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Colyliform Crystalline 2D Covalent Organic Frameworks with Quasi-3D Topologies for Rapid I₂ Adsorption

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Abstract: Constructing three-dimensional (3D) structural characteristics on two-dimensional (2D) covalent organic frameworks (COFs) is a smart approach to effectively improve the pore permeability and mass transfer rate of the materials and realize the rapid adsorption for guest molecules, while avoiding the high cost and monomer scarcity in preparing 3D COFs. Herein, we report for the first time a series of colyliform crystalline 2D COFs with quasi-threedimensional (Q-3D) topologies, consisting of unique "stereoscopic" triangular pores, large interlayer spacings and flexible constitutional units which makes the pores elastic and self-adaptable for the object transmission. The as-prepared QTD-COFs have fairly faster adsorption rate (2.51 g/h) for iodine than traditional 2D COFs, with an unprecedented maximum adsorption capacity of 6.29 g/g. The excellent adsorption performance, as well as the prominent irradiation stability enable the QTD-COFs to be reliably applied to the rapid removal of radioactive iodine under special circumstances of emergency response to nuclear accidents.

Introduction

As a major gaseous fission product, radioactive iodine is one of the most important radioactive pollutants in nuclear waste disposal and nuclear accident. Due to its characteristics of easy volatilization, strong fluidity and fast diffusion, it is very difficult to deal with in the actual environment. In addition, the extremely long radioactive half-life (129 I-1.57 × 10⁷ years), high radiation (131 I) and biocompatibility of radioactive iodine also make it a potential threat to the safety of the ecological environment and human health. If not properly handled, it will seriously restrict the development and application of nuclear energy.^[1] On the other hand, radioactive iodine has important application value in the medical field. For example, 131 I can be used for the examination of thyroid function and the treatment of malignant tumor.^[2] The low-energy γ ray emitted by ¹²⁵I can be used for simple, high accuracy and low dose-rate bone mineral density determination. Various types of iodine-labeled compounds also play important roles in the diagnosis and treatment of diseases.^[3] Therefore, whether from the point of view of the sustainable development of nuclear energy and the environmental protection, or from the perspective of enhancing the added value of the nuclear power, it is of great practical significance to separate and enrich radioactive iodine produced in the nuclear reactor quickly and efficiently.

Covalent organic frameworks (COFs)^[4] are a class of crystalline porous material with periodic structure formed by the polymerization of organic building units. Due to its large specific surface area, excellent physical and chemical stability, designability of structure and active adsorption sites, COFs have great potential applications in gas storage,^[5] separation,^[6] electronic devices^[4c] and catalysis.^[7] In recent years, COFs have also attracted wide attention in the field of gaseous iodine adsorption owing to the advantages of simple operation, high adsorption capacity and easy recycling.^[1b] Compared with threedimensional (3D) COFs, two-dimensional (2D) COFs have lower cost, richer monomer species and more designable and adjustable structures. Therefore, current studies on iodine enrichment are mainly focused on 2D COFs, with emphases on improving the adsorption capacity of iodine through structural design, and exploring the influence of structure on the iodine adsorption performance.^[8] However, while focusing on the increase of iodine adsorption capacity of these COFs, researchers ignored or avoided the problem of the very slow iodine adsorption rate of most of the materials studied, especially the 2D structural materials. Under the typical iodine adsorption conditions (75°C, 1bar), it usually takes dozens of hours for 2D COFs to reach the basic equilibrium of adsorption.^[9] Some materials with high adsorption capacity, such as TPB-DMTP COF, even need up to 100 hours.^[8a] The slow adsorption rate makes it difficult for these materials to meet the needs of rapid treatment

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Scheme 1. The design strategy of "quasi-three-dimensional" structure. The inherent stereoscopic characteristics of pentavalent phosphorus bonding in the phosphazene ring (left) and the diagrams of two theoretically possible configurations, Type I and Type II (right). The partial enlarged diagrams of Type I and Type I are the views of their pores from different directions (the narrow lateral pore for Type I and the unique oblique triangular pore for Type II).

and disposal of iodine in the case of actual emergency such as radioactive iodine leakage in nuclear accident, which greatly limits their practical applications. Therefore, how to reasonably design the structure of 2D COFs to effectively improve their adsorption rate for iodine while ensuring their adsorption capacity is one of the key problems to be solved urgently.

