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SYNTHESIS OF ONE COVALENT ORGANIC FRAMEWORK (COF) BASED ON C=N BONDS AND ITS EXCELLENT PERFORMANCE OF IODINE ADSORPTION

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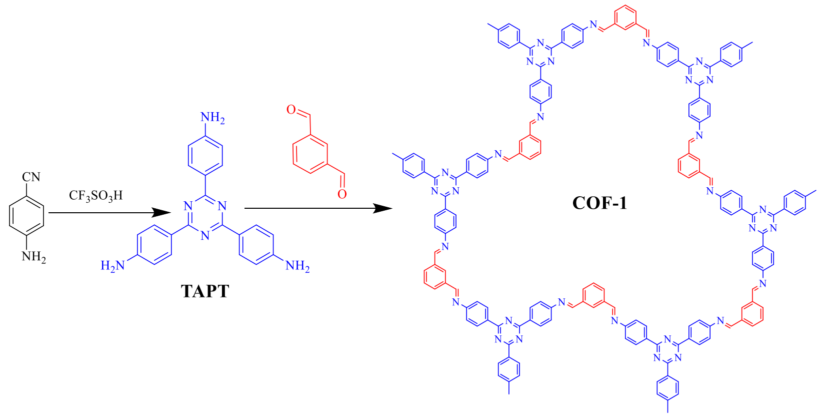
Abstract – Radioactive iodine is one of the main substances existed in nuclear wastes. It can quickly diffuse into the atmosphere causing great harm to environment and human health. Therefore, how to capture radioactive iodine efficiently has become a research hotspot. Herein, a covalent organic framework (**COF**) material (**COF-1**) has been synthesized by aldimine condensation reaction using the 1,3,5-triazine structure compound and isophthalaldehyde as starting materials. The nitrogen-rich **COF-1** possesses medium specific surface area (321.78 m^2/g), a pore diameter of 1.98 nm and relatively regular layered stack structure, which provide good conditions for iodine adsorption ability. The maximum iodine uptake of **COF-1** is 2647 mg/g, which is higher than most iodine adsorbents reported. Subsequently, the release of iodine can be achieved in methanol indicating the iodine adsorption of **COF-1** is a reversible process. It is also shown that **COF-1** can be recycled. These characteristics maybe make **COF-1** materials as a good iodine capturer in practical applications.

Nuclear energy is a very important source of energy and its use will inevitably produce waste materials containing radioactive materials, of which the radionuclides ^{129}I and ^{131}I are the main components. Their half-lives are 15.7 million years and 8 days respectively. They can diffuse into the air quickly and exist for an extremely long time.[1] Radioactive iodine can also enter the human body through water, food, etc, and cause serious harm to environment and human health.[2,3] Thus, the research on iodine adsorption has attracted broad interests. The earliest iodine adsorbents were mainly inorganic adsorption materials, activated carbon,[4] zeolite[5] etc. Recent studies have shown that the large pore size and strong affinity for iodine are important factors of affecting the iodine adsorption performance.[6] Therefore, porous materials such as metal-organic framework (**MOF**),[7] conjugated microporous polymers[8] have also been used for iodine adsorption research, and have become hot research topics. Being a kind of periodic and crystalline organic porous polymers connected by covalent bonds, covalent organic framework (**COF**) has the characteristics of low density and good stability, and has good application prospects in gas storage.[9] Moreover, the nitrogen-rich structure and electron-rich π-π conjugated system can provide effective binding sites for iodine adsorption.[10,11] Herein, **COF-1** possessing has been synthesized by aldimine condensation reaction using the 1,3,5-triazine structure compound and isophthalaldehyde as starting materials (**Scheme 1**). Meanwhile, the adsorption performance of **COF-1** to iodine has been investigated by iodine vapor adsorption experiment.



Scheme 1

In the Fourier-transform infrared spectra (**Figure S1**), 3048 cm^{-1} is the stretching vibration peak of =C-H; 1670 cm^{-1} is assigned to the stretching vibration peak of -C=N-; 1612 cm^{-1}, 794 cm^{-1} and 742 cm^{-1} are assigned to the vibration peaks of meta-substituted benzene ring. These indicate that TAPT and isophthalaldehyde were successfully linked by imine bonds.

