Efficient and simultaneous capture of iodine and methyl iodide achieved by a covalent organic framework

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Radioactive molecular iodine (I\(_2\)) and organic iodides, mainly methyl iodide (CH\(_3\)I), coexist in the off-gas stream of nuclear power plants at low concentrations, whereas few adsorbents can effectively adsorb low-concentration I\(_2\) and CH\(_3\)I simultaneously. Here we demonstrate that the I\(_2\) adsorption can occur on various adsorptive sites and be promoted through intermolecular interactions. The CH\(_3\)I adsorption capacity is positively correlated with the content of strong binding sites but is unrelated to the textural properties of the adsorbent. These insights allow us to design a covalent organic framework to simultaneously capture I\(_2\) and CH\(_3\)I at low concentrations. The developed material, COF-TAPT, combines high crystallinity, a large surface area, and abundant nucleophilic groups and exhibits a record-high static CH\(_3\)I adsorption capacity (1.53 g·g\(^{-1}\) at 25 °C). In the dynamic mixed-gas adsorption with 150 ppm of I\(_2\) and 50 ppm of CH\(_3\)I, COF-TAPT presents an excellent total iodine capture capacity (1.51 g·g\(^{-1}\)), surpassing various benchmark adsorbents. This work deepens the understanding of I\(_2\)/CH\(_3\)I adsorption mechanisms, providing guidance for the development of novel adsorbents for related applications.
Nuclear reactors have been continuously providing ~10% of the world’s energy over the last decade. As a sustainable and low-carbon energy supply, nuclear energy is expected to play a more important role in the future. However, safety concerns still challenge its operation. One of the major safety issues is the volatile radioactive waste produced during the reprocessing of spent nuclear fuels, which primarily consists of radionuclides, such as $^{129}$I and $^{131}$I in the form of molecular iodine (I$_2$) or organic iodides (e.g., methyl iodide (CH$_3$I) and ethyl iodide)\(^{6-8}\). These compounds are harmful to the environment ($^{129}$I has an extremely long half-life of approximately 1.57 x 10\(^7\) years) or severely affect human metabolism by damaging the thyroid gland, and must be removed before the off-gas is discharged\(^{9-11}\).

Compared with traditional liquid scrubbing processes to capture radioactive iodine, adsorption-based processes require a simpler operation and lower maintenance costs and avoid highly corrosive solutions\(^6\). Therefore, researchers have increasingly focused on the development of various adsorbents for iodine capture, including materials containing silver (Ag)\(^{12-14}\), ceramics\(^{13,15,16}\), zeolites\(^{17,18}\), aerogels\(^{19-21}\), metal-organic frameworks\(^{8,22-26}\) and conjugated polymers\(^{27-31}\). Most of these studies have focused on the adsorption capacity of the developed adsorbent for I$_2$, whereas only a few studies have addressed the capture of CH$_3$I, and even fewer studies have examined the simultaneous capture of I$_2$ and CH$_3$I. Given that radioactive molecular iodine and organic iodides coexist in off-gas streams, it is particularly important to develop adsorbents that can capture them simultaneously and efficiently.

Various strategies have been adopted to promote the adsorption of iodine species. For I$_2$, effective strategies include the following: (i) using adsorbents containing Ag to precipitate I$_2$ in the form of silver iodide (AgI)\(^{2,12,13}\), (ii) introducing electron-rich heteroatoms (e.g., nitrogen (N), sulfur (S), and oxygen(O)) or n-donors (e.g., double/triple bonds, benzene rings, and other aromatic compounds) in adsorbents to adsorb electron-deficient I$_2$ by forming charge-transfer complexes\(^{32-41}\), and (iii) modifying the adsorbent with ionic groups (e.g., [RN-(CH$_3$)$_3$]$^+$Br$^-$) to adsorb I$_2$ via Coulomb interactions\(^{42}\). Compared with I$_2$, CH$_3$I is more difficult to capture because of the weaker intermolecular forces\(^43\). Currently, the capture of CH$_3$I is primarily achieved either through catalytic decomposition on adsorbents containing Ag to form AgI\(^{13,34-46}\) or through an N-methylation reaction on nucleophilic N sites to form pyridinium\(^{34}\) or quaternary ammonium salts\(^{1,31,47-49}\). Based on these insights, we speculate that adsorbents containing abundant Ag sites or nucleophilic N sites may exhibit high capture capacity for both I$_2$ and CH$_3$I. Given the high cost and poor recyclability of Ag-based adsorbents, developing N-rich adsorbents is a better choice for simultaneously capturing I$_2$ and CH$_3$I.