As is known to all, the dimension and topological structure of materials have important effects on their potential applications.^[10] 3D COFs have three-dimensional open spatial structures and multidirectional and interconnected pore properties, which enables the materials to have better permeability. The threedimensional pore characteristics are conducive to the diffusion of the target adsorbate in the structure, accelerating the mass transfer rate and shortening the equilibrium time.^[10e, 11] However, 3D COFs usually use monomers with tetrahedral or similar stereoscopic configurations as building units, resulting in a very limited selection of monomer structures and types. Therefore, the number of 3D COFs reported so far is less than one-tenth of the total COFs. Moreover, the limited available 3D monomers are complex and difficult to synthesize, and quite expensive to obtain commercially. The above disadvantages, as well as the difficulty in structural analysis of 3D COFs, especially those with interpenetration structure, have severely restricted their development and practical application. The conventional 2D COFs are composed of discrete planar sheets stacked between non-covalent layers and have been widely studied and reported owing to the abundance of building monomers and the simplicity and lower cost of material synthesis. However, due to the high planarization degree and crystallinity of 2D COFs, their pores are usually located in the same plane, and the orientations of their pore channels are extremely uniform and consistent. Compared with stereo channels of 3D COFs, this unidirectional and uniform channel characteristics make the 2D COFs have lower intracavity diffusion and guest adsorption efficiency.

In view of this situation, we wonder if it is possible to construct structures and channel characteristics similar to those of three

dimensions in 2D COFs through ingenious structural design, so as to effectively improve the pore permeability and mass transfer rate of the 2D COFs, and thus increase the adsorption rate to iodine and other guests. The presence of COF building blocks centered on cyclotriphosphazene structure provides the possibility for our hypothesis. In this study, hexa(4-formylphenoxy)cyclotriphosphazene (CTP-6-CHO) with symmetric structure similar to C₆ was used to synthesize COFs. Due to the stereoscopic bonding properties of P atom in the monomer, the aromatic ring plane dominated by the cyclotriphosphazene structure is perpendicular to the plane formed by the two noncyclic P-O single bonds (O-P-O plane). This unique structure causes the 2D planar structure of the formed COFs to twist regularly, so as to construct new vertical multiple channels beyond the one-way extension channels of traditional 2D COFs. This quasi-three-dimensional (Q-3D) structure with 3D pore characteristics can greatly improve the porous permeability and mass transfer rate of the materials, and shows excellent adsorption efficiency and commendable adsorption rate in the field of enrichment and separation of gaseous iodine.

Results and Discussion

In order to achieve the goal of building 2D COFs with 3D structural characteristics, we elaborately selected CTP-6-CHO with the structure of six cross side arms outside the central plane as the node module of the COFs (Scheme 1 and Figure 1a; see the Supporting Information (SI) for details, Section 2). CTP-6-CHO is formed by the condensation of hexachlorocyclotriphosphazene and p-hydroxybenzaldehyde and has a unique stereoscopic structure in which the O-P-O plane (β plane) is perpendicular to the aromatic ring plane of cyclotriphosphazene N₃P₃ (α plane) (Scheme 1). Because of the unique structure of CTP-6-CHO, the as-prepared COFs are not traditional 2D planar structure. Theoretically, to realize the

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Figure 1. Structure diagram (a) and crystal structure (b) of QTD-COF-1. Experimental (black), Pawley refined (red) and predicted (blue) PXRD patterns, and the differences between the experimental and refined PXRD patterns in dark cyan (inset: views of space-filling models along the c-axis with the layer distances). FT-IR spectra (c), high resolution XPS spectrum of N1s (d) and pore-size distribution (e) for QTD-COF-1.

construction of COFs with long-range ordered structure, there are mainly two connection configurations between CTP-6-CHO and the C₂-symmetric linkers, namely Type I and Type II (Scheme 1). Type I is constructed by CTP-6-CHO in a C₃-like symmetric way. The two side chains anchored at the O-P-O bonds are parallel. forming a heteropore structure with frontal hexagonal main pores and lateral narrow pores. Type II is constructed in a symmetric configuration similar to C₆, and the six stereoscopic side chains from three nodes are cross-linked upper and lower to form a colyliform structure with oblique triangular pores. In fact, since the formation of Type I needs to overcome the huge spatial tension of the O-P-O bonds, it is difficult to get such kind of configuration. The formation of Type II involves a torsion process of the β plane. Under the influence of the stretching effect and the spatial limiting effect during the formation of the continuous extensional framework structure, the β plane rotates laterally relative to the plane a. However, due to the inherent 3D structural features of pentavalent phosphorus bonding and the existence of spatial steric hindrance, it is impossible for the two planes to coincide completely, resulting in a unique "Q-3D" structure between two and three dimensions. Compared with the traditional 2D structure, the novel Q-3D structure has abundant stereoscopic lateral channels which can greatly increase the pore permeability of the material and improve its adsorption and mass transfer rate for guest molecule.

