Supporting Information for

Facile Post-Synthesis of Isomeric Covalent Organic Frameworks *via* Precise Pore Surface Engineering

Yuhao Liu,*[a] Yaze Chen,[a] Ke Shi,[a] Haijiao Peng,[a] and Chao Lu*[a, b]

[a]Pingyuan Laboratory, College of Chemistry, Zhengzhou University, No.100 Science Avenue, 450001, Zhengzhou, China

[b]State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, No.15 Beisanhuan East Road, 100029, Beijing, China

E−mail: yuhaoliu@zzu.edu.cn; luchao@mail.buct.edu.cn.

Table of Contents

Experimental Section

Materials

All regents were commercially available and directly employed.

Synthesis of D-A-COF

A 10 mL Schlenk tube was charged with 2,4,6-Tris(4-aminophenyl)triazine (17.8 mg, 0.05 mmol), tris(4-formylphenyl)amine (16.5 mg, 0.05 mmol), 0.2 mL o-dichlorobenzene and 0.6 mL 1-butanol. The resulting mixture was sonicated for 5 min and then the 0.1 mL 3 M acetic acid aqueous solution was added. The tube was flash frozen at 77 K (liquid nitrogen bath), evacuated and sealed. Upon warming to room temperature, the tube was heated at 120 °C for 3 days. The solid was filtered out and washed with THF, MeOH, and H_2O several times. The obtained solid was dried under vacuum at 80 °C for 8 h to afford D-A-COF as yellow powder (28 mg, 81%).

Synthesis of COF-BA

D-A-COFs (20 mg), (2-ethynylphenyl) boronic acid, (3-ethynylphenyl) boronic acid or (4-ethynylphenyl) boronic acid (36.5 mg, 0.25 mmol), $BF_3•OEt_2$ (20 μL, 0.15 mmol), chloranil (40 mg, 0.15 mmol), and 2 mL of solvents were added to a clean Schlenk tube. The tube was sealed and heated under N_2 with different synthesis conditions (Table S1). The mixture was cooled to room temperature and the precipitate was isolated *via* filtration. The reaction mixture was then washed with THF and quenched with saturated $NaHCO_3$ solution (10 mL × 3). Subsequently, the solids were washed with THF using a Soxhlet extractor for 12 h and dried under vacuum to obtain COF-o-BA, COF-m-BA or COF-p-BA.

Sample characterization

The FT-IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Thermo Scientific Nicolet iS5. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation at 40 kV, 40 mA power. Scanning electron microscopy (SEM) images were obtained on a ZEISS sigma500. Transmission electron microscopy (TEM) images were obtained with a Talos F200 X. Solid ^{13}C NMR experiments were carried out on

Bruker AVANCE (3) 400 WB. The porous properties of the COFs were investigated by nitrogen adsorption and desorption at 77 K using a Quantachrome autosorb iQ. The pore-size-distribution curves were calculated from nitrogen adsorption isotherms using the quenched solid density functional theory (QSDFT) model. Before the adsorption measurement, the samples were activated at 120 °C under vacuum (< 10^{-3} torr) for 12 h. The fluorescence measurements were performed with an Edinburgh instruments FLS1000. The UV/vis spectra were measured on a Shimadzu UV-2700i spectrophotometer. Thermogravimetric analyses (TGA) were carried out in a N_2 atmosphere with a heating rate of 10 °C min^{-1} on a NETZSCH STA 449 F5. X-ray photoelectron spectroscopy (XPS) was performed with a Shimadzu AXIS SUPRA electron spectrometer.

Fluorescence spectra of COFs at different pH values. The stock solutions of COFs were prepared by dispersing COFs in DMF with the concentration of 1.0 mg mL^{-1}. The stock solution of COF (200 μL) and aqueous solutions with different pH values ranging from 2 to 10 were put into quartz cuvettes, and the total volume of the detection system was 2.0 mL. The fluorescence spectra were collected with the excitation wavelength of 300 nm.

Adsorption experiments. The COF-BA (10 mg) was dispersed in a buffer solution of $NaHCO_3$/NaOH (pH = 10, 2.0 mL) with different nucleosides substances (uridine, thymidine, cytidine, inosine, guanosine, and adenosine) ($1*10^{-4}$ M). The as-prepared solution was shaken in a thermostatic oscillator (TS 100, Ruicheng, China) with a speed of 1500 rpm at room temperature for 96 h. At different time intervals of 0.5, 1, 2, 3, 4, 6, 8, 24, 48, 72 and 96 h, the remaining concentration of the adsorbates in the solution was filtered and measured through a UV/vis spectrophotometer (Shimadzu UV-2700i).

Recycling experiments. The COF-BA sample after adsorption was dispersed in a mixed solution of HOAc/NaOAc buffer solution (pH = 3.6, 2.0 mL) for a certain time until the complete desorption of nucleoside from COF-BA. The COF-BA after desorption was recycled for the next run of nucleoside adsorption, which was implemented under the same conditions as the first run.

General procedure for fluorescence titration with NaOH (aq.). The titration experiments were carried out by adding 10.0 μL 0.15 M NaOH solution of substrates to a solution of D-A-COF or COF-BA (0.1 mg mL^{-1} in DMF, 2 mL) every two minutes. The fluorescence spectra were collected with the excitation wavelength of 300 nm.

General procedure for fluorescence titration with nucleosides. The titration experiments were carried out by adding 25.0 μL nucleoside substrates (1.0×10^{-3} M in DMF) to a solution of COF-BA (0.1 mg mL^{-1} in DMF, 2 mL) and 100 μL 0.15 M NaOH solution every two minutes. The fluorescence spectra were collected with the excitation wavelength of 300 nm.

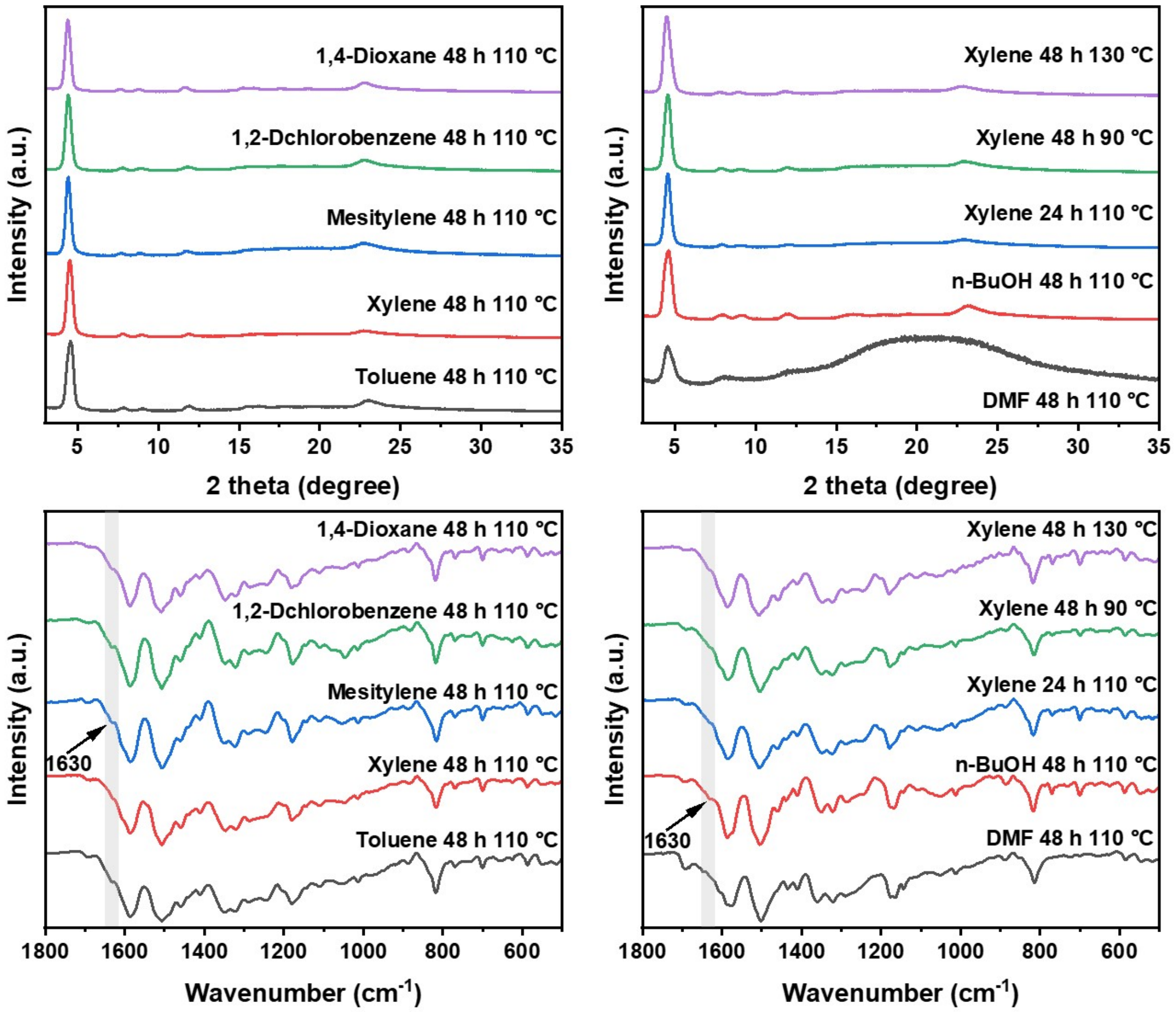

Fig. S1. PXRD patterns and FTIR spectra of COF-BA under different synthetic conditions.

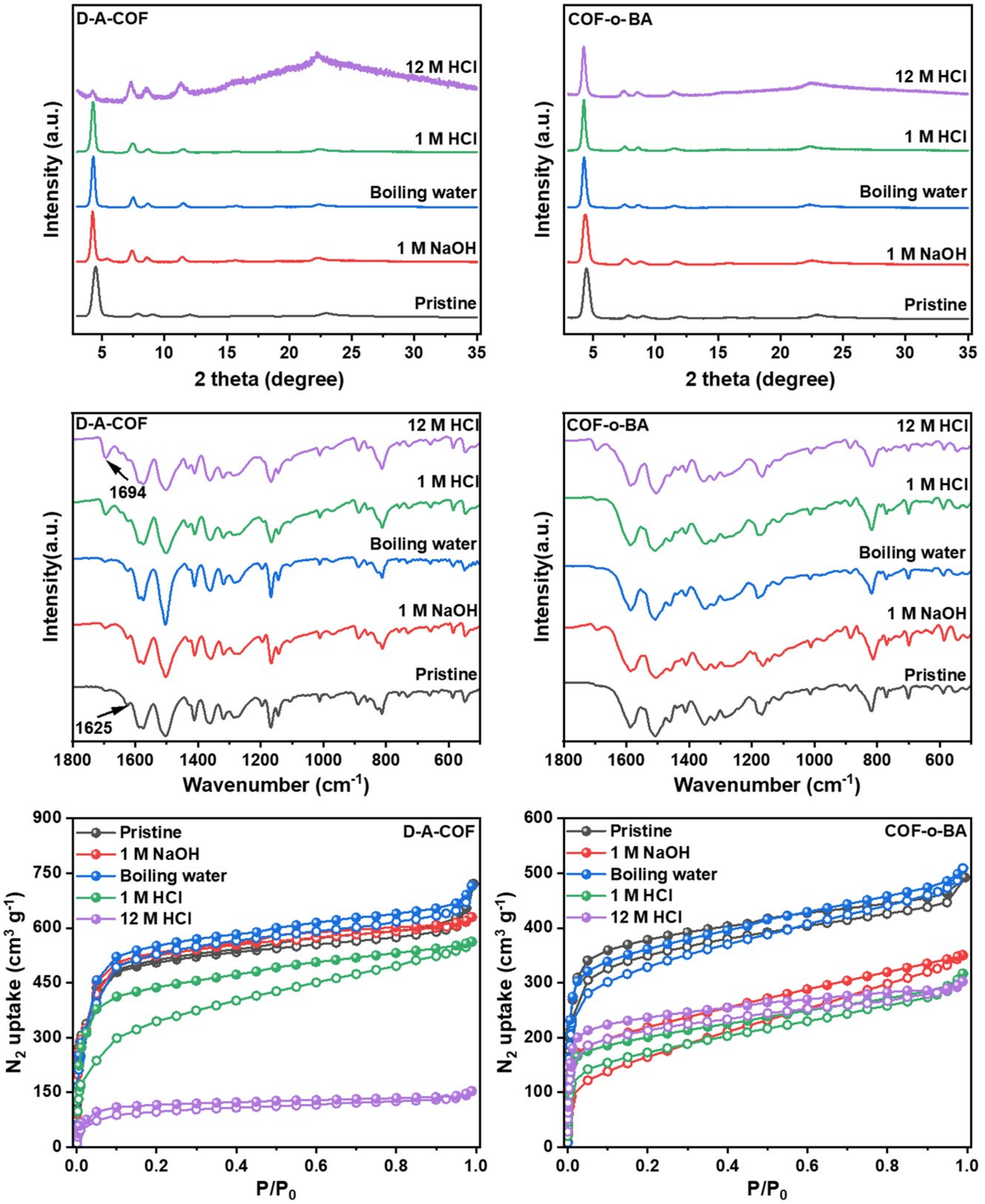

Fig. S2. PXRD patterns, FTIR spectra, and N_2 adsorption−desorption isotherms (77 K) of D-A-COF and COF-o-BA under the 12 M HCl, 1 M HCl, boiling water and 1M NaOH.