In addition to the characteristics of adsorption sites that determine binding strength, the density of the adsorption sites and the textural properties (e.g., surface area, pore size, and pore volume) of the adsorbent are crucial because these factors collectively determine the number of accessible adsorption sites (i.e., the adsorption capacity) and adsorption kinetics. Therefore, an ideal adsorbent for simultaneously capturing I$_2$ and CH$_3$I should possess a high concentration of nucleophilic N sites along with a large surface area and a highly open porous structure.

As an emerging class of porous materials, covalent organic frameworks (COFs) provide an ideal platform for developing high-performance adsorbents because their porous structures and surface functionalities can be easily engineered to meet the requirements of specific applications\(^{50-52}\). Several COFs have been prepared as adsorbents for I$_2$ capture, in which the binding sites are π-conjugated moieties, various N-containing functional groups, and ionic groups\(^{34,35,38,42}\). Although some of these COFs exhibited high I$_2$ adsorption capacities in the measurement performed in a static closed system with high partial pressure of I$_2$, their performance for low-concentration I$_2$ capture under a dynamic condition was not measured. More importantly, like other recently developed adsorbents, the CH$_3$I adsorption properties of these COFs have not been investigated.

To the best of our knowledge, there is only one COF material (SCU-COF-2) evaluated for both I$_2$ and CH$_3$I adsorption\(^{34}\). In SCU-COF-2, there are pyridine and imine moieties, which bind to I$_2$ and CH$_3$I through charge-transfer interaction and N-methylation reactions, respectively. At room temperature, SCU-COF-2 adsorbed 0.979 g g$^{-1}$ I$_2$ from flowing N$_2$ (carrier gas) containing 400 ppm of I$_2$ or 0.564 g g$^{-1}$ of CH$_3$I from flowing N$_2$ containing 200,000 ppm of CH$_3$I. These moderately high adsorption capacities were obtained from single-component measurements, whereas the adsorption performance of SCU-COF-2 in the coexistence of I$_2$ and CH$_3$I has not been explored.

In this report, we designed and synthesized two COFs, namely COF-TAPB and COF-TAPT, for the simultaneous capture of I$_2$ and CH$_3$I. The framework of COF-TAPB was constructed through imine linkages formed between two monomers, tris(4-formylphenyl)amine (TFPA) and 1,3,5-tris(4-aminophenyl)benzene (TAPB); COF-TAPT is a structural analog of COF-TAPB, constructed from TFPA and 2,4,6-tri(4-aminophenyl)-1,3,5-triazine (TAPT) (see Fig. 1). Through a literature search, we found

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**Fig. 1 Schematic illustration of the synthesis of COF-TAPT and COF-TAPB.** In the structural model, different N sites are marked with different colors.
that these two COF materials have previously been synthesized for CO₂ adsorption and photocatalytic hydrogen evolution³³–³⁵, whereas the synthetic methods are not exactly the same as those used in this study. The two COFs exhibit the same crystal structure and textural properties, being different only in N content, allowing the investigation of the role of N in the adsorption of I₂ and CH₃I.

