Supporting materials

Rational design of multivariate covalent organic frameworks with enhanced light-harvesting for selective detection and photocatalytic reduction of Cr(VI)

Zhenyu Lu,[a] Xue Liu,[ab] Xiaohui Zhu,*[b] Li Yang,[a] Hao Lu,[b] Binbin Zhang,[a] Xing Kang,*[c] Mingrong Yue,[b] and Yunjiang Yu*[bd]

[a] School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453000, China

[b] Key Laboratory of Environmental Pollution Health Risk Assessment, South China Institute of Environmental Sciences, Ministry of Ecology and Environment, Guangzhou, 510655, China

[c] Zhangjiang Laboratory, Shanghai, 201204, China；orcid.org/0000-0001-5320-2376

[d] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China

*Corresponding Authors

E-mail: zhuxiaohui@scies.org; yuyunjiang@scies.org; kangxing@zjlab.ac.cn

Table of Content

Experimental Section

Materials and Chemicals

1, 3, 6, 8 - tetra - (p-aminophenyl) – pyrene (TPAPy), 3, 3'- dihydroxy- [1, 1'-biphenyl] - 4, 4' -dicarbaldehyde (DHBD), benzo [c] [1, 2, 5] thiadiazole - 4, 7-dicarbaldehyde (BTD), 1,2-Dichlorobenzene (*o*-DCB), *n*-Butanol were purchased from Shanghai Macklin Biochemical Co., Ltd.; Potassium dichromate was Shanghai Aladdin Biochemical Technology Co., Ltd.. All chemicals and solvents were analytical-grade reagents obtained from commercial sources and used without further purification.

Characterization.

The crystal structure of the COFs was determined by powder X-ray diffraction (PXRD) using a Bruker D8 Advance diffractometer (Germany) with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 40 mA. Data were collected over a 2θ range of 2° to 40° with a step size of 0.02°. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu IRTracer-100 spectrometer (Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific ESCALab 250Xi spectrometer (USA) equipped with a monochromated Al Kα X-ray source. Nitrogen (N_2) adsorption-desorption isotherms at 77 K were measured on a Beishide 3H-2000PS2 analyzer (China). The specific surface area was calculated from the adsorption data using the Brunauer-Emmett-Teller (BET) model. Thermogravimetric analysis (TGA) was conducted on a Netzsch STA 449 F5 instrument (Germany). Prior to analysis, samples were dried at 80 °C in air for 12 hours. TGA measurements were performed under a N_2 atmosphere from 25 °C to 800 °C at a heating rate of 10 °C/min.

The morphology of the COFs was examined by field-emission scanning electron microscopy (FE-SEM) using a Hitachi S-4800 microscope (Japan) and transmission electron microscopy (TEM) using an FEI Talos F200X microscope (USA). Zeta potential measurements were carried out on a Malvern Zetasizer Nano ZS90 instrument (UK). Steady-state fluorescence spectra were recorded on an Agilent Cary Eclipse spectrofluorometer (Shanghai), while time-resolved photoluminescence (PL) spectra were obtained using an Edinburgh Instruments FS5 spectrofluorometer (UK). UV-Vis absorption spectra were measured on a Persee U-1901 spectrophotometer (Beijing).

Fluorescence detection of Cr(VI).

BTD-OH-COF was dispersed in DMF solution to prepare a suspension with a concentration of 0.01 mg/mL. 2.85 mL of the suspension was taken and mixed with 150 μL of Cr(VI) solutions at varying concentrations to yield final Cr(VI) concentrations of 0.2, 1.0, 5.0, 10.0, 20.0, 30.0, 40.0, 50.0, 75.0, 100.0, 150.0, 200.0, and 300.0 μmol/L in the mixture. After incubation at room temperature for 3 s, the fluorescence emission spectra were immediately recorded. All fluorescence sensing experiments were performed with excitation at λex = 415 nm, and the corresponding emission spectra were scanned and recorded over the wavelength range λem = 400-700 nm.

Photocatalytic measurements.

Photocatalytic performance was evaluated in a reaction system equipped with a 300 W xenon lamp and cutoff filter (λ > 420 nm). Exactly 5 mg of COF photocatalyst was ultrasonically dispersed in 50 mL of Cr(VI) aqueous solution (15 mg/L, pH 3).

After stirring in the dark for 1 h to achieve adsorption equilibrium, the light irradiation experiment was initiated. During illumination, 1 mL dispersion solution were periodically collected and filtered through 0.22 μm membranes. The Cr(VI) concentration in the supernatant was quantified colorimetrically at 540 nm using UV-Vis spectrophotometry with reference to a standard calibration curve. Photocatalytic reduction efficiency was calculated as Eq 1:

$$\text{Reduction efficiency (\%)} = [(C_0 - C_t)/C_0] \times 100\% \quad (1)$$

where C_0 (mg/L) and C_t (mg/L) represent initial and instantaneous concentrations at reaction time t (min), respectively.

Computational methods.

DFT calculations were performed using the Gaussian 09 software package at the B3LYP/6-311G (d, p) level of theory to characterize the optimized geometry and electronic properties of all COFs. Molecular electrostatic potential (MEP) maps and molecular orbital distributions were subsequently analyzed and visualized using the Multiwfn software.