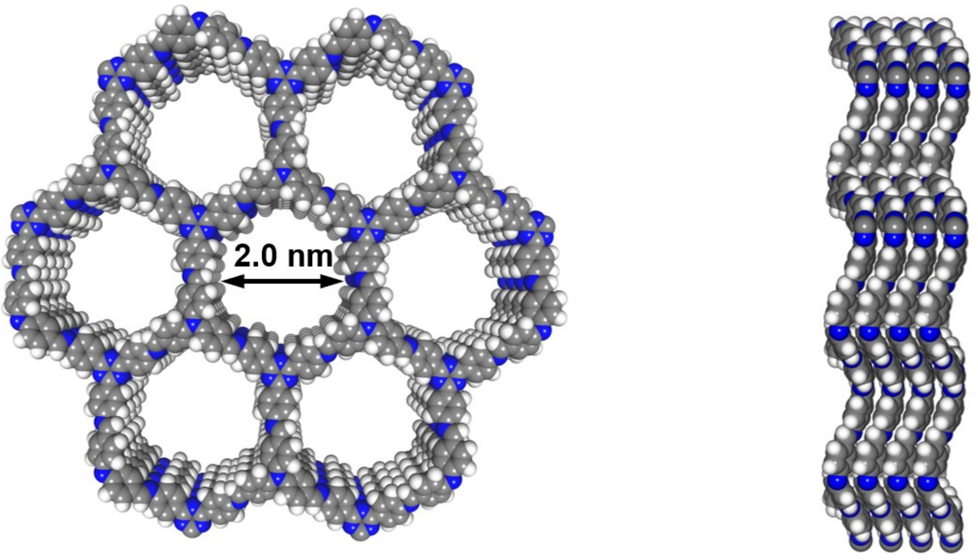

Fig. S3. Refined crystal structures of D-A-COF.

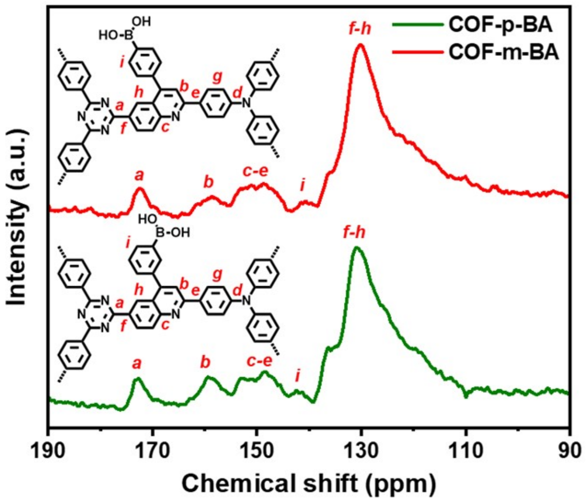

Fig. S4. Solid-state ^{13}C NMR spectra of COF-p-BA and COF-m-BA.

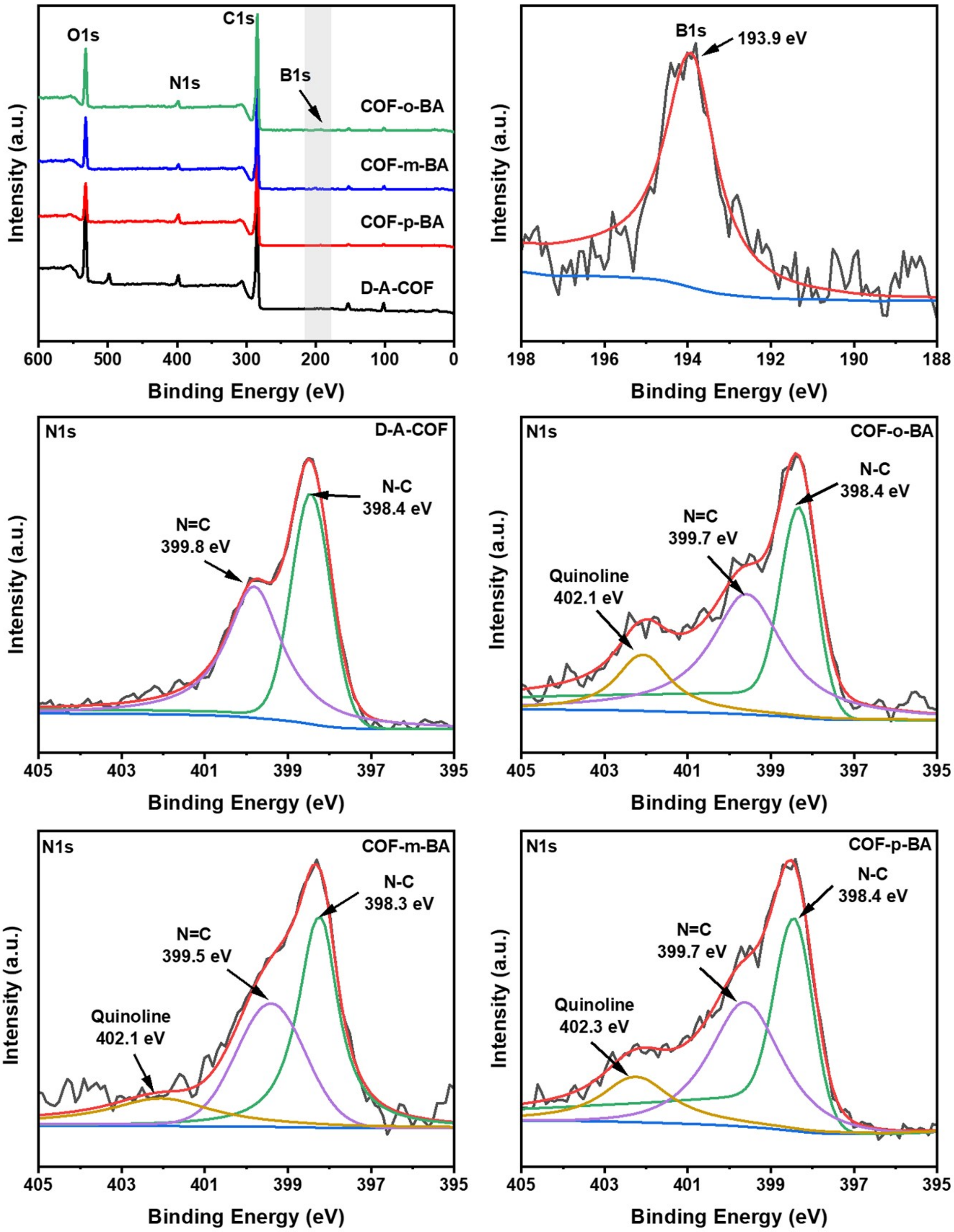

Fig. S5. XPS full spectra of D-A-COF and COF-BA and the binding energy region of the B1s and N1s electrons.

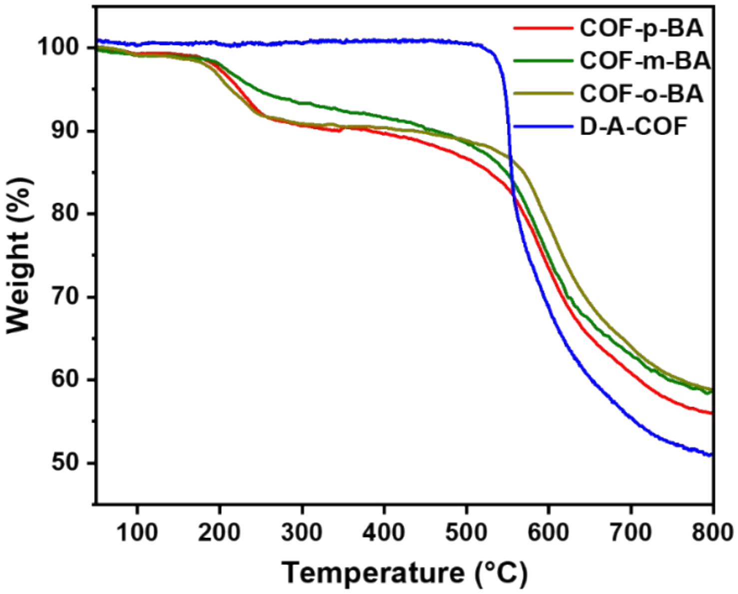

Fig. S6. TGA curves of D-A-COF and COF-BA.

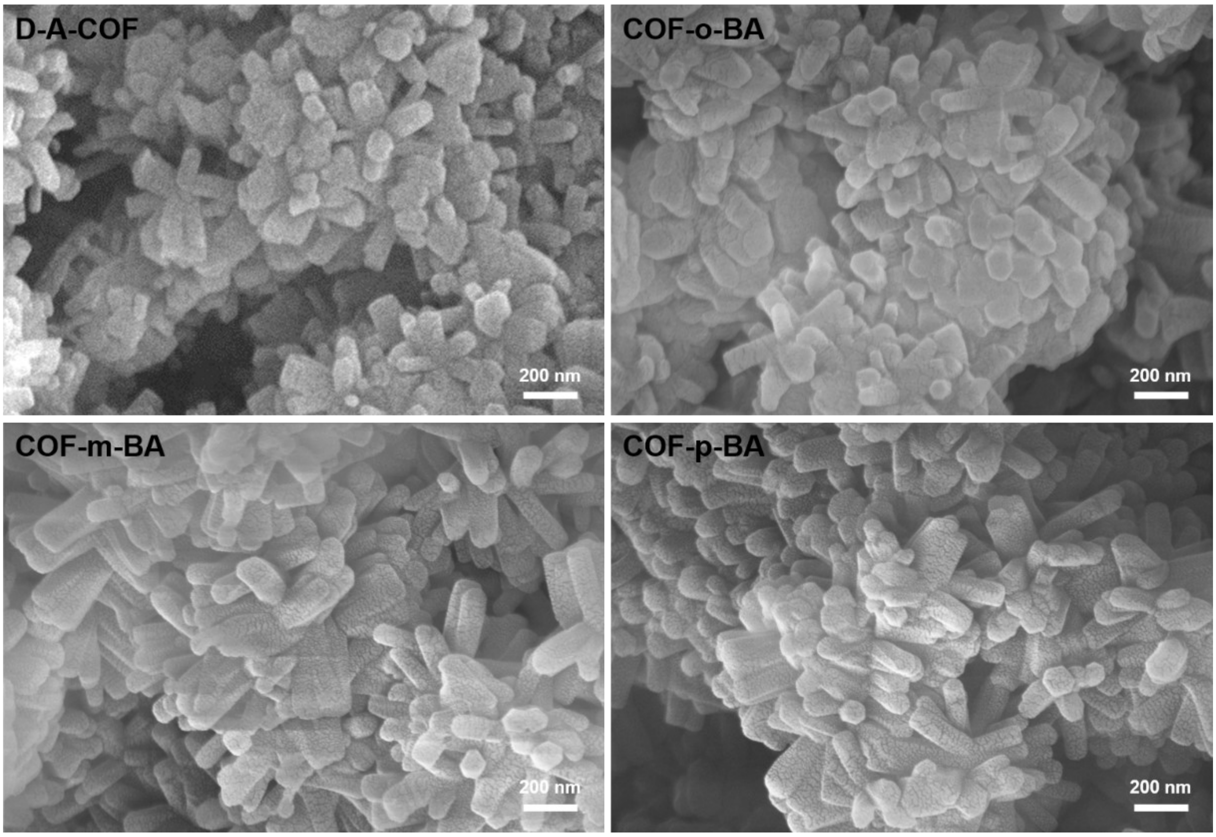

Fig. S7. SEM images of COFs.

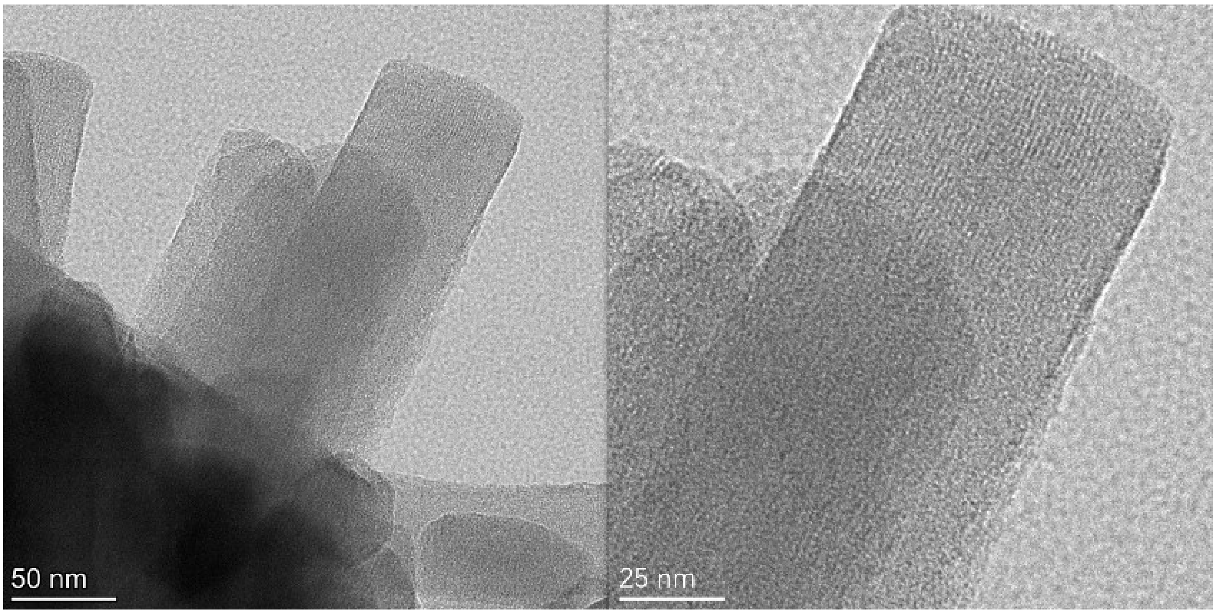

Fig. S8. HRTEM images of D-A-COF.

