Supporting Information

Rapid, High-Capacity Adsorption of lodine from Aqueous Environments with Amide Functionalized Covalent Organic Frameworks

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1. General Methods and Instrumentation

Potassium iodide and iodine were purchased from Fischer scientific. All chemicals purchased from commercial sources were used without purification. COFamide-1, COFamide-2 and PyCOFamide were synthesized according to previously reported procedures.^{1,2}

Nuclear Magnetic Resonance Spectroscopy

¹H and ¹³C NMR spectra for all the synthesized compounds were carried out on a Bruker Advance III HD 600 MHz spectrometer.

UV-Vis Spectrophotometry

UV-Vis measurements of all the COF powders were performed using a Cary 5000 UVvis-NIR spectrophotometer.

Powder X-Ray Diffraction

PXRD measurements of COF powders were collected using Bruker D8 Advance diffractometer with a (Cu K α , λ = 0.154 nm) radiation source, a low background sample holder, and a Lynxeye XE detector. Measurements were taken from 2° to 30° 2 θ .

Fourier Transform Infrared

FTIR spectra of all the COF powders were collected using the attenuated total reflectance (ATR) method on a Cary 600 Series FTIR spectrophotometer.

Supercritical CO₂ Activation

Super critical activation processing was performed by a Leica EM CPP300. The COF powders were pretreated by ethanol and kept in specimen holders. The holders were then placed in the drying chamber and filled with liquid CO_2 . The chamber was sealed and the temperature was raised to 40°C (above the CO_2 critical temperature.) The samples were kept there for 1 hour and 55 mins to afford dry COF powder.

Scanning Electron Microscopy

The surface morphology of the samples was evaluated by scanning electron microscopy (SEM). The images were obtained with a Zeiss SIGMA 500 VP scanning electron microscope (Carl Zeiss Microscopy). The samples were mounted on 15 mm aluminum stubs using double-sided adhesive copper tape. EDX was performed with a Zeiss SIGMA 500 VP scanning electron microscope (Carl Zeiss Microscopy) and an Octane Electron Scanning system (AMETEK). EDX was done with a 15kV gun intensity and a 200 second scan time.

Thermogravimetric Analysis

TGA was performed Mettler Toledo SDT using 2-10 mg samples loaded into alumina crucibles and was conducted with a heating rate of 10 °C/min, from 25 to 700 °C under N2 atmosphere with a flow rate of 100 mL/min.

2. Synthesis and characterization of COFamides

Synthesis of COFamides

All the COFs were synthesized as previously reported in the literature.¹⁻²

Charcterization of COFamides

PXRD and BET surface analysis are as mentioned in Fig S1. These results are in agreement with the previous literature.¹



Figure S1. (A) BET surface analysis shows the surface area to be 1202 m²/g, 1390 m²/g and 1909 m²/g for COFamide-1, COFamide-2 and PyCOFamide respectively. (B) PXRD data of COFamide-1, COFamide-2 and PyCOFamide.

3. Iodine Capture and Release Studies

In order to monitor the I_2 capture of COFamides in aqueous solution, a time-dependent measurement was carried out on a UV-Vis spectrophotometer. COFamides (3.0 mg) were added to a saturated aqueous I_2 solution (1.2mM) with stirring. The UV-Vis spectrum of the solution was measured every 3 minutes in the first 30 minutes, and at 4 h and 24 h. The I_2 concentration was decreased from 40 ppm to less than 20 ppm within 30 min and below 1, 5.95 and 8.89 ppm after 24 h, for COFamide-1, COFamide-2, and PyCOFamide respectively as shown in Fig S2



Figure S2. Time-dependent UV spectra of a saturated aqueous iodine solution (1.2mM, 3mL) after adding (a) COFamide-1 (3.0 mg) (b) COFamide-2 (3.0 mg) (c) PyCOFamide (3.0 mg) Purple: iodine saturated aqueous solution, t = 0 min, grey: t = 4 h, brown: t = 24 h

Max Iodine Adsorption In Aqueous Iodine Solution

In order to find the maximum capacity of iodine uptake, the mass increase of COFamides was measured after immersing COF powders in highly concentrated iodine solution. Typically, 5 mg COFamides was soaked in 35 mM I_2 / 65 mM KI/ 2mL aqueous solution. Fig S3 shows the max uptake of iodine in COFamides. Fig S4 shows the time-dependent UV vis of maximum iodine uptake in 35 mM I_2 / 65 mM KI/ 2mL aqueous solution after adding COFamides (5.0 mg)



Figure S3: Images show the iodine uptake of COFamides in 35 mM I_2 / 65 mM KI/ 4mL aqueous solution.