The porosity of **COF-1** has been investigated by nitrogen adsorption-desorption experiment at 77 K (**Figure 1**). **COF-1** exhibits a type I isotherm, which is indicative of microporous materials.

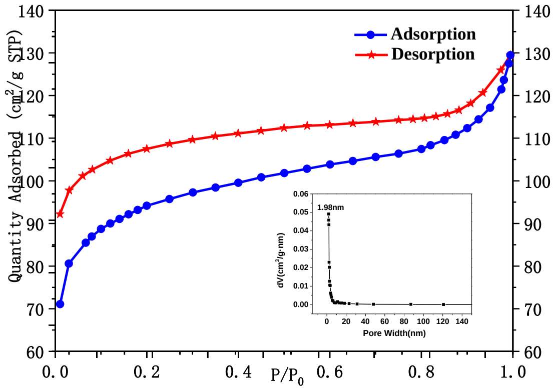


Figure 1. N_2 adsorption and desorption isotherm curve of **COF-1**

The experiment results show that the single-point surface area (P/P0=0.20) is 327.8004 m^2/g; the BET surface area is 321.78 m^2/g. The pore size is 1.98 nm calculated by the non-local density function theory (NLDFT) and the total pore volume is 0.18 cm^3/g.

The morphology of **COF-1** is characterized by scanning electron microscope (SEM) (**Figure 2**). From the figure, it can be see that **COF-1** possesses a relatively regular and lamellar stacked structure.

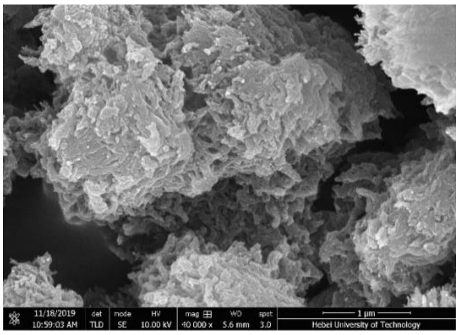


Figure 2. SEM image of **COF-1**

Thermogravimetric analysis (TG) indicates that **COF-1** is thermally stable up to 230 ℃ (**Figure S2**). From room temperature to about 100 ℃, there is a small loss of weight, which is the evaporation of water on the surface of the material.[12] When the temperature continues to be raised to 335 ℃, 74.42% of weight is lost, and the structure has decomposed. The weight decreases about 8.21% as the temperature raise to 500 ℃, the triazine structures begin to be damaged. It is basically completely decomposed at 590 ℃.

The crystallinity of **COF-1** is examined by X-ray diffraction (XRD) (**Figure 3**). There are only two bulging peaks in the XRD spectrum of **COF-1**. The comparison between the experiment and simulated values shows that the crystallinity of **COF-1** is not ideal and it is an amorphous material.

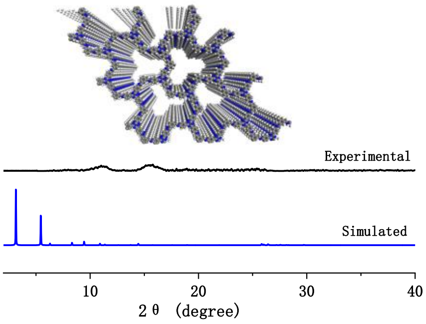


Figure 3. The XRD of **COF-1**

According to the iodine adsorption test, **COF-1** is exposed to iodine vapor at 348 K, then is cooled and weighted at room temperature at intervals. **COF-1** powder changes from yellow to dark brown after absorbing iodine vapor. The curve of iodine adsorption with time is shown in the **Figure 4**. The amount of iodine adsorption increases rapidly at 0 ~ 810 min, then the adsorption rate levels off and the adsorption capacity gradually reaches saturation after 810 min. The maximum adsorption uptake can reach 2647 mg/g (72.58 wt%). The adsorption capacity of **COF-1** is higher than many adsorbents such as activated carbon, zeolite and MOFs (**Table S1**). The high adsorption capacity of **COF-1** may be caused by the inherent π–π conjugate and high nitrogen content.[10,11,13,14]

