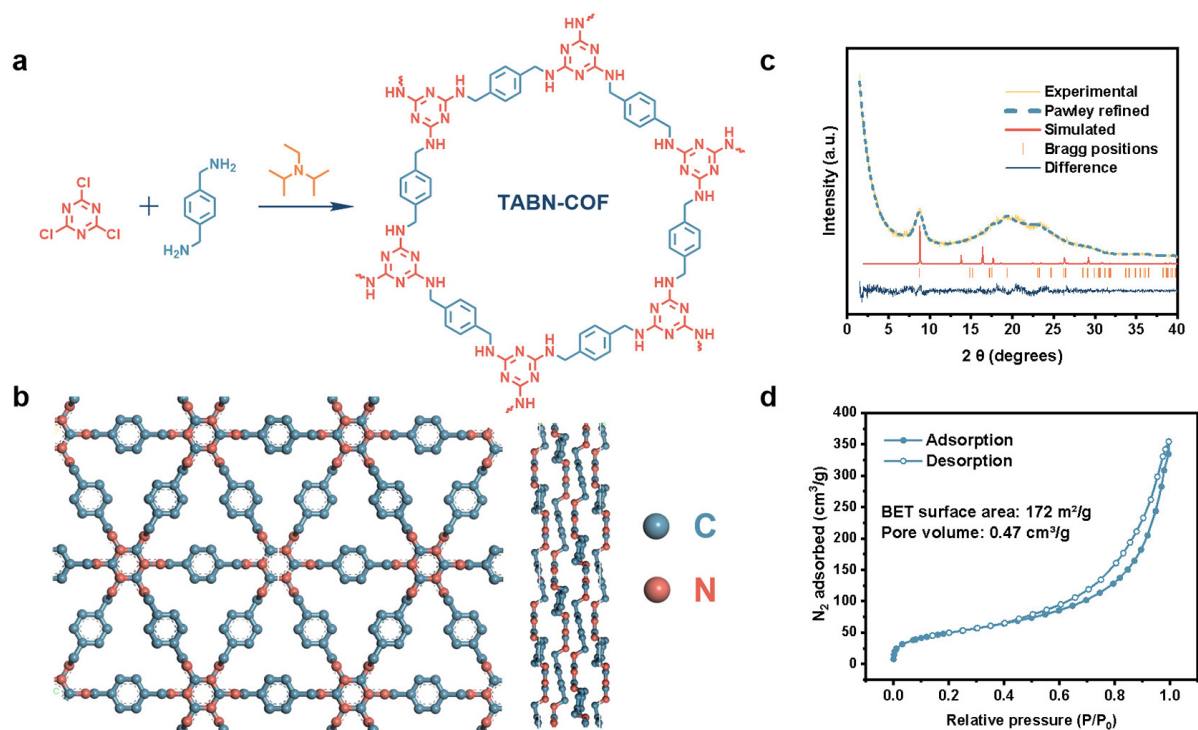


Figure 3 (a) The synthetic pathway; (b) the PXRD pattern and its simulation; (c) the simulation structure given by Materials Studio; (d) the nitrogen adsorption-desorption isotherm curve of TABN-COF.

(Figure 3c, and Figures S2, S3 for the AA and AB stacking simulation). The refined parameters for the unit cell were determined as $a = b = 20.07 \text{ \AA}$, $c = 6.91 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. Pawley refinements were made with low residuals ($R_p = 5.84 \%$, $R_{wp} = 7.55 \%$), indicating consistency between TABN-COF and the simulation structure. Nitrogen adsorption and desorption tests were performed at 77 K. As shown in Figure 3d, the calculated Brunauer-Emmett-Teller (BET) surface area was approximately $172 \text{ m}^2/\text{g}$, with a pore volume of about $0.47 \text{ cm}^3/\text{g}$, indicating significant porosity characteristics. The morphology of TABN-COF was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). TABN-COF showed spheroidal and flower-like structures stacked with smaller sheet-like structures in SEM results (Figure 4a, b and Figures S9, S10). As shown in TEM images (Figure 4c, d), the material exhibited layered, small flaky structures, consistent with the SEM observations.