We evaluated the adsorption properties of the two COFs for I₂ and CH₃I under different conditions (static and dynamic adsorption at different temperatures and adsorbate concentrations) for a direct comparison with benchmark adsorbents reported in the literature. Under the static high-concentration conditions, COF-TAPB and COF-TAPT exhibited similar high I₂ adsorption capacities, and their static I₂ uptake values (7.94 and 8.61 g g⁻¹, respectively) are among the highest reported for various adsorbents. Unlike the case of I₂ adsorption, COF-TAPT exhibited a significantly higher CH₃I uptake capacity than COF-TAPB, suggesting that the N content in the adsorbent plays a vital role in CH₃I adsorption. The further systematic analysis confirmed that the CH₃I adsorption capacity is positively correlated with the N content in the adsorbent. Remarkably, COF-TAPT exhibits a record-high CH₃I adsorption capacity (1.53 g g⁻¹; static conditions at 25 °C), which can be attributed to the combined effect of its high N content (16.1 wt%) and large surface area (~2300 m² g⁻¹). In the dynamic CH₃I adsorption measurement, COF-TAPT demonstrated the highest capacity of all tested adsorbents. When used to simultaneously capture low-concentration I₂ (150 ppm) and CH₃I (50 ppm) from a carrier gas stream, COF-TAPT outperformed all tested adsorbents except an ionic COF in terms of total iodine capture. The adsorbed I₂ and CH₃I can be easily extracted by ethanol or acetone from COF-TAPT to fully restore its adsorption capacity for subsequent adsorption cycles. The density functional theory (DFT) calculations revealed that the CH₃I binding energy at different N sites in COF-TAPT follows the order imine N > triazine N > sp³ N.

Results

Characterization. Powder X-ray diffraction (PXRD) indicated that COF-TAPT and COF-TAPB are highly crystalline, both exhibiting four clearly discernible peaks before 12° (2θ) and two weak peaks at around 16° and 25° (Fig. 2a, c). We performed structural modeling based on PXRD to corroborate that the synthesized COFs have the designed structures. The results revealed that for both materials, the based on PXRD to corroborate that the synthesized COFs have the designed structures. The two COFs exhibit very similar PXRD patterns and N₂ adsorption isotherms, with the designed structure and PXRD results. The two COFs exhibit very similar PXRD patterns and N₂ adsorption isotherms, indicating that they have comparable structural and textural properties (Supplementary Table 3). High-resolution transmission electron microscopy confirmed that they both possess a hexagonal structure containing one-dimensional channels (Supplementary Fig. 1). The completion of the Schiff base reaction between TFFA and TAPT/TAPB was evidenced by the disappearances of bands at 3359 to 3428 cm⁻¹ (amine groups) and 1685 cm⁻¹ (aldehyde groups) and the synchronous appearance of the characteristic -C=N- stretching band at ~1625 cm⁻¹ in the Fourier transform infrared (FTIR) spectra (Fig. 2f). The successful construction of the designed COF frameworks and the presence of different N species in the frameworks were further confirmed by solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy and N 1s X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 2). In addition, the elemental analysis revealed that the carbon (C), hydrogen (H), and N content in COF-TAPT and COF-TAPB closely agreed with the theoretical values (Supplementary Table 4). These COFs retained high crystallinity after treatment with concentrated HNO₃ aqueous solution (5 M) or β-irradiation (200 kGy), exhibiting the excellent stability required to capture radioactive iodine from the off-gas stream (Supplementary Fig. 3).

Static I₂ and CH₃I adsorption. In most previous studies, I₂ adsorption was performed in a static closed system with saturated I₂ vapor at 75 °C, and the adsorption capacity was determined based on the mass increase subsequently measured under ambient conditions at room temperature. To directly compare with the previously developed adsorbents, we evaluated COF-TAPB and COF-TAPT using the same experimental setup (see the Experimental section in the Supporting Information for detailed methods). The results revealed that COF-TAPT and COF-TAPB adsorbed 7.94 and 8.61 g g⁻¹ I₂ within 96 h, respectively (Fig. 3a and Supplementary Table 3). These values rank high among all adsorbents tested under the same conditions (Fig. 3c and Supplementary Table 5). It is worth noting that under this commonly used evaluation condition, where the concentration of I₂ is rather high (~16,000 ppm), the adsorption is dominated by the intermolecular interactions of I₂; consequently, the capacity is largely determined by the pore volume of the adsorbent in addition to the characteristics of the binding sites.