The geometry of COFs and COF-$Cr_2O_7^{2-}$ complex was fully optimized at the b3lyp/def2tzvpp level. Calculations of vibrational frequencies at the identical theoretical level found no imaginary frequencies for these optimized structures. Based on the optimized geometries, the interaction energy was calculated at the b3lyp/def2tzvpp level. Then, the binding energy (Ebinding) for $Cr_2O_7^{2-}$ to COF can be calculated as Eq.2:

$$E_{binding}E_{complex} - E_{COF} - E_{Cr(VI)}$$

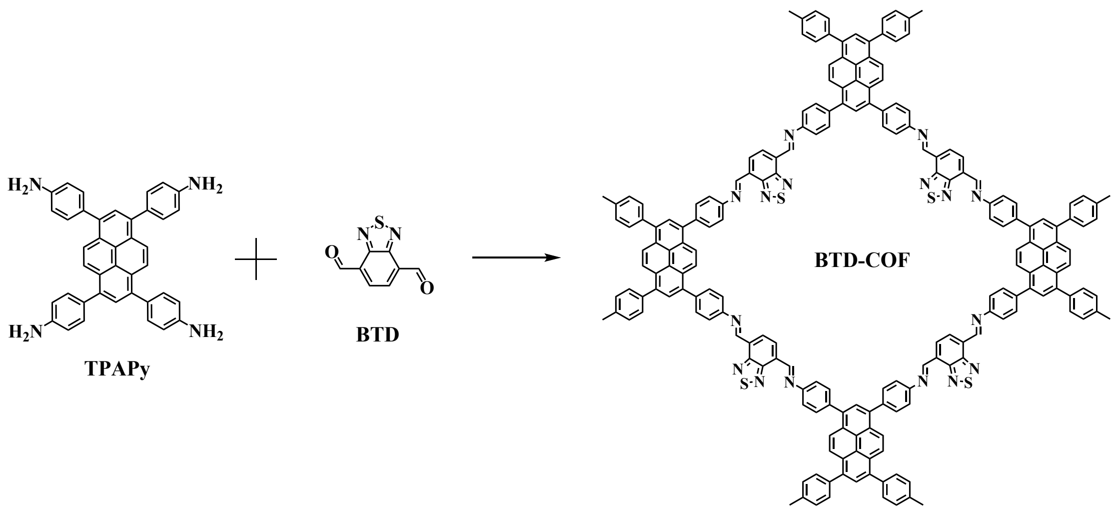
where Ecomplex, ECOF, and ECr(VI) are the total energies of the optimized COF-$Cr_2O_7^{2-}$ system, the COFs, and the $Cr_2O_7^{2-}$, respectively.

Preparation of actual sample

To evaluate the practical application value of the sensor, three categories of real water samples comprising lake water, tap water, and Wei River water were used to assess its detection performance. The lake water was collected from the campus pond of Henan Institute of Science and Technology, tap water was obtained from the municipal water supply system, and Wei River water was sampled from local sections of the river. All water samples were centrifuged and filtered through 0.22 μm membranes to remove particulate matter without further purification. Spike recovery experiments were performed by adding Cr(VI) standard solutions at concentrations of 0.50, 1.00, and 5.00 μmol/L. Following sample preparation, all specimens were analyzed according to the procedures described in Sections 2.3 of this work.

Synthesis of COFs

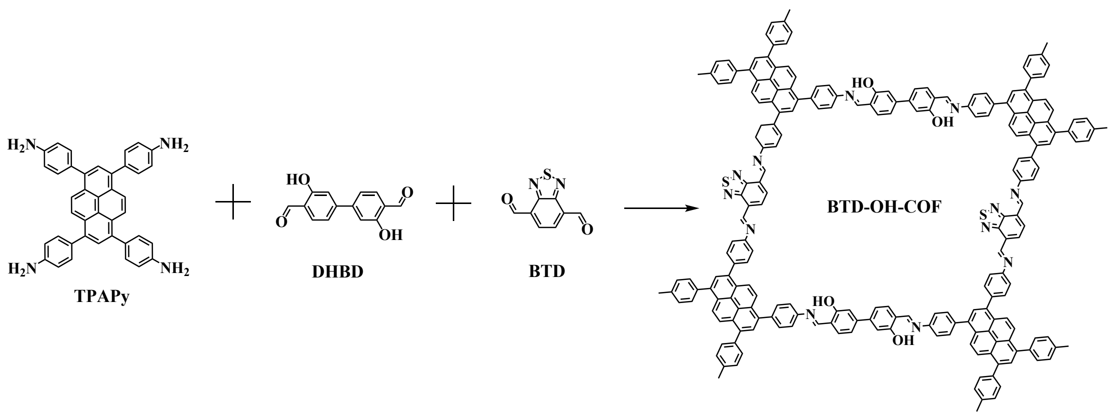
Synthesis of BTD-COF:



Scheme S1. The synthetic routes of BTD-COF

In a 10 mL glass tube, TPAPy (0.025 mmol,14.2mg), BTD (0.05mmol, 9.6 mg) were dispersed in a mixed solvent solution (2.2 mL) consisting of *o*-DCB/*n*-BuOH/ AcOH (6 M) with a volume ratio of 5/5/1. After 15 min of sonication, the mixture was subjected to three freeze-pump-thaw cycles to remove dissolved gases, flame-sealed under an inert atmosphere, and heated at 120°C for 3 days. After cooling to room temperature, the resulting solid (BTD-COF) was washed sequentially with tetrahydrofuran (THF) and acetone several times, collected by vacuum filtration, and dried overnight at 40°C under vacuum.

