

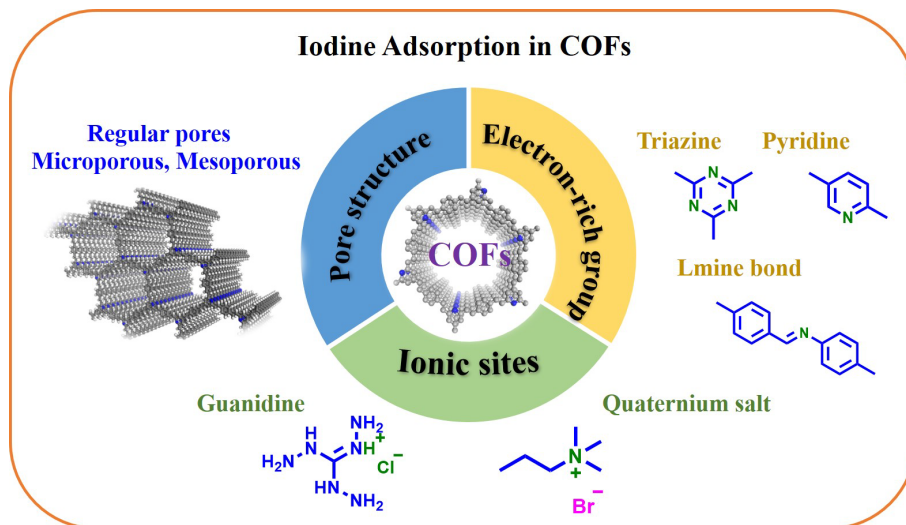
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Structure-activity relationship of covalent organic frameworks (COFs) for gaseous iodine adsorptionSiyu Chen^{1,2}, Liyong Yuan^{1,*} & Weiqun Shi¹¹Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China;²College of Nuclear Science and Technology, Harbin Engineering University, Harbin 150001, China*Corresponding author (email: yuanly@ihep.ac.cn)

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Radioactive iodine (such as ^{129}I and ^{131}I) is one of the major gaseous contaminants resulting from the utilization of nuclear energy and/or nuclear accidents. During the initial dissolution process in the spent fuel reprocessing, for example, most of the iodine is released into the off-gas system in the form of highly volatile I_2 and small amounts of organic iodine compounds (such as methyl iodide, ethyl iodide, butyl iodide). The remaining iodine in the dissolution solution exists in the forms of I_2 , IO_3^- , I^- , IO^- , and iodine colloids (AgI , PdI_2). When the iodine in the dissolution solution enters the subsequent solvent extraction process, it can lead to solvent degradation, organic iodine formation, and reduction in the quality of uranium and plutonium products. Therefore, during the dissolution stage of spent fuel elements, it is generally preferred to convert as much iodine in the dissolution solution as possible into I_2 and drive it into the off-gas. Overall, in the current nuclear fuel cycle system, radioactive iodine produced by nuclear fission mainly exists in the gaseous form. In the event of an accident, this radioactive iodine can easily leak, which presents a potential threat to the environment and public health due to its long half-life (e.g., ^{129}I has a half-life of 1.57×10^7 years), high mobility, ease of dispersion through air and water, and tendency to accumulate in living organisms [1]. Consequently, the development of efficient and recyclable adsorbent materials for the capture and fixation of radioactive iodine has become a research priority in the fields of nuclear environmental remediation, nuclear emergency response, and nuclear fuel cycle management. Covalent organic frameworks (COFs), as a novel class of crystalline porous materials, have demonstrated promising potential for the capture of gaseous radioactive iodine due to their distinctive physicochemical properties [2,3]. Specifically, COFs are composed of organic monomers connected by covalent bonds, providing high chemical and thermal stability. And the highly conjugated structure of COFs can significantly improve their resistance to irradiation [4]. These enable them to maintain structural integrity and functionality under various extreme environments, making them suitable for handling complex radioactive contamination scenarios. This enables them to maintain structural integrity and functionality under various extreme environments, making them suitable for handling complex radioactive contamination scenarios. Furthermore, the designability of COF skeletons allows for the



Scheme 1 Schematic of radioactive iodine capture on a covalent organic framework material.