A comprehensive series of tests were conducted to assess the stability of TABN-COF. Firstly, the thermal stability of the framework was examined through thermogravimetric analysis (TGA), as shown in Figure 5a. The results indicated that the TABN-COF could retain 70% of its mass even subjected to high temperatures up to 400°C , demonstrating its good thermal stability. Subsequently, the acid-base and salt stability of TABN-COF were thoroughly investigated. Specifically, 5 mg of TABN-COF was soaked in 2 mL of different concentrations of acids, bases, and simulated seawater for 5 days. Upon subsequent cleaning, filtration, and drying processes, no significant mass loss was observed. The FT-IR and PXRD analyses (Figure 5b, c and Figure S4) also showed that the structure and crystallinity of TABN-COF did not change, indicating that TABN-COF possessed high acid-base resistance and could remain stable in real environments like marine environments. Meanwhile, to investigate the stability of the material under extreme conditions, the TABN-

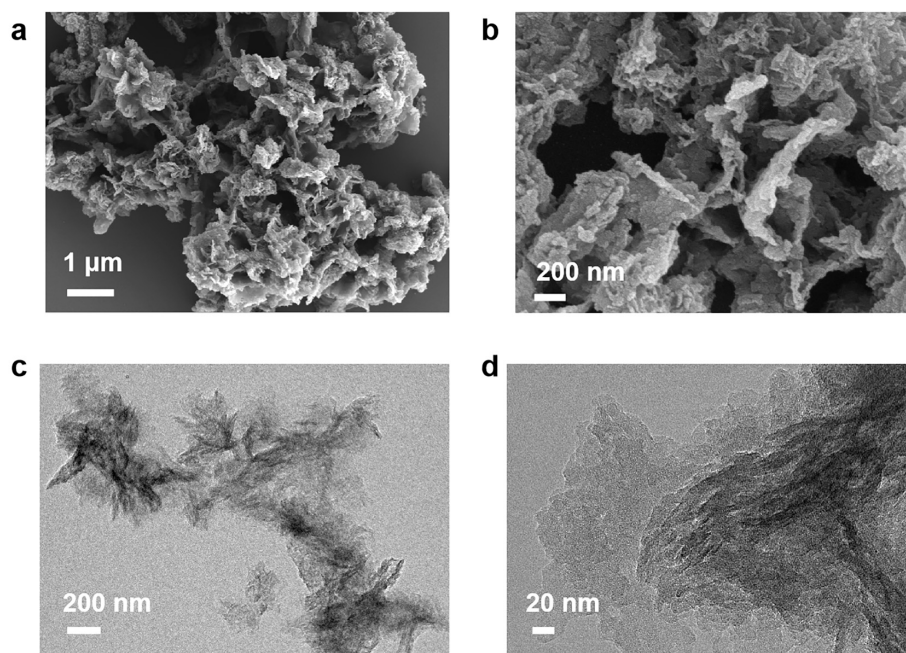


Figure 4 SEM images in (a) and (b), and TEM images in (c) and (d) for TABN-COF.

