



Article Construction of Ketoenamine-Based Covalent Organic Frameworks with Electron-Rich Sites for Efficient and Rapid Removal of Iodine from Solution

Qi Tao^{1,*}, Xiao Zhang², Liping Jing^{3,*}, Lu Sun⁴ and Peipei Dang⁵

- ¹ College of Energy and Electrical Engineering, Hohai University, Nanjing 211100, China
- ² Key Laboratory of Applied Surface and Colloid Chemistry Ministry of Education (MOE), School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China
- ³ College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161006, China
- ⁴ Department of Chemistry, Northeast Normal University, Changchun 130024, China
- ⁵ State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
- * Correspondence: 20220924@hhu.edu.cn (Q.T.); 03707@qqhru.edu.cn (L.J.)

Abstract: Porous covalent organic frameworks (COFs) have been widely used for the efficient removal of iodine from solution due to their abundance of electron-rich sites. In this study, two kinds of ketoenamine-based COFs, TpBD-(OMe)2 and TpBD-Me2, are successfully synthesized via Schiff base reaction under solvothermal conditions using 1, 3, 5-triformylphoroglucinol as aldehyde monomer, otolidine and o-dianisidine as amino monomers. The ability of TpBD-(OMe)2 and TpBD-Me2 to adsorb iodine in cyclohexane or aqueous solutions has been quantitatively analyzed and interpreted in terms of adsorption sites. TpBD-Me₂ possesses two adsorption sites, -NH- and -C=O, and exhibits an adsorption capacity of 681.67 mg/g in cyclohexane, with an initial adsorption rate of 0.6 g/mol/min with respect to COF unit cell. The adsorption capacity of TpBD-(OMe)₂ can be as high as 728.77 mg/g, and the initial adsorption rate of TpBD-(OMe)₂ can reach 1.2 g/mol/min in the presence of oxygen atoms between the methyl group and the benzene ring. Compared with TpBD-Me₂, the higher adsorption capacity and adsorption rate of TpBD-(OMe)2 towards iodine are not only reflected in organic solvents, but also in aqueous solutions. It is proven through X-ray photoelectron spectroscopy and Raman spectroscopy that iodine exists in the form of I_2 , I_3^- , and I_5^- within TpBD-(OMe)₂ and TpBD-Me2 after adsorption. This work not only expands the application of COFs in the field of iodine adsorption, but also provides research ideas and important an experimental basis for the optimization of iodine adsorption sites.

Keywords: ketoenamine-based; covalent organic frameworks; adsorption; iodine

1. Introduction

The rapid development of the nuclear industry has gravely harmed the environment and posed a hazard to human health due to nuclear waste, making its removal an urgent issue that needs to be addressed [1–3]. The nuclear reaction process generates the radioactive isotopes ¹²⁹I and ¹³¹I, ¹²⁹I having a significantly longer half-life [2,4]. Iodine isotopes entering the human body without the right safeguards in place may lead to serious health conditions, such as acute radiation sickness and tumor formation [5,6]. In addition, iodine leakage into water bodies in the form of ions causes severe environmental pollution, while its solubility in organic solvents provides a considerable obstacle to industrial production and solvent recycling [7,8]. Therefore, the efficient removal of iodine from solution has emerged as a matter of widespread concern.

The commonly used iodine adsorbent consists of activated carbon impregnated with triethylenediamine (TEDA) or KI [9–11]. However, the accumulation of TEDA or KI within the adsorbents could lead to pore blockage in the activated carbon, thereby reducing



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). their adsorption capacity over time [12]. Ag-based adsorbents include Ag-exchanged zeolites [13,14], titanosilicates [15], silver-doped porous oxide materials [16–18], silverfunctionalized silica aerogels [19,20], and so on. The adsorption of iodine by silver-based adsorbents results in the formation of stable AgI [21,22], which exhibits low desorption efficiency when using suitable solvents for iodine, thereby limiting the recyclability of Agbased adsorbents. The functional macroreticular resin exhibits a high specific surface area and exceptional stability [23,24]. Moreover, the amino, amide, and cationic components grafted onto the resin effectively enhance its adsorption capacity for iodine. Importantly, the absorbed iodine can be desorbed using an appropriate solvent, enabling the reuse of the resin material [24,25]. Newly developed metal organic frameworks (MOFs) [26–29] and porous organic polymers (POPs) [2,30–33] have gained significant attention due to their exceptional designability as monomers, high specific surface area, adjustable pore size, and pore volume, making them highly suitable for iodine adsorption in both vapor and solution systems. Covalent organic frameworks (COFs) connected by robust covalent bonds using multidentate organic building units emerge as significant adsorbents for iodine in solution owing to their excellent crystallinity, high specific surface area, one-dimensional open pores, low density, and exceptional thermal stability [34,35].

Considering the facile modifiability of COF monomers, electron-rich non-metallic heteroatoms, such as P, N, O, and S, were commonly incorporated into the skeleton of COFs. The incorporation of these elements effectively enhances the adsorption capacity of COFs towards iodine by leveraging the interaction between lone-pair electrons and iodine molecules [36-40]. The enol form of COFs, derived from the Schiff base reaction between 1, 3, 5-triformylphoroglucinol (Tp) and binary amino monomers, can undergo a conversion into a more thermodynamically stable ketone form, resulting in the formation of ketoenamine-based COFs [34]. The oxygen atom, as an electron-rich atom, is typically found in ketoenamine-based COFs in the form of a carbonyl or ether bond, which serve as important binding sites for iodine molecules. Since the oxygen in the ether bond possesses more lone electron pairs, its role in iodine adsorption cannot be overlooked. Current studies have primarily focused on investigating the influence of COFs' pore size and specific surface area on their iodine adsorption performance [41], while there is a lack of clear experimental result to elucidate the impact of electron-rich sites on the adsorption performance. In this study, two types of COFs, namely TpBD-Me₂ and TpBD-(OMe)₂, were synthesized through the Schiff base reaction between Tp and o-tolidine (BD-Me₂) and o-dianisidine (BD-(OMe)₂), respectively. These COFs exhibit excellent crystallinity, high specific surface area, and remarkable thermal stability. We investigated their adsorption capacity and rate towards iodine in solution. It was observed that the presence of ether oxygen atoms in COFs led to enhanced adsorption capacity and faster adsorption kinetics for iodine uptake. This study provides new insights into understanding how TpBD-Me₂ and TpBD-(OMe)₂ interact with iodine at an atomic level while offering two novel materials for the efficient removal of iodine from solutions.

2. Results and Discussion

2.1. The Structure of TpBD-Me₂ and TpBD-(OMe)₂

To study the iodine adsorption performance of COFs from the perspective of adsorption sites, it is necessary to select suitable monomers to construct COFs in order to facilitate comparing the effects of differences in molecular structure on iodine adsorption. The structural differences between the already-reported TpBD-Me₂ and TpBD-(OMe)₂, which only exist in the oxygen atoms, allow us to simultaneously reveal the influence of both the ketoenamine-based skeletons and the ether oxygen atoms on iodine adsorption properties. The synthesis of TpBD-Me₂ and TpBD-(OMe)₂ was achieved by reacting Tp with BD-Me₂ and BD-(OMe)₂ (Figure 1a), respectively, under solvothermal conditions, as previously reported in the literature [34,38]. The molar ratio of Tp to BD-Me₂ or BD-(OMe)₂ in the reaction was 2:3, indicating that two molecules of Tp reacted with three molecules of BD-Me₂ or BD-(OMe)₂ to form a COF unit cell. TpBD-Me₂ possesses two electron-rich functional groups consisting of secondary amine (-NH-) and carbyl oxygen (C=O), which serve as binding sites for iodine adsorption in solution. The incorporation of a methoxy component into the COF structure for TpBD-(OMe)₂ additionally introduces ether oxygen sites (-O-), which could effectively enhance its adsorption capacity and rate of iodine (Scheme 1).



Figure 1. (a) Synthetic conditions and molecular structure of TpBD-Me₂ and TpBD-(OMe)₂; (b) PXRD results obtained from the experiments and simulations of TpBD-Me₂ (top) and TpBD-(OMe)₂ (bottom). Inset: AA stacking structural models of TpBD-Me₂ and TpBD-(OMe)₂.



Scheme 1. Two kinds of ketoenamine-based covalent organic frameworks (COFs) with electron-rich sites, namely TpBD-Me₂ (double adsorption sites) and TpBD-(OMe)₂ (triple adsorption sites) for iodine adsorption in solution.