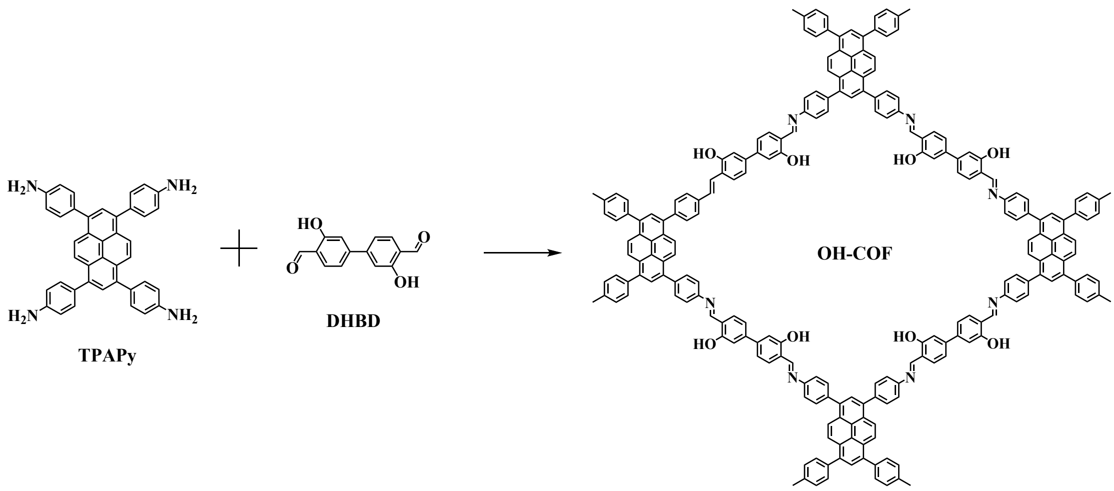
Synthesis of BTD-OH-COF:



Scheme S2. The synthetic routes of BTD-OH-COF

In a 10 mL glass tube, 1, 3, 6, 8 - tetra - (p-aminophenyl) – pyrene (0.025 mmol, 14.2 mg), 3,3'- dihydroxy- [1, 1'-biphenyl] - 4, 4' -dicarbaldehyde (0.025 mmol, 6 mg), benzo[c][1,2,5]thiadiazole - 4, 7 - dicarbaldehyde (0.025 mmol, 4.8 mg) were dispersed in a mixed solvent solution (2.2 mL) consisting of o-DCB/n-BuOH/ AcOH (6 M) with a volume ratio of 5/5/1. After 15 min of sonication, the mixture was subjected to three freeze-pump-thaw cycles to remove dissolved gases, flame-sealed under an inert atmosphere, and heated at 120°C for 3 days. After cooling to room temperature, the resulting solid (BTD-OH-COF) was washed sequentially with tetrahydrofuran (THF) and acetone several times, collected by vacuum filtration, and dried overnight at 40°C under vacuum.

Synthesis of OH-COF:



Scheme S3. The synthetic routes of OH-COF

In a 10 mL glass tube, TPAPy (0.025 mmol, 14.2 mg), DHBD (0.05 mmol, 12 mg) were dispersed in a mixed solvent solution (2.2 mL) consisting of *o*-DCB/*n*-BuOH/ AcOH (6 M) with a volume ratio of 5/5/1. After 15 min of sonication, the mixture was subjected to three freeze-pump-thaw cycles to remove dissolved gases, flame-sealed under an inert atmosphere, and heated at 120°C for 3 days. After cooling to room temperature, the resulting solid (OH-COF) was washed sequentially with tetrahydrofuran (THF) and acetone several times, collected by vacuum filtration, and dried overnight at 40°C under vacuum.

Figures

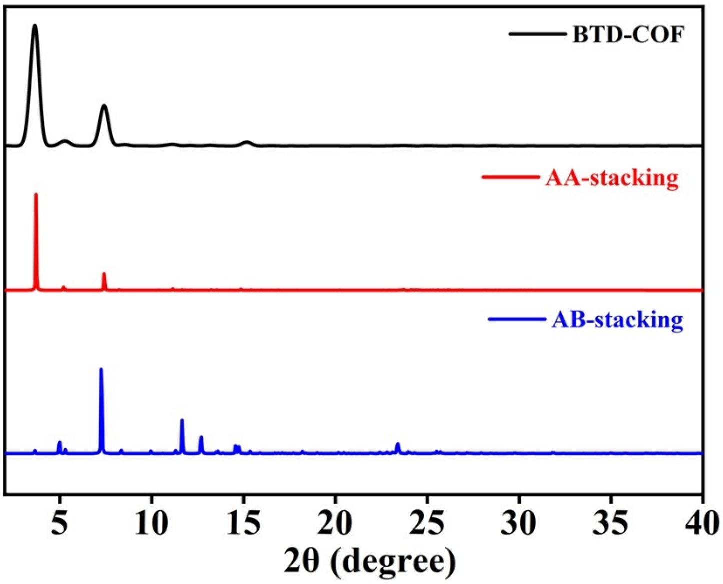


Fig. S1. The simulated PXRD patterns of BTD -COF with AA and AB stacking models

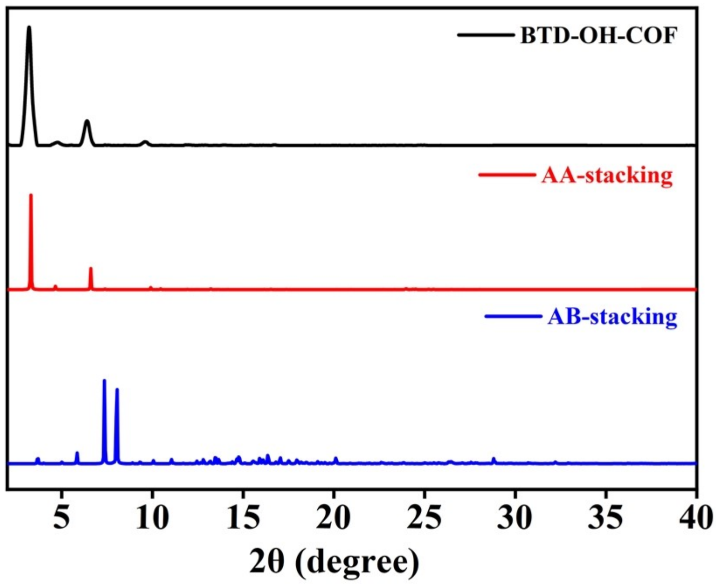


Fig. S2. The simulated PXRD patterns of BTD-OH-COF with AA and AB stacking models