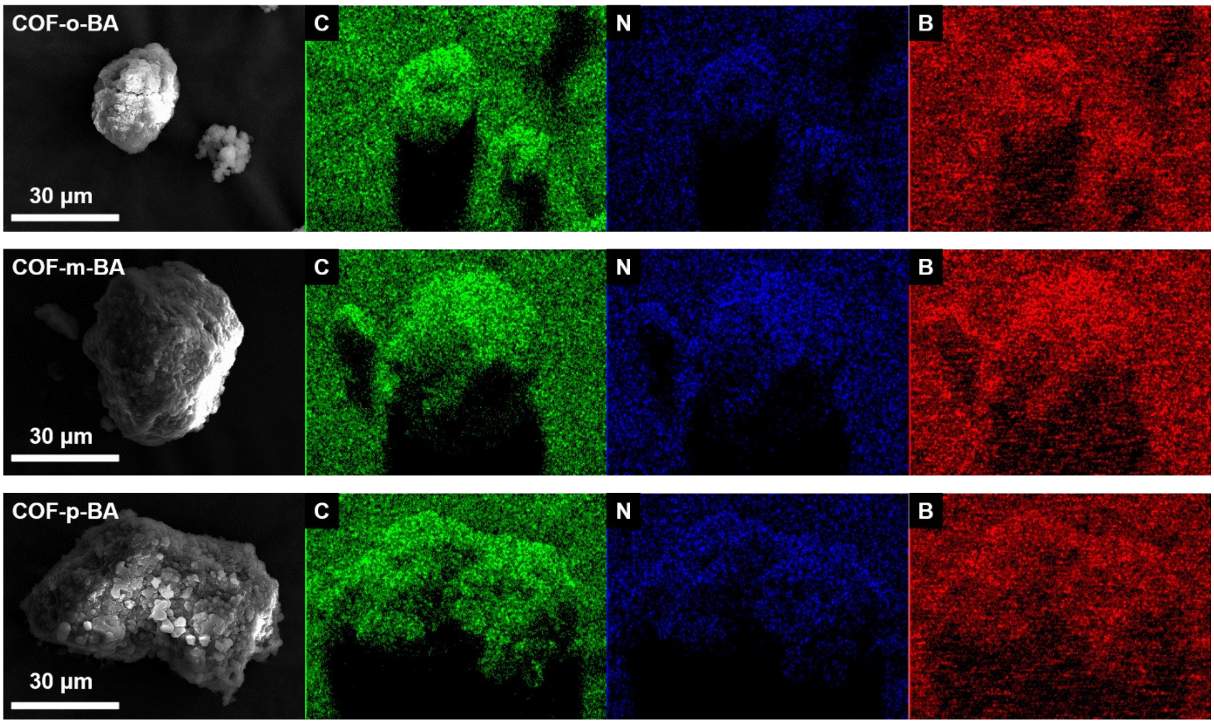

Fig. S9. SEM elemental mapping images of COF-o-BA, COF-m-BA, and COF-p-BA.

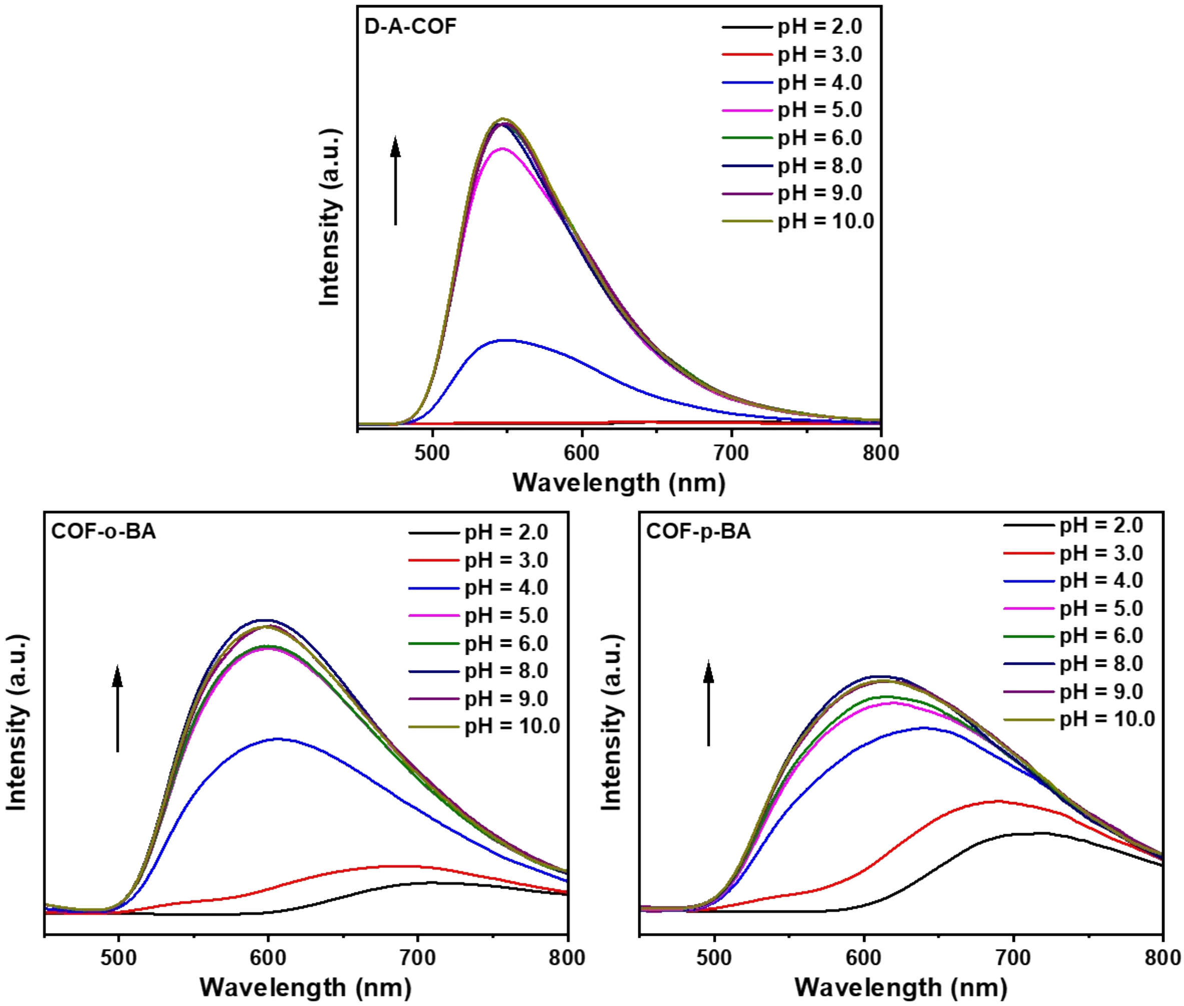

Fig. S10. Fluorescence spectra of COFs at different pH values.

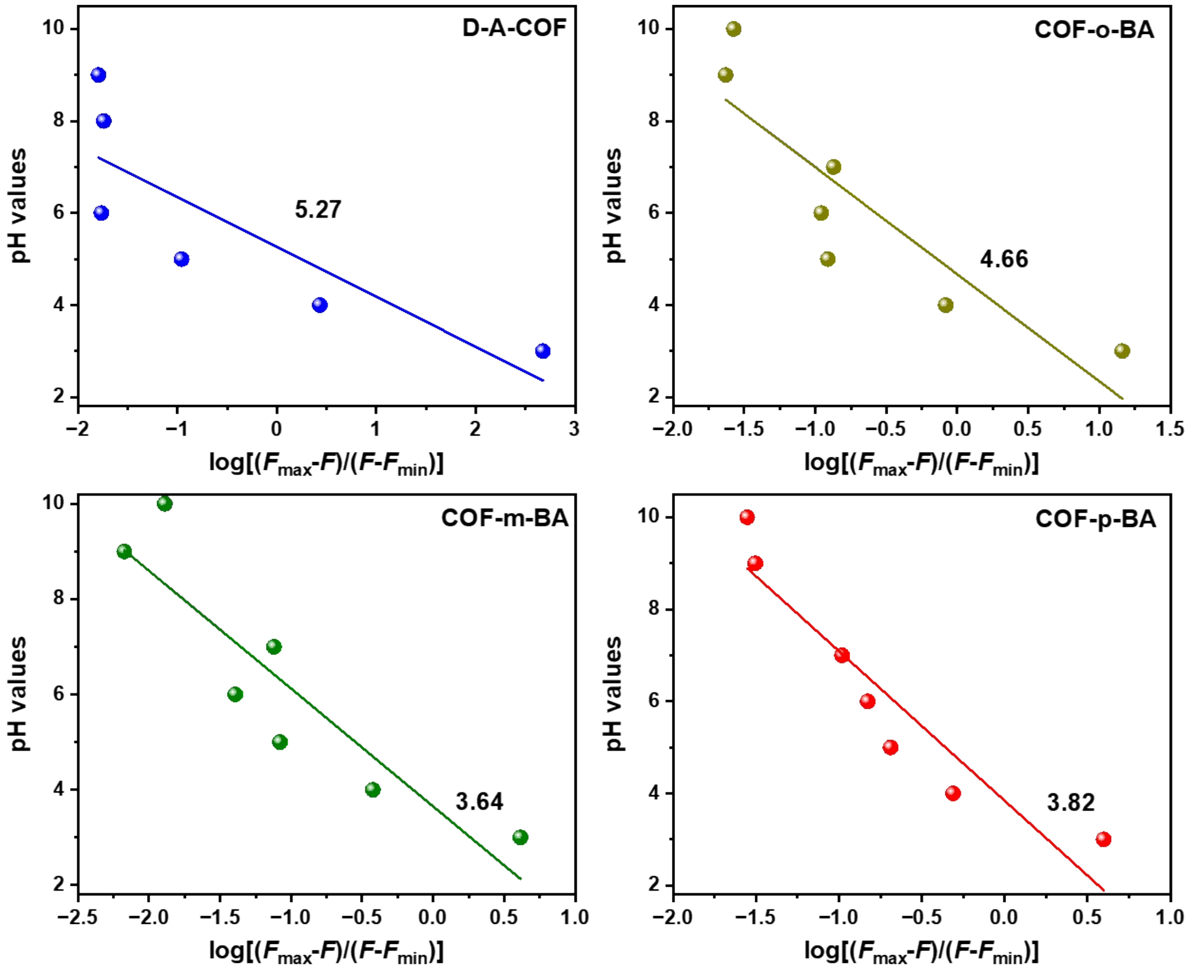

Fig. S11. linear relationship between log[(F_{max}-F)/(F-F_{min})] and pH values.

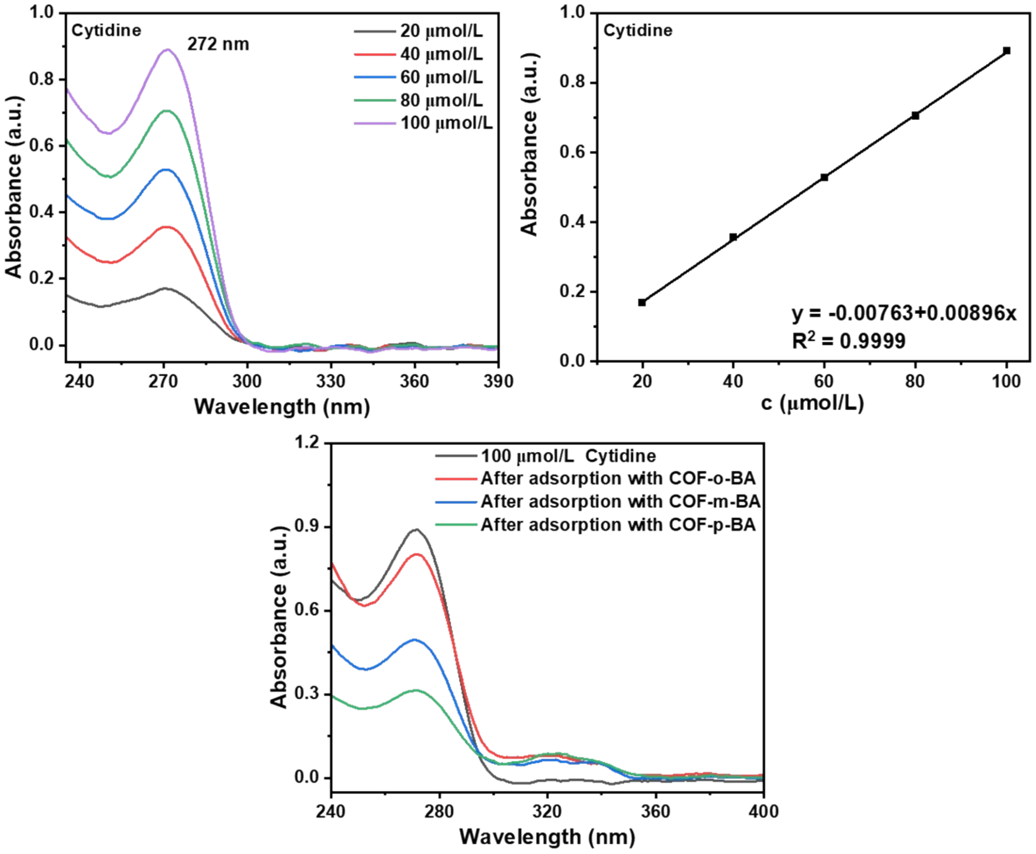

Fig. S12. Standard curve of cytidine and curve of cytidine adsorption by COF-BA.

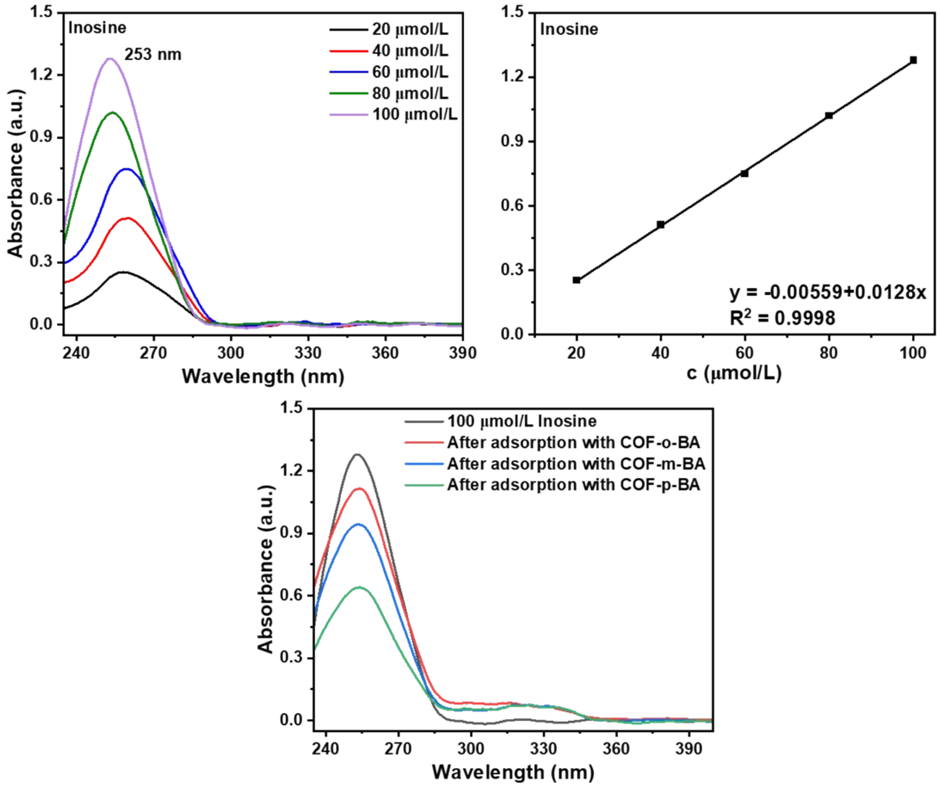

Fig. S13. Standard curve of inosine and curve of inosine adsorption by COF-BA.