Figure S4: Time dependent UV spectra of a saturated iodine solution (35 mM I2/ 65 mM KI/ 2mL) after adding COFamides (5.0 mg). Blue: Iodine saturated solution, t= 0 min, red: t= 5 days.







Figure S5: Maximum iodine absorption of (a) COFamide-1 (4.62 g/g) (b) COFamide-2 (5.91 g/g) (c) PyCOFamide (6.53 g/g).

I₂ Release from COFamides

Time-dependent UV-Vis measurements were carried out in DMSO and ethanol to determine the release of I_2 from COF $\subseteq I_2$. Typically, I_2 was immersed in ethanol or DMSO (10 ml) in a reaction vial with stirring. Fig. S7a shows the release of iodine in DMSO and Fig. S7b in ethanol. The release of iodine was faster in ethanol than DMSO because of its better solubility in the former. Images of this release process over time are shown in Figure S8.



Figure S6: UV spectra of a saturated aqueous iodine solution (1.2mM, 3mL) after adding COF control (3.0 mg). Purple: iodine saturated aqueous solution, t= 0 min, brown: t= 30 min.



Figure S7: (a) Iodine release of COF \subset I₂ in 10 ml DMSO (b) COF \subset I₂ in 10 ml ethanol.



Figure S8: (a) iodine release from COFamides in ethanol over course of 30 min (b) iodine release from COFamides in DMSO over course of 30 min

FT-IR Studies of lodine Loaded COFamides

In order to observe the interactions that are expected to exist in between the framework and the iodine in the COFamides, we used FT-IR as shown in Figure S9. Here we have focused our discussions on COFamide-2. When the FT-IR spectra of the iodine loaded COF was compared to the parent COF, it was found that the one with iodine loading exhibits enhanced N-H stretching vibrations, the center of the peak shifted from 3305 to 3292 cm⁻¹ and C=C red shifts slightly from 1590 cm⁻¹ to 1505 cm⁻¹, with increasing uptake of iodine



Figure S9: The FT-IR data represents the interaction of iodine and nitrogen rich moieties by red shifting the peak center of N-H vibrations.

PXRD profiles of lodine Loaded and Regenerated COFamides

The recovered COF was reactivated by super critical carbon dioxide ($scCO_2$) to get rid of leftover ethanol and DMSO and the PXRD profile of recovered COF powders were compared to the original crystalline COF and was found to be well-preserved for

COFamide 1 and 2 and not for PyCOFamide (as shown in fig S10) because of its fragile framework.



Figure S10. PXRD patterns of COFamides before loading with I_2 , after loading, and after regeneration in ethanol or DMSO. (a) COFamide-1, (b) COFamide-2, and (c) PyCOFamide.

Scanning Electron Microscopy Images and Energy Dispersive Spectroscopy Profiles of Iodine Loaded COFamides







Thermogravimetric Analysis curves of iodine loaded COFamides

Figure S12. TGA curves of the iodine loaded (A) PyCOFamide (B) COFamide-1 (C) COFamide-2

Table S1. Comparison of COFamide iodine adsorption capacity with selected examples from the literature.