introduction of diverse functional groups, which can enhance iodine adsorption performance. Again, the regular and tunable pore structure of COFs can effectively prevent pore blockage, significantly facilitate the diffusion of iodine molecules within the material's pores, thereby accelerating adsorption kinetics and increasing the utilization rate of functional groups [4] (Scheme 1). In order to design and prepare more efficient and practical COF materials for gaseous iodine adsorption, it is of the utmost importance to gain a comprehensive understanding of the structure-activity relationship during the adsorption process. Although some positive results have been achieved in the study on the mechanisms of iodine adsorption in COFs, many issues remain to be clarified. This paper presents a systematic analysis of the structure-activity relationship of COFs in iodine adsorption. It explores the main factors influencing adsorption performance and discusses key issues about iodine adsorption in COFs. Finally, it provides an outlook on the future development directions of COFs for the capture and fixation of radioactive iodine.

In considering the principal factors influencing the iodine adsorption performance of COFs, the pore structure of COFs is of paramount importance. It is well documented that COFs with non-interpenetrating 1D open channels can effectively prevent pore blockage, thereby significantly enhancing iodine adsorption capacity. Wang *et al.*, for example, concluded that the key factor influencing the iodine adsorption capacity of COFs in the gas phase is the pore volume of the COFs. They compared the iodine adsorption performance of five COF materials (TPB-DMTP, TTA-TTB, TTA-TFB, TFBCz-PDA, ET TA-TPA, Figures 1 and 2) in relation to their physical properties. These five COFs have different pore channel topologies, including hexagonal, quadrangular, and triangular structures, with pore sizes ranging from micropores to mesopores. The results indicated that the iodine uptake is positively correlated with the pore volume of the COFs, which is mainly attributed to the regular and non-interpenetrating 1D pore channel structures of these COFs [4]. The regular pore structure of the material facilitates the diffusion of iodine molecules within the material's pores, effectively reducing mass transfer resistance and ensuring the full utilization of COF pores. From the perspective of physical adsorption, iodine molecules are more inclined to be adsorbed in the micropores and mesopores of the material, and cannot be adsorbed in larger pores. Liu *et al.* successfully transformed microporous 3D COFs (NM-COF-300) into COFs with ordered macropores (OM-COF-300) using a tem-