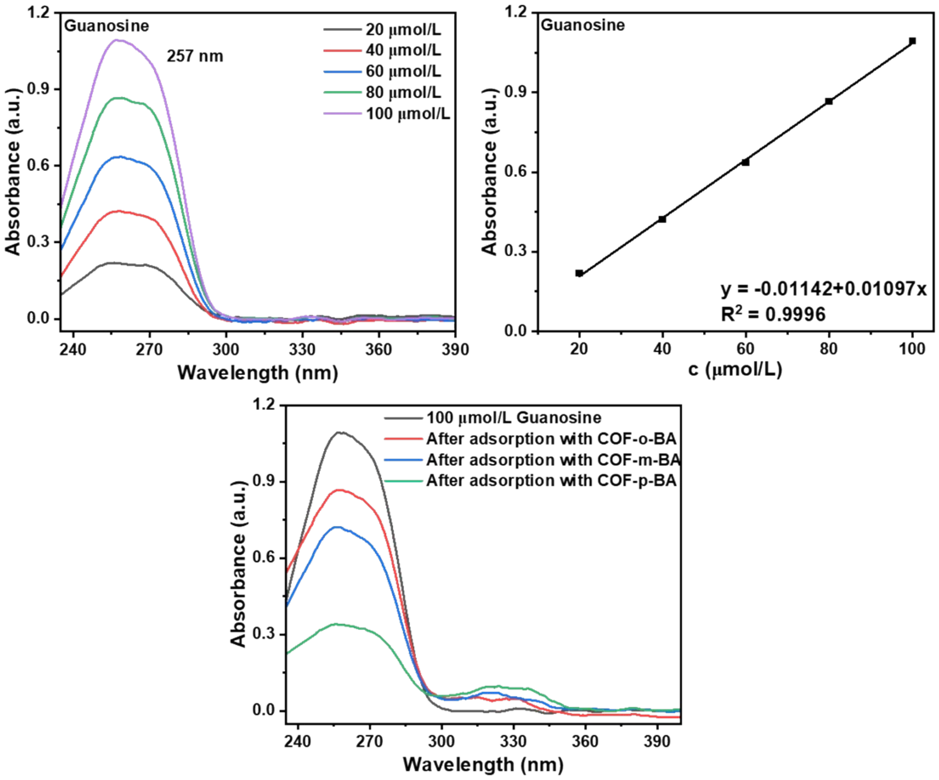

Fig. S14. Standard curve of guanosine and curve of guanosine adsorption by COF-BA.

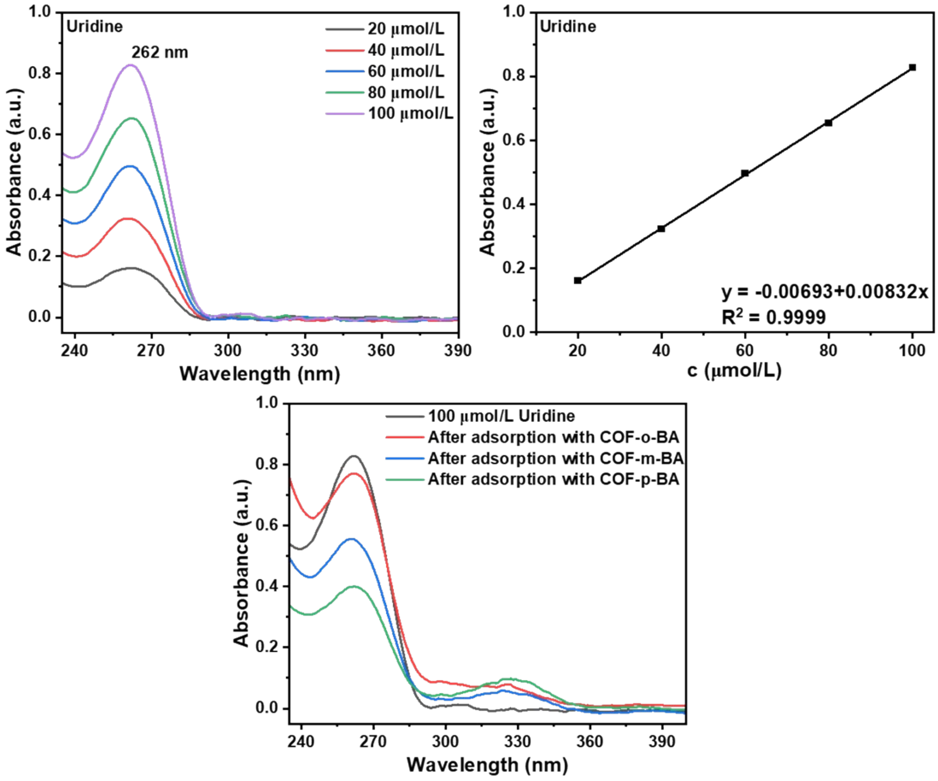

Fig. S15. Standard curve of uridine and curve of uridine adsorption by COF-BA.

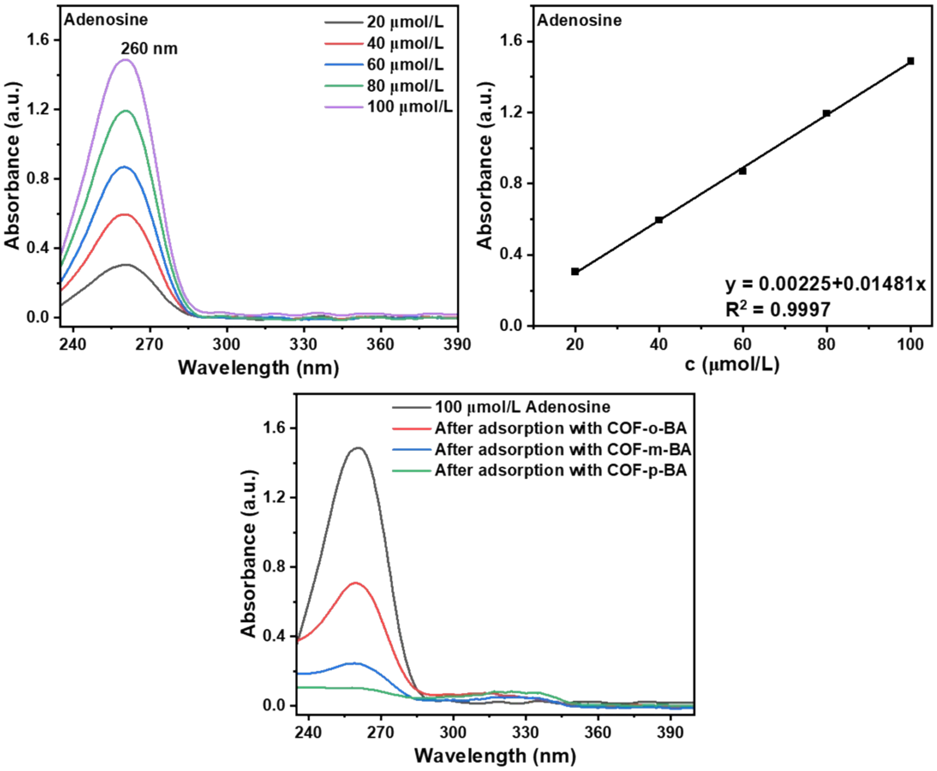

Fig. S16. Standard curve of adenosine and curve of adenosine adsorption by COF-BA.

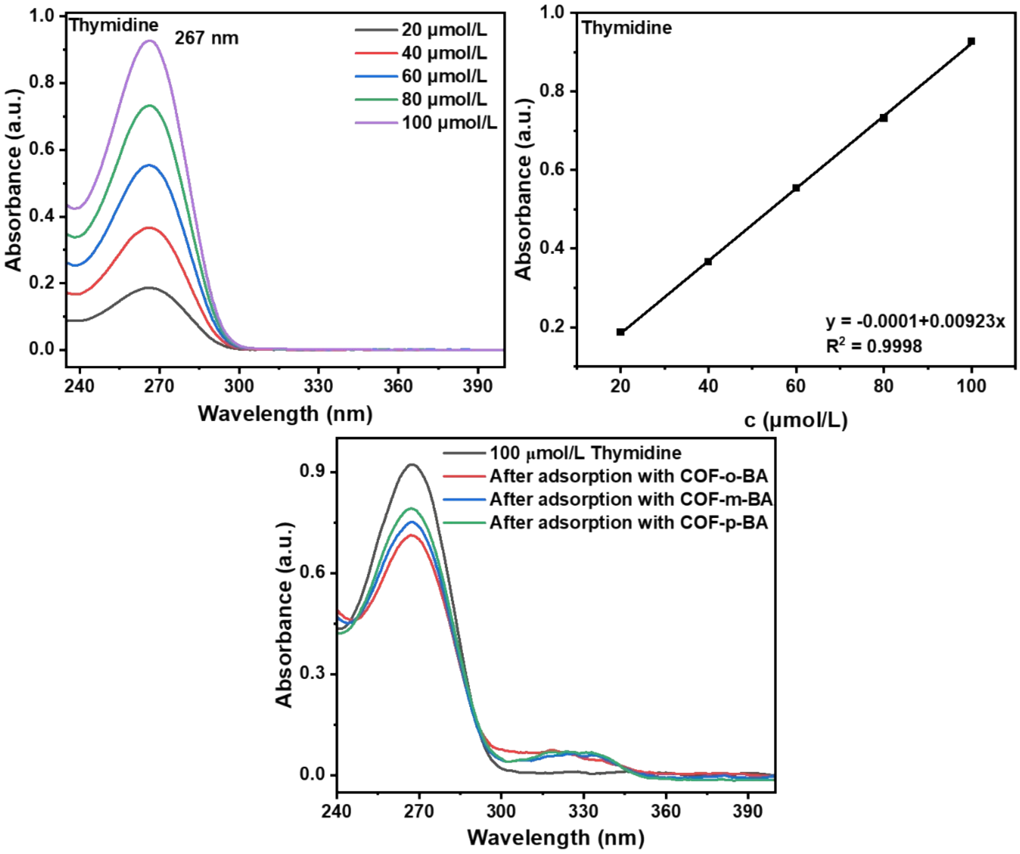

Fig. S17. Standard curve of thymidine and curve of thymidine adsorption by COF-BA.

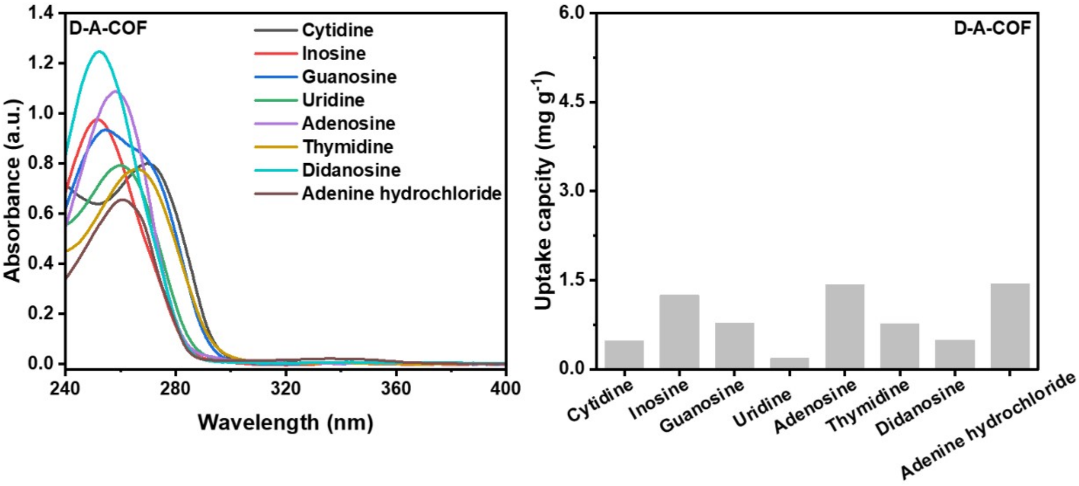

Fig. S18. The curve of different substrates adsorption by D-A-COF.