We used the average adsorption rate determined at 80% of the full adsorption capacity (Kₙ₅₀) to describe the adsorption kinetics of the adsorbents. Despite their similar porous structures, COF-TAPT exhibited a higher Kᵥ₅₀ value than COF-TAPB (0.48 vs. 0.33 g g⁻¹ h⁻¹), which can be attributed to its higher N content promoting the initial adsorption of I₂. The measured I₂ adsorption kinetics of COF-TAPT and COF-TAPB are faster than those of many previously reported microporous adsorbents (Supplementary Table 5) due to their highly crystalline structures that facilitate mass transport. To investigate the effect of porosity on the adsorption capacity and adsorption kinetics, we prepared a control sample, which was synthesized using the same process as COF-TAPT, except that N,N-dimethylformamide (DMF) instead of mixed ethanol and o-dichlorobenzene was used as the solvent. The obtained material (denoted as TFPA-TAPT) has the same chemical composition as COF-TAPT but a much lower porosity (BET specific surface area: 1284 m² g⁻¹; total pore volume: 0.19 cm³ g⁻¹) due to its poor crystallinity (Fig. 4a, b). Under the same conditions, TFPA-TAPT exhibited a lower I₂ adsorption capacity (4.31 g g⁻¹) and a slower adsorption rate (Kᵥ₅₀: 0.098 g g⁻¹ h⁻¹) than COF-TAPT (Supplementary Fig. 4c). This result demonstrates the significant influence of textural properties of the adsorbent on its I₂ adsorption behavior.

We also evaluated the CH₃I adsorption performance of COF-TAPT and COF-TAPB in a static closed system with a saturated CH₃I vapor at 75 °C, as used in the previous study, for direct comparison. The results demonstrated that COF-TAPT adsorbed 1.53 g g⁻¹ of CH₃I (Fig. 3b), exceeding the capacity of the state-of-the-art CH₃I adsorbent SCU-COF-2 (1.45 g g⁻¹). In contrast, COF-TAPB adsorbed only 0.81 g g⁻¹ of CH₃I under the same...
The control sample TFPA-TAPT exhibited a CH$_3$I adsorption capacity of 1.37 g g$^{-1}$, although its BET surface area is only half of that of COF-TAPT (Supplementary Fig. 4d). These results collectively indicate that, unlike I$_2$ adsorption, CH$_3$I adsorption capacity depends on the number of strong binding sites of the adsorbent rather than its surface area or pore volume. This conclusion was further verified by the plots of CH$_3$I uptake vs. the BET surface area (Supplementary Fig. 5a) and CH$_3$I uptake vs. N content (Supplementary Fig. 5b), based on the data for seven adsorbents, which clearly indicate that the CH$_3$I uptake is irrelevant to the surface area but positively correlated with the N content of the adsorbent (Supplementary Table 3). In addition, at their full adsorption capacity, the CH$_3$I/N ratios in COF-TAPT and COF-TAPB were 0.97 and 0.89, respectively, whereas the I$_2$/N molar ratios were 3.05 and 4.89, respectively. These results collectively indicate the essential difference between I$_2$ adsorption and CH$_3$I adsorption. The nearly one-to-one correspondence between CH$_3$I and N suggests that CH$_3$I molecules are only adsorbed on N sites, presumably by forming salts. In contrast, I$_2$ adsorption can occur at other sites in the π-conjugated frameworks (e.g., benzene rings) or be promoted by forming polyiodide species, resulting in high I$_2$/N ratios.