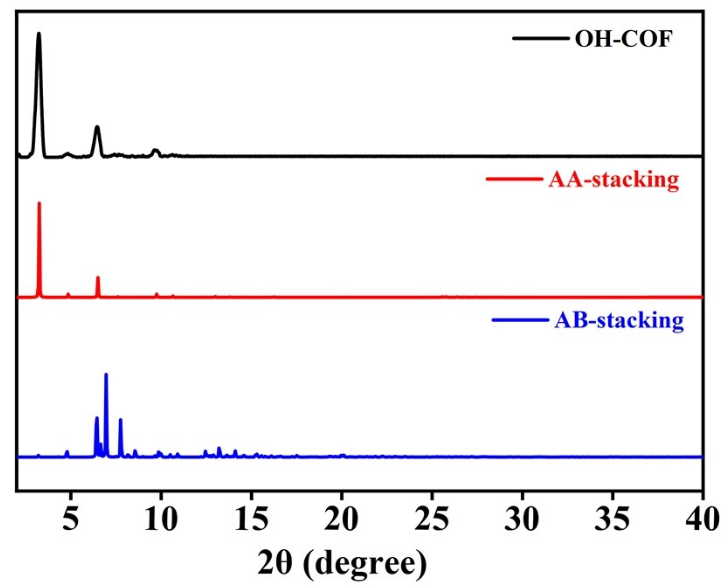


Fig. S3. The simulated PXRD patterns of OH-COF with AA and AB stacking models

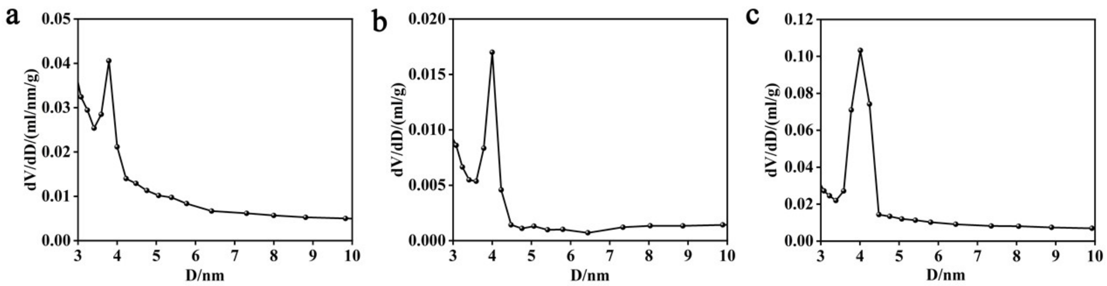


Fig. S4. Pore size distribution profiles of BTD-COF(a), BTD-OH-COF(b), and OH-COF(c)