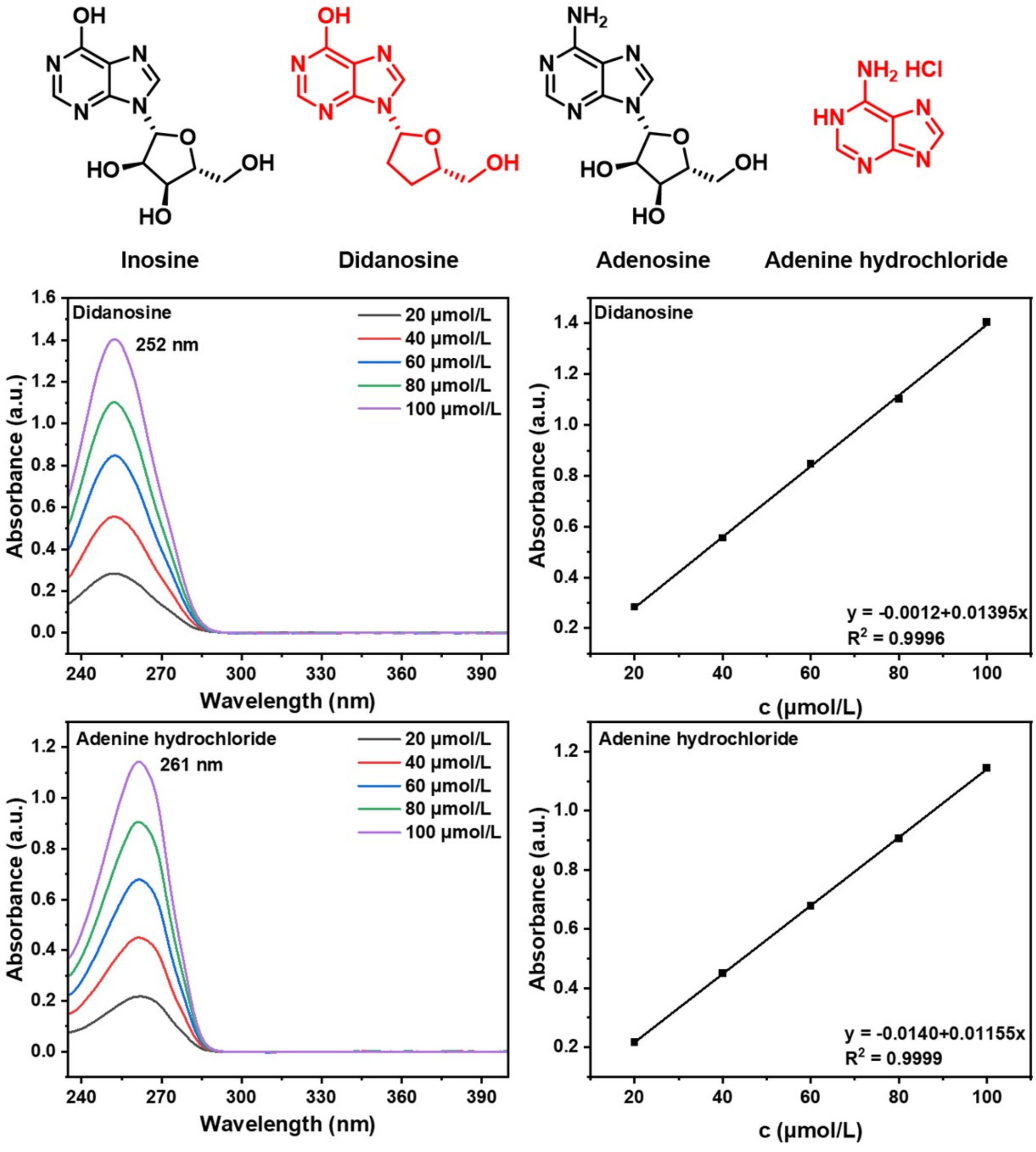

Fig. S19. Standard curve of didanosine and adenine hydrochloride.

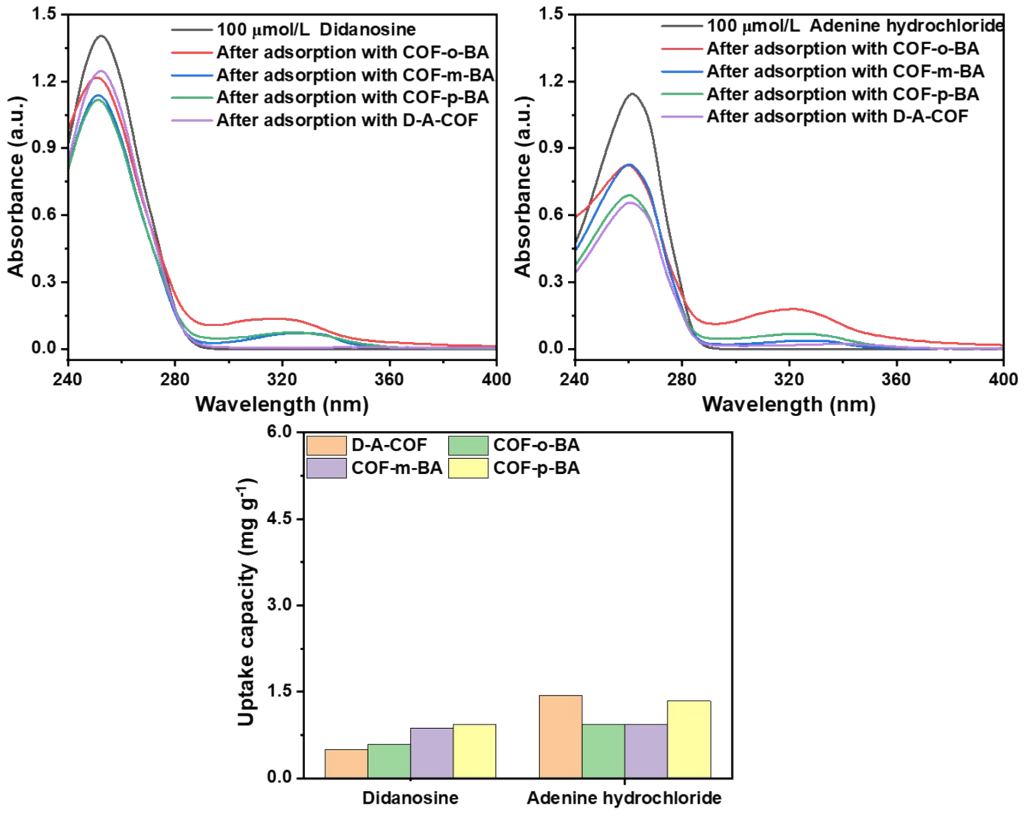

Fig. S20. The curve of didanosine and adenine hydrochloride adsorption by D-A-COF and COF-BA.

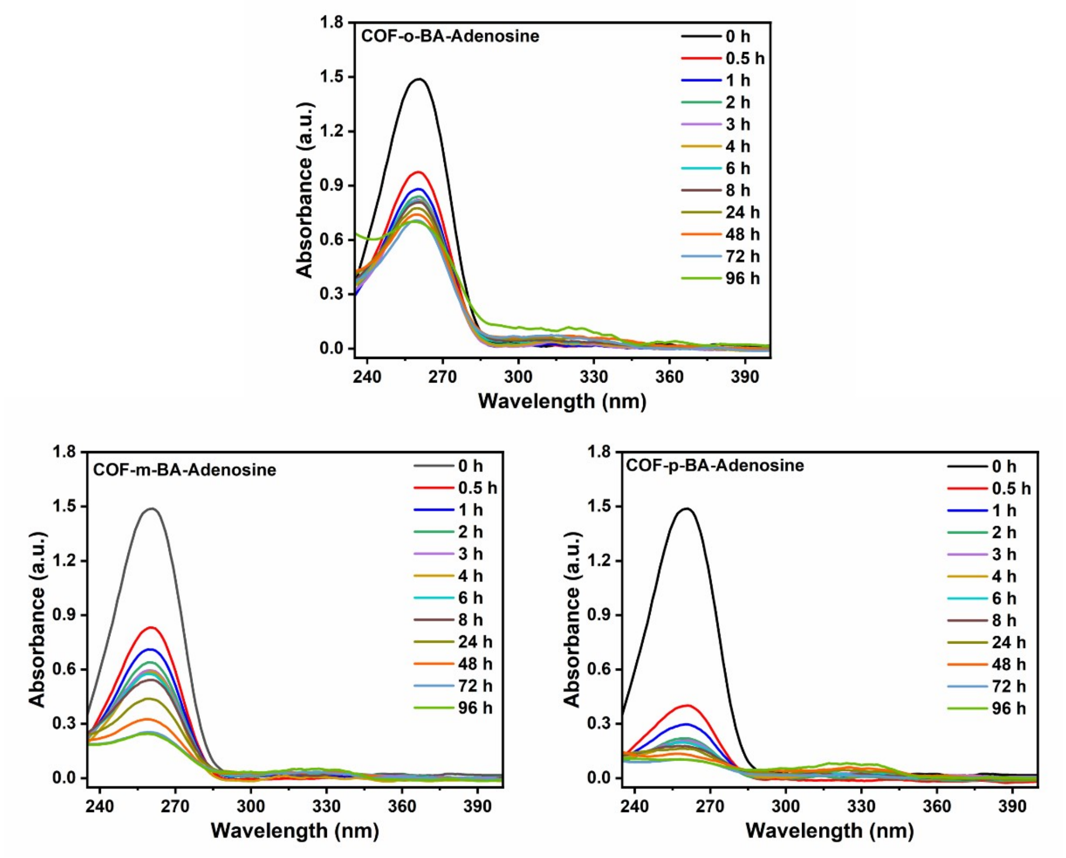

Fig. S21. Curve of adenosine adsorption by COF-BA with different times.

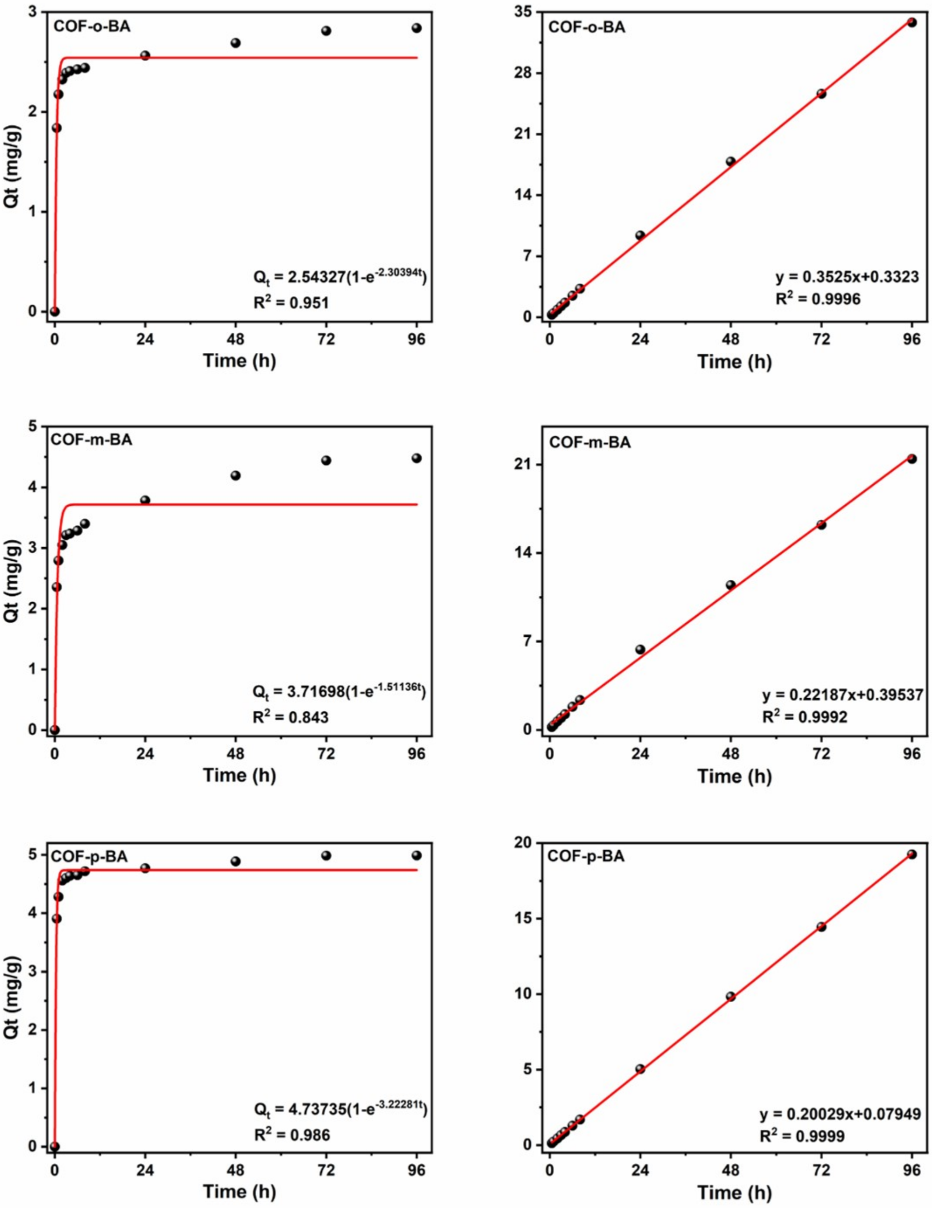

Fig. S22. Linear fitting curves with pseudo-first-order kinetic model and pseudo-second-order kinetic model for adenosine adsorption using COF-BA.

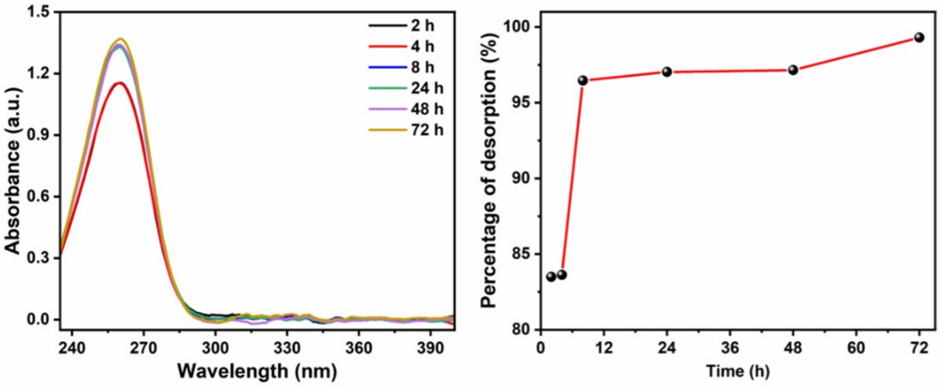

Fig. S23. Curve of adenosine desorption by COF-p-BA with different times.

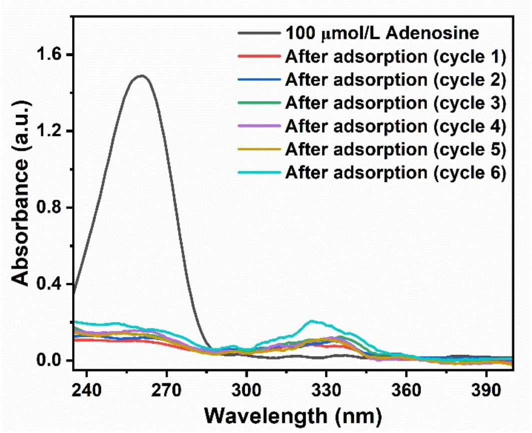

Fig. S24. Cyclic curve of adenosine adsorption by COF-p-BA.