**Dynamic I$_2$ and CH$_3$I adsorption.** Given the low concentrations of molecular iodine and organic iodides (usually <200 ppm) in the off-gas stream$^{2,57,58}$, it is more meaningful to test the adsorption behavior of adsorbents at low I$_2$ (or CH$_3$I) concentrations related to practical applications. To explore the potential of the developed COFs for practical applications, we evaluated their I$_2$ and CH$_3$I adsorption capacities under dynamic...
conditions using a fixed-bed column-breakthrough configuration, which allowed the concentration of I₂ and CH₃I, the temperature of the adsorbent bed, and humidity to be freely adjusted. To directly compare the developed COFs with benchmark adsorbents, we conducted dynamic adsorption at 25 °C with 400 ppm of I₂ in N₂ flow (adsorbent: 30.0 mg; flow rate: 10.0 mL min⁻¹). Under these conditions, COF-TAPB exhibited a steep breakthrough step after 45 h with a total I₂ uptake of 2.18 g g⁻¹, and COF-TAPT demonstrated a similar breakthrough profile, whereas its breakthrough time was 50 h, corresponding to a total I₂ uptake of 2.38 g g⁻¹ (Fig. 4a). The observed I₂ adsorption capacities are significantly higher than those of most reported adsorbents under similar measurement conditions (Supplementary Fig. 6 and Supplementary Table 6). In addition, the presence of water vapor only caused a slight decrease in the I₂ uptake of COF-TAPT (from 2.38 g g⁻¹ to 2.32 g g⁻¹) and COF-TAPB (from 2.18 to 2.13 g g⁻¹) (Fig. 4b), indicating that they are both tolerant to moisture, which is important for practical applications.

We performed dynamic CH₃I adsorption using the same column-breakthrough setup, with the CH₃I concentration controlled at 200,000 ppm. The results revealed that, under dry conditions, the CH₃I uptakes of COF-TAPB and COF-TAPT were 0.71 and 1.30 g g⁻¹, respectively (Fig. 4c, d). The CH₃I adsorption capacity of COF-TAPT (1.30 g g⁻¹) is higher than that of all reported adsorbents except MIL-101-Cr-HMTA (Supplementary Fig. 7 and Supplementary Table 7). The ultrahigh CH₃I adsorption capacity of MIL-101-Cr-HMTA is attributed to the combination of a large surface area and abundant tertiary amine groups that can strongly and specifically interact with CH₃I. However, MIL-101-Cr-HMTA exhibits a limited adsorption capacity for I₂ (Supplementary Fig. 8 and Supplementary Table 6) due to the lack of effective I₂ binding sites other than tertiary amines. When water vapor was introduced into the feed stream (relative humidity = 50%), the CH₃I adsorption capacity of COF-TAPT decreased from 1.30 to 1.06 g g⁻¹, indicating competitive adsorption between H₂O and CH₃I. This result is because the adsorption of CH₃I primarily occurs on N sites, which also adsorb H₂O molecules. The dynamic adsorption measurements indicate that COF-TAPT has a similar I₂ uptake capacity but a significantly higher CH₃I uptake capacity than COF-TAPB. This outcome is consistent with the results of the static adsorption experiments and further validates the above conclusion about the difference between I₂ adsorption and CH₃I adsorption.

The adsorbed I₂ and CH₃I in COF-TAPT can be fully extracted by ethanol to regenerate its adsorption capacities. When the I₂-saturated COF-TAPT (I₂@COF-TAPT) or CH₃I-saturated COF-TAPT (CH₃I@COF-TAPT) was immersed in ethanol, the I₂ or CH₃I desorption process proceeded spontaneously and accelerated with the assistance of sonication. As a commonly used method for regenerating adsorbents after I₂ adsorption, extraction with ethanol can also efficiently remove CH₃I from COF-TAPT because the N-methylation reaction is reversible in protic solvents. The regenerated COF-TAPT (COF-TAPT-Re) restored its original physiochemical properties, as evidenced by the FTIR, PXRD, and N₂ sorption characterizations. Correspondingly, the exceptionally high adsorption capacity of COF-TAPT can be fully restored in four successive adsorption/extraction cycles under the above conditions (Supplementary Figs. 9, 10).

Simultaneous capture of low-concentration I₂ and CH₃I. After evaluating the adsorption performance of the developed COFs for I₂ and CH₃I under commonly used conditions, we explored their ability to capture I₂ and CH₃I at much lower concentrations (150 and 50 ppm, respectively) relevant to practical off-gas treatment applications. Several state-of-the-art adsorbents for I₂ or CH₃I applications.