Before studying the iodine absorption property, we characterized the as-synthesized TpBD-Me₂ and TpBD-(OMe)₂ and compared the results with those in the literature to confirm their successful preparation. As shown in Figure 1b, the experimental powder X-ray diffraction (PXRD) results of TpBD-Me₂ and TpBD-(OMe)₂ are consistent with the theoretical simulations based on the AA stacking model using the Materials Studio 2020 software package, which can prove that they have good crystallinity. Fourier transform infrared spectroscopy (FT-IR) was employed for the characterization of the functional groups present in as-prepared TpBD-Me₂ and TpBD-(OMe)₂ (Figure S1). We carried out ¹³C solid-state nuclear magnetic resonance (NMR) spectroscopy to verify the atomic-

level construction of as-prepared COFs (Figure S2). The thermal stability of the two types of COFs were assessed via thermogravimetric analysis in ambient air, revealing that TpBD-Me₂ and TpBD-(OMe)₂ exhibited notable thermal stability up to 300 °C without any discernible mass loss, which is comparable to that of other reported imine-based COFs [34,42] (Figure S3). The X-ray photoelectron spectroscopy (XPS) analysis of both types of COFs reveals the presence of C, N, and O elements (Figure S4, Table S1). The high-resolution XPS analysis of C element in TpBD-Me₂ and TpBD-(OMe)₂ reveals that the C1s signals can be categorized into three distinct carbon environments (Figure S5). The surface irregular flocculation morphology of TpBD-Me₂ and TpBD-(OMe)₂ was observed via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figures S6 and S7). In addition, it was demonstrated using PXRD that TpBD-Me₂ and TpBD-(OMe)₂ remained well stabilised in different solvents (Figure S8).

According to nitrogen adsorption-to-desorption isotherms (Figure S9a), both COFs exhibit a typical type I reversible isotherm, indicating significant nitrogen adsorption at low relative pressure and the existence of micropores in these materials. The N₂ desorption curve of TpBD-(OMe)₂ shows a slight hysteresis compared to TpBD-Me₂, suggesting the presence of narrowly distributed mesopores. The Brunauer–Emmet–Teller (BET) plots to calculate surface area are shown in Figure S10. The surface area of TpBD-Me₂ is 942.81 g/m², surpassing that of TpBD-(OMe)₂ (539.30 g/m²) (Table S2). The surface area of TpBD-Me₂ is approximately twice as high as that of TpBD-(OMe)₂, because integrating the ether oxygen atoms in the pore walls of the COFs further blocks the pores. The primary pore size of TpBD-Me₂ is 1.83 nm, while that for TpBD-(OMe)₂ is 1.88 nm, with a discernible presence of mesoporous regions (Figure S9b), which is consistent with the N₂ desorption profile. Considering that the pore size of both COFs exceeds the molecular diameter of I₂ (0.53 nm), the removal of I₂ in solutions by TpBD-Me₂ and TpBD-(OMe)₂ could be attributed to chemisorption, while the influence of pore size on adsorption can be disregarded.

2.2. Adsorption of Iodine by TPBD-Me₂ and TPBD-(OMe)₂ in Cyclohexane

To facilitate the separation and collection process, TpBD-Me₂ or TpBD-(OMe)₂ was compressed into a flaky shape for efficient iodine adsorption, and their morphologies are shown in Figure S11. The PXRD of the COFs in flake form is consistent with that of powders, indicating that they still maintain their original ordered structure (Figure S12). The thermogravimetric analysis of the flaky TpBD-Me and TpBD-(OMe)₂ reveals that their decomposition temperatures remain above 300 °C, indicating that the applied pressure has not compromised their skeleton structure (Figure S13). The flecks of TpBD-Me₂ and TpBD-(OMe)₂ were immersed in a 100 mg/L iodine cyclohexane solution, respectively. Over time, the color intensity of the solutions gradually decreased. Notably, after 48 h of adsorption, it is evident that TpBD-(OMe)₂ exhibits a significantly higher iodine absorption capacity compared to TpBD-Me₂ (Figure 2a,b). UV-vis spectroscopy was used to monitor the concentration of iodine in cyclohexane to quantify the amount of iodine absorbed by COFs (Figure S14). A standard equation, based on UV-vis absorption values at various iodine concentrations, was employed to determine the concentration of iodine in cyclohexane solution during COF-mediated iodine uptake (Figure S15). The time-dependent change in adsorption capacity per unit mass (q_t) of 10 mg TpBD-Me₂ and TpBD-(OMe)₂ in a 100mg/L iodine cyclohexane solution is depicted in Figure 2c (Table S3). Adsorption equilibrium is achieved within approximately 30 h, with the adsorption capacity of TpBD-(OMe)₂ for iodine being significantly higher compared to that of TpBD-Me₂. The iodine absorption capacity of TpBD-(OMe)₂ with respect to unit cell $(q_t^{\mu c})$ is significantly higher than that of TpBD-Me₂, suggesting the crucial role played by the ether oxygen atoms in the process of iodine adsorption (Table S3). Based on the molar ratio of iodine molecule to COF unit cell (q_t^{Mol}) , TpBD-(OMe)₂ exhibits an additional adsorption capacity of 0.8 mol I₂ per unit cell compared to TpBD-Me₂ at equilibrium. The maximum adsorption capacities (q_e and $q_e^{\mu c}$) at equilibrium were determined by simulating the values of q_t and q_t^{uc} using both pseudofirst-order and pseudo-second-order kinetic models (Tables S4 and S5). It is observed that the temporal changes in q_t and q_t^{uc} were better described by the pseudo-second-order kinetic model, suggesting a multi-site adsorption mechanism for iodine on the two COF materials, with charge transfer occurring between iodine molecules and adsorption sites. By calculating the adsorption rate of COFs of iodine ($\Delta q_t^{uc} / \Delta t$), it is evident that the initial adsorption rate of TpBD-(OMe)₂ (1.2 g/mol/min) exhibits a twofold increase compared to that of TpBD-Me₂ (0.6 g/mol/min), while maintaining a consistent adsorption rate even after 100 min (Figure 2d).



Figure 2. (**a**,**b**) The photographs of the process of I₂ uptake after 10 mg TpBD-Me₂ (**a**) and TpBD-(OMe)₂ (**b**) were immersed in 10 mL of cyclohexane solution of I₂ at the initial concentration of 100 mg·L⁻¹; the incubation times are marked on the photos. (**c**) The values of q_t (black) and q_t^{uc} (red) were plotted against time for the adsorption kinetics of TpBD-Me₂ (square) and TpBD-(OMe)₂ (circle), which were fitted using pseudo-first-order (solid curves) and pseudo-second-order (dash curves) kinetic models. (**d**) Plots of the values of $\Delta q_t^{uc} / \Delta t$ for TpBD-Me₂ (black square) and TpBD-(OMe)₂ (red circle) in cyclohexane solution versus adsorption time. (**e**) Plots of the values of q_t^{N+CO} (black square) for TpBD-Me₂, q_t^{N+O} (red circle) and q_t^{EO} (blue triangle) for TpBD-(OMe)₂ in cyclohexane solution versus adsorption time of $\Delta q_t^{N+CO} / \Delta t$ (black square) for TpBD-Me₂, $\Delta q_t^{N+O} / \Delta t$ (red circle), and $\Delta q_t^{EO} / \Delta t$ (blue triangle) for TpBD-(OMe)₂ in cyclohexane solution versus adsorption time, which were fitted by pseudo-first-order (solid curves) and pseudo-second-order (dash curves) kinetic models. (**f**) Plots of the values of $\Delta q_t^{N+CO} / \Delta t$ (black square) for TpBD-Me₂, $\Delta q_t^{N+O} / \Delta t$ (red circle), and $\Delta q_t^{EO} / \Delta t$ (blue triangle) for TpBD-(OMe)₂ in cyclohexane solution versus adsorption time. The arrows are used to mark the horizontal and vertical coordinates of the corresponding curves.

By analyzing the iodine molecule binding sites within the crystal structure of both COFs, it is found that TpBD-Me₂ possesses two distinct binding sites for iodine molecules (-NH-(N) and -C=O(CO)), while TpBD-(OMe)₂ exhibits three binding sites (-NH-(N), -C=O(CO), and -O-Me (EO)). Each unit cell of the COFs contains six electron-rich sites of the same atoms for iodine adsorption. The value of q_t^{uc} is divided by six to obtain the mass of adsorbed iodine per mole of adsorption sites (q_t^A) (Figure 2e). For TpBD-Me₂, the adsorption capacity per mole of iodine binding site is represented by q_t^{N+CO} , whereas for TpBD-(OMe)₂, it is denoted as q_t^{N+O} . By calculating the difference between q_t^{N+O} and q_t^{N+CO} , the quantity of iodine adsorbed by each mole of oxygen atom in the ether bond (q_t^{EO}) could be determined (Table S6). According to experimental results and kinetic fitting, the maximum value of q_e^{N+O} is greater than that of q_e^{N+CO} , indicating that the oxygen atoms in the methoxyl group play a crucial role in the iodine adsorption process (Table S7). The kinetic fitting results of q_t^{N+O} and q_t^{N+CO} are in better agreement with the pseudo-secondorder kinetic model, providing further evidence for the multi-site adsorption nature of iodine molecules on COFs. Time-dependent calculation of the value of initial adsorption rate as for adsorption sites $(\Delta q_t^A / \Delta t)$ reveals that $\Delta q_t^{N+O} / \Delta t$ for TpBD-(OMe)₂ at the three adsorption sites surpass that of TpBD-Me₂ at the two sites, while the initial adsorption rate for oxygen atoms alone $(\Delta q_t^{EO} / \Delta t)$ exceeded that of TpBD-Me₂ (Figure 2f). The above results demonstrate that the introduction of an oxygen atom not only enhances the iodine adsorption capacity, but also accelerates the adsorption rate. Although TpBD-Me₂ has a higher surface area, its adsorption capacity and rate of iodine are lower than those of TpBD-(OMe)₂, indicating that the adsorption site is the decisive factor in the process of the removal of iodine in solution.