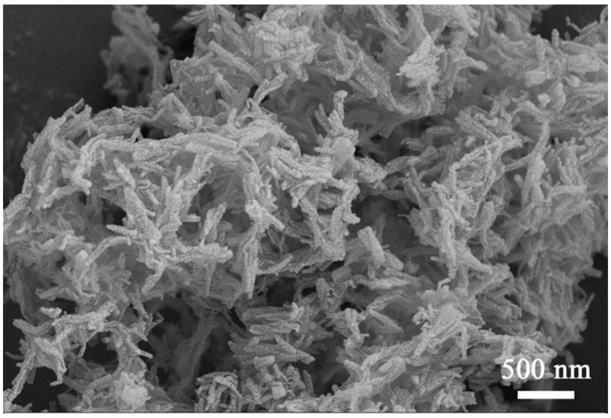


Fig. S5. SEM image of BTD-COF

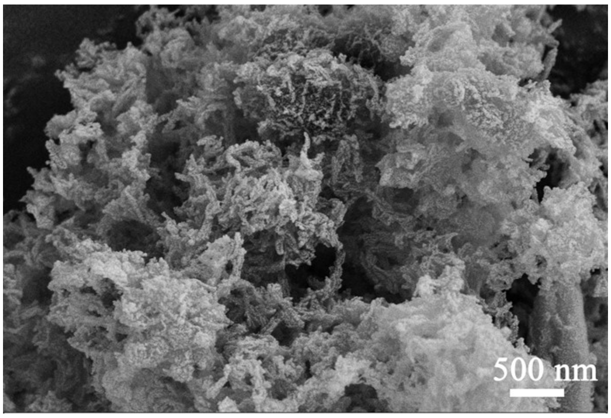


Fig. S6. SEM image of BTD-OH-COF

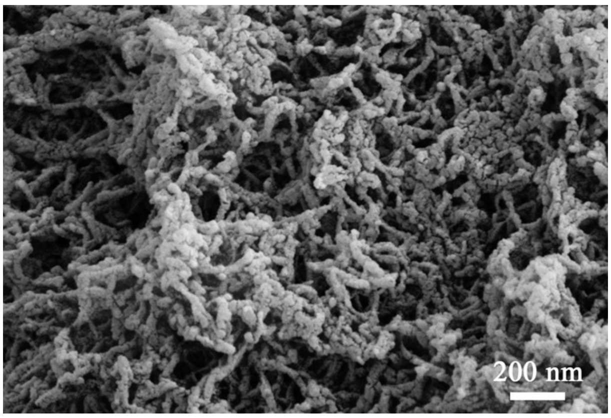


Fig. S7. SEM image of OH-COF

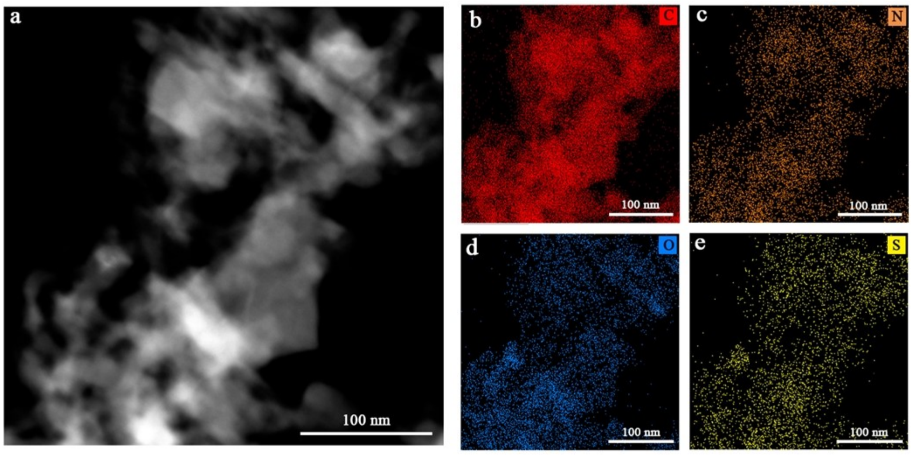


Fig. S8. EDS mapping images of BTD-OH-COF

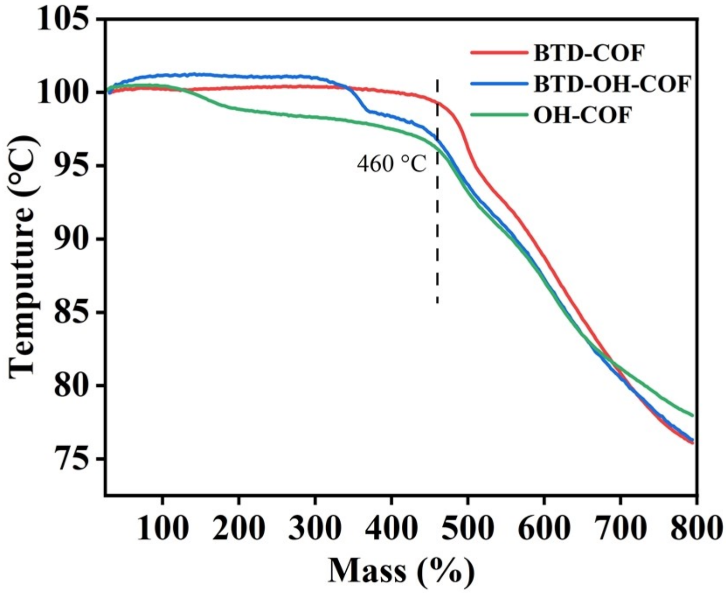


Fig. S9. TGA curves of BTD-COF, BTD-OH-COF and OH-COF

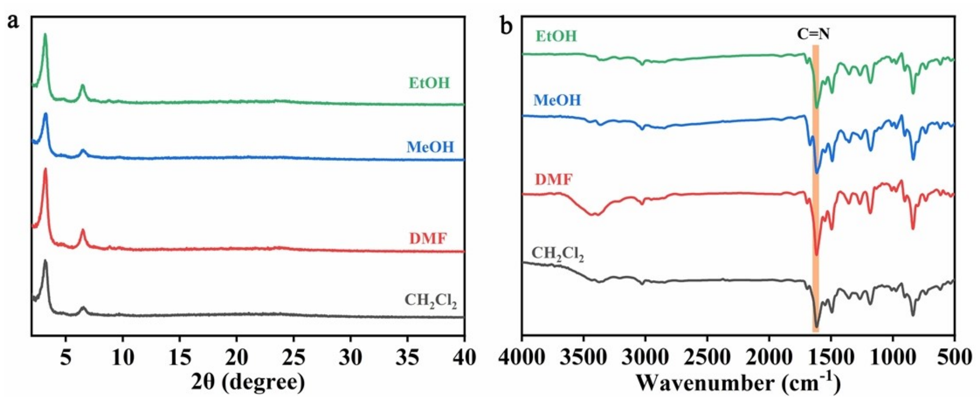


Fig. S10. Chemical stability of BTD-OH-COF after treatment with various organic solutions for 24 h

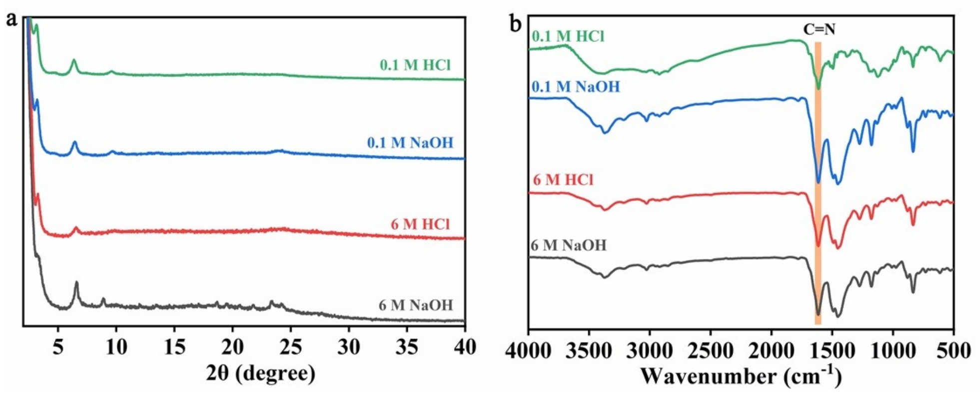


Fig. S11. Chemical stability of BTD-OH-COF after treatment with 0.1 M HCl or 6 M NaOH for 6 h