Several state-of-the-art adsorbents for I₂ or CH₃I adsorption.
capture, including MIL-101-Cr-HMTA, SCU-COF-2, and iCOF-AB-50, were evaluated under the same conditions for comparison. We started with single-component measurements, introducing only I\(_2\) (150 ppm) or CH\(_3\)I (50 ppm) in the feed stream for capture. The results revealed that, for I\(_2\) capture, the order of adsorption capacity of the tested adsorbents is iCOF-AB-50 (1.52 g g\(^{-1}\)) > COF-TAPT (1.25 g g\(^{-1}\)) > COF-TAPB (1.12 g g\(^{-1}\)) > MIL-101-Cr-HMTA (0.83 g g\(^{-1}\)) > SCU-COF-2 (0.49 g g\(^{-1}\)) > TFPA-TAPT (0.42 g g\(^{-1}\)) (Fig. 5a and Supplementary Table 8).

This order is consistent with that derived from the static adsorption measurements (Fig. 3c). The exceptionally high I\(_2\) uptake of iCOF-AB-50 is attributed to the presence of abundant ionic groups that effectively promote I\(_2\) adsorption via strong Coulomb interactions. The results of various adsorbents capturing CH\(_3\)I, as summarized in Fig. 5b and Supplementary Table 8, indicate that COF-TAPT ranks second among all tested adsorbents. The specific CH\(_3\)I adsorption capacities are as follows: MIL-101-Cr-HMTA (0.51 g g\(^{-1}\)) > COF-TAPT (0.39 g g\(^{-1}\)) > TFPA-TAPT (0.18 g g\(^{-1}\)) > COF-TAPB \(\approx\) iCOF-AB-50 (0.12 g g\(^{-1}\)) > SCU-COF-2 (0.08 g g\(^{-1}\)).

These results further confirm that the adsorption behaviors of I\(_2\) and CH\(_3\)I are different. The adsorption of I\(_2\) can be initiated through specific functional groups (e.g., ionic groups) in the adsorbent and further promoted through strong intermolecular interactions. Therefore, the type of binding sites and textural capture, including MIL-101-Cr-HMTA, SCU-COF-2, and iCOF-AB-50, were evaluated under the same conditions for comparison. We started with single-component measurements, introducing only I\(_2\) (150 ppm) or CH\(_3\)I (50 ppm) in the feed stream for capture. The results revealed that, for I\(_2\) capture, the order of adsorption capacity of the tested adsorbents is iCOF-AB-50 (1.52 g g\(^{-1}\)) > COF-TAPT (1.25 g g\(^{-1}\)) > COF-TAPB (1.12 g g\(^{-1}\)) > MIL-101-Cr-HMTA (0.83 g g\(^{-1}\)) > SCU-COF-2 (0.49 g g\(^{-1}\)) > TFPA-TAPT (0.42 g g\(^{-1}\)) (Fig. 5a and Supplementary Table 8).

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properties of the adsorbent both critically influence the I$_2$ uptake. In contrast, the adsorption of CH$_3$I is primarily determined by the type and number of binding sites and is not much related to the textural properties of the adsorbent. In addition, ionic groups can strongly promote the adsorption of I$_2$ but have a little promotional effect on the adsorption of CH$_3$I because I$_2$ can be easily induced to form charge species, such as I$_3^-$ and I$_5^-\text{N}$, whereas CH$_3$I cannot.

Finally, we measured the simultaneous capture of iodine species on various adsorbents by co-feeding I$_2$ (150 ppm) and CH$_3$I (50 ppm). Considering the excellent capture ability of COF-TAPT for I$_2$ and CH$_3$I in the single-component measurements, good performance in the co-capture of these two species is expected. Indeed, COF-TAPT exhibited a significantly higher total iodine (I$_2$ + CH$_3$I) capture capacity (1.51 g g$^{-1}$) than other tested adsorbents, except iCOF-AB-50 (Fig. 5c and Supplementary Table 8). The total uptake of iCOF-AB-50 primarily derives from the contribution of I$_2$ adsorption; thus, it is conceivable that COF-TAPT is more suitable for feed streams containing a high fraction of organic iodides. Similar to the single-component measurement results, the high performance of the COF-TAPT in simultaneous capture of I$_2$ and CH$_3$I can be fully regenerated in successive tests (Supplementary Fig. 11).