Reference	Linkage	Pore size	Type of pore	S _{BET}	l₂ uptake	
		(nm)		(m²g⁻¹)	(g g-1)	
Bhaumik <i>et al-</i> 2023 ³	imine (C=N)	1.8	microporous	1058	4.83	
Huang <i>et al</i> - 2023 ⁴	imine	2.18	mesoporous	1061	4.16	
Xinle Li <i>et al</i> - 2023⁵	imine	2.3	mesoporous	210	7.83 (l ₂ vapor)	
Pei-Zhou <i>et al-</i> 2023 ⁶	imine	2.9	mesoporous	451	3.15	
Pei-Zhou <i>et al-</i> 2023 ⁶	imine	2.9	mesoporous	464	2.6	

Chenfeng <i>et al-</i>	Thiol (S-	-	mesoporous -		2.1
2017 ⁷	H)				
Guang <i>et al</i> - 2022	imine	3.5	mesoporous	1410	3.15
Jun Hu <i>et al</i> - 2019 ⁸	imine	4.7	mesoporous 926		3.3
Yu Han <i>et al</i> - 2021 ⁹	imine	3.3	mesoporous 1390		10.21(I ₂
					vapor)
Yu Han <i>et al</i> - 2021 ⁹	imine	3.3	mesoporous	1580	9 (I ₂ vapor)
This work	Azine	2.3	mesoporous	1390	4.6
	imine	3.3	mesoporous	1202	5.9
	imine	6.5	mesoporous	1682	6.5

4. Computational Modelling

We have taken two COF models for investigating the binding phenomena of I_2 and its counter anions. The monomeric unit (**ML**) is the exact replica of the COF monomer whereas two layers of modelled monomeric unit (hexyl group is substituted by the methyl group, designated as **BL**, has been considered also for I_2 capture.

For modeling of COF without amide bonds, we have taken monomeric unit only (ML^{NO_NH}) and substituted the -CONH-Hex part with methyl group.

lodine capture process with linkers is taken care of explicitly. Three types of linkers are reported here; one with azide(COFamide-1), another is linked with benzene (COFamide-2) and the 3rd one is pyrene derivative (PyCOF). The aromatic moieties of the linkers can adsorb iodine through non-covalent interactions, which is thoroughly investigated using DFT.

From the structural analysis it has been found that there are two benzene units (core benzene and side benzene) and three -NH of amide bonds (two are available for binding) on which lodine can be captured through non-covalent interactions. Through DFT we are going to investigate all possible binding modes and associated Interaction Energies (IE) of different anionic and neutral forms of iodine on the COF units.

5. Method and computational Details

All the electronic structure optimization have been done using Gaussian 16 rev. A. 03^{10} employing ω B97XD¹¹ in conjunction with 6-31+G(d)¹²⁻¹³ for (C, H, N, O) and def2svp¹⁴ for I atoms. The C, N, and O atoms were kept fixed while only the hydrogens and iodine atom(s) were allowed to relax. Symmetry adapted perturbation theory (SAPT) analysis¹⁵⁻¹⁶ has been done using PSI4 1.2.1.¹⁷ Non-covalent interaction plot has been done using NCI plot4.¹⁸ To predict the stability, we have calculated interaction energy (IE_{COF-X}) of the complexes by employing the following equation.

$$IE_{COMP-X} = E_{COMP-X}^{opt} - E_{COMP}^{Frag} - E_{X}^{Frag}$$

Complexation energy is computed between COF and X after complexation which is reported after BSSE correction.¹⁹⁻²⁰ From SAPT (DFT) analysis we have also reported dispersion (D), induced(I) and electrostatic (I) energy contributed between **COMP** (COF, LINKER, No_H_COF) and **X** (X=I⁻, I_3^- , I_2 , I_5^- , I_7^- ,).





Figure S14. Constrained Optimized geometries of (A) I-, (B) I₃-, (C) I2 absorbed on monomeric unit of no_NH_COF at ω B97xD/ 6-31+G(d) (C,H,N,O)/def2svp(I). IE are in kcal/mol.



Table S2. Fragmentation of energies between two fragments at ω B97xD/ 6-31+G(d)
(C,H,N,O)/def2svp(I)) from SAPT(DFT) analysis. Energies are in kcal/mol.

Frag1	Frag2	Electrostatic	Dispersion	Induction	Exchange	Total		
_	_	Kcal/mol						
BL	- -	-24.9	-6.5	-15.4	19.5	-27.4		
BL	I ₃ -	-18.1	-9.9	-9.3	15.5	-21.8		
BL	I ₂	-4.9	-7.4	-1.5	8.2	-5.6		
MLI-	2l ₂	-54.2	-16.4	-50.4	82.2	-38.8		

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