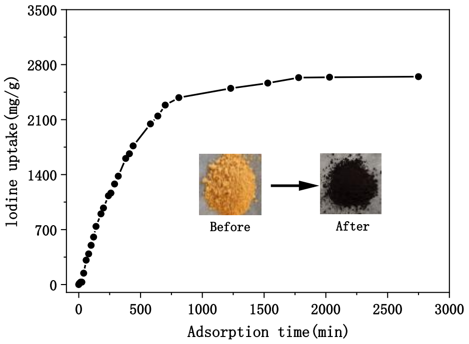


Figure 4. Iodine uptake of **COF-1** over time at 348 K

Then an iodine release experiment shows that the solution immediately changes from colorless to brown after adding **I_2@COF-1**, and gradually deepenes which means that I_2 has been continuously released into methanol solvent. The color of liquid does not change after 180 min (**Figure S3**). The release process is monitored by UV-vis spectrum (**Figure 5**, **Figure S4** and **S5**). The concentration of I_2 in methanol increases exponentially with the time (**Figure 5b**). The release of iodine increases linearly with time during the first 11 minutes, indicating that the release of iodine is mainly dominated by the interaction between the lodging and the object (inset of **Figure 5a**).[15,16] As the process to be continued, the release rate of iodine slowed down, suggesting that the diffusion at this stage is mainly controlled by free diffusion. These results reveal that the process of **COF-1** adsorption of iodine can be reversible.

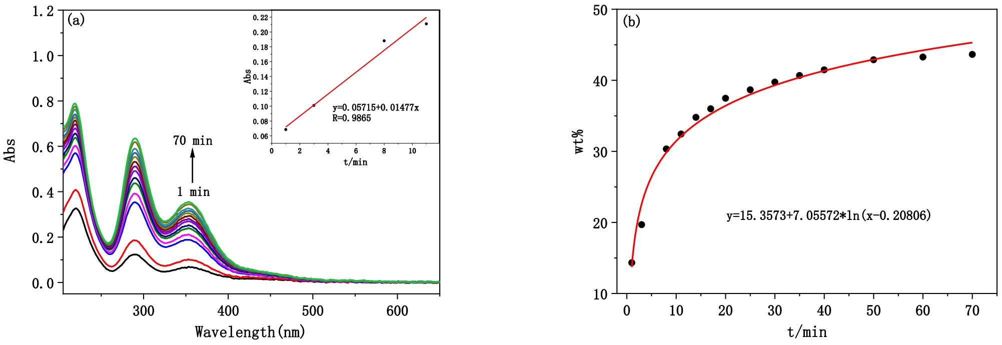


Figure 5. (a) Release of iodine from **I_2@COF-1** monitored by UV-vis absorption spectra; (b) the release behavior of iodine with time in MeOH.

Subsequently, experiments on the recycling performance of **COF-1** for adsorbing iodine vapor have been performed (**Figure 6**). The iodine uptake of **COF-1** is still 2080 mg/g after four cycles, maintaining a good adsorption capacity. Therefore **COF-1** material can be reused in terms of adsorbing iodine vapor, displaying good recycle performance.

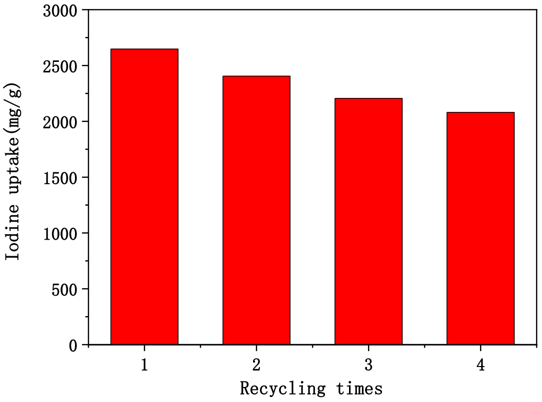


Figure 6. Reusability of **COF-1** for iodine uptake

In summary, **COF-1** linked by imine bonds has been successfully prepared by solvothermal method, possessing conjugated system and high nitrogen content. It has the characteristics of regular structure and good thermal stability. Furthermore, **COF-1** exhibits high iodine adsorption performance (up to 2647 mg/g) at 348 K and atmospheric pressure. Although the experimental results show that **COF-1** can be recycled and its interaction process with iodine is reversible, there is still a long way to go before the material can be used in practical applications due to the cost of recovery. Especially the pollution to the environment caused by spreading the radioactive substances of the adsorbent that adsorbed iodine still requires great attention.