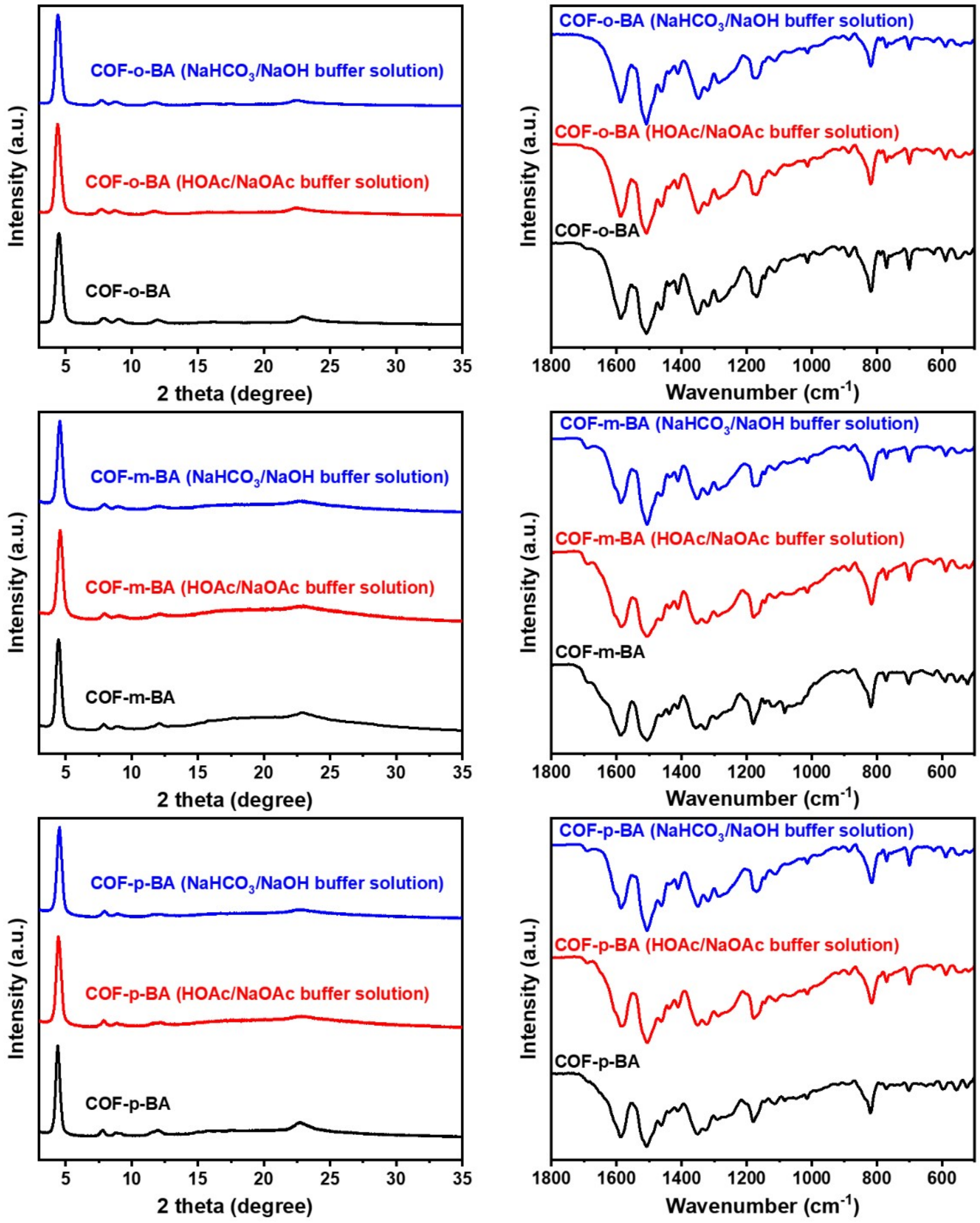

Fig. S25. PXRD patterns and FTIR spectra of COF-BA under the $NaHCO_3$/NaOH buffer solution (pH 10.0) and HOAc/NaOAc buffer solution (pH 3.6).

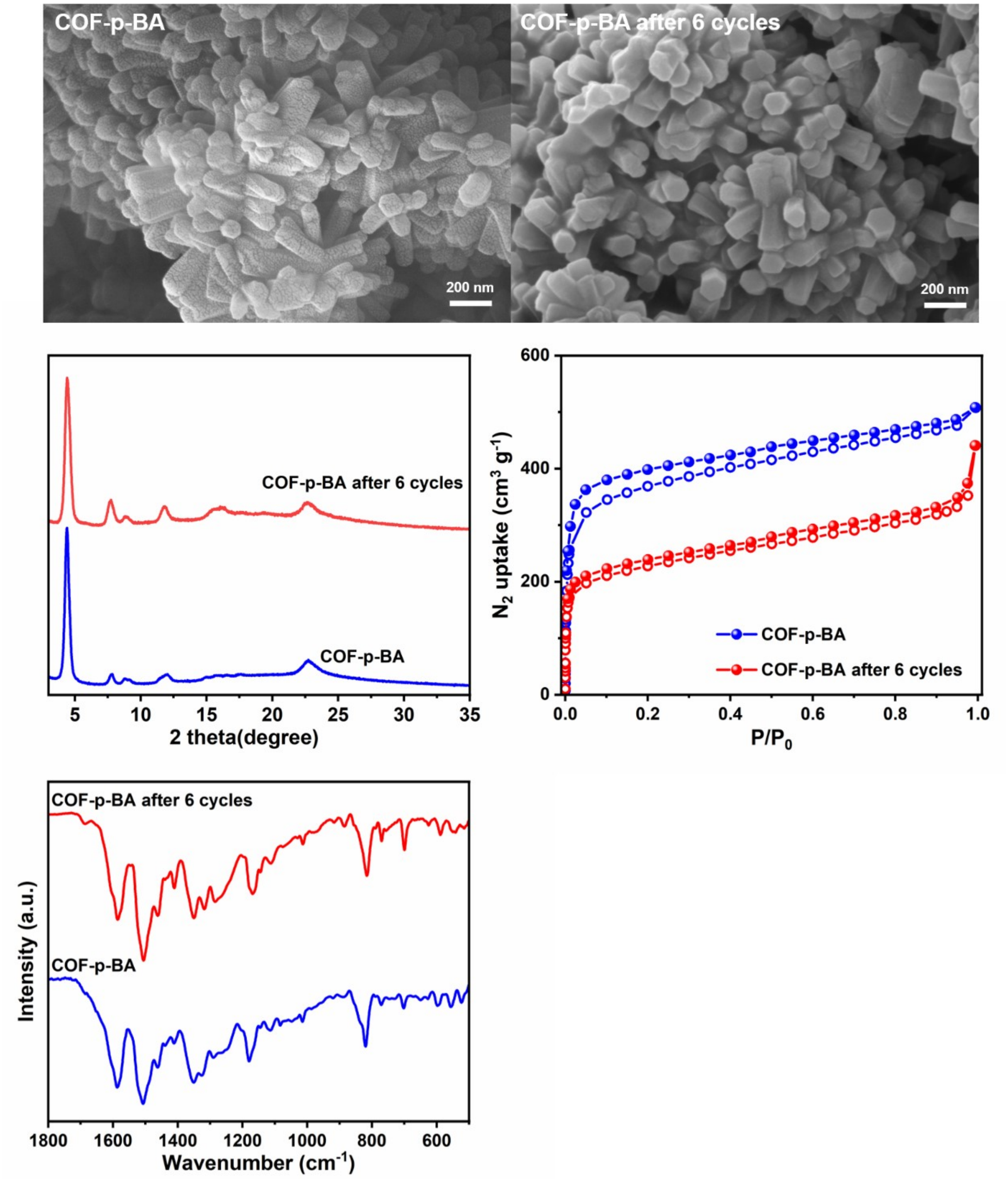

Fig. S26. Cyclic stability of COF-p-BA.

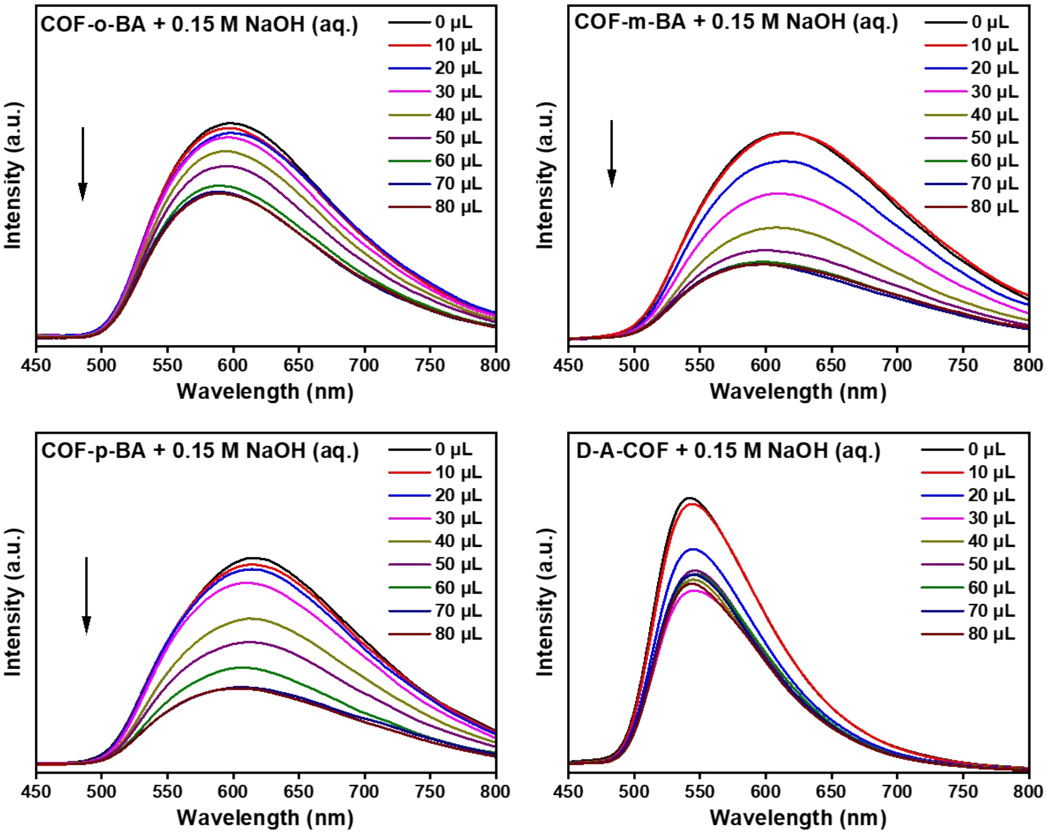

Fig. S27. The fluorescence emission spectra of COFs quenched by NaOH (aq.).

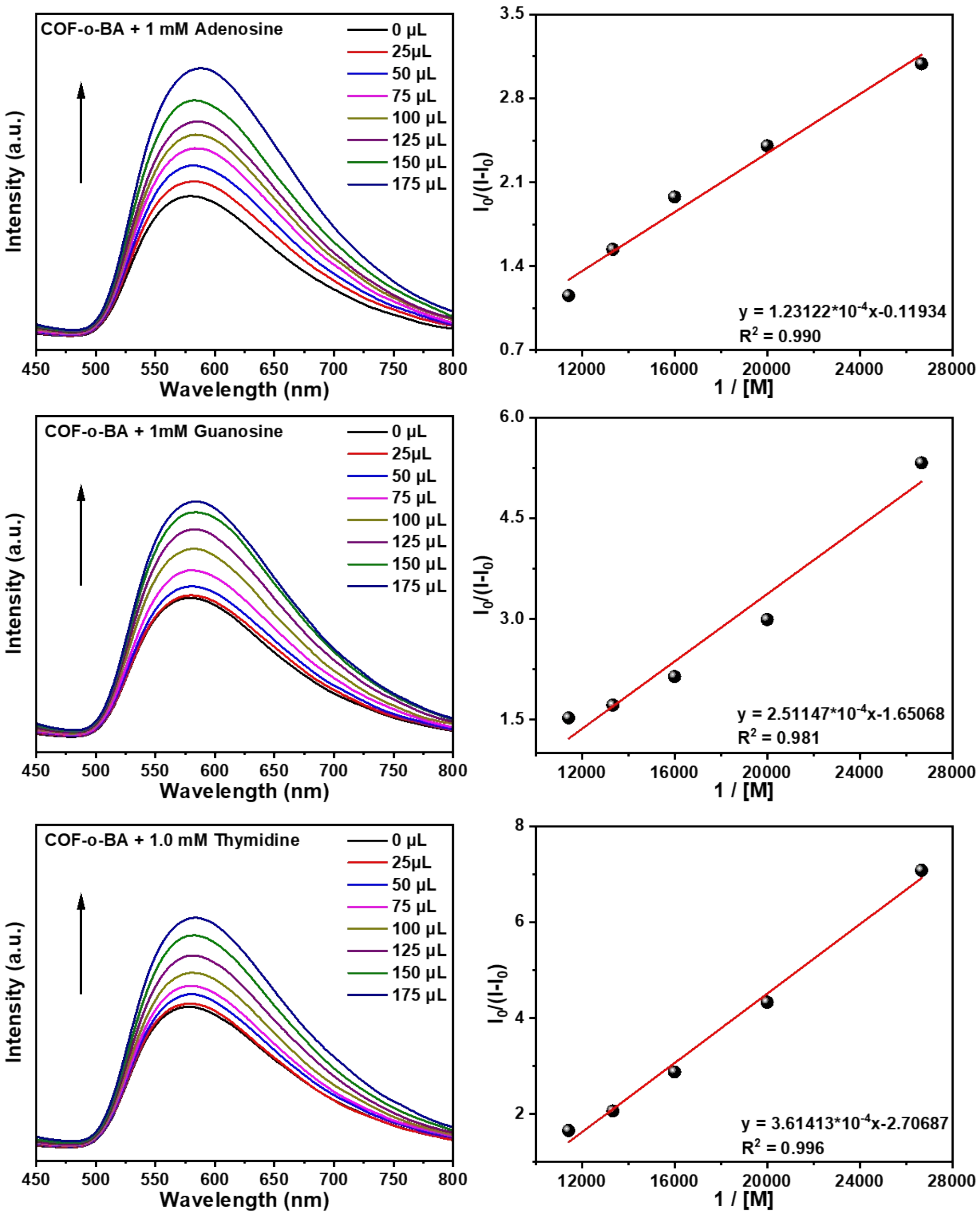

Fig. S28. The fluorescence emission spectra of COF-o-BA in the presence of varying concentrations of adenosine, guanosine, and thymidine in suspension.