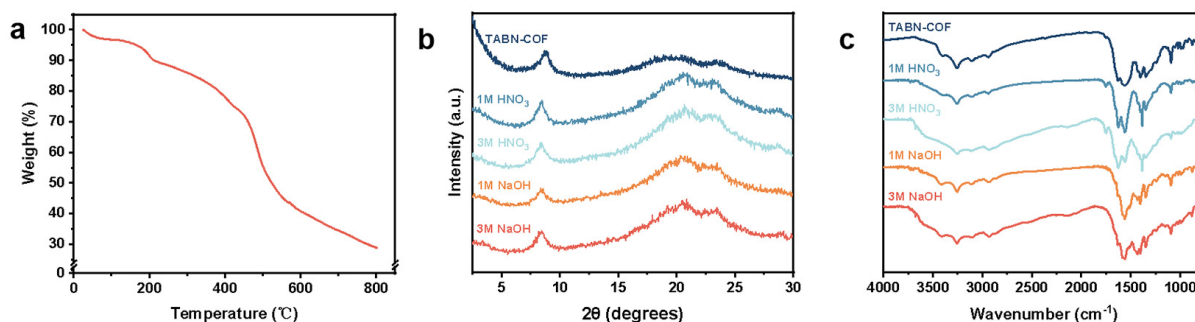


Figure 5 (a) The TGA curve of the TABN-COF from 25 to 800 °C; (b) the PXRD patterns and (c) the FT-IR spectra of TABN-COF after being immersed in acids and bases for 5 days.

COF was immersed in solutions containing both a reducing agent (Na_2SO_3) and an oxidizing agent (H_2O_2). Analysis of the FT-IR and PXRD patterns (Figure S4) of the treated samples revealed no significant alterations, thus reaffirming the exceptional stability of TABN-COF even in the face of harsh chemical environments.

I_3^- adsorption performance

Adsorption kinetics of I_3^-

The adsorption kinetics of the TABN-COF towards I_3^- was initially investigated. As shown in Figure 6a, TABN-COF reached the adsorption equilibrium after approximately one hour. To further analyze the adsorption behavior of TABN-COF for I_3^- , the adsorption data was fitted by pseudo-first-order and pseudo-

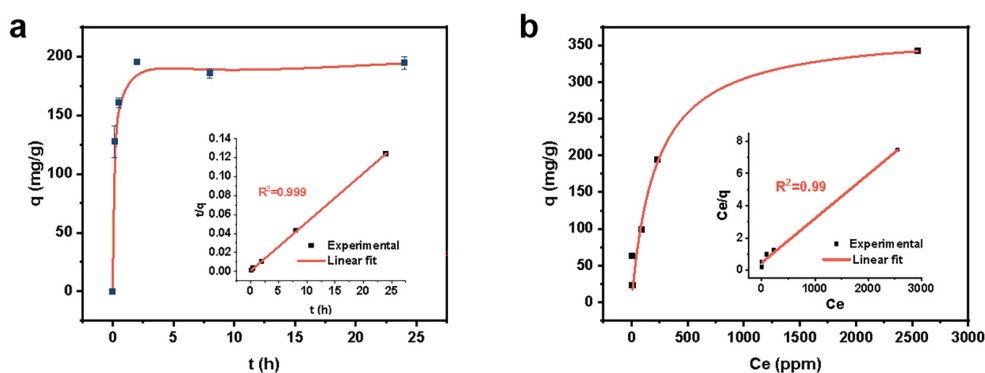


Figure 6 (a) The adsorption kinetics of I_3^- by TABN-COF and the pseudo-second-order linear fitting (25 °C, $C_0 = 600$ ppm, $m = 10$ mg, $V = 5$ mL); (b) the adsorption isotherm of I_3^- by TABN-COF and the Langmuir linear fitting (25 °C, $C_0 = 57, 137, 293, 624, 1637, 2017, 3235$ ppm, $m = 10$ mg, $V = 5$ mL).

second-order adsorption kinetics models. It was observed that the simulation results of the pseudo-second-order adsorption kinetics (Figure S5 and Table S1) were more favorable ($R^2 = 0.999$), indicating that the adsorption of I_3^- by TABN-COF was predominantly chemical adsorption [35].