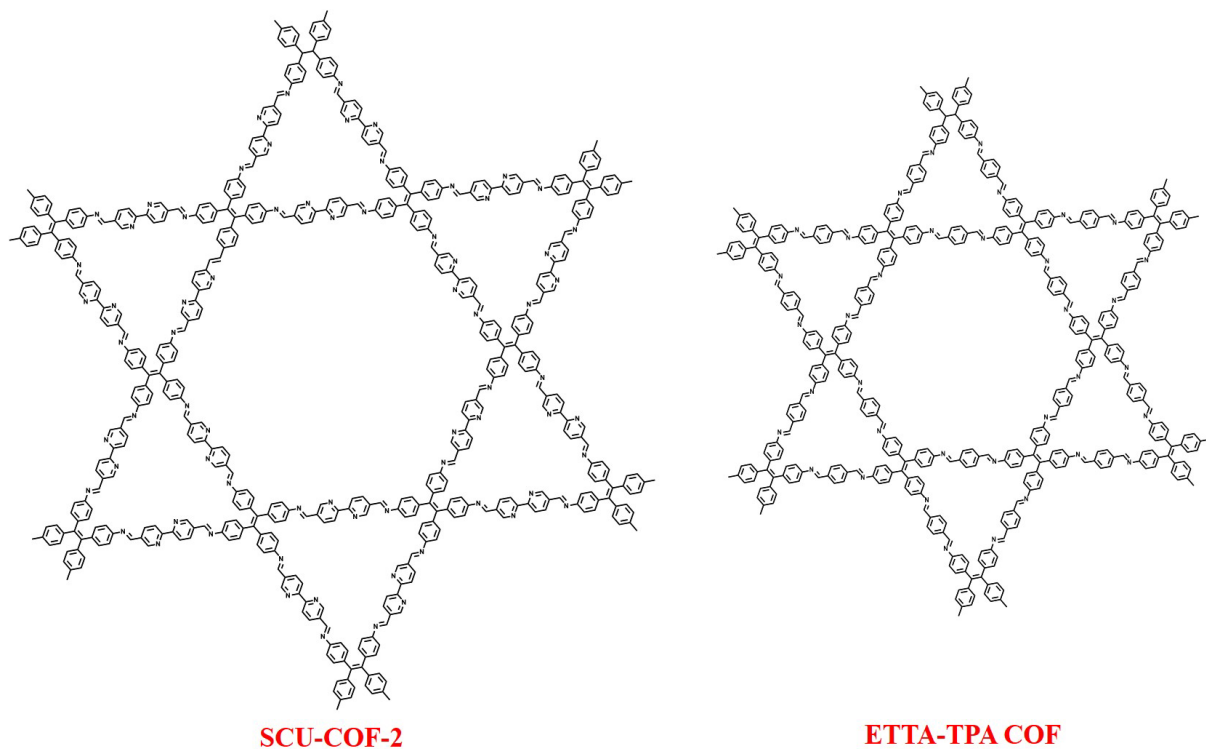


Figure 1 The structural formulas of SCU-COF-2 and ETTA-TPA COF.

plate-assisted regulation strategy. Gas-phase iodine adsorption tests were then conducted on both NM-COF-300 and OM-COF-300. The results showed that after 72 hours, the maximum iodine adsorption capacity was 1.48 g/g for NM-COF-300 but 3.15 g/g for OM-COF-300. That is, the introduction of macropores significantly enhanced the iodine adsorption in COF-300. However, the two COFs have almost identical pore volumes (0.62 cm³/g vs 0.63 cm³/g), corresponding to almost identical theoretical iodine adsorption capacities (3.06 g/g vs 3.15 g/g). In that case, the only plausible explanation for the enhanced iodine adsorption after the introduction of macropores is that the ordered macroporous structure effectively facilitates the diffusion of iodine within the channels, thereby allowing full utilization of the micropores [5]. The findings here suggest that the design of suitable pore structures is of crucial importance for the development of COF-based iodine adsorption materials.

Another significant factor influencing the iodine adsorption performance of COFs is the presence of electron-rich groups within their framework. Iodine molecules possess unsaturated valence electrons, which renders them Lewis acids. In accordance with the principles of Lewis acid-base theory, iodine molecules are readily capable of undergoing chemical reactions with electron-rich groups. Consequently, the incorporation of electron-rich groups into COFs has emerged as a principal approach to augment the iodine adsorption performance of COFs. A significant body of research has demonstrated that the incorporation of electron-rich groups, such as imine bonds and heteroatoms like nitrogen, can markedly enhance the iodine adsorption capacity of COFs. Among these, the imine bond is the most frequently reported. The imine bond (C=N bond) is a pivotal component in the structure of imine-based COFs, typically synthesized from aromatic amines and aldehydes through condensation reactions. Imine bonds possess a high electron density, which enables them