To further assess the iodine adsorption capacity of COFs, the iodine adsorption isotherm was determined by measuring the maximum amount of iodine adsorption at various equilibrium concentrations (Table S8, Figure 3a). Here, both the adsorption capacity with respect to the unit mass (q_e) and unit cell (q_e^{uc}) of these two COFs were compared, and Langmuir and Freundlich models were used to fit them (Tables S9 and S10). The maximum value of q_e obtained by fitting the Langmuir model for TpBD-Me₂ and TpBD-(OMe)₂ are 681.67 mg/g and 728.77 mg/g, respectively. Additionally, the maximum values of q_e^{uc} are determined to be 646.99 g mol⁻¹ and 761.68 g mol⁻¹, corresponding to 2.5 and 3.0 I₂ per unit cell for TpBD-Me2 and TpBD-(OMe)2. The adsorption curve was fitted using the Langmuir equation with a correlation coefficient (R^2) of 0.982 for TpBD-Me₂ and 0.921 for TpBD-(OMe)₂, while it was fitted using the Freundlich equation with a correlation coefficient (R²) of 0.992 for TpBD-Me₂ and 0.998 for TpBD-(OMe)₂. The adsorption data for the COF materials exhibit a higher degree of conformity with the Freundlich model rather than the Langmuir model, implying that iodine adsorption takes place in multiple layers within the pores of the COF materials. The value of 1/n fell within the range of 0.1 to 0.5 for Freundlich model, indicating a pronounced affinity between iodine molecules and the sites within the COF channels. The cyclability of COFs was evaluated by subjecting them to three cycles of elution using ethanol to achieve the complete desorption of the iodine molecule, followed by subsequent iodine adsorption in cyclohexane. The adsorption capacity of iodine in cyclohexane for TpBD-Me₂ and TpBD-(OMe)₂, as shown in Figure 3b, remains unchanged compared to the freshly prepared sample after three cycles, indicating their excellent cyclability and reusability.



Figure 3. (a) Adsorption isotherms of TpBD-Me₂ (square) and TpBD-(OMe)₂ (circle) towards I₂ in cyclohexane obtained by the values of q_e (black) and q_e^{uc} (red) at different equilibrium I₂ concentration (C_e), which were fitted by Langmuir (solid curves) and Freundlich models (dashed curves). Inset: correlation coefficient of adsorption isotherms fitted by Langmuir and Freundlich models for TpBD-Me₂ and TpBD-(OMe)₂. (b) Recyclability of TpBD-Me₂ (green) and TpBD-(OMe)₂ (red) for I₂ adsorption in the cyclohexane solution at the initial concentration of 100 mg·L⁻¹.

The surface morphology of TpBD-Me₂ and TpBD-(OMe)₂ after iodine adsorption in cyclohexane (referred to as TpBD-Me2@I2 and TpBD-(OMe)2@I2) was observed using SEM, and their morphologies remain consistent with freshly prepared samples (Figure 4a,b). The PXRD patterns of TpBD-Me₂@I₂ and TpBD-(OMe)₂@I₂ show that they still have good crystallinity, indicating that the COF materials do not change their ordered structure after adsorption of iodine (Figure S16). The elemental distribution of TpBD-Me₂@I₂ and TpBD-(OMe)₂@I₂ was confirmed using energy dispersive spectroscopy (EDS). Notably, the variations in C, N, and O contents originate from the COFs themselves. Moreover, the higher iodine content observed in TpBD-(OMe)₂@I₂ compared to that in TpBD-Me₂@I₂ further substantiates the superior iodine absorption capacity of TpBD-(OMe)₂ (Figure 4a,b). Raman spectroscopy was employed for the investigation of iodine molecule presence within COF channels (Figure 4c). The vibration peaks at 108 cm⁻¹ and 140 cm⁻¹ correspond to the symmetric and asymmetric stretching vibrations of I_3^- ions, respectively. Additionally, a prominent peak at 165 cm^{-1} is observed, which corresponds to the stretching vibrations of I_5^- ($I_2 + I_3^-$) ions. The chemical state of iodine in COF material after iodine adsorption was further confirmed via X-ray photoelectron spectroscopy (XPS). The comparison of XPS spectra of TpBD-Me₂ and TpBD-(OMe)₂ before and after iodine uptake reveals that TpBD-Me₂@I₂ and TpBD-(OMe)₂@I₂ exhibit I 3d peaks at 631 eV and 620 eV, corresponding to I $3d_{3/2}$ and I $3d_{5/2}$, respectively, indicating the successful adsorption of iodine molecules (Figure S17). The atomic concentrations of various elements are presented in Table S11. Notably, the atomic concentration of iodine in TpBD-(OMe)₂@I₂ surpasses that of TpBD-Me₂@I₂, thereby reaffirming the superior adsorption capacity of TpBD-(OMe)₂ towards iodine. The high-resolution XPS spectrum for I 3d reveals two splitting peaks in I $3d_{3/2}$ and I $3d_{5/2}$. The peaks with binding energies at 618.84 eV and 630.86 eV correspond to I_3^- , while the peaks at 620.39 eV and 632.40 eV represent I_2 (Figure 4d). The XPS results for the analysis of chemical state of iodine in COF are consistent with those obtained from Raman spectroscopy.



Figure 4. (**a**,**b**) SEM images and corresponding elemental mapping images of TpBD-Me₂@I₂ (**a**) and TpBD-(OMe)₂@I₂ (**b**) and atomic concentrations of different elements were marked on the photos. (**c**) Raman spectra of TpBD-Me₂@I₂ (black) and TpBD-(OMe)₂@I₂ (red) after adsorption equilibrium. (**d**) High-resolution XPS I3d spectrum of TpBD-Me₂@I₂ (bottom) andTpBD-(OMe)₂@I₂ (top). In (**a**–**d**), the I₂ adsorption was carried out at the initial concentration of 500 mg·L⁻¹ in cyclohexane solution.

The iodine adsorption capacity of TpBD-Me₂ and TpBD-(OMe)₂ in cyclohexane is compared with the those reported in the literature for COFs [36,39,40,43–47], revealing that while their adsorption capacity does not reach the level of P-COF, they surpass most other COFs (Figure 5). The high adsorption capacity of TpBD-Me₂ and TpBD-(OMe)₂ could be attributed to their multiple binding sites for iodine molecules, as well as their large pore size and volume. Comparing TpBD-Me₂ and TpBD-(OMe)₂ with other porous materials, it is found that their iodine absorption capacity in organic solutions exceeds that of most MOFs and POPs (Table S12). Due to their inherent stability and recyclability as adsorption materials, COFs have been widely used in the field of iodine adsorption.



Figure 5. Comparison of maximum adsorption capacity (q_e^{max}) towards iodine for different COFs in organic solvent. Red stars are used to label TpBD-Me₂ and TpBD-(OMe)₂ prepared in this paper [36,39,40,43–46].

2.3. Adsorption of I_3^- by TPBD-Me₂ and TPBD-(OMe)₂ in Aqueous Solution

Although I_2 is poorly soluble in water, it can form I_3^- with I^- ions, which in turn dissolves in water and becomes one of the major pollutants in water bodies. To expand the application scope of COF materials for solvent-based iodine adsorption, the iodine adsorption capacity of TpBD-Me2 and TpBD-(OMe)2 in aqueous solution was further investigated here. To enhance the solubility of iodine in water, I₂ was dissolved in an aqueous solution containing KI (with a molar ratio of I₂ to I⁻ as 1:5) to generate I_3^- for subsequent adsorption. The flakes of TpBD-Me₂ and TpBD-(OMe)₂ were placed into the I_3^- solution, and it was found that the solution became basically colorless after 24 h, indicating that both COFs possessed high removal efficiency for I_3^- ions (Figure 6a,b). Depending on the concentration of iodine dissolved in the KI solution, the UV-vis spectrum of the I_3^- solution was acquired and a standard curve was employed to quantify the iodine content in the solution (Figure S18). According to the standard curve, the quantity of iodine adsorbed by COF was determined based on the UV-vis absorbance of the solution (Figure S19). The temporal evolution of adsorption capacity per unit mass of COFs (Q_t) and per COF unit cells (Q_t^{tc}) towards I₂ are depicted in Figure 6c (Table S13). The Q_t and $Q_{\ell}^{\mu c}$ values of TpBD-Me₂ and TpBD-(OMe)₂ show a time-dependent increase, eventually reaching equilibrium. Notably, the Q_t value of TpBD-(OMe)₂ is slightly greater than that of TpBD-Me₂, while the $Q_t^{\mu c}$ values display more pronounced differences between the two COFs. These findings suggest that TpBD-(OMe)₂ offers enhanced advantages in adsorbing iodine from aqueous solution. The temporal evolutions of Q_t and $Q_t^{\mu c}$ values exhibit greater conformity with the pseudo-second-order kinetic model, thereby further substantiating the existence of multiple iodine molecule binding sites within COFs and highlighting the occurrence of charge sharing and transfer between iodine molecules and these binding sites (Tables S14 and S15). The time-dependent iodine adsorption rate with respect to COF unit cell $(\Delta Q_{\mu}^{tc}/\Delta t)$ is presented in Figure 6d, where the initial adsorption rate of TpBD-(OMe)₂ is twice as high as that of TpBD-Me₂, and both rates reach equilibrium rapidly. It is noteworthy that both COFs exhibit a higher rate of iodine adsorption in water compared to cyclohexane, attributed to the poor solubility of iodine molecules in aqueous solutions.