Adsorption isotherm study

To determine the I_3^- adsorption capacity of TABN-COF, a series of adsorption experiments using different concentration of I_3^- solution were conducted at room temperature (25 °C). As shown in Figure 6b and Table S2, the experimental adsorption data fitted well with the Langmuir model, with a commendable linear fitting $R^2 > 0.99$. Calculations revealed that the TABN-COF could achieve a maximum I_3^- adsorption capacity of up to 365 mg/g. Additionally, within the range of I_3^- solution concentrations from 100 to 250 ppm, the removal rate of the system had exceeded 90%, indicating that the TABN-COF possessed considerable adsorption capacity and could effectively remove I_3^- from aqueous phases.

pH and competitive ions study

The variation in pH value can potentially affect the removal rate of sorbents. To evaluate the impact of different pH values on the adsorption performance of TABN-COF, a series of I_3^- solutions with pH ranging from 5 to 9 were prepared. As shown in Figure 7a, TABN-COF consistently maintained a removal rate of approximately 95% within the pH range of 5 to 9, indicating minimal influence of pH on the adsorption performance of TABN-COF. This suggested a robust performance of TABN-COF with high removal rates maintained under diverse pH conditions. To further explore whether the removal rate of TABN-COF would be affected in the presence of competitive ions, I_3^- solutions with a concentration ratio of competitive ions to I_3^- of 10:1 and an I_3^- solution in simulated seawater were prepared for adsorption (Figure 7b and Figure S8). Remarkably, it was observed that removal rate of TABN-COF remained around 95% in these different solutions, demonstrating the resistance of TABN-COF to interference from competitive ions. Additionally, the high removal rate in simulated seawater also highlighted its potential for practical applications in real-world environments.