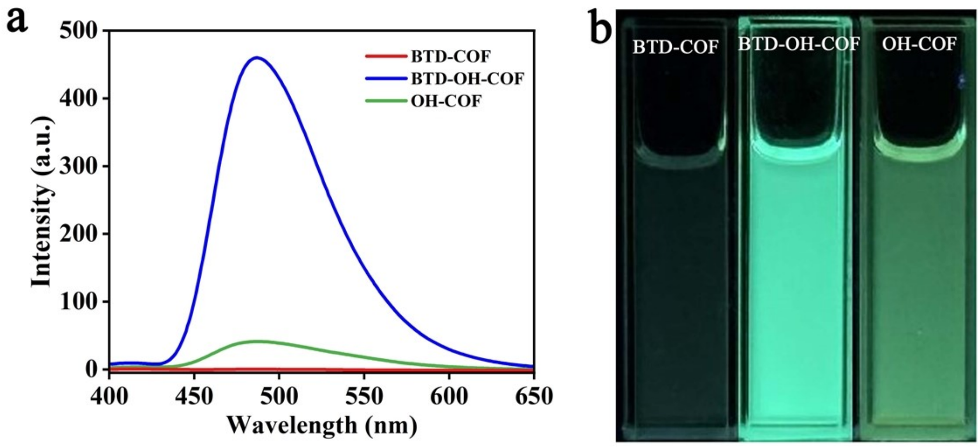


Fig. S12. The emission spectra(a) and the photographs (b) of BTD-COF, BTD-OH-COF and OH-COF in DMF solutions (λex= 415 nm).

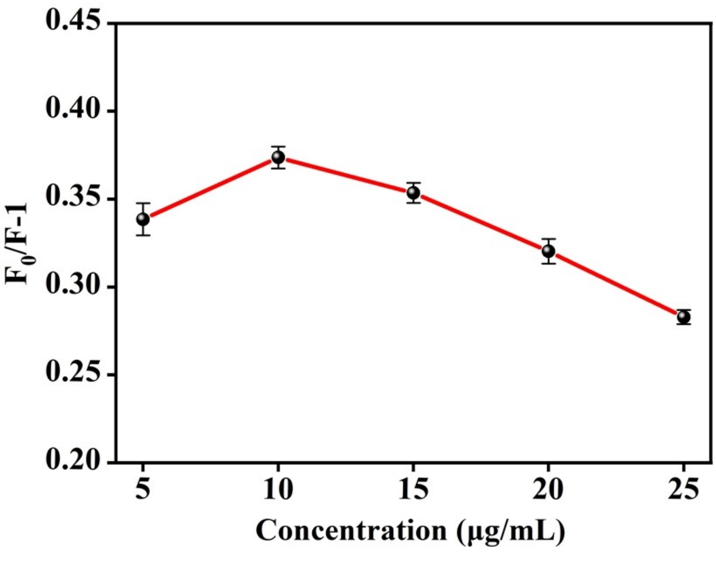


Fig. S13. Fluorescence response of BTD-OH-COF to Cr(VI) under different material concentrations (λex= 415 nm; $C_{Cr(VI)}$ = 50 μmol/L).

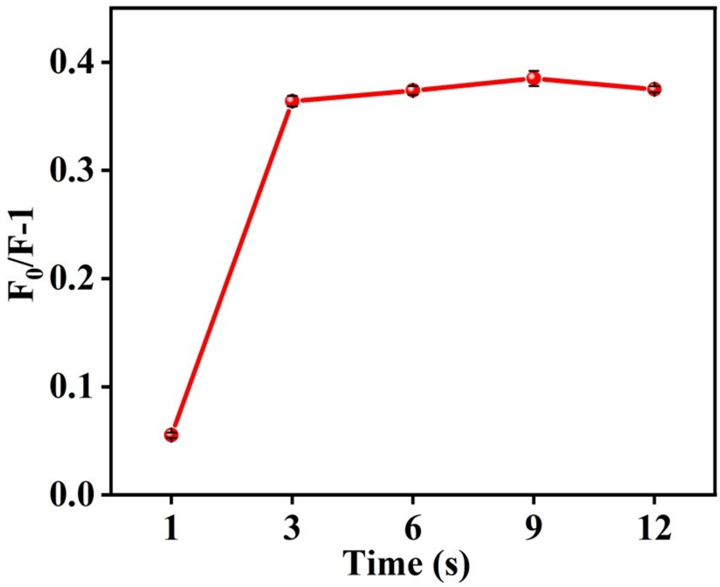


Fig. S14. Fluorescence response of BTD-OH-COF to Cr(VI) under different incubating time (λex= 415 nm; $C_{\mathrm{Cr(VI)}}$ = 50 μmol/L).