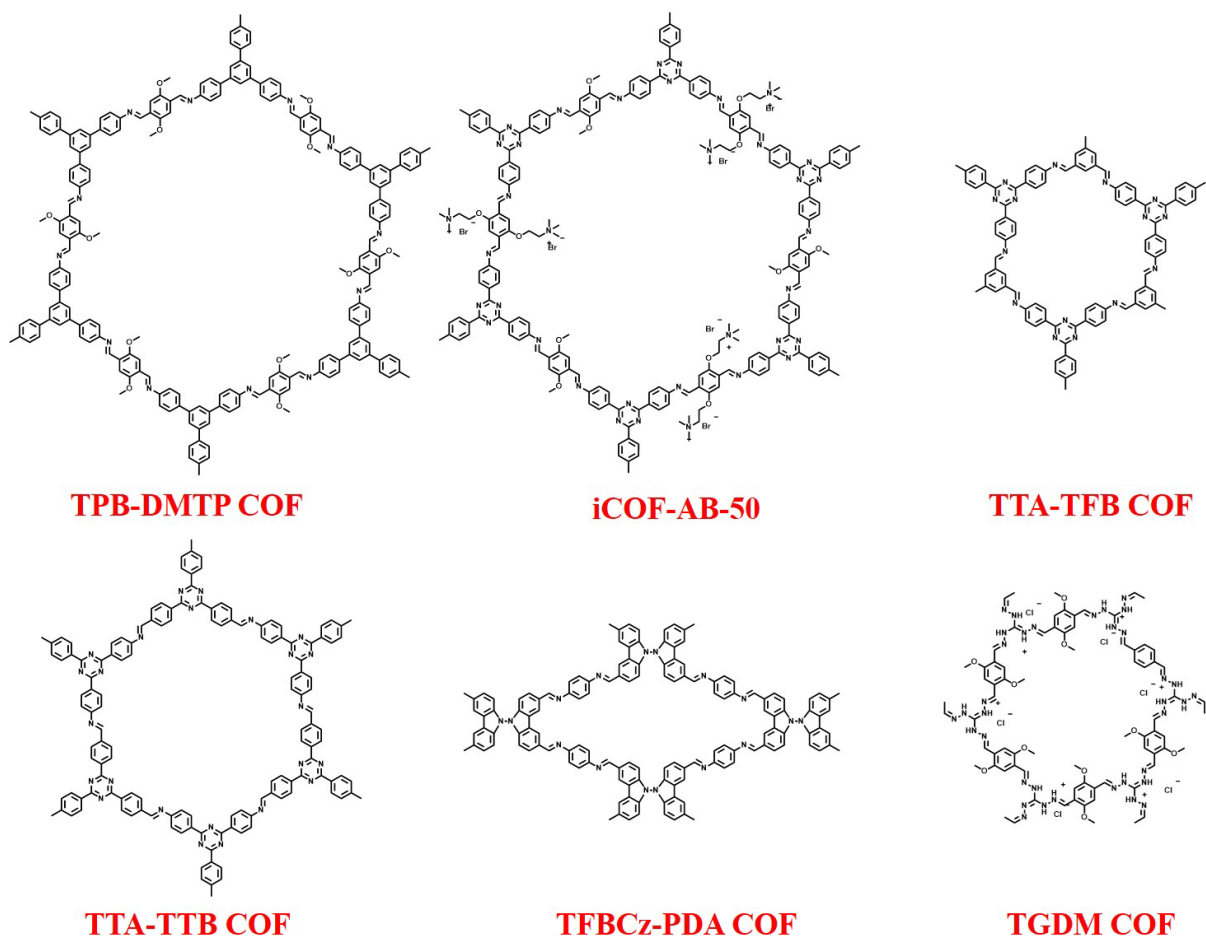


Figure 2 The structural formulas of TPB-DMTP COF, iCOF-AB-50, TTA-TFB COF, TTA-TTB COF, TFBCz-PDA COF and TGDM COF.

to effectively interact with iodine molecules during adsorption [6,7]. Besides imine bonds, pyridine groups are also considered effective electron-rich functional groups that can promote iodine adsorption in COFs [7–10]. For example, He *et al.* reported a nitrogen-rich covalent organic framework (SCU-COF-2, Figure 1) that enhanced electron pair interactions with iodine by introducing bipyridine groups, significantly improving iodine capture capability [11]. Density Functional Theory (DFT) calculations and XPS spectroscopy analyses have verified the adsorption effect of pyridine groups on iodine molecules. Additionally, triazine, aromatic rings, oxygen, and other electron-rich groups are also considered to have a definite promoting effect on iodine adsorption [12,13].

In addition to electron-rich groups, the ionic sites present in the COF structures also have a direct impact on the performance of iodine adsorption. For example, the presence of (2-bromoethyl)trimethylammonium bromide and guanidine in COF structures has been demonstrated to significantly enhance iodine adsorption through coulombic interactions. Xie *et al.* synthesized an ionic COF material, (iCOF-AB-50, Figure 2), using a “multi-component” synthesis strategy combined with post-synthetic modification. This material possesses a large surface area, high pore volume, and abundant iodine binding sites, achieving a static iodine adsorption capacity of up to 10.21 g/g, which is currently the highest recorded iodine adsorption capacity. XPS, Raman

Table 1 Parameters and iodine uptake capacities of COFs

COFs	Pore size (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Experimental capacity 75°C (g g^{-1})
SCU-COF-2	2.3	413	–	6.0
TTA-TTB	2.2	1733	1.04	5.0
TPB-DMTP	3.3	1927	1.28	6.2
iCOF-AB-50	3.3	1390	1.21	10.2
TTA-TFB	1.6	1163	0.55	2.7
TFBCz-PDA	1.5	1441	0.74	3.7
ETTA-TPA	1.4 and 2.7	1822	0.95	4.7

spectroscopy, and DFT calculations confirmed the Coulombic interactions between the ionic sites and iodine [12]. Subsequently, the same research group reported a guanidine salt-based COF (TGDM, Figure 2) capable of efficient iodine adsorption under high-temperature conditions. At 150°C and 150 ppmv (Parts Per Million by Volume) iodine, TGDM exhibited an iodine adsorption capacity of 332 mg/g. Using XPS, Raman spectroscopy, infrared spectroscopy, and theoretical calculations, they confirmed that the ionic sites in TGDM could bind with iodine through strong Coulombic interactions under high-temperature conditions. In addition, the results also showed that, compared to electron-rich groups, ionic sites are more conducive to binding with iodine at high temperatures [14]. The detailed comparison of iodine adsorption performance of the above materials is shown in Table 1.