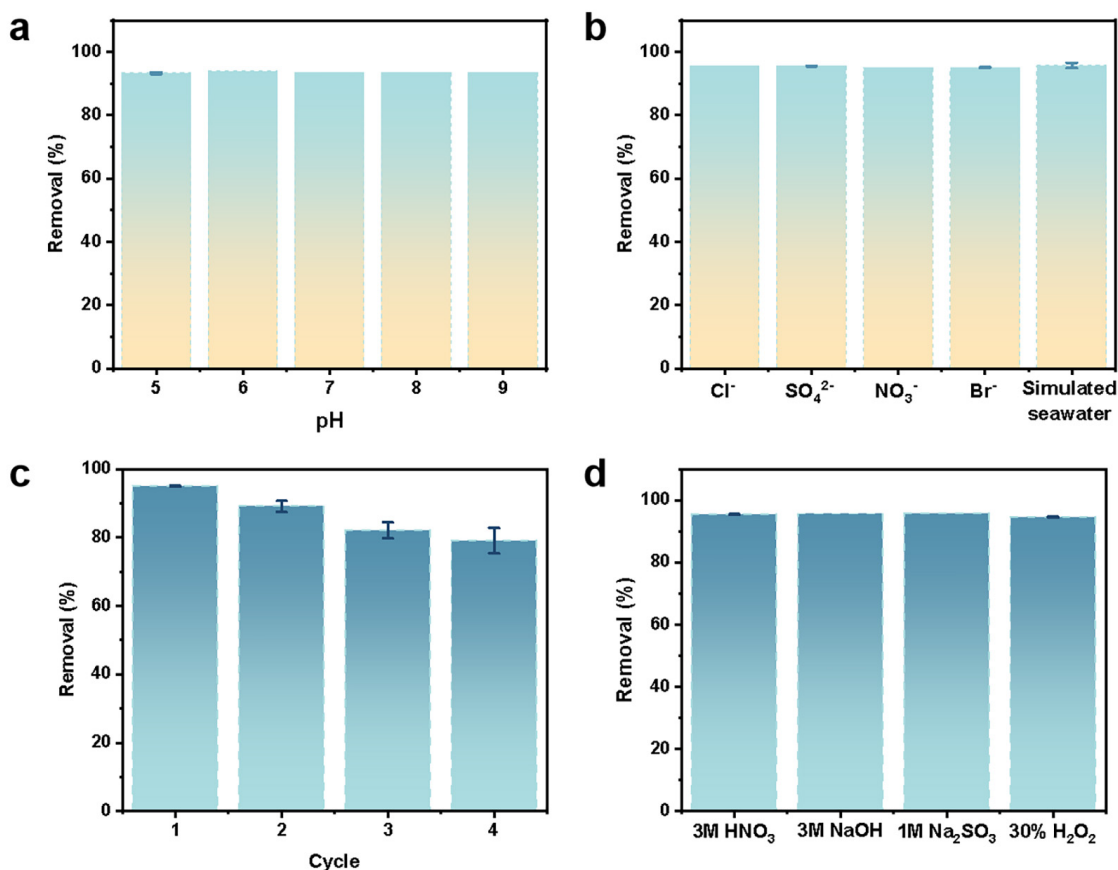


Figure 7 The removal rate of TABN-COF in (a) pH range 5–9 (25 °C, $C_0 = 6$ mM, $m = 10$ mg, $V = 5$ mL); (b) different competitive ions and simulated seawater (25 °C, $C_0 = 0.6$ mM, $C_{\text{competitive}} = 6$ mM, $m = 10$ mg, $V = 5$ mL); (c) recycle tests (25 °C, $C_0 = 6$ mM, $m = 10$ mg, $V = 5$ mL) and (d) removal rate of I_3^- by TABN-COF after treatment with acids, base, oxidant and reductant (25 °C, $C_0 = 6$ mM, $m = 10$ mg, $V = 5$ mL).

Recycle tests of TABN-COF

To investigate the reusable performance of TABN-COF, the I_3^- -adsorbed TABN-COF (named $\text{I}_3^-@$ TABN-COF) were desorbed by ethanol and DMF, and then added into I_3^- solution again for adsorption. The color of the material changed from pale yellow to dark yellow after adsorption, and it returned to its original pale yellow after being washed with ethanol and DMF for desorption, indicating a relatively thorough desorption (Figure S6). The results of the recycle experiments were shown in Figure 7c, revealing a notable initial removal rate of 90% after the first cycle, which remained consistently high at around 80% even after four cycles, underscoring the stable cyclic performance of TABN-COF.

Moreover, due to its high stability, TABN-COF maintained its crystallinity even when subjected to treatments with acids, bases, and oxidant or reductant. To verify whether the removal performance of TABN-COF was retained, adsorption experiments were conducted subsequent to subjecting TABN-COF in 3 M HNO_3 , 3 M NaOH , 30% H_2O_2 , and 1 M Na_2SO_3 solutions for 8 hours. Following washing and drying, the observed removal rate of I_3^- remained consistently high, indicating the potential of TABN-COF for application in challenging harsh environments (Figure 7d).

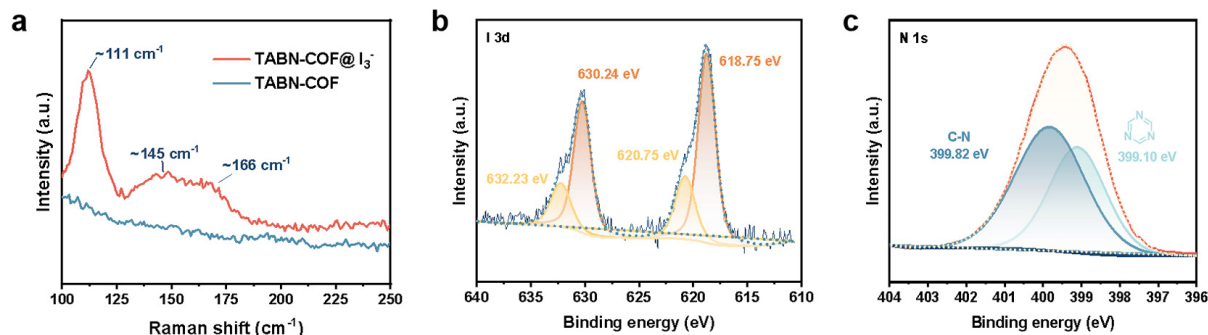


Figure 8 (a) The Raman spectra of TABN-COF and I₃⁻@TABN-COF; (b) the I 3d spectrum of I₃⁻@TABN-COF; (c) the N 1s spectra of I₃⁻@TABN-COF.