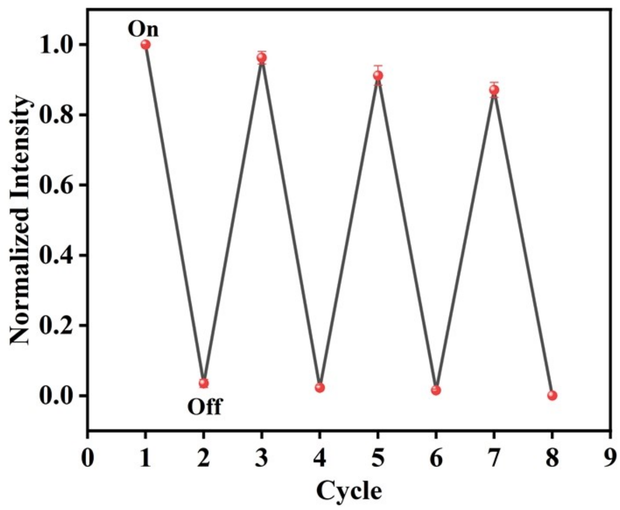


Fig. S15. Performance test of Cr(VI) using the BTD-OH-COF cycle for four times.

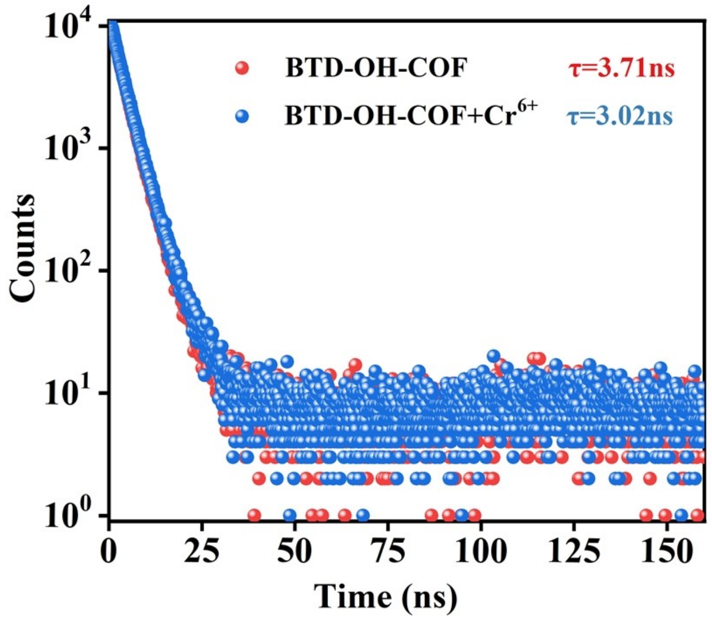


Fig. S16. Time resolved fluorescence decay curves of BTD-OH-COF in the absence and presence of Cr(VI) in DMF solution

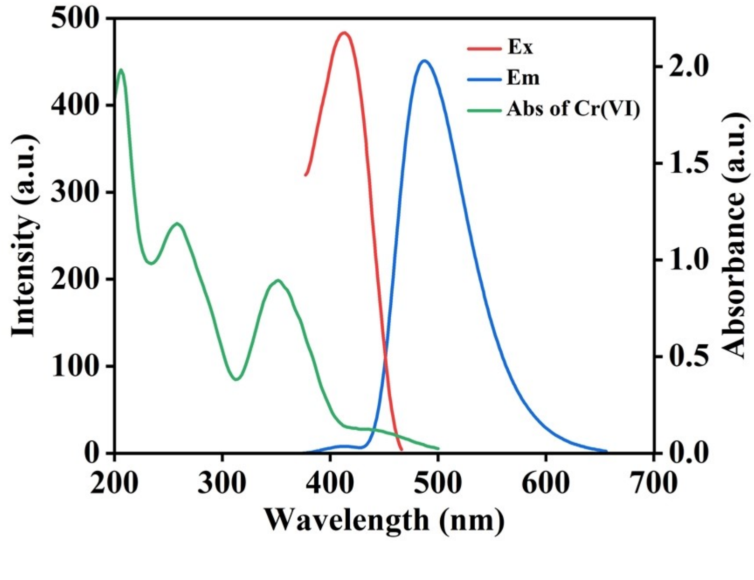


Fig. S17. Fluorescence excitation and emission spectra of BTD-OH-COF and UV-vis absorption spectrum of Cr(VI)