In this study, QTD-COF-1, a quasi-three-dimensional COF, was prepared by self-assembly polymerization under solvothermal conditions with CTP-6-CHO as the node and *p*-phenylenediamine as the linker (Figure 1a, SI, Section 2).

Meanwhile, a small molecule model compound CTP-M with similar structure was prepared for comparative analysis (SI, Section 2). It is shown by Fourier transform infrared spectroscopy (FT-IR) that the characteristic diffraction peaks of the amino group and the aldehyde group of QTD-COF-1 largely disappeared, and the characteristic peak of the -C=N- stretching band newly appeared at 1624 cm⁻¹ is fundamentally the same as that of the model compound CTP-M (Figures 1c and S1a). X-ray photoelectron spectroscopy (XPS) analysis revealed that there are only imine nitrogen (-C=N-, 398.8 eV) and phosphazene nitrogen (-P=N-, 398.1 eV) peaks in the N1s spectrum, with a ratio of 2:1 and no amino peak (~400 eV) (Figures 1d and S3b). And there is an imine carbon peak at ~152 ppm in the solid-state ¹³C NMR spectrum, indicating that the condensation reaction of aldehydes and amines has been successfully achieved (Figure S2a). In addition, the result of elemental analysis (EA) shows that the experimental values of element contents are close to the theoretical values, suggesting that the monomers have virtually reacted according to the feed ratio (Table S2).

The crystallinity of QTD-COF-1 was confirmed by powder X-ray diffraction (PXRD) analysis. As shown in Figure 1b, the obvious diffraction peaks at 4.72°, 9.52°, 12.12° and 21.08° demonstrate that QTD-COF-1 has high degree of crystallinity. And this is also the first synthesis of phosphazene COF with high crystallinity. Materials Studio (MS) software was used to simulate the crystal structure of COFs and the results show that the experimental values are in good agreement with the simulated values of the eclipsed (AA) stacking structure of the Type II configuration (Figure S6a), and the corresponding diffraction peaks are

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attributed to (100), (200), (210) and (001) facets, respectively. Pawley refinement produced unit cell parameters of a = b = 21.38 Å, c = 4.22 Å, $\alpha = \beta = 90^{\circ}$, and $\gamma = 120^{\circ}$, with good agreement factors of R_{P} = 2.68% and R_{WP} = 3.45% (Table S1a). Therefore, it can be determined that QTD-COF-1 belongs to Type II configuration and forms a colyliform structure with oblique triangular channels, rather than Type I configuration with a hexagon framework structure (Figure S4c). Different from the conventional 2D COFs, the atoms of the same layer of QTD-COF-1 are not in the same plane, and there are abundant oblique triangular pores observed from both the front and the interlayer directions of the COF layers. The interlayer stacking distance also increases significantly from ~3-3.5 Å of the traditional 2D COFs to 4.21 Å (Figure 1b), realizing the transition from 2D structure to the Q-3D structure.



Figure 2. SEM images (a-c), TEM images (d, e, inset: SAED patterns) and ACTEM images (f, inset: the corresponding lattice distances and the fast Fourier transformation) of QTD-COF-1

Scanning electron microscopy (SEM) analysis shows that QTD-COF-1 is composed of homogeneous spherical particles formed by stacking of sheets, with a diameter of 2 µm (Figure 2ac). The high-resolution transmission electron microscope (HR-TEM) images also show that it is formed by ordered stacking of layers, with good lattice patterns and obvious electron diffraction spots (Figures 2d,e and S8a). In order to further reflect the structure of QTD-COF-1 accurately, the spherical aberration corrected transmission electron microscope (ACTEM) was adopted and the existence of the interlayer lateral pores can be clearly observed in the ACTEM images (Figures 2f and S9), which is very similar to the interlayer image simulated by MS (Figures 1b and 2f). And the interlayer distance is found to be 4.28 Å which is consistent with the theoretical value. The pore-size distribution curve shows that the average pore diameters are 1.35 nm and 1.71 nm, and the two sizes of pores are actually consistent with the triangular pores of 1.36 nm and 1.66 nm in the simulated wheel-shaped structure (Figure 1e). SEM, HR-TEM and pore-size distributions further prove that QTD-COF-1 is a quasi-threedimensional COF with a colyliform structure consisting of oblique triangular pores.