Adsorption mechanism of I₃⁻

The species and active sites of iodine in the I₃⁻@TABN-COF were characterized using Raman spectroscopy and XPS. Initially, Raman spectroscopy was employed to analyze the iodine species within the I₃⁻@TABN-COF, as shown in the Figure 8a, three characteristic peaks at 111 cm⁻¹, 145 cm⁻¹, and 167 cm⁻¹ appeared in I₃⁻@TABN-COF, with the first two corresponding to the symmetric and asymmetric stretching vibrations of I₃⁻, respectively, and the peak at 167 cm⁻¹ associated with the stretching vibration of I₅⁻ [36,37]. The presence of these peaks indicated that after adsorption, some I₃⁻ may have undergone charge exchange, leading to the formation of I₅⁻ [38]. This hypothesis was further confirmed by XPS analysis. As shown in the Figure 8b and Figure S7, the XPS total spectrum of the I₃⁻@TABN-COF exhibited an I 3d peak, which, upon deconvolution, resolved into two sets of peaks at 630.24 eV and 618.75 eV, and 632.23 eV and 620.75 eV, corresponding to I₃⁻ and I₅⁻, respectively [39]. Further examination of the N 1s spectra revealed that the C–N and triazine peak of I₃⁻@TABN-COF shifted relative to that of TABN-COF after iodine adsorption (Figure 8c), suggesting an interaction between the nitrogen atoms in the material and iodine species.

In order to further explore the interaction sites between TABN-COF and I₃⁻, we carried out a calculation using density functional theory (DFT). Through electrostatic potential distribution (ESP) analysis, we found the TABN-COF fragment showed an opposite charge to I₃⁻ (Figure 9a, b) [40]. The positive charged areas were mainly around the melamine units and the amine linkage. This finding suggested that the I₃⁻ may be effectively adsorbed at active sites near the amine linkages through electrostatic interactions. Additionally, we calculated the binding energy between TABN-COF and I₃⁻ (Figure 9c). The results showed that the binding energy of I₃⁻ to TABN-COF is −5.23 kcal/mol, indicating a strong binding capability of TABN-COF towards I₃⁻.

CONCLUSIONS

In summary, we have successfully synthesized an amine-linked COF with melamine units, which named TABN-COF, through a one-pot reaction with cyanuric chloride and p-xylylenediamine. The amine linkages in TABN-COF endowed it with exceptional stability, maintaining its crystallinity even after treatment with acids, bases, reducing agents, and oxidizing agents. Simultaneously, the melamine units and amine bonds in

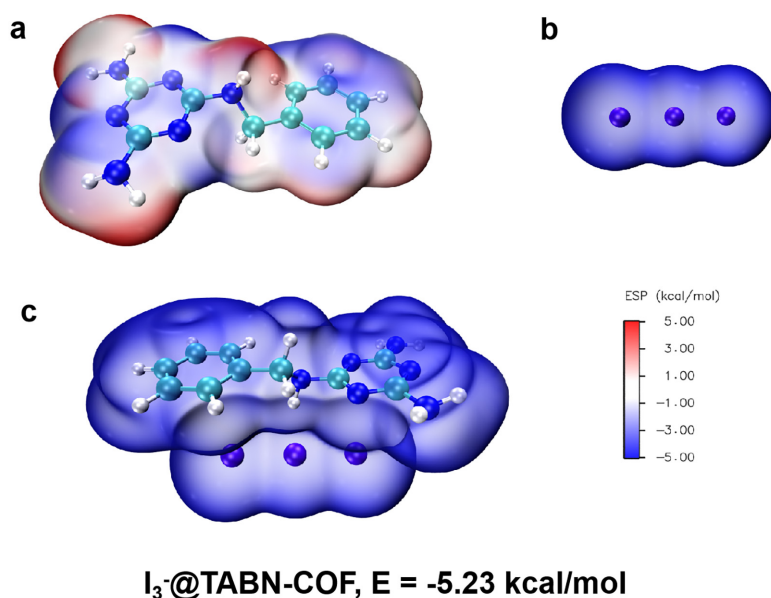


Figure 9 Electrostatic potential (ESP) distributions of (a) TABN-COF and (b) I_3^- ; (c) the ESP and binding energy of I_3^- @TABN-COF.