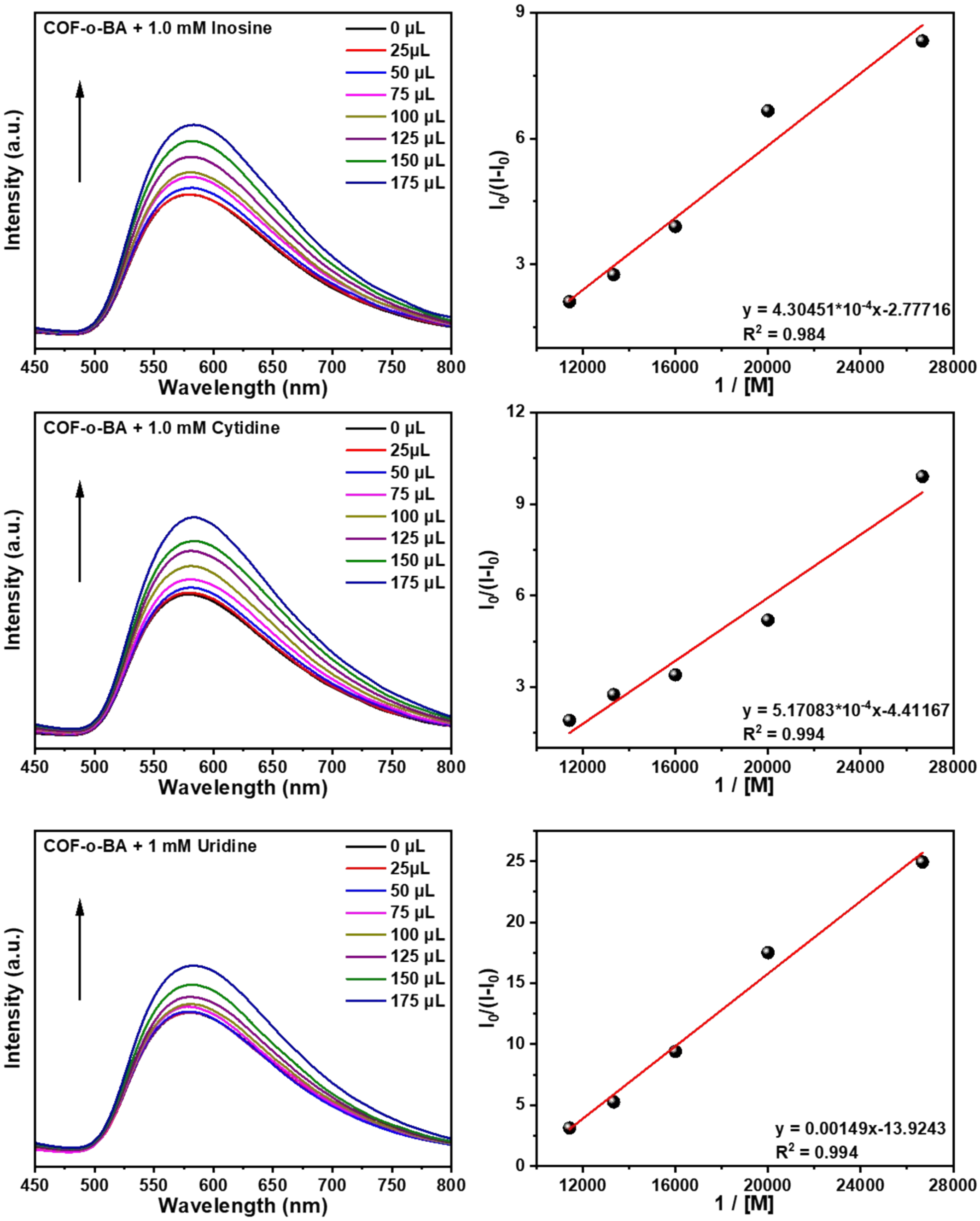

Fig. S29. The fluorescence emission spectra of COF-o-BA in the presence of varying concentrations of inosine, cytidine, and uridine in suspension.

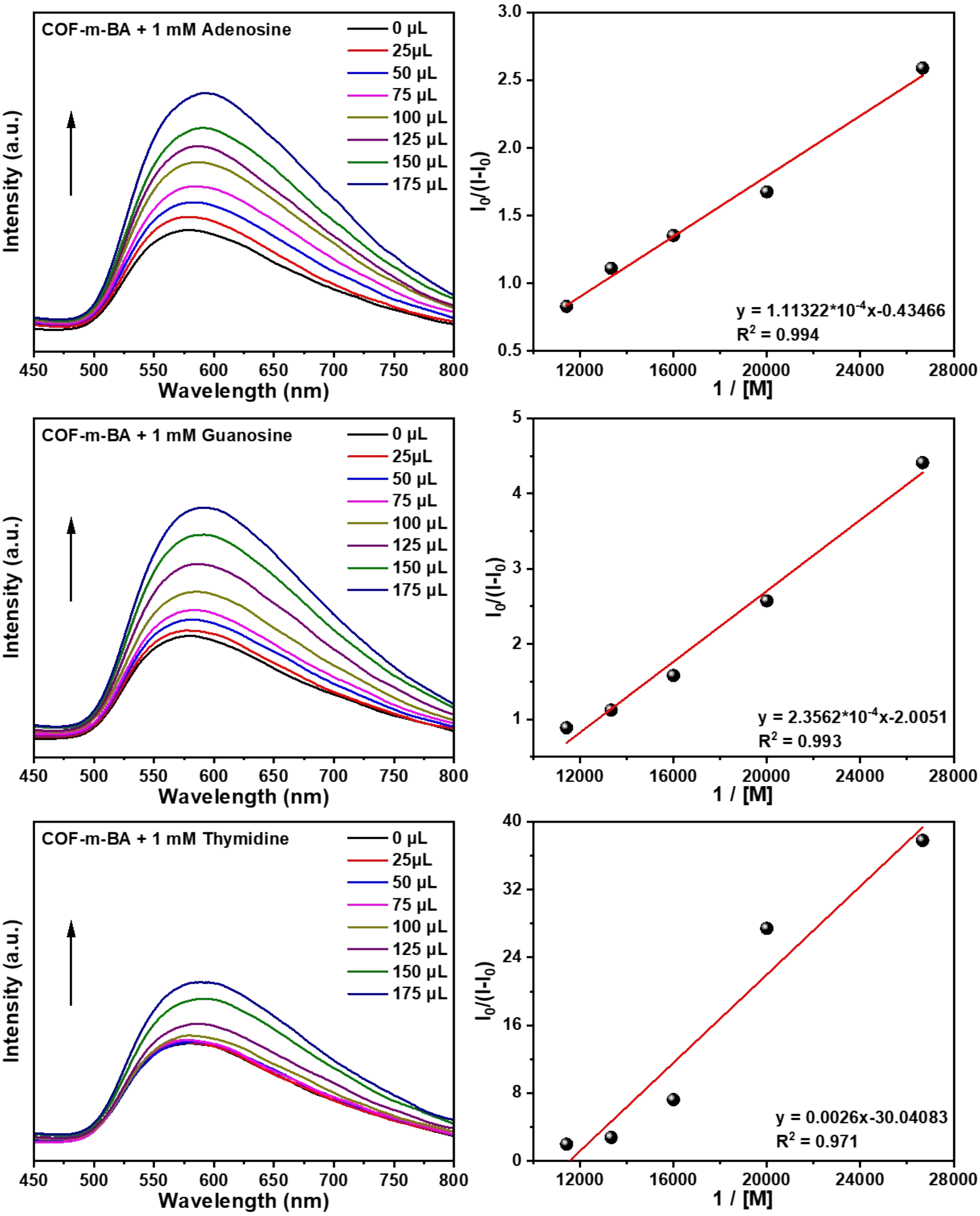

Fig. S30. The fluorescence emission spectra of COF-m-BA in the presence of varying concentrations of adenosine, guanosine, and thymidine in suspension.

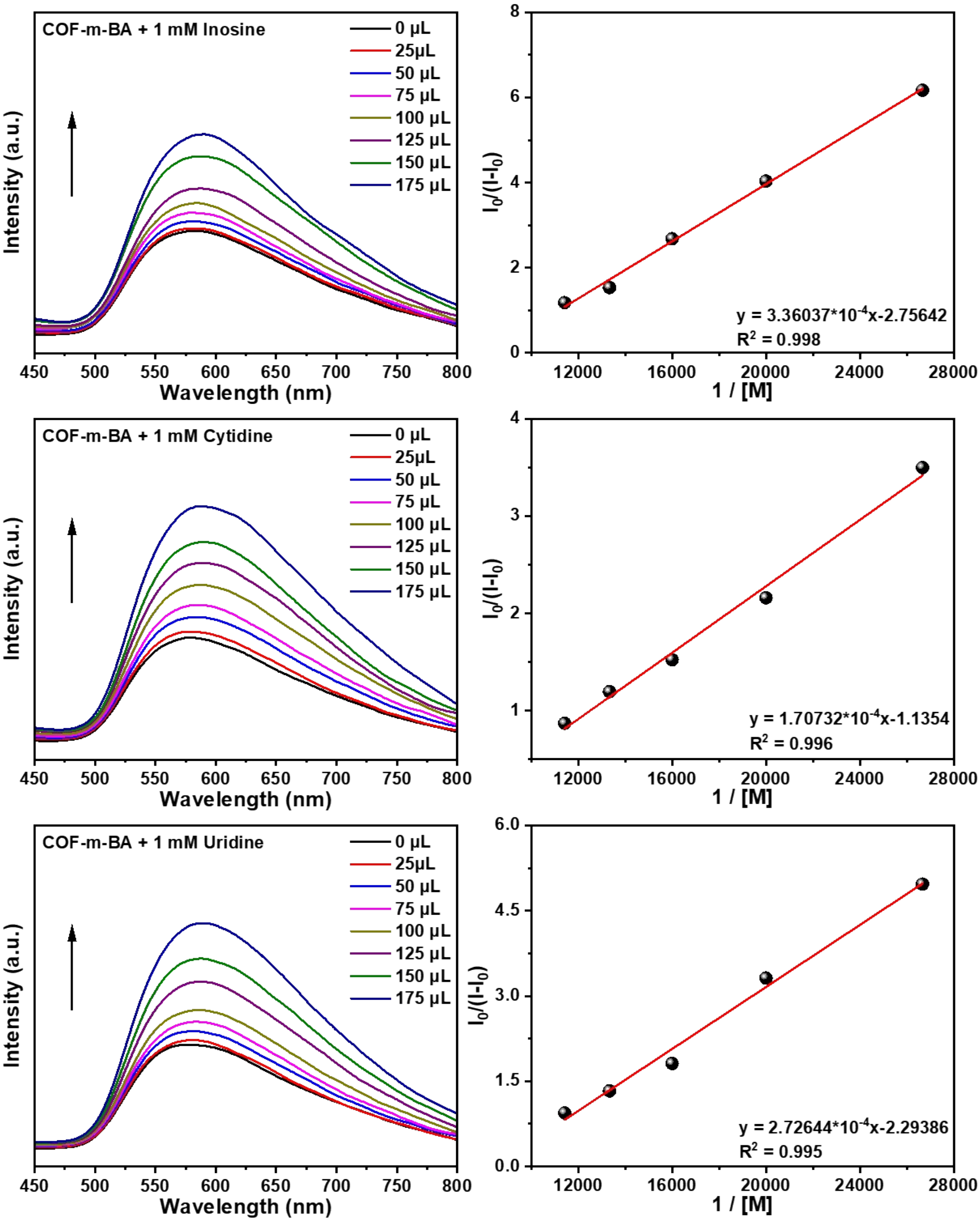

Fig. S31. The fluorescence emission spectra of COF-m-BA in the presence of varying concentrations of inosine, cytidine, and uridine in suspension.

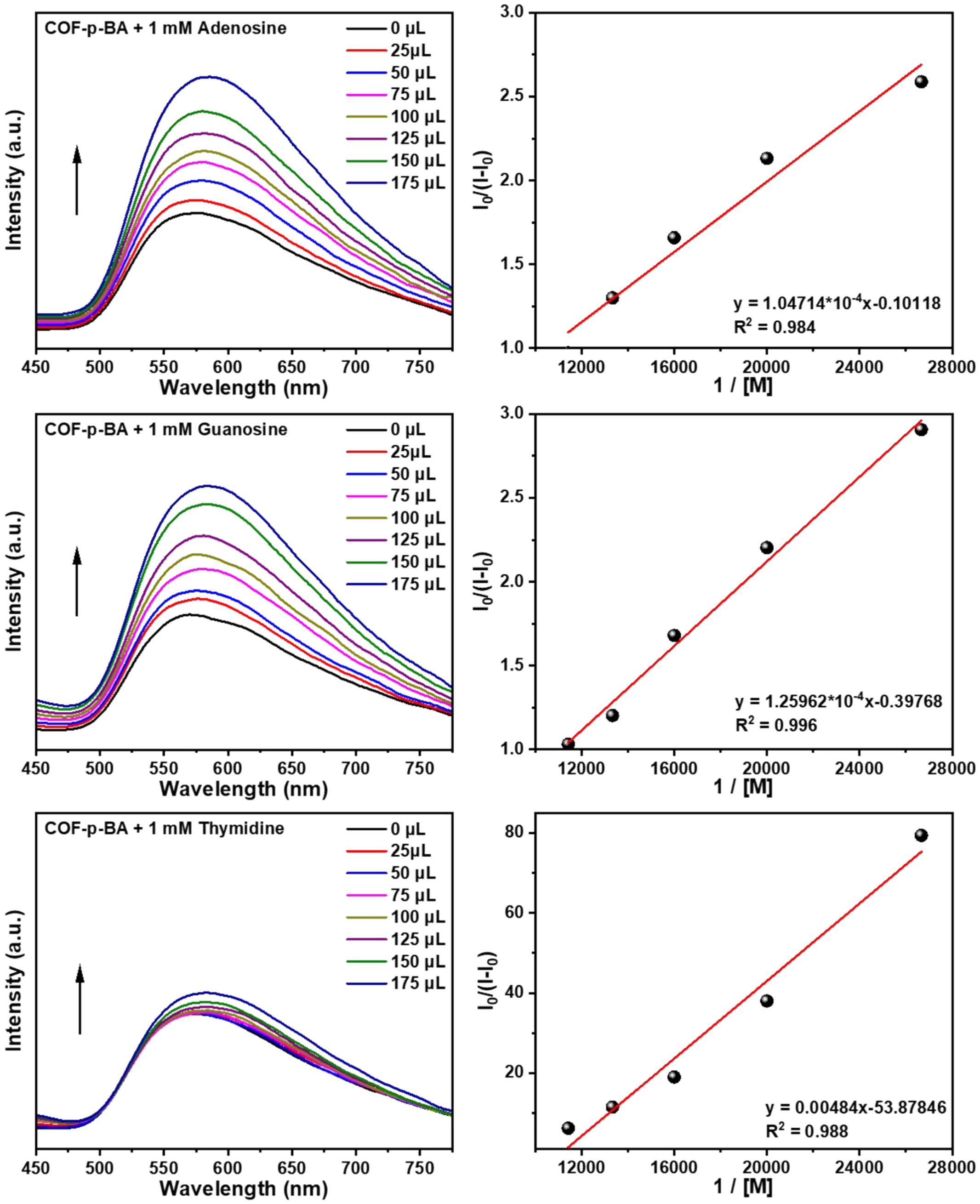

Fig. S32. The fluorescence emission spectra of COF-p-BA in the presence of varying concentrations of adenosine, guanosine, and thymidine in suspension.