The unique structure of QTD-COF-1 formed by Type II configuration has abundant frontal-lateral pores which are oblique triangular and face both the front and the side. Compared with traditional 2D COFs, the big hexagon framework in Type II configuration is divided evenly into six small triangular regions, which effectively increases the density of the active binding sites on the framework. Moreover, the Q-3D structure with frontallateral pores facing forward and sideways allows the guest molecules to enter the structural framework of the material through both the frontal and the lateral pathways, which greatly increases the permeability and mass transfer rate of the pores and makes the interaction between host-guest molecules more orderly and efficiently. Interestingly, we found that due to the introduction of flexible building units in the COF structure, the quest solvents such as acetone and tetrahydrofuran can cause a reversible structural transformation of QTD-COF-1 (Figure S5). This phenomenon indicates that the COF pores constructed by the flexible units underwent a self-adaptive reversible structural change with the entry of guest molecules, which further confirmed the flexible characteristic of the COF structure.^[12] Compared with the rigid structure, the flexible structure makes the COF more adaptable to the object, and thus increases its affinity to guest molecules.



Figure 3. Iodine adsorption and desorption experiments. (a) Gravimetric iodine uptake of QTD-COF-X (X= 1, 2, 3, 4, V) as a function of time at 75°C and ambient pressure. (b) Comparison of the saturated adsorption capacity and the K_{80%} of various COF materials. (c) Photographs show the color change of iodine enrichment progress of QTD-COF-1 in hexane. (d) Schematic diagram of iodine adsorption by QTD-COF-1 in an open atmosphere. (e) Controlled release of iodine upon heating the I₂-laden QTD-COFs at 125°C.

Since the Q-3D structure can increase the permeability and mass transfer rate of the channel, theoretically, the adsorption rate of the sorbent to the target adsorbate will also be improved effectively. To verify this ratiocination, the adsorption performance of QTD-COF-1 was investigated in detail using iodine as the target adsorbate. As shown in Figure 3a, the iodine adsorption

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Figure 4. Structure diagram (a) and crystal structures (b-e) of QTD-COF-X (X= 2, 3, 4, V). Experimental (black), Pawley refined (red) and predicted (blue) PXRD patterns, and the differences between the experimental and refined PXRD patterns in dark cyan. (f) Interlayer distances of QTD-COF-X (X=1, 2, 3, 4, V) calculated with Materials Studio.

capacity of QTD-COF-1 increased almost linearly in the initial stage and reached 80% of the saturated adsorption capacity within just 3 hours. And an obvious turning point of adsorption occurred at about 5 hours, indicating that the adsorption equilibrium was basically reached. The measured saturated adsorption capacity of QTD-COF-1 is 4.62 g/g, which is at a high level in the iodine adsorption materials reported. In order to compare and evaluate the adsorption performance of the materials more scientifically and reasonably, the average adsorption rate before the adsorption capacity reaches 80% of the saturated adsorption capacity was determined as the benchmark and defined as $K_{80\%}$ ($K_{80\%}$ = 80% of saturated adsorption capacity / adsorption time, and the unit is g h⁻¹) (See SI Section 16 for detail). Figure 3b shows the relationship between the saturated adsorption capacity and $K_{80\%}$ of the typical 2D COFs for iodine adsorption reported previously. It can be seen from the diagram that QTD-COF-1 has a large $K_{80\%}$ value of 1.23 g h⁻¹, which is better than all the 2D COFs reported so far (Figure S13).