Figure 6. (**a**,**b**) The photographs of the process of I_3^- uptake after 5 mg TpBD-Me₂ (**a**) and TpBD-(OMe)₂ (**b**) were immersed in 10 mL of aqueous solution of I_2/KI at the initial concentration of 67 mg·L⁻¹ of I_2 ; the incubation times were marked on the photos. (**c**) The values of Q_t (black) and $Q_t^{\mu c}$ (red) were plotted against time for the adsorption kinetics of TpBD-Me₂ (square) and TpBD-(OMe)₂ (circle), which were fitted by pseudo-first-order (solid curves) and pseudo-second-order (dash curves) kinetics models. (**d**) Plots of the values of $\Delta Q_t^{\mu c}/\Delta t$ for TpBD-Me₂ (black square) and TpBD-(OMe)₂ (red circle) in aqueous solution versus adsorption time. (**e**) Adsorption isotherms of TpBD-Me₂ (square) and TpBD-(OMe)₂ (circle) towards I_2 in KI/I₂ aqueous solution obtained by the values of Q_e (black) and $Q_e^{\mu c}$ (red) at different equilibrium I₂ concentration (C_e), which were fitted by Langmuir and Freundlich models for TpBD-Me₂ and TpBD-(OMe)₂. (**f**) Effect of typical competing anions on the removal percentage of iodine for TpBD-Me₂ (green) and TpBD-(OMe)₂ (blue) at an initial I₂ concentration of 67 mg·L⁻¹, in which the concentration of competing anions is 0.1 M.

The adsorption isotherms for iodine adsorption in aqueous solution by TpBD-Me₂ and TpBD-(OMe)₂ were determined based on the maximum values of Q_e and Q_e^{uc} at various equilibrium concentrations (Table S16, Figure 6e). The maximum iodine uptake of TpBD-Me₂ and TpBD-(OMe)₂, as determined by the Langmuir model, are 939.56 mg/g and 997.13 mg/g, respectively (Table S17). These values significantly exceed the iodine uptake in cyclohexane, indicating that water, despite being considered an undesirable solvent for iodine, exhibits a more favorable propensity for iodine adsorption. The maximum values

of Q_e^{uc} obtained from Langmuir model simulations for TpBD-Me₂ and TpBD-(OMe)₂ are 891.77 g/mol and 1042.15 g/mol, respectively, and TpBD-(OMe)₂ exhibits a superior adsorption capability (Table S18). Based on the correlation coefficient (R²) obtained from the fitting analysis (Figure 6e), it is evident that the adsorption of iodine in water by COFs aligns more closely with the Freundlich model, implying a multilayered adsorption behavior of iodine molecules within the pores of COFs. Freundlich model simulations reveal that TpBD-Me₂ and TpBD-(OMe)₂ exhibit adsorption strengths of 1/n less than 0.5, thereby demonstrating the favorable affinity between the active adsorption sites in the COFs and iodine. Different types of ions tend to dissolve in water when COFs were employed for iodine uptake. However, the efficiency of iodine removal by the COFs in aqueous solutions is found to be unaffected by different anions, indicating that the presence of anionic species does not interfere with the iodine uptake ability of TpBD-Me₂ and TpBD-(OMe)₂ (Figure 6f and Figure S20).

Raman spectroscopy and X-ray photoelectron spectroscopy were employed to confirm the presence of iodine species in TpBD-Me₂ and TpBD-(OMe)₂ after the adsorption of I₃⁻ ions (designated as TpBD-Me₂@I₃⁻ and TpBD-(OMe)₂@I₃⁻) in an aqueous medium. The Raman spectrum reveals that the peaks observed at 108 cm⁻¹ and 140 cm⁻¹ correspond to the symmetric and asymmetric stretching vibrations of I₃⁻, respectively, while the peaks detected at 160 cm⁻¹ are attributed to the vibrations of I₅⁻ (I₂ + I₃⁻) (Figure 7a). The two peaks observed at 632 eV and 620 eV in the XPS of TpBD-Me₂@I₃⁻ and TpBD-(OMe)₂@I₃⁻ correspond to I 3d_{3/2} and I 3d_{5/2}, respectively (Figure S21). High-resolution XPS is able to separate I 3d_{3/2} and I 3d_{5/2} into two characteristic peaks, respectively, with the peaks at binding energies of 618.79 eV and 630.28 eV corresponding to I₃⁻ and the peaks at binding energies of 620.67 eV and 632.28 eV corresponding to I₂ (Figure 7b). The atomic concentrations of TpBD-Me₂@I₃⁻ and TpBD-(OMe)₂ still exhibits a higher affinity for adsorbing I₃⁻ ions (Table S19). The adsorption capacities of TpBD-Me₂ and TpBD-(OMe)₂ exhibit variations in different solvents, while the chemical state of iodine within the COF channels remains consistent.



Figure 7. (a) Raman spectra of TpBD-Me₂@I₃⁻ (black) and TpBD-(OMe)₂@I₃⁻ (red) after adsorption equilibrium. (b) The high-resolution XPS spectrum of I 3d for TpBD-Me₂@I₃⁻ (bottom) and TpBD-(OMe)₂@I₃⁻ (top).

3. Materials and Methods

3.1. Materials

2,4,6-Trihydroxylbenzene-1,3,5-tricarbaldehyde (Tp), o-Tolidine (BD-Me₂), and o-Dianisidine (BD-(OMe)₂) were purchased from Jilin Province Yanshen Technology Co., Ltd, Changchun, China. Iodine, Mesitylene, 1,4-dioxane, NaCl, NaBr, NaNO₃, CH₃COONa, and Na₂SO₄ were purchased from Sigma-Aldrich, Shanghai, China. EtOH, THF, DCM, Acetone, Cyclohexane, and CH₃COOH were purchased from Beijing Chemical Industry Group Co. Ltd., Beijing, China. All the chemicals and materials were used without further purification. Water with resistivity of $18 \text{ M}\Omega \cdot \text{cm}^{-1}$ was prepared using a Millipore Milli-Q system and used in all experiments.

3.2. Characterization

Powder X-ray diffraction (PXRD) was performed using D8 Advance X-ray Diffractometer (Bruker AXS, Karlsruhe, Germany) using Cu-K α radiation ($\lambda = 1.5418$ Å), operating at 40 kV and 40 mA with a scanning rate of 1° ·min⁻¹ (2 θ). FT-IR spectra was recorded on a Bruker IFS 66v/S Fourier transform infrared spectrometer. ¹³C NMR spectra were obtained on a Bruker Avance III model 400 MHz solid-state nuclear magnetic resonance (NMR) spectrometer at a magic angle spinning (MAS) rate of 5 kHz. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha XPS (XPS, ESCALAB 250, Thermofisher, Waltham, U.S.) with a characteristic energy of 1486.7 eV. UV-vis absorption spectroscopy was performed by a UV-2450 spectrophotometer (HITACHI, Tokyo, Japan). Thermogravimetric analysis (TGA) was performed on a Netzch Sta 449c thermal analyzer system in the temperature range from 30 °C to 800 °C at a heating rate of $10 \,^{\circ}\text{C}\cdot\text{min}^{-1}$ in an air atmosphere. The N₂ adsorption–desorption isotherms were measured on a Quantachrome Autosorb-iQ2 analyzer. For N2 adsorption measurements, the masses of TpBD-Me₂ and TpBD-(OMe)₂ used were 69.2 mg and 61.8 mg, respectively. Prior to measurements, the COFs were degassed under vacuum at 120 °C for 8 h in order to remove the gas adsorbed on the surface of the materials. Raman spectroscopy was performed on a Horiba LabRAM HR evolution instrument in the wavenumber range of $50-1000 \text{ cm}^{-1}$ by using 633 nm laser (50 mW). The accumulation time of 600 s was applied to collect all the spectroscopic data. Scanning electron microscopy (SEM) imaging and energy dispersive spectroscopic (EDS) elementary mapping were performed on a Hitachi FE-SEM S-4800 scanning electron microscope with an acceleration voltage of 3 kV. The TEM images were observed on JEM-2100F, JEOL transmission electron microscopy.

3.3. Synthesis of TpBD-Me₂ and TpBD-(OMe)₂ Powders

In the typical synthesis, a Pyrex tube (o.d. \times i.d. = 10 \times 8 mm² and length 18 cm) was charged with 0.2 mM 1,3,5-triformylphloroglucinol (Tp, 42.0 mg), 0.3 mM o-tolidine (BD-Me₂, 63.7 mg), or o-dianisidine (BD-(OMe)₂, 73.3 mg), 1.5 mL of mesitylene, 1.5 mL of 1,4-dioxane and 0.2 mL of 6 M aqueous acetic acid. This reaction mixture was sonicated for 10 min to obtain a homogeneous dispersion. After being frozen at 77 K (liquid N₂ bath) and degassed by three freeze–pump–thaw cycles, the reaction tube was flame-sealed, reducing the total length by ca. 8.0 cm. Upon warming to room temperature, the reaction tube was then heated to 120 °C for 3 days. After cooling down to room temperature, the precipitates were isolated through filtration and washed with THF/DCM/acetone thrice. The products obtained were further purified through Soxhlet extraction using THF as the solvent for two days. After that, the products were dried in vacuo at 120 °C for 24 h to produce TpBD-Me₂ in 90.4% yield and TpBD-(OMe)₂ in 91.2% yield.