EXPERIMENTAL

Bruker AC 400MHz Nuclear Magnetic Resonance Spectrometer (manufactured by Bruker, Germany, TMS, DMSO-d_6); Bruker Vector-22 Fourier exchange infrared spectrometer (KBr pellet); SDT-TG Q600 Thermogravimetric Analyzer (produced by American TA Company); ASAP2020M+C specific surface and porosity analyzer (produced by Micromeritics, USA); Nova Nano SEM450 electron microscope (produced by FEI, USA); D8 Discover X-ray Powder diffractometer (manufactured by Bruker AXS, Germany, Cu Kα-ray); 6100 UV-Vis spectrophotometer (Shanghai Yuan Analysis Instrument Co., Ltd.).

p-aminobenzonitrile, trifluoromethanesulfonic acid and isophthalaldehyde are all from commercially available analytical grade. Other reagents are used after purification by standard methods.

Synthesis of 1,3,5-tri-(4-aminophenyl)triazine (TAPT). 4-Aminobenzonitrile (3.86 g, 0.0325 mol) was placed in a 150 mL single-mouth bottle. Circulate the exhaust body three times to make it full of argon gas. Trifluoromethanesulfonic acid (15 mL, 0.1667 mol) was added dropwise in an ice bath. The ice bath was then removed and allowed to react at room temperature for 24 h. Then 25 mL of distilled water was added, an orange-yellow precipitate was produced, and neutralized to pH=7 with a 2 mol/L NaOH solution.[17] The precipitate dissolves and then turns into a pale yellow solid. Performed with 300 mL of distilled water, filtered and washed several times to get a pale yellow solid. It was dried under vacuum at 55 °C for 12 h, and the yield is 3.32 g, yield 86%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.339-8.360 (d, J=8.4 Hz, 6H), 6.677-6.698 (d, J=8.4 Hz, 6H), 5.918 (s, 6H).

Synthesis of COF-1. A sealed pressure vial was charged with TAPT (0.354 g, 1.0 mmol) and isophthalaldehyde (0.194 g, 1.45 mmol). A mixed solvent of 60 mL 1,4-dioxane, 12 mL 1,3,5-mesitylene and 5 mL acetic acid was added to the vial. After three cycles of liquid nitrogen freezing and thawing, reacted for 72 h at 120 °C under inert environment. After cooling to room temperature, a yellow solid was obtained by suction filtration. The solid was repeatedly washed with ethanol and immersed in acetone for 24 h, and dried under vacuum at 60 °C for 6 h.

Uptake of iodine.[2,18] 20 mg **COF-1** powder was loaded into a small vial (2 mL), then place the vial into a wide-mouth vial containing 2 g iodine. The wide-mouth vial was sealed and placed in oven at 348 K. Taking out the vial containing **COF-1** powder and weighing it at regular intervals, then return to the wide-mouth bottle to continue adsorption until the mass of small vial did not change. The iodine adsorption amount is obtained by the following formula.

$$C_{exp} = \frac{W_2 - W_1}{m}$$

Where C_{exp}: iodine adsorption; W_1: mass of vial containing **COF-1** before iodine adsorption; W_2: mass of vial containing **COF-1** after iodine adsorption; m: mass of **COF-1**.

Release of iodine. 0.1 mg **I_2@COF-1** powder was immersed in 6 mL MeOH, and the iodine continuously released into the MeOH. The concentration of I_2 in the solution increased with time and monitored by UV-vis spectroscopy.

Recycle of iodine adsorption. **I_2@COF-1** powder was washed in anhydrous MeOH at normal temperature. The methanol was replaced every 1 h until the solution was colorless. After centrifugation, the solid was dried under vacuum at 60 °C for 8 h, and then reused for the next cycle.

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