To further prove the rapid and efficient adsorption performance of QTD-COF-1, we compared the adsorption of iodine at room temperature between QTD-COF-1 and TPT-BD COF, a reported iodine adsorbent with outstanding adsorption performance which contains similar flexible ether bond structure and has a high saturated adsorption capacity of 5.43 g/g and K_{80%} of 0.75 g h⁻¹ (Figure 3b).^[8b] It was found that the adsorption rate and adsorption capacity of QTD-COF-1 are much higher than TPT-BD

COF at room temperature (Figure S14c), which may be attributed to the blockage of the characteristic one-dimensional channel in the traditional 2D TPT-BD COF by iodine. However, the QTD structure of QTD-COF-1 overcomes this shortcoming and the guest iodine can enter the COF structure through unique stereoscopic channels, which leads to the significant improvement in adsorption capacity and rate. Moreover, QTD-COF-1 also showed a fast iodine adsorption rate in hexane solution. The iodine can be adsorbed completely within about 4 h by QTD-COF-1. While, TPT-BD COF did not fully adsorb the iodine after 48 h and the solution was still pale red (Figures 3c and S15). Therefore, the construction of Q-3D COFs is an effective method to improve the iodine adsorption rate of 2D COFs. In addition, the iodine adsorption experiments in an open atmosphere also confirmed the faster adsorption rate and higher affinity of QTD-COF-1 for iodine, along with quick and obvious color changes (Figure 3d), which is expected to be applied to the enrichment and disposal of radioactive iodine under various emergency conditions.

In order to further verify the general applicability of the Q-3D COFs construction strategy, we prepared a series of phosphazene QTD-COF-X (X = 2, 3, 4, V) with high crystallinity and different cell sizes by replacing the amine linking units, as shown in Figure 4. FT-IR and EA analysis were used to confirm the bonding modes and compositions of the materials, and the analysis results are similar to those of QTD-COF-1 (Figure S1 and

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Table S2). That is to say, the aldehyde and amine monomers of this series of QTD-COF-X (X = 2, 3, 4, V) have virtually reacted completely to form imine bonds according to the feed ratio. Solid-state ¹³C NMR spectrum and XPS analysis further corroborated this conclusion (Figures S2 and S3).

The crystallinity and structure of QTD-COF-X (X = 2, 3, 4, V) were analyzed and studied by PXRD and MS simulation. As shown in Figure 4b-e, QTD-COF-X (X = 2, 3, 4, V) have a number of obvious diffraction peaks. Regardless of the different positions of the peaks, the patterns are almost the same as that of QTD-COF-1, indicating that the stacking modes of the series of materials are consistent except for the different cell sizes. The MS simulation in Figures 4 and S6 also proves this result. The experimental values of PXRD patterns coincide well with the simulation values of AA stacking mode of the Type II configuration which has very small refined parameters. The results confirm that QTD-COF-X (X = 2, 3, 4, V) take CTP-6-CHO as the node and form Q-3D COFs with the colvliform framework structure equipped with abundant oblique triangular channels. It was found from the pore-size-distribution curves that the pore diameters of QTD-COF-X (X = 2, 3, 4, V) increase from 1.36 to 1.72 nm with the increasing length of the linking monomers (Figure S10b). The pore diameters are fundamentally consistent with the theoretical oblique triangular pore structure, which further confirms their topological structure. Therefore, the strategy of constructing Q-3D COFs by monomers possessing flexible six-arm structure similar to CTP-6-CHO is feasible and universal. In addition, TGA analyses show that QTD-COF-X (X = 1, 2, 3, 4, V) have excellent thermal stability in air or nitrogen atmosphere (Figures 5a and S11), which may be related to the flame retardant property of organic-inorganic phosphazene heterocyclic ring. Moreover, there are almost no changes in the PXRD patterns and FT-IR spectra of the QTD-COFs before and after y-ray irradiation, which indicates that the as-prepared COFs possess excellent antiirradiation performance and can withstand 10⁵ Gy γ-ray irradiation, revealing their potentials to capture radioactive iodine, such as ¹²⁹I or ¹³¹I, in specific emergency circumstance of nuclear accident (Figure S12).

Further analysis of PXRD shows that the (001) diffraction peaks of QTD-COF-X (X = 1, 2, 3, 4, V) were 21.1°, 21.8°, 20.6°, 20.3°, 19.5°, respectively. In other words, with the increase of the length of linking monomers and the number of substituent groups, the diameters of the Q-3D lateral pores and the related interlayer stacking distances increase gradually. And the interlayer spacings of QTD-COF-X (X = 1, 2, 3, 4, V) are significantly higher than that of the traditional COFs (0.34 nm) and reach ~0.42, 0.41, 0.43, 0.44 and 0.45 nm (Figures 1 and 4b-e), respectively, which are consistent with the interlayer distances calculated by MS (Figure 4f). TEM images of QTD-COF-V proved that the material is layered with better lattice patterns and regular electron diffraction spots, and the interlayer distance is ~4.53 Å which is fairly close to the experimental value of the PXRD pattern and the MS simulated value (Figure S8b). Studies on iodine adsorption of the QTD-COFs show that the iodine adsorption rate ($K_{80\%}$) mainly keeps increasing with the increase of the interlayer spacings, suggesting that the iodine adsorption rate of 2D materials can be controlled through the regulation of the interlayer distance. The adsorption rate of QTD-COF-3 is lower than that of QTD-COF-1, which may be due to the strong interlayer stabilizing effect^[12a, 13] of the biphenylene linker which limits the adaptive structural transformation of the material during the adsorption process.