3.4. Study of Iodine Adsorption Property of TpBD-Me2 and TpBD-(OMe)2 in Cyclohexane

To avoid iodine sublimation, all iodine adsorption experiments in different solutions were carried out in dark brown bottles at room temperature. The absorption intensity of I₂ cyclohexane solution with different concentrations of 5, 10, 25, 50, 100, 250, 500 mg/L was measured using UV-vis absorption spectroscopy, and the absorption intensity was plotted against the concentration to obtain the standard curve of I₂ cyclohexane solution. After asprepared TpBD-Me₂ and TpBD-(OMe)₂ were placed into the I₂ cyclohexane solutions, the I₂ concentration in cyclohexane were monitored by means of UV-vis absorption spectroscopy. The I₂ concentration in cyclohexane solutions at a given adsorption time (t, min) was calculated from the standard curve. The I₂ adsorption capacity with respect to the mass of COFs (q_t , mg·g⁻¹) and molar number of COF unit cells (q_t^{uc} , g·mol⁻¹) and the ratio of

$$q_t = \left((C_0 - C_t) V \right) / W_{COF} \tag{1}$$

$$q_t^{uc} = ((C_0 - C_t)V) / (W_{COF} / M_{COF})$$
⁽²⁾

$$q_t^{mol} = \left((C_0 - C_t) V / M_{I_2} \right) / (W_{COF} / M_{COF})$$
(3)

where C_0 is the initial concentration of I₂ cyclohexane solution, C_t is the concentration of the solution at any time during the adsorption process, V is the volume of solution used for adsorption, W_{COF} is the mass of the COFs and M_{COF} is the molar mass of COF unit cell, which are 949.06 g/mol and 1045.06 g/mol, respectively, for TpBD-Me₂ and TpBD-(OMe)₂ according to the molar ratio of the reactive monomers. M_{I_2} is the molar mass of the I₂ molecule, the value of which is 253.8 g/mol.

The measured adsorption kinetics data of TpBD-Me₂ and TpBD-(OMe)₂ were fitted using pseudo-first-order and pseudo-second-order models, as shown in Equations (4) and (5), respectively.

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{4}$$

$$t/q_t = 1/k_2(q_e)^2 + t/q_e$$
(5)

In these equations, q_t and q_e are the adsorption capacity at a given time (t, min) and at equilibrium state. When q_t is the adsorption capacity with respect to COF unit cell (q_t^{uc}), q_e is defined as adsorption capacity per molar number of COF unit cell (q_e^{uc}), and k_1 and k_2 are the pseudo-first-order rate constant (min⁻¹) and the pseudo-second-order rate constant ($g \cdot mg^{-1} \cdot min^{-1}$), respectively.

When adsorption equilibrium is reached, adsorption capacity with respect to the mass of COFs (q_e) and the molar number of COF unit cell (q_e^{uc}), and the ratio of the molar number of adsorbed I₂ molecules to that of COF unit cells (q_e^{mol}) at different initial concentrations (C_0) can be calculated using Equations (1)–(3) according to different equilibrium concentrations (C_e). The Langmuir isotherm is used to study the adsorption process occurring on the surface of the adsorbent (Equation (6)). In this equation, K_L is the Langmuir constant, q_m (mg·g⁻¹, g·mol⁻¹) is the maximum adsorption capacity, and C_e (mg·L⁻¹) is the iodine concentration at equilibrium state.

$$q_e = q_m K_L C_e / (1 + K_L C_e) \tag{6}$$

The Freundlich isotherm is often used to study multi-layer adsorptions, as described in Equation (7),

$$lnq_e = 1/nlnC_e + lnK_F \tag{7}$$

where 1/n represents the adsorption intensity (mg·L⁻¹), K_F is the Freundlich constant (mg·g⁻¹, g·mol⁻¹), and C_e (mg·L⁻¹) is the equilibrated concentration of iodine.

3.5. Study of Iodine Adsorption Property of TpBD-Me₂ and TpBD-(OMe)₂ in Aqueous Solution

The absorption intensity of KI/I₂ aqueous solutions with different concentrations of I₂ at 10, to 20, 30, 40, 50, 60, and 80 mg/L was measured using UV-vis absorption spectroscopy, and the absorption intensity was plotted against the concentration to obtain the standard curve. After as-prepared TpBD-Me₂ and TpBD-(OMe)₂ were placed into the KI/I₂ aqueous solutions, the I₂ concentration in the solution was monitored by means of UV-vis absorption spectroscopy. The I₂ concentration in aqueous solutions at a given adsorption time (t, min) was calculated from the standard curve. The I₂ adsorption capacity in KI/I₂ aqueous solution with respect to the mass of COFs (Q_t , mg·g⁻¹) and molar number of COF unit cells (Q_t^{uc} , g·mol⁻¹) was calculated using Equations (1)–(3) using I₂ concentration in solution at any time (C_t). The adsorption kinetics of I₂ in aqueous solution can also be fitted through the pseudo-first-order and pseudo-second-order models (Equations (4) and (5)).

The maximum adsorption capacity towards I_2 with respect to the mass of COFs (Q_e) and the molar number of COF unit cell (Q_e^{uc}) in KI/I₂ aqueous solutions can also be

calculated using Equations (1) and (2) according different I₂ concentrations at equilibrium states (C_e). The adsorption isotherms could be simulated by Langmuir and Freundlich models to obtain the maximum adsorption capacity (Q_m) and the adsorption intensity (1/n) in aqueous solutions (Equations (6) and (7)).

3.6. Study of the Reusability of Iodine Uptake by $TpBD-Me_2$ and $TpBD-(OMe)_2$ in Cyclohexane

Freshly prepared TpBD-Me₂ and TpBD-(OMe)₂ were immersed in a cyclohexane solution containing 100 mg/L of I₂ for three days to achieve adsorption equilibrium. Afterwards, TpBD-Me₂ and TpBD-(OMe)₂, which were saturated with adsorbed iodine, were immersed in ethanol for desorption. The ethanol was replaced every 12 h for a total of five cycles to ensure complete desorption of iodine molecules existed in the pores of COF materials. Next, TpBD-Me₂ and TpBD-(OMe)₂ were again immersed in 100 mg/L of I₂ cyclohexane solution for I₂ adsorption. This cycle was repeated 3 times, and the amount of iodine adsorbed by TpBD-Me₂ and TpBD-(OMe)₂ each time was compared with that of fresh preparation.

3.7. Evaluation of the Resistance to Anionic Interference on the Iodine Absorption Property in Aqueous Solutions

The KI/I₂ solution, containing an I₂ concentration of 67 mg/L, was supplemented with 0.1 M NaCl, NaBr, NaNO₃, CH₃COONa, and Na₂SO₄, respectively. Subsequently, 5 mg of TpBD-Me₂ and TpBD-(OMe)₂ were immersed in the aforementioned mixed solution. After a period of 3 days, the adsorption equilibrium was established, and the I₂ concentration in the solution was determined using UV-vis spectroscopy. Subsequently, the adsorption capacity of iodine (Q_e) by COFs after mixing other anions in the KI/I₂ solution was calculated based on Equation (1). The removal efficiency of iodine can be determined using Equation (8).