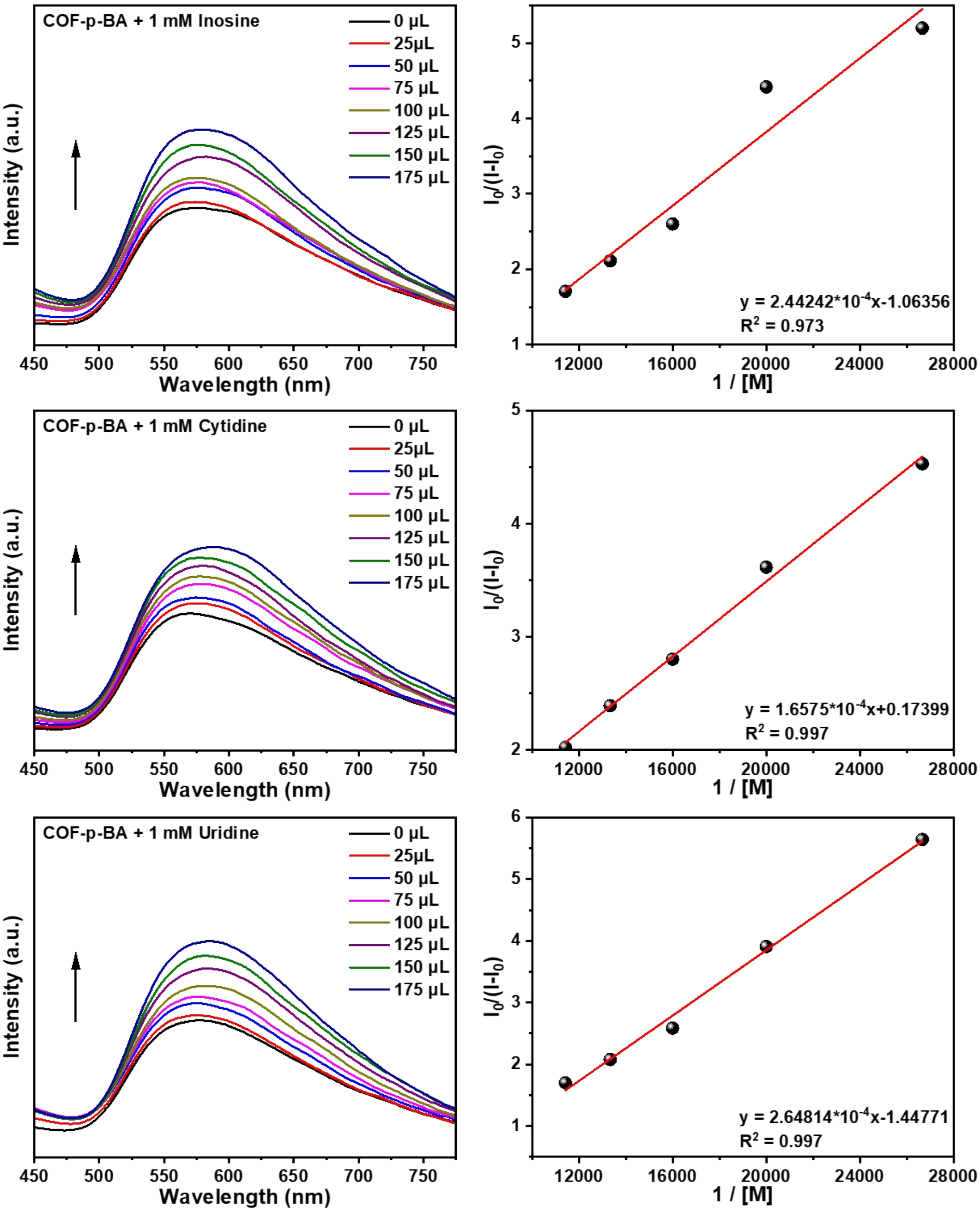

Fig. S33. The fluorescence emission spectra of COF-p-BA in the presence of varying concentrations of inosine, cytidine, and uridine in suspension.

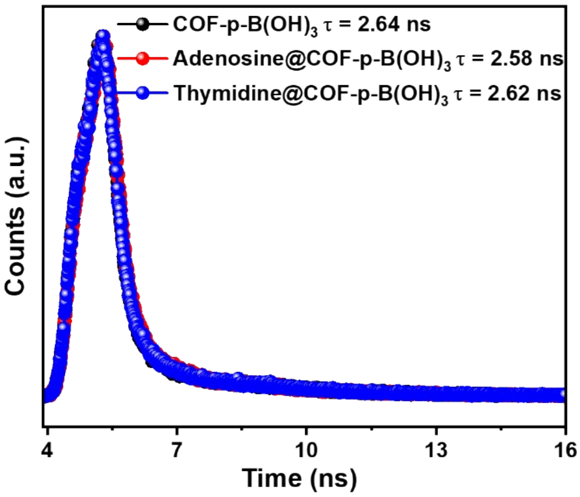

Fig. S34. The fluorescence decay curves of COF-p-B(OH)$_3$ and before and after the bonding with adenosine and thymidine.

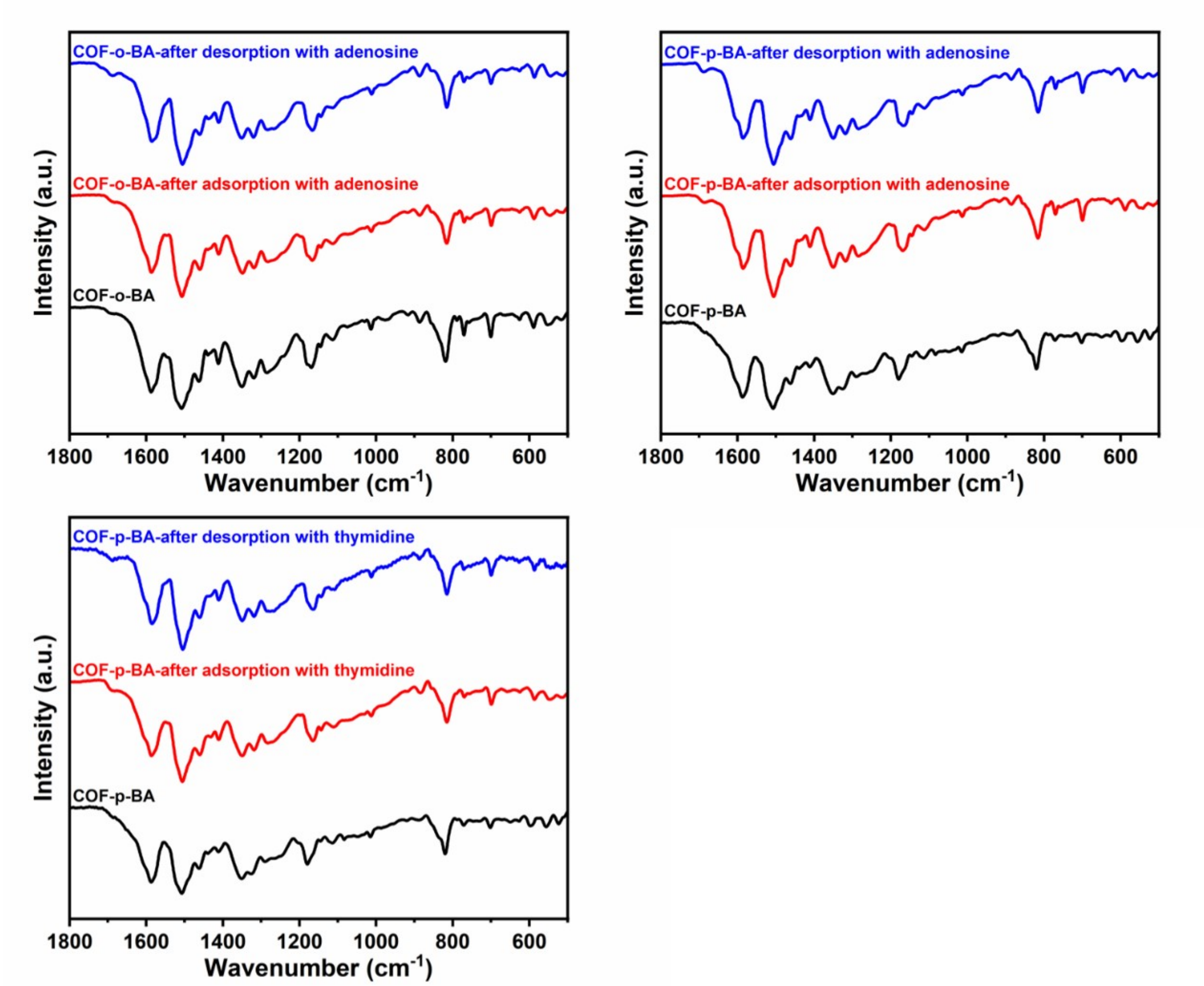

Fig. S35. FT-IR spectra of COF-BA after adsorption and desorption with nucleoside substances.

Table S1. Screened synthetic conditions for the synthesis of COF-BA.

Entry	Solvent (mL)	Reaction Time	Reaction Temperature	Crystallinity
1	Toluene	48 h	110 °C	Medium
2	Xylene	48 h	110 °C	High
3	Mesitylene	48 h	110 °C	Medium
4	1,2-Dichlorobenzene	48 h	110 °C	High
5	1,4-Dioxane	48 h	110 °C	High
6	DMF	48 h	110 °C	low
7	n-BuOH	48 h	110 °C	Medium
8	Xylene	24 h	110 °C	High
9	Xylene	48 h	90 °C	Medium
10	Xylene	48 h	130 °C	High

Table S2. FE-SEM/EDS analyses of COF-o-BA, COF-m-BA, and COF-p-BA.

Entry	**Element**	**Atomic Fraction (%)**	**Mass Fraction (%)**	**Error (%)**
COF-p-BA	B	8.096	7.171	2.950
	C	77.276	76.034	0.853
	N	14.554	16.699	4.233
	O	0.073	0.096	1.376
COF-m-BA	B	7.782	6.891	2.703
	C	77.864	76.603	0.802
	N	14.129	16.211	4.147
	O	0.225	0.295	1.359
COF-o-BA	B	7.672	6.776	2.674
	C	77.553	76.082	0.773
	N	13.307	15.224	3.923
	O	1.468	1.919	1.229

Table S3. Fractional atomic coordinates and unit cell parameters of D-A-COF.

D-A-COF			
$a = b = 22.60$ Å, $c = 3.95$ Å $\alpha = \beta = 90°$, $\gamma = 120°$			
Atom	x	y	z
N1	1.36155	-0.32945	0.42249
C2	1.43621	-0.29366	0.40095
C3	1.32576	-0.29058	0.40095
C4	1.32267	-0.40412	0.40095
C5	1.35435	-0.22409	0.53573
C6	1.32511	-0.18345	0.47374
C7	1.26536	-0.20883	0.28195
C8	1.23359	-0.2764	0.16676
C9	1.26357	-0.31628	0.22413
C10	1.47411	-0.32225	0.53573
C11	1.544	-0.29301	0.47374
C12	1.57836	-0.23327	0.28195
C13	1.54256	-0.20149	0.16676
C14	1.4727	-0.23148	0.22413
C15	1.25619	-0.44202	0.53573
C16	1.21554	-0.5119	0.47374
C17	1.24092	-0.54627	0.28195
C18	1.30849	-0.51047	0.16676
C19	1.34837	-0.44061	0.22413
C20	1.23909	-0.16342	0.18691
N21	1.18688	-0.18509	-0.01397
C22	1.15856	-0.14522	-0.14021
C23	1.19551	-0.61795	0.18691
C24	1.65005	-0.207	0.18691
N25	1.21719	-0.64848	-0.01397
C26	1.17732	-0.71668	-0.14021
N27	1.68058	-0.15479	-0.01397
C28	1.74877	-0.12646	-0.14021
C29	1.19648	-0.07351	-0.15491

C30	1.16592	-0.0368	-0.2688
C31	1.09706	-0.07103	-0.36955
C32	1.06065	-0.14281	-0.37327
C33	1.09148	-0.17945	-0.26122
C34	1.1056	-0.75046	-0.15491
C35	1.06889	-0.81774	-0.2688
C36	1.10312	-0.85237	-0.36955
C37	1.1749	-0.817	-0.37327
C38	1.21154	-0.74953	-0.26122
C39	1.78256	-0.16439	-0.15491
C40	1.84983	-0.13383	-0.2688
C41	1.88446	-0.06497	-0.36955
C42	1.8491	-0.02856	-0.37327
C43	1.78163	-0.05938	-0.26123
C44	1.06158	-0.03227	-0.43159
N45	0.99234	-0.06512	-0.43008
C46	1.06436	-0.92661	-0.43159
N47	1.09721	-0.963	-0.43008
C48	1.95871	-0.02948	-0.43159
N49	1.9951	0.03976	-0.43008