Furthermore, in addition to the fast adsorption rate, the adsorption capacity of QTD-COF-X (X = 1, 2, 3, 4, V) are also satisfactory, which are 4.67, 2.87, 5.16, 4.85 and 6.29 g/g, with the corresponding iodine percentage contents of 82.3 wt%, 74.2 wt%, 83.8 wt%, 82.9 wt% and 86.3 wt%, respectively (Figure S14b). The adsorption capacity of the QTD-COFs are at a high level among all the reported iodine adsorption materials, which was also proved by TGA analysis (Figures 5a and S11).



Figure 5. TGA curves of QTD-COF-V before (in N₂ and air atmosphere) and after iodine adsorption (in N₂ atmosphere). (b) Raman spectra of iodine and QTD-COF-V before and after volatile iodine adsorption. (c) FT-IR spectra of QTD-COF-V before and after iodine adsorption. (d) Reusability of QTD-COF-1 and QTD-COF-V for iodine capture.

In particular, it is the first time that two flexible monomers, a flexible aldehyde and a flexible amine, were combined and copolymerized to prepare the highly crystalline QTD-COF-V with V-shaped linking units and spiral fan structure (Figure S6e,f). Compared with the traditional linear monomers, the introduction of V-shaped monomer not only increases the overall flexibility and self-adaptive ability of the material's framework, but also reduces the π - π interaction between the interlayers to a greater extent, resulting in the decrease of interlayer stabilization and the obvious increase of interlayer spacing. Therefore, among the series of QTD-COFs, the interlayer distance of QTD-COF-V is the largest and up to 0.45 nm (Figure 4b,f and Table S1b). It was also found through iodine adsorption experiments that the adsorption rate and capacity of QTD-COF-V are much higher than that of all the reported 2D COFs, with the adsorption rate of 2.51 g/h (K_{80%}) and the adsorption capacity of 6.29 g/g (75°C, 1bar) (Figure 3a,b). The excellent adsorption performance of QTD-COF-V can also be proved by iodine adsorption at room temperature, with an adsorption capacity of 4.56 g/g, which is also better than QTD-COF-1 (Figure S14c). Therefore, the increase of lateral pore diameter, interlayer spacing and flexible self-adaptive ability can significantly increase the adsorption rate and capacity of COFs to iodine. More importantly, the iodine adsorption capacity of QTD-COF-V after irradiation was 6.02 g/g which was not different from that before irradiation, indicating its application potential for radioactive iodine adsorption in practical environment. Of course, similar phenomena and results were also observed in the other QTD-COFs (Figure S14d).

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Scheme 2. Schematic diagram of the rapid iodine adsorption process and mechanism by QTD-COFs.