$$Removal \ \% = Q_e / (C_0 V) \tag{8}$$

4. Conclusions

The present study successfully synthesized two COFs, namely TpBD-Me₂ and TpBD-(OMe)₂, through the Schiff base reaction under solvothermal conditions. PXRD analysis, thermogravimetry, and N_2 adsorption–desorption confirmed their high crystallinity, excellent thermal stability, large specific surface area, and presence of open pores. Considering the abundance of electron-rich N and O atoms in both COFs, their potential for efficient iodine absorption in cyclohexane and aqueous solution was explored. Both in water and in cyclohexane, TpBD-OMe₂ exhibited higher iodine uptake and faster iodine uptake rates relative to TpBD-Me2, which was attributed to the existence of ether oxygen atoms increasing the number of its adsorption sites. The present study confirmed the crucial role of ether oxygen atoms in multiple COF monomers for iodine adsorption. Comparing the iodine adsorption of TpBD-(OMe)₂ with other porous materials, it was found that its adsorption capacity was able to exceed that of most of the POPs (including COFs) and MOFs, making it a preferred material for iodine adsorption. Raman spectroscopy and XPS analysis revealed that iodine predominantly existed as monomeric species and their aggregates (I_2, I_3^-, I_3^-) I_5^-) within the pores of the COFs. In this work, the adsorption capacities of TpBD-Me₂ and TpBD-(OMe)₂ in solutions were investigated for the first time from the perspective of adsorption sites, which improved the experimental basis and research ideas for the design of COF materials for iodine adsorption and provided new materials for the efficient removal of iodine from solutions.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/molecules28248151/s1, Figure S1: FT-IR spectra of COFs; Figure S2: Solidstate ¹³C CP-MAS NMR spectra of COFs; Figure S3: TGA profiles of COFs; Figure S4: XPS spectra of COFs; Figure S5: High-resolution XPS spectra of C1s; Figure S6: SEM images of COFs; Figure S7: TEM images of COFs; Figure S8: PXRD patterns of COFs in different solvents; Figure S9: Nitrogen adsorption-desorption isotherms curves and the pore size distribution of COFs; Figure S10: Plots of BET surface area of COFs; Figure S11: Photos of disk-shaped sheet of COFs; Figure S12: PXRD patterns of COF sheets; Figure S13: TGA profiles of COF sheets; Figure S14: Temporal absorption spectral evolution of cyclohexane solution of I_2 during the adsorption process; Figure S15: UV-Vis spectra of cyclohexane solutions of I2 and plot of the absorption intensity versus the I₂ concentration; Figure S16: PXRD patterns of COFs@I₂; Figure S17: XPS spectra of COFs@I₂; Figure S18: UV-vis spectra of I₃⁻ aqueous solution and plot of the absorbance intensity of I_3^- aqueous solution versus I_2 concentration; Figure S19: Temporal absorption spectral evolution of aqueous solution of I_2/KI during the adsorption process; Figure S20: Plots of the values of $Q_{\rm e}$ in the presence of different kinds of competing anions; Figure S21: XPS spectra of COFs@I₃⁻; Table S1: Summary of C, N, O atomic concentration of COFs; Table S2: Summary of the BET fitting results of nitrogen adsorption isotherms of COFs; Table S3: Summary of the values of q_t , q_t^{uc} and q_t^{Mol} ; Table S4: Summary of the experimental values of q_e and calculated value of q_e from fitting of their adsorption kinetics profiles; Table S5: Summary of the experimental values of $q_{\mu}^{\mu c}$ and the calculated value of q_e^{uc} from fitting of their adsorption kinetics profiles; Table S6: Summary of the values of q_t^{N+CO} of TpBD-Me₂ and q_t^{N+O} , q_t^{EO} of TpBD-(OMe)₂; Table S7: Summary of the values of q_e^{N+CO} of TpBD-Me₂ and the values of q_e^{N+O} and q_e^{EO} of TpBD-(OMe)₂ and the calculated value of q_e^{N+O} , q_e^{N+O} and q_e^{EO} from fitting of their adsorption kinetics profiles; Table S8: Summary of the q_e , q_e^{uc} and q_e^{Mol} values at different initial I₂ concentrations; Table S9: Summary of the fitting results of I₂ adsorption isotherms in terms of q_e ; Table S10: Summary of the fitting results of I₂ adsorption isotherms in terms of $q_e^{\mu c}$; Table S11: Summary of the element atomic concentration of COFs@I₂; Table S12: Summary of I₂ adsorption capacity of reported porous materials in organic solvent; Table S13: Summary of the values of Q_t , $Q_t^{\mu c}$; Table S14: Summary of the experimental values of Q_e and the calculated value of Q_e from fitting of their adsorption kinetics profiles; Table S15: Summary of the experimental values of Q_e^{uc} and the calculated value of Q_e^{uc} from fitting of their adsorption kinetics profiles; Table S16: Summary of the Q_e and Q_e^{uc} values; Table S17: Summary of the fitting results of I₂ adsorption isotherms in terms of Q_{ei} ; Table S18: Summary of the fitting results of I_2 adsorption isotherms in terms of Q_e^{uc} ; Table S19: Summary of the element atomic concentration of COFs@I₃⁻. References [48–76] are cited in the supplementary materials.

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References

- Bates, J.K.; Bradley, J.P.; Teetsov, A.; Bradley, C.R.; Buchholtz Ten Brink, M. Colloid Formation During Waste Form Reaction: Implications for Nuclear Waste Disposal. *Science* 1992, 256, 649–651. [CrossRef] [PubMed]
- Wang, C.; Jiang, S.; Ma, W.; Liu, Z.; Liu, L.; Zou, Y.; Xu, B.; Tian, W. Polymorphic Covalent Organic Frameworks: Molecularly Defined Pore Structures and Iodine Adsorption Property. *Molecules* 2023, 28, 449. [CrossRef] [PubMed]
- Dehner, G.; McBeth, M.K.; Moss, R.; Woerden, I. A Zero-Carbon Nuclear Energy Future? Lessons Learned from Perceptions of Climate Change and Nuclear Waste. *Energies* 2023, 16, 2025. [CrossRef]
- Fujiwara, H. Observation of Radioactive Iodine (I-131, I-129) in Cropland Soil after the Fukushima Nuclear Accident. *Sci. Total Environ.* 2016, 566, 1432–1439. [CrossRef] [PubMed]
- Vienna, J.D. Nuclear Waste Vitrification in the United States: Recent Developments and Future Options. *Int. J. Appl. Glass. Sci.* 2010, 1, 309–312. [CrossRef]