In summary, the iodine capture by COF materials is a complex process that encompasses both chemical and physical adsorption. In order to design a COF material with enhanced iodine adsorption performance, a number of factors must be taken into account. With regard to chemical adsorption, the incorporation of electron-rich groups, such as C=N, $-\text{NH}_2$, triazine, and pyridine, can enhance the iodine adsorption capacity of COFs through Lewis acid-base interactions, while ionic sites can enhance the adsorption capacity through Coulombic interactions with iodine. Nevertheless, the expansion of the number of active sites in COFs has a limited impact on the enhancement of iodine adsorption. Firstly, if the pore channels of the COF material are too narrow or poorly ordered, iodine adsorption on the material's surface during the adsorption process may block the pores, preventing iodine molecules from entering the material's interior and rendering the active sites ineffective. Secondly, even if the COF material has regular pore channels and appropriate pore sizes, iodine adsorbed on the active sites may not occupy all the pore channels, with the remaining space being filled by physically adsorbed iodine. This indicates that increasing the number of active sites may only enhance adsorption firmness, while the upper limit of adsorption capacity is determined by the pore volume of the material. Therefore, it can be seen that the main factor influencing the iodine adsorption capacity of COFs materials is their pore structure. To achieve higher iodine adsorption capacity, this factor should be primarily considered in the design of COFs. A focus on the physical properties of the material alone, however, may result in materials that rely mainly on physical adsorption, with a relatively lower proportion of chemical adsorption. Physical adsorption is usually achieved by weak van der Waals forces, which have relatively small binding forces and are therefore highly susceptible to the natural desorption of iodine, a process that can potentially lead to secondary pollution. Consequently, it is of paramount importance to integrate the advantages of physical and chemical adsorption when developing porous materials for the capture of radioactive iodine.

Future research on iodine adsorption based on COFs materials should focus on the following aspects:

Firstly, research on the physical adsorption of iodine is currently limited. The specific pore size that can achieve efficient physical adsorption of gaseous iodine remains unclear, and there is considerable controversy regarding the exact principles of physical adsorption. Further experimental and theoretical research is therefore required with the utmost urgency. Secondly, with regard to chemical adsorption, there is a paucity of comparative studies on the binding capacities of different functional groups with iodine molecules. It is essential to gain a more profound comprehension of the specific contributions of various functional groups in enhancing iodine adsorption performance. Thirdly, iodine molecules (I_2) can react with iodine ions (I^-) to form various polyiodides, including I_3^- and I_5^- . These reactions frequently occur during the iodine adsorption process in COFs, and numerous studies have documented the presence of these polyiodides, typically validated by XPS and Raman spectroscopy [1–5,8,9,11,12,14]. Besides iodine ions, other halide ions (Br^- and Cl^-) can also react with iodine molecules to form corresponding polyiodides such as $[I_2Cl]^-$, $[2I_2Cl]^-$, $[I_2Br]^-$ and $[2I_2Br]^-$ [12,14]. The polyiodides exhibit varying degrees of stability and reactivity during the adsorption process. A detailed understanding of these reactions is essential for elucidating the interactions between adsorption materials and iodine molecules. Fourth, all current COF adsorption experiments use high concentrations of non-radioactive iodine. There is a lack of research on the adsorption of trace amounts of radioactive iodine. The trace radioiodine experiment might lead to some different conclusions. To better reflect real-world application scenarios, future research should focus more on the removal of trace radioiodine. Finally, research on iodine adsorption should not be overly focused on saturation adsorption capacity. In many practical applications, the concentration of iodine is low, and materials therefore do not require a saturation adsorption capacity that is particularly high. It is recommended that further research be conducted on adsorption rates and dynamic adsorption capacities at low concentrations, with the objective of optimising the performance of materials in practical applications.

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Conflict of interest

The authors declare no conflict of interest.

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