Discussion

To analyze the adsorption sites of COF-TAPT, we characterized the I$_2$-saturated COF-TAPT sample (I$_2$@COF-TAPT) with PXRD after the static adsorption measurement. The obtained PXRD pattern did not exhibit diffraction peaks related to the original crystalline structure of COF-TAPT (Supplementary Fig. 9b), indicating the loss of structural order due to the incorporation of I$_2$ into the porous channels. Moreover, no diffraction peaks associated with I$_2$ were observed, ruling out the possibility that the high I$_2$ adsorption capacity of COF-TAPT was caused by the recrystallization of I$_2$ outside its porous structure. Solid-state $^{13}$C NMR spectra revealed that the chemical shifts of all carbon atoms in COF-TAPT changed originating from CH$_3$I that formed salts at various N sites (Fig. 6b), suggesting that I$_2$ molecules interacted with various sites throughout the entire π-electron conjugated framework$^{27,34}$. The N 1s XPS indicated that after the adsorption of I$_2$, the peak fractions at 398.6 and 399.5 eV, assigned to imine/triazine N and sp$^3$ N in COF-TAPT$^{33,34}$, shifted to 400.7 and 401.4 eV, respectively (Fig. 6b), suggesting the formation of charge-transfer complexes between I$_2$ and various N species in COF-TAPT. In the FTIR spectra, the adsorption of CH$_3$I caused the bands of C=N at 1625 cm$^{-1}$, C=C at 1586 cm$^{-1}$, C-(in N-ph$_3$) at 1361 cm$^{-1}$, and C=N (in ph-N-C) at 1195 cm$^{-1}$ to decrease in intensity or shift (Fig. 6c), indicating that all functional groups in the entire framework of COF-TAPT interact with I$_2$.$^{27,33,34}$ The Raman spectrum of I$_2$@COF-TAPT exhibited characteristic bands at 107.5, 142.2, and 166.7 cm$^{-1}$, which can be assigned to the symmetric stretching vibration of I$_3^-$, asymmetric stretching vibration of I$_5^-\text{N}$, and stretching vibration of I$_5^-\text{N}$, respectively (Fig. 6d)$^{60,61}$. These spectroscopic observations indicate that various functional groups in COF-TAPT, including phenyl rings, imine and triazine moieties, and sp$^3$ N, were all involved in forming the charge-transfer complex with I$_2$ and that polyiodide species were produced during the adsorption process.

The CH$_3$I-saturated COF-TAPT sample (CH$_3$I@COF-TAPT) was also characterized using $^{13}$C NMR, N 1s XPS, and FTIR. Compared to the original material, CH$_3$I@COF-TAPT exhibited an intense new signal at ~589.9 ppm in the $^{13}$C NMR spectrum, originating from CH$_3$I that formed salts at various N sites through methylation reactions (Fig. 6a)$^{34}$. In addition, after the adsorption of CH$_3$I, the N 1s electron binding energies of imine/triazine N and sp$^3$ N in COF-TAPT increased by 1.3 and 3.7 eV, respectively, providing additional evidence for the binding of CH$_3$I on N species (Fig. 6b)$^{33,34}$. Compared with I$_2$ adsorption, CH$_3$I adsorption resulted in a less pronounced peak shift for imine/triazine N and a more pronounced peak shift for sp$^3$ N, implying differences in affinity of I$_2$ and CH$_3$I at different N sites. In FTIR, the adsorption of CH$_3$I on COF-TAPT also resulted in the intensity change or shift of the characteristic bands of C=N and C=N bonds, and the appearance of a band at ~939 cm$^{-1}$ indicated the formation of new C=N bonds on the heterocycles in COF-TAPT (Fig. 6c)$^{31,34}$. Notably, the bands of C≡C at 1560–1590 cm$^{-1}$ were unchanged upon the adsorption of CH$_3$I. These spectroscopic results support the conclusion that CH$_3$I molecules are not adsorbed on the benzene ring moieties in COF-TAPT but are specifically bonded to the nucelophilic N sites through N-methylation reactions. The CH$_3$I-adsorbed COF-TAPT exhibits strong anion-exchange ability (Supplementary Fig. 12), confirming the generation of exchangeable iodide ions.