- Ewing, R.C.; Hippel, F.N. Nuclear Waste Management in the United States-Starting Over. Science 2009, 325, 151–152. [CrossRef] [PubMed]
- Teien, H.C.; Wada, T.; Kashparov, V.; Lopez-Gutierrez, J.M.; Garcia-Tenorio, R.; Hinton, T.G.; Salbu, B. Transfer of 129 I to Freshwater Fish Species within Fukushima and Chernobyl Exclusion Zones. J. Environ. Radioact. 2023, 207, 107269. [CrossRef]
- 8. Zhou, W.; Li, A.; Zhou, M.; Xu, Y.; Zhang, Y.; He, Q. Nonporous Amorphous Superadsorbents for Highly Effective and Selective Adsorption of Iodine in Water. *Nat. Commun.* **2023**, *14*, 5388. [CrossRef]
- 9. Nandanwar, S.U.; Coldsnow, K.; Utgikar, V.; Sabharwall, P.; Aston, D.E. Capture of Harmful Radioactive Contaminants from Off-gas Stream Using Porous Solid Sorbents for Clean Environment—A Review. *Chem. Eng. J.* **2016**, *306*, 369–381. [CrossRef]
- 10. Herdes, C.; Prosenjak, C.; Román, S.; Müller, E.A. Fundamental Studies of Methyl Iodide Adsorption in DABCO Impregnated Activated Carbons. *Langmuir* **2013**, *29*, 6849–6855. [CrossRef]
- González-García, C.M.; Román, S.; González, J.F.; Sabio, E.; Ledesma, B. Surface Free Energy Analysis of Adsorbents Used for Radioiodine Adsorption. *Appl. Surf. Sci.* 2013, 282, 714–717. [CrossRef]
- 12. Huve, J.; Ryzhikov, A.; Nouali, H.; Lalia, V.; Auged, G.; Daou, T.J. Porous Sorbents for the Capture of Radioactive Iodine Compounds: A Review. *RSC Adv.* **2018**, *8*, 29248–29273. [CrossRef]
- Jabraoui, H.; Hessou, E.P.; Chibani, S.; Cantrel, L.; Lebegue, S.; Badawi, M. Adsorption of Volatile Organic and Iodine Compounds over Silver-Exchanged Mordenites: A Comparative Periodic DFT Study for Several Silver Loadings. *Appl. Surf. Sci.* 2019, 485, 56–63. [CrossRef]
- 14. Yadav, A.; Chong, S.; Riley, B.J.; MoCloy, J.S.; Goel, A. Iodine Capture by Ag-Loaded Solid Sorbents Followed by Ag Recycling and Iodine Immobilization: An End-to-End Process. *Ind. Eng. Chem. Res.* **2023**, *62*, 3635–3646. [CrossRef]
- 15. Wu, L.; Sawada, J.A.; Kuznicki, D.B.; Kuznicki, T.; Kuznicki, S.M. Iodine Adsorption on Silver-Exchanged Titania-Derived Adsorbents. *J. Radioanal. Nucl. Chem.* **2014**, 302, 527–532. [CrossRef]
- Muhire, C.; Reda, A.T.; Zhang, D.; Xu, Y.; Cui, C. An Overview on Metal Oxide-Based Materials for Iodine Capture and Storage. Chem. Eng. J. 2022, 431, 133816. [CrossRef]
- 17. Liu, S.; Kang, S.; Wang, H.; Wang, G.; Zhao, H.; Cai, W. Nanosheets-Built Flowerlike Micro/Nanostructured Bi₂O_{2.33} and Its Highly Efficient Iodine Removal Performances. *Chem. Eng. J.* **2016**, *289*, 219–230. [CrossRef]
- Bo, A.; Sarina, S.; Zheng, Z.; Yang, D.; Liu, H.; Zhu, H. Removal of Radioactive Iodine from Water Using Ag₂O Grafted Titanate Nanolamina as Efficient Adsorbent. *J. Hazard. Mater.* 2013, 246, 199–205. [CrossRef]
- 19. Asmussen, R.M.; Matyas, J.; Qafoku, N.P.; Kruger, A.A. Silver-Functionalized Silica Aerogels and Their Application in the Removal of Iodine from Aqueous Environments. *J. Hazard. Mater.* **2019**, *379*, 119364. [CrossRef] [PubMed]
- Tang, S.; Choi, S.; Nan, Y.; Tavlarides, L.L. Adsorption of Methyl Iodide on Reduced Silver-Functionalized Silica Aerogel: Kinetics and Modeling. AIChE J. 2021, 67, e17137. [CrossRef]
- Buck, T.; Chibani, S.; Paul, J.-F.; Cantrel, L.; Badawi, M. Dissociative Iodomethane Adsorption on Ag-MOR and the Formation of Agl Clusters: An &ITab Initio&IT Molecular Dynamics Study. *Phys. Chem. Chem. Phys.* 2017, 19, 27530–27543.
- Wang, B.; Zhu, H.; Duan, T.; He, G.; Wei, Y.; Zhou, J. Multi-Layer Active Interface Construction with Polyphenols and Nano-Silver on Nano Collagen Fiber for Efficient Capturing Iodine Vapor. *Appl. Surf. Sci.* 2022, 596, 153585. [CrossRef]
- 23. Yu, X.; Cui, W.; Zhang, F.; Guo, Y.; Deng, T. Removal of Iodine from the Salt Water Used for Caustic Soda Production by Ion-Exchange Resin Adsorption. *Desalination* **2019**, *458*, 76–83. [CrossRef]
- 24. Chen, D.; Ma, T.; Zhao, X.; Jing, X.; Zhao, R.; Zhu, G. Multi-Functionalization Integration into the Electrospun Nanofibers Exhibiting Effective Iodine Capture from Water. *ACS Appl. Mater. Interfaces* **2022**, *14*, 47126–47135. [CrossRef]
- Xiang, Y.; Wang, Y.; Chen, H.; Fu, J.; Zhu, Q.; Yang, X.; Xu, X.; Qin, S.; He, L.; Tao, G. Efficient Enrichment of Iodine by Supported Ionic Liquid with Three Effective Adsorption Sites: Heteroatoms, Fused Aromatic Rings and Ionic Bond. *Chem. Eng. J.* 2023, 456, 140979. [CrossRef]
- Zhang, X.; Maddock, J.; Nenoff, T.M.; Denecke, M.A.; Yang, S.; Schroder, M. Adsorption of Iodine in Metal–Organic Framework Materials. *Chem. Soc. Rev.* 2022, *51*, 3243. [CrossRef]
- 27. Yu, R.; Li, Q.; Li, Z.; Wang, X.; Xia, L. Analysis of Radioactive Iodine Trapping Mechanism by Zinc-Based Metal–Organic Frameworks with Various N-Containing Carboxylate Ligands. *ACS Appl. Mater. Interfaces* **2023**, *15*, 35082–35091. [CrossRef]
- Zhang, Y.; Cui, X.; Xing, H. Recent Advances in the Capture and Abatement of Toxic Gases and Vapors by Metal–Organic Frameworks. *Mater. Chem. Front.* 2021, 5, 5970. [CrossRef]
- Li, Z.; Ju, Y.; Yu, B.; Wu, X.; Lu, H.; Li, Y.; Zhou, J.; Guo, X.; Zhang, Z.; Lin, J.; et al. Modulated Synthesis and Isoreticular Expansion of Th-MOFs with Record High Pore Volume and Surface Area for Iodine Adsorption. *Chem. Commun.* 2020, 56, 6715. [CrossRef] [PubMed]
- 30. Du, W.; Qin, Y.; Ni, C.; Dai, W.; Zou, J. Efficient Capture of Volatile Iodine by Thiophene-Containing Porous Organic Polymers. *ACS Appl. Polym. Mater.* **2020**, *2*, 5121–5128. [CrossRef]
- Kurisingal, J.F.; Yun, H.; Hong, C.S. Porous Organic Materials for Iodine Adsorption. J. Hazard. Mater. 2023, 458, 131835. [CrossRef] [PubMed]
- 32. Wang, H.; Qiu, N.; Kong, X.; Hu, Z.; Zhong, F.; Li, Y.; Tan, H. Novel Carbazole-Based Porous Organic Polymer for Efficient Iodine Capture and Rhodamine B Adsorption. *ACS Appl. Mater. Interfaces* **2023**, *15*, 14846–14853. [CrossRef] [PubMed]
- Yan, Z.; Yuan, Y.; Tian, Y.; Zhang, D.; Zhu, G. Highly Efficient Enrichment of Volatile Iodine by Charged Porous Aromatic Frameworks with Three Sorption Sites. *Angew. Chem. Int. Ed.* 2015, 54, 12733–12737. [CrossRef] [PubMed]

- Chandra, S.; Kandambeth, S.; Biswal, B.P.; Lukose, B.; Kunjir, S.M.; Chaudhary, M.; Babarao, R.; Heine, T.; Banerjee, R. Chemically Stable Multilayered Covalent Organic Nanosheets from Covalent Organic Frameworks via Mechanical Delamination. *J. Am. Chem. Soc.* 2013, 135, 17853–17861. [CrossRef]
- Liu, T.; Zhao, Y.; Song, M.; Pang, X.; Shi, X.; Jia, J.; Chi, L.; Lu, G. Ordered Macro–Microporous Single Crystals of Covalent Organic Frameworks with Efficient Sorption of Iodine. J. Am. Chem. Soc. 2023, 145, 2544–2552. [CrossRef] [PubMed]
- Song, S.; Shi, Y.; Liu, N.; Liu, F. Theoretical Screening and Experimental Synthesis of Ultrahigh-Iodine Capture Covalent Organic Frameworks. ACS Appl. Mater. Interfaces 2021, 13, 10513–10523. [CrossRef] [PubMed]
- 37. Zhang, Z.; Dong, X.; Yin, J.; Li, Z.; Li, X.; Zhang, D.; Pan, T.; Lei, Q.; Liu, X.; Xie, Y.; et al. Chemically Stable Guanidinium Covalent Organic Framework for the Efficient Capture of Low-Concentration Iodine at High Temperatures. *J. Am. Chem. Soc.* **2022**, 144, 6821–6829. [CrossRef]
- Xie, Y.; Pan, T.; Lei, Q.; Chen, C.; Dong, X.; Yuan, Y.; Shen, J.; Cai, Y.; Zhou, C.; Pinnau, I.; et al. Ionic Functionalization of Multivariate Covalent Organic Frameworks to Achieve an Exceptionally High Iodine-Capture Capacity. *Angew. Chem. Int. Ed.* 2021, 60, 22432–22440. [CrossRef]
- Li, Y.; Li, X.; Li, J.; Liu, W.; Cheng, G.; Ke, H. Phosphine-Based Covalent Organic Framework for Highly Efficient Iodine Capture. *Micropor. Mesopor. Mater.* 2021, 325, 111351. [CrossRef]
- 40. Yan, X.; Yang, Y.; Li, G.; Zhang, J.; He, Y.; Wang, R.; Lin, Z.; Cai, Z. Thiophene-Based Covalent Organic Frameworks for Highly Efficient Iodine Capture. *Chin. Chem. Lett.* **2023**, *34*, 107201. [CrossRef]
- 41. Sun, Y.; Song, S.; Xiao, D.; Gan, L.; Wang, Y. Easily Constructed Imine-Bonded COFs for Iodine Capture at Ambient Temperature. ACS Omega 2020, 5, 24262–24271. [CrossRef] [PubMed]
- 42. Ding, S.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.; Su, C.; Wang, W. Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki-Miyaura Coupling Reaction. *J. Am. Chem. Soc.* **2011**, 133, 19816–19822. [CrossRef] [PubMed]
- 43. Jing, L.; Cheng, C.; Wang, B.; Wang, S.; Xie, R.; Xia, H.; Wang, D. Controlled Iodine Phase Transfer of Covalent Organic Framework Membranes for Instant but Sustained Disinfection. *Langmuir* **2023**, *39*, 597–609. [CrossRef] [PubMed]
- 44. Wu, Z.; Wei, W.; Ma, J.; Luo, J.; Zhou, Y.; Zhou, Z.; Liu, S. Adsorption of Iodine on Adamantane-Based Covalent Organic Frameworks. *Chem. Select* 2021, *6*, 10141–10148. [CrossRef]
- Liu, X.; Zhang, A.; Ma, R.; Wu, B.; Wen, T.; Ai, Y.; Sun, M.; Jin, J.; Wang, S.; Wang, X. Experimental and Theoretical Insights into Copper Phthalocyanine-Based Covalent Organic Frameworks for Highly Efficient Radioactive Iodine Capture. *Chin. Chem. Lett.* 2022, 33, 3549–3555. [CrossRef]
- 46. Mokhtari, N.; Dinari, M. Developing Novel Amine-Linked Covalent Organic Frameworks towards Reversible Iodine Capture. Sep. Purif. Technol. 2022, 301, 121948. [CrossRef]
- 47. Song, S.; Shi, Y.; Liu, N.; Liu, F. C=N Linked Covalent Organic Framework for the Efficient Adsorption of Iodine in Vapor and Solution. *RSC Adv.* **2021**, *11*, 10512. [CrossRef]
- Wang, Z.; Huang, Y.; Yang, J.; Li, Y.; Zhuang, Q.; Gu, J. The Water-Based Synthesis of Chemically Stable Zr-Based MOFsUsing Pyridine-Containing Ligands and Their Exceptionally High Adsorption Capacity for Iodine. *Dalton Trans.* 2017, 46, 7412–7420. [CrossRef]
- Xu, T.; Li, J.; Jia, M.; Li, G.; Liu, Y. Contiguous Layer Based Metal–Organic Framework with Conjugated π-Electron Ligand for High Iodine Capture. *Dalton Trans.* 2021, 50, 13096–13102. [CrossRef]
- 50. Ju, Y.; Li, Z.; Qiu, J.; Li, X.; Yang, J.; Zhang, Z.; He, M.; Wang, J.; Lin, J. Adsorption and Detection of Iodine Species by a Thorium-Based Metal–Organic Framework. *Inorg. Chem.* **2023**, *62*, 8158–8165. [CrossRef]
- 51. Zhao, Y.; Zhang, N.; Wang, Y.; Bai, F.; Xing, Y.; Sun, L. Ln-MOFs with Window-Shaped Channels Based on Triazine Tricarboxylic Acid as a Linker for the Highly Efficient Capture of Cationic Dyes and Iodine. *Inorg. Chem. Front.* 2021, *8*, 1736–1746. [CrossRef]
- 52. Xu, L.; Zheng, Q.; Wang, Y.; Jiang, L.; Jiang, J.; Qiu, J. A Pillared Double-Wall Metal-Organic Framework Adsorption Membrane for the Efficient Removal of Iodine from Solution. *Sep. Purif. Technol.* **2021**, 274, 118436. [CrossRef]
- 53. Zhang, N.; Sun, L.; Xing, Y.; Bai, F. A Double-Walled Thorium-Based Metal—Organic Framework as a Promising Dual-Function Absorbent for Efficiently Capturing Iodine and Dyes. *Cryst. Growth Des.* **2019**, *19*, 5686–5695. [CrossRef]
- Cai, H.; Zeng, G.; You, Z.; Wang, C.; Sun, L.; Bai, F.; Xing, Y. Cu(II) and Zn(II) Frameworks Constructed by Directional Tuning of Diverse Substituted Groups on a Triazine Skeleton and Supermassive Adsorption Behavior for Iodine and Dyes. *Dalton Trans.* 2022, 51, 5457–5470. [CrossRef] [PubMed]
- Zhang, N.; Sun, L.; Bai, F.; Xing, Y. Thorium-Organic Framework Constructed with a Semirigid Triazine Hexacarboxylic Acid Ligand: Unique Structure with Thorium Oxide Wheel Clusters and Iodine Adsorption Behavior. *Inorg. Chem.* 2020, 59, 3964–3973. [CrossRef]
- 56. Liu, M.; Cai, H.; Jiang, S.; Xing, Y.; Bai, F. Construction of a Triazine Polycarboxylate Co-MOF with Flexible and Rigid Coordination Arms as well as Excellent Catalytic Reduction and Adsorption Properties. *Dalton Trans.* **2023**, *52*, 6773–6781. [CrossRef]
- 57. Li, Z.; Yue, Z.; Ju, Y.; Wu, X.; Ren, Y.; Wang, S.; Li, Y.; Zhang, Z.; Guo, X.; Lin, J. Ultrastable Thorium Metal–Organic Frameworks for Efficient Iodine Adsorption. *Inorg. Chem.* **2020**, *59*, 4435–4442.
- 58. Huang, J.; Hu, H.; Deng, S.; Cai, S.; Fan, J.; Zhang, W.; Zheng, S. A Ni(II) metal–organic framework with helical channels for the capture of iodine via guest exchange induced amorphization. *New J Chem.* **2022**, *46*, 7144–7152. [CrossRef]
- 59. Hu, H.; Chen, F.; Zhang, Z.; Liu, D.; Liang, Y.; Chen, Z. Heterometallic Metal-Organic Framework Based on [Cu₄I₄] and [Hf₆O₈] Clusters for Adsorption of Iodine. *Front. Chem.* **2022**, *10*, 864131. [CrossRef]