TABN-COF together formed a nitrogen-rich framework that exhibits strong affinity for I_3^- . The TABN-COF achieved the highest I_3^- adsorption capacity of up to 365 mg/g in aqueous phase, with the best removal rate reaching 96%. Due to the outstanding stability of TABN-COF, it could still maintain approximately 95% high I_3^- removal rate under various solution environments, including varying pH levels, exposure to different competitive ions, and simulated seawater. Furthermore, even under extreme conditions such as exposure to 3 M HNO_3 , 3 M $NaOH$, 1 M Na_2SO_3 , and 30% H_2O_2 , TABN-COF displayed sustained performance. Additionally, TABN-COF showed good cyclic performance, retaining 79% of its removal rate after four cycles. The high stability, high removal rate, and good cyclic performance of TABN-COF suggested its potential for removing I_3^- in real environments, with broad application prospects in marine systems.

MATERIALS AND METHODS

Materials

All the reagents used in this study were of analytical grade and did not undergo further purification. Cyanuric chloride, benzylamine, N,N-diisopropylethylamine, potassium iodide and iodine were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tetrahydrofuran (THF), methanol, ethanol and N,N-dimethylformamide (DMF) were purchased from Chengdu Changlian Chemical Reagent Co., Ltd. P-xylylenediamine was purchased from Rhawn Reagent.

Synthesis of model compound TABN

Cyanuric chloride (18.4 mg, 0.1 mmol) and benzylamine (64.3 mg, 0.6 mmol) were mixed in 5 mL THF and refluxed for 8 h. After removing organic solvent in vacuo, the residue was washed by $KHSO_4$ (1 M, 10 mL),

water (10 mL), 5% NaHCO₃ (10 mL) and brine. Following evaporation to eliminate any remaining organic solvents, the resulting product was dried overnight in a vacuum oven at 60 °C. ¹H NMR (d6-DMSO, δ) 4.42 (m, 6H), 7.25 (m, 15H); ¹³C NMR (d6-DMSO, δ) 44.1, 127.2, 127.8, 128.7, 139.8, 165.9.

Synthesis of TABN-COF

Cyanuric chloride (36.9 mg, 0.2 mmol) and p-xylylenediamine (40.9 mg, 0.3 mmol) were uniformly dispersed in 3 mL acetonitrile. After that, 415 μL N,N-diisopropylethylamine was added and then the reaction was protected by nitrogen gas. The reaction mixture was then heated at 80 °C for 3 days, subsequently cooled down to room temperature, and subjected to washing with appropriate amount of ethanol, methanol and DMF for 2–3 cycles. TABN-COF was collected by filtration, followed by drying in vacuum at 60 °C for 12 h to obtain pale yellow solid.

Adsorption of I₃[−]

The I₃[−] solution was freshly prepared according to a published literature [1,3]. After that, 10 mg TABN-COF was added into 5 mL I₃[−] solution, then the mixture was stirred for 24 h. The I₃[−] concentration before and after adsorption was determined by UV-Vis spectrophotometry.

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Author contributions

L.M. and Y.L. conceived the idea. H.L. optimized the synthesis condition of materials and carried out the structure simulation. Z.H., H.L. and M.W. synthesized the materials. Z.H. did iodine adsorption experiments and wrote the manuscript. J.Z. carried out the DFT calculation.

Conflict of interest

The authors declare no conflict of interest.

Supplementary information

The supporting information is available online at <https://doi.org/10.1360/nso/20240023>. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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