There are three types of nucleophilic N species (i.e., imine, triazine, and sp$^3$ N) in COF-TAPT, all of which can bind to CH$_3$I. To gain more insight into the preferential binding sites of CH$_3$I, we performed DFT calculations to assess their binding energies with CH$_3$I. The calculations were conducted at the B3LYP level of the exchange functional, using TPF-A-T as the model molecule to represent COF-TAPT (Fig. 7). The calculated binding energy is $-15.0$ kcal mol$^{-1}$ for imine, $-5.4$ kcal mol$^{-1}$ for triazine, and $-2.6$ kcal mol$^{-1}$ for sp$^3$ N sites, indicating that the imine groups in the COF are the most favorable adsorption sites for CH$_3$I (Fig. 7). This result suggests that introducing imine groups and maximizing their content in the adsorbent may be a good choice to improve the ability to capture low-concentration CH$_3$I. In previous studies, sp$^3$ N promoted the capture of CH$_3$I, where N was connected with alkyl chains.$^{47,48}$ However, in TPF-A-T, sp$^3$ N is connected with three benzene rings; thus, its nucleophilicity is greatly reduced due to the conjugation effect. We note that the XPS data (Fig. 6b) suggest that CH$_3$I interacts more strongly with sp$^3$ N than with imine/triazine N (more pronounced peak shift). This discrepancy is not fully understood and requires further exploration.

In conclusion, the development of high-performance adsorbents for the simultaneous capture of molecular iodine and organic iodides relies on understanding the similarities and differences between these two processes. Based on previous studies, we hypothesized that N-rich carbonaceous adsorbents are conducive to simultaneously capturing I$_2$ and CH$_3$I. Further studies revealed that I$_2$ could be relatively easily adsorbed on a variety of electron-donor sites, including various N species and aromatic moieties, by forming charge-transfer complexes and polyiodides. Therefore, the characteristics of binding sites and textural properties (e.g., surface area and pore volume) of the adsorbent both affect I$_2$ uptake. The adsorption of CH$_3$I occurs specifically on nucelophilic N sites through N-methylation reactions to form salts and is unrelated to the textural properties of the adsorbent. In addition, ionic groups can strongly promote the adsorption of I$_2$ but have little promotional effect on the adsorption of CH$_3$I.

These findings motivated the development of a COF-based adsorbent, COF-TAPT, which combines a high surface area and numerous nucelophilic N sites, including imine, triazine, and sp$^3$ N, thereby exhibiting excellent adsorption capacity for I$_2$ and CH$_3$I. We evaluated COF-TAPT for I$_2$ and CH$_3$I adsorption under different conditions and found that it outperforms most state-of-the-art adsorbents in all measurements, especially at low-concentration conditions relevant to practical applications. In addition, we calculated the binding energies of CH$_3$I at different
N sites, and the results revealed that imine groups might be the most preferred adsorption sites.

**Data availability**
All data supporting the findings of this study are available within the article and the Supplementary information file, or available from the corresponding authors on request.

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Author contributions
Y.X. and Y.H. conceived the project and designed the experiments. Y.X. and W.A.M. prepared and characterized the materials. Y.X., T.P., and X.D. conducted the adsorption experiments. C.C. performed TEM measurement and analysis. Y.X. and Y.Y. performed PXRD simulations and analysis. L.Z. helped the irradiation treatments. L.C. performed the DFT calculations. Y.X., Q.L., I.P., and Y.H. wrote the manuscript with contributions from all the authors.

Competing interests
The authors declare no competing interests.

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