- 60. Falaise, C.; Volkringer, C.; Facqueur, J.; Bousquet, T.; Gasnot, L.; Loiseau, T. Capture of Iodine in Highly Stable Metal–Organic Frameworks: A Systematic Study. *Chem. Commun.* **2013**, *49*, 10320–10322. [CrossRef]
- 61. Li, Z.; Ju, Y.; Lu, H.; Wu, X.; Yu, X.; Li, Y.; Wu, X.; Zhang, Z.; Lin, J.; Qian, Y. Boosting the Iodine Adsorption and Radioresistance of Th-UiO-66 MOFs via Aromatic Substitution. *Chem. Eur. J.* **2020**, *27*, 1286–1291. [CrossRef]
- Wang, G.; Huang, J.; Huang, X.; Deng, S.; Zheng, S.; Cai, S.; Fan, J.; Zhang, W. A Hydrolytically Stable Cage-Based Metal–Organic Framework Containing two Types of Building Blocks for the Adsorption of Iodine and Dyes. *Inorg. Chem. Front.* 2021, *8*, 1083–1092. [CrossRef]
- 63. Chen, H.; Fan, L.; Zhang, X.; Ma, L. Robust Heterometallic Tb^{III}/Mn^{II}–Organic Framework for CO₂/CH₄ Separation and I₂ Adsorption. *ACS Appl. Nano Mater.* **2020**, *3*, 2680–2686. [CrossRef]
- 64. Yu, R.; Li, Q.; Zhang, T.; Li, Z.; Xia, L. Zn, O Co-Adsorption Based on MOF-5 for Efficient Capture of Radioactive Iodine. *Process* Saf. Environ. 2023, 174, 770–777. [CrossRef]
- Yang, Y.; Tu, C.; Shi, J.; Zhao, T.; Liu, Z.; Cheng, F.; Luo, F. Highly Stable Cd(II)-MOFs Based on 2,6-Naphthanlenedisulfonate and Bisimidazole Ligands: A New Platform for Selective Detection of Cu²⁺ and Efficient Removal of Iodine. *J. Solid State Chem.* 2021, 302, 122439. [CrossRef]
- 66. Zhang, N.; Xing, Y.; Bai, F. A Uranyl-Organic Framework Featuring Two-Dimensional Graphene-like Layered Topology for Efficient Iodine and Dyes Capture. *Inorg. Chem.* 2019, *58*, 6866–6876. [CrossRef]
- 67. Li, M.; Yuan, G.; Zeng, Y.; Yang, Y.; Liao, J.; Yang, J.; Liu, N. Flexible surface-supported MOF membrane via a convenient approach for efficient iodine adsorption. *J. Radioanal. Nucl. Ch.* **2020**, 324, 1167–1177. [CrossRef]
- 68. Al Lafi, A.G.; Assfour, B.; Assaad, T. Metal Organic Framework MIL-101(Cr): Spectroscopic Investigations to Reveal Iodine Capture Mechanism. *J. Inorg. Organomet. P.* **2020**, *30*, 1218–1230. [CrossRef]
- 69. Li, L.; Sun, Z.; Yang, A.; Zhang, X.; Zhu, X.; Li, W.; Liu, Y.; Luan, J. A Novel Azo-Linked Polymer Bearing Trifluoromethyl Groups for I₂ Capture. *Macromol. Rapid Comm.* **2023**, *44*, 2200982. [CrossRef] [PubMed]
- 70. Thurakkal, L.; Cheekatla, S.; Porel, M. Superfast Capture of Iodine from Air, Water, and Organic Solvent by Potential Dithiocarbamate-Based Organic Polymer. *Int. J. Mol. Sci.* 2023, 24, 1466. [CrossRef] [PubMed]
- 71. Pan, X.; Ding, C.; Zhang, Z.; Ke, H.; Cheng, G. Functional Porous Organic Polymer with High S and N for Reversible Iodine Capture. *Micropor. Mat.* 2020, 300, 110161. [CrossRef]
- 72. Yang, X.; Duan, L.; Ran, X.; Ran, B.; Yi, S. Two Nitrogen-Rich Conjugated Microporous Polymers for Efficient Iodine Sequestration and Removal. *J. Polym. Res.* 2022, 29, 499. [CrossRef]
- 73. Sigen, A.; Zhang, Y.; Li, Z.; Xia, H.; Xue, M.; Liu, X.; Mu, Y. Highly Efficient and Reversible Iodine Capture Using a Metalloporphyrin-Based Conjugated Microporous Polymer. *Chem. Commun.* **2014**, *50*, 8495–8498.
- 74. Liu, L.; Song, C.; Kong, A. Nitrogen and Sulfur-Enriched Porous Bithiophene-Melamine Covalent Organic Polymers for Effective Capture of CO₂ and Iodine. *Mater. Lett.* **2020**, 277, 128291. [CrossRef]
- 75. Mohan, A.; Al-Sayah, M.H.; Ahmed, A.; El-Kadri, O.M. Triazine-Based Porous Organic Polymers for Reversible Capture of Iodine and Utilization in Antibacterial Application. *Sci. Rep.* 2022, *12*, 2638. [CrossRef]
- Yang, M.; Shi, W.; Liu, S.; Xu, K. Multifunctional Diphenyl Ether-Based, Cross-Linked Polyisocyanide for Efficient Iodine Capture and NO₂⁻/SO₃²⁻ Electrochemical Probing. *Colloid Surface A* 2022, 642, 128680. [CrossRef]

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