Through the analyses of Raman spectroscopy (RM), FT-IR and XPS, the mechanism of iodine capture and transmission path were studied. During the adsorption process, iodine is dispersed in the air in form of molecular iodine and interacts with the adsorbent, thus being absorbed and immobilized by the material. It was found in the literature that the straight-chain diameter of the iodine molecule is 3.35 Å^[14] which is far less than the lateral pore diameters and interlayer spacings of all the QTD-COFs from 0.41 to 0.45 nm. This implies that iodine molecule can enter the materials from not only the same frontal channels of the QTD-COFs as the traditional 2D material, but also the Q-3D lateral channels between the layers during the adsorption process. Meanwhile, due to the strong self-adaptive ability of the flexible COFs to guest molecule, the pore sizes of the materials can be adjusted according to the size of guest molecule within a certain range, so that the guest iodine can pass through the frontal-lateral channels at a faster rate, enter into the structural frameworks of the COFs, and be loaded at the adsorption active sites. The species of iodine loaded on the adsorbents was detected through RM analysis. It was found that after the adsorption of iodine by the QTD-COFs, the characteristic peaks of I5⁻ appeared at ~110 and 167 cm⁻¹ in the RM spectra, which was quite different from the 182 cm⁻¹ of molecular iodine (Figures 5b and S17), indicating the charge transfer interaction between the adsorbents and iodine.^[15] The FT-IR spectra of the QTD-COFs show that the peak positions of the C=N bond, the C=C/C-H bonds on benzene ring and the P=N/P-O-Ar bonds on phosphazene ring have obvious shifts before and after adsorption (Figures 5c and S1).^[16] Moreover, the binding energy of I₂-laden QTD-COFs in the XPS spectra also indicates the formation of I5⁻. The binding energy of 13d_{5/2} and 13d_{3/2} of the QTD-COFs after iodine adsorption are located at ~617.9 eV and ~629.4 eV, respectively, which have larger shifts compared with the values of 618.6 eV and 630.1 eV of iodine elements and can be attributed to the formation of I5-(Figure S3e).^[17] In addition, the binding energy of C, N, P and O in the COFs also shifted to some degrees, indicating their interaction with iodine, which is consistent with the FT-IR results (Figure S3f-i). Thus, it can be concluded that the charge transfer between iodine and the adsorbents occurred in the electron-rich groups and conjugated systems. The possible mechanism of iodine enrichment by the QTD-COFs was proposed based on the conclusion. As shown in Scheme 2 and Video S1, the iodine molecules enter the Q-3D channels of the adsorbent through both the frontal and the lateral pathways and interact with the electron-rich conjugated systems and groups to form I_5^- charge-transfer complex.

In addition, QTD-COFs can be recycled through thermal desorption and solvent desorption. Under the thermal desorption condition of 125°C, the desorption equilibrium can be reached within 2 h and the desorption rate is as high as over 90% (Figure 3e). The materials are also capable of being recovered by ethanol desorption, and agitation and ultrasound can greatly accelerate the desorption rate (Figures 3e and S16). Meanwhile, QTD-COFs have the advantages of good reusability (Figure 5d and S14g) and easy preparation in large scale (See SI Section 2 and 17 for detail). Based on the results, it is clear that the QTD-COFs are a kind of excellent iodine adsorbent with high efficiency, large capacity and recyclability, and have great application potentials.

Conclusion

In conclusion, to improve the permeability and mass transfer rate of 2D COFs, a series of phosphazene COF materials with high crystallinities was prepared for the first time in this study by using CTP-6-CHO as the node module and stereo source center. The as-prepared QTD-COFs have unique oblique triangular frontal-lateral pores and larger interlayer distances (0.41~0.45 nm), presenting a colyliform Q-3D structure, which successfully achieves the construction of 3D structural features on 2D materials, and greatly increases the permeability and mass transfer rate of 2D COFs. The unique pore structure of the COFs enables the guest molecules to enter the framework of the materials through both the frontal and the lateral pathways, thus making the interaction between the host-guest molecules more orderly and efficiently. Adsorption experiments show that the iodine adsorption rate of QTD-COFs are fairly better than traditional 2D COFs, and the adsorption capacity are also very prominent. Especially for QTD-COF-V, the adsorption rate parameter of K_{80%} can reach 2.51 g/h and the adsorption capacity is up to 6.29 g/g, with excellent material reusability and irradiation stability. It was found by comparative study that the lateral pore diameter and interlayer spacing, as well as the iodine adsorption rate of QTD-COFs increased along with the increasing length and flexibility of the linking monomers, indicating that the regulation of the guest adaptive ability and adsorption property of the COFs were successfully realized through the control of chain length and flexibility of the monomers. The design and construction strategy of Q-3D materials proposed in this study can not only greatly reduce the preparation cost and limitation of COF materials, but also effectively improve the iodine adsorption rate and capacity of 2D COFs, which provides an applicable solution for the rapid enrichment and separation of radioactive iodine in emergencies such as nuclear accident. And this strategy is also of great scientific significance for the rapid adsorption of other gas molecules and the design and preparation of other mass storage materials.

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A novel type of COFs with colyliform quasi-three-dimensional (Q-3D) topologies equipped with "stereoscopic" oblique triangular pores and larger interlayer spacings are reported. The unique Q-3D structure effectively improve the pore permeability and mass transfer rate of the COFs and lead to a fairly faster adsorption rate (2.51 g/h) for iodine than traditional 2D COFs, with an unprecedented maximum adsorption capacity of 6.29 g/g.