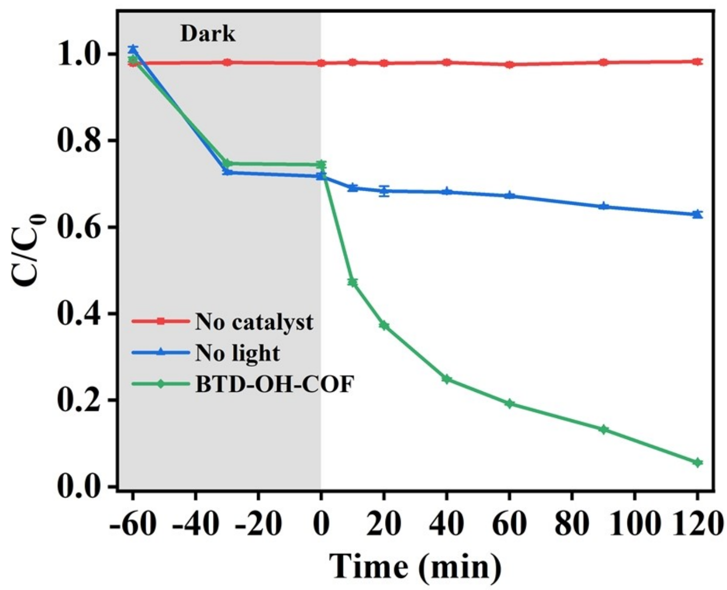


Fig. S18. Photocatalytic reduction of Cr(VI) at different conditions

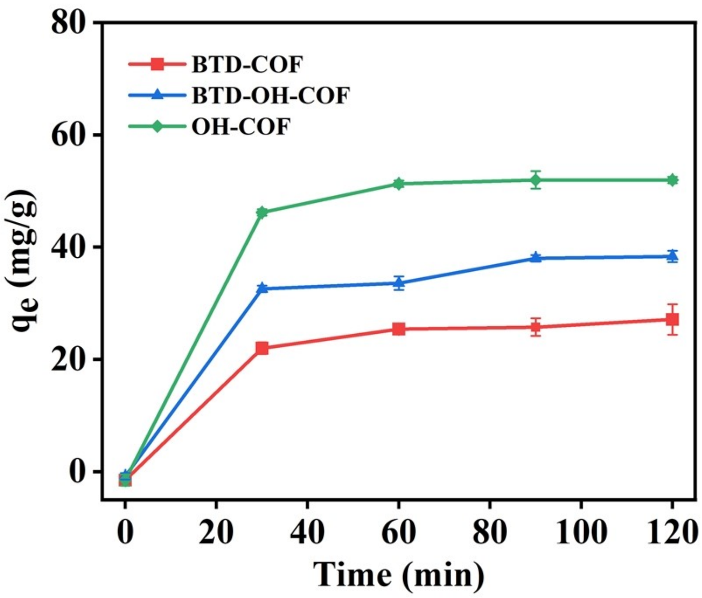


Fig. S19. Adsorption kinetics on BTD-COF, BTD-OH-COF and OH-COF for Cr(VI) in darkness (pH = 3, $C_{Cr(VI)}$ = 15 mg/L, t = 120 min, dosage = 5 mg).

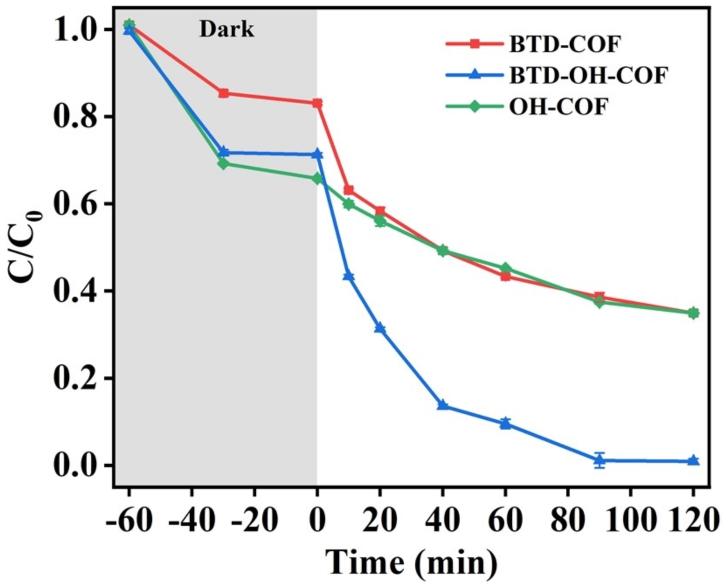


Fig. S20. Photocatalytic reduction of Cr(VI) using different catalysts (pH = 3, $C_{Cr(VI)}$ = 15 mg/L, t = 120 min, dosage = 5 mg).

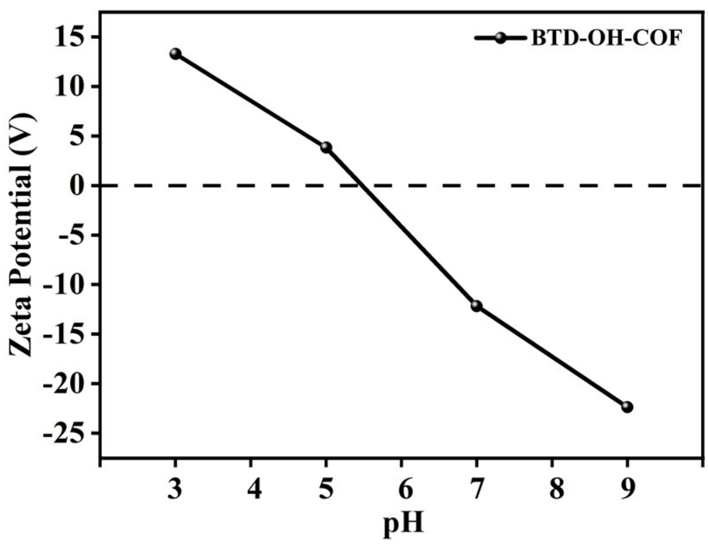


Fig. S21. Zeta potential of BTD-OH-COF under different pH

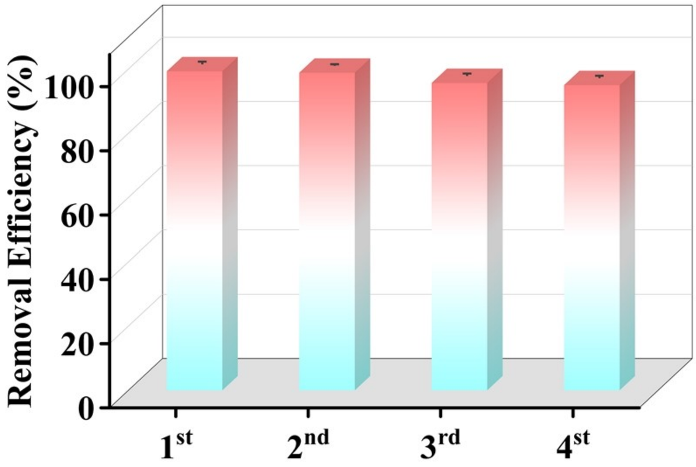


Fig. S22. Recyclable ability of BTD-OH-COF to Cr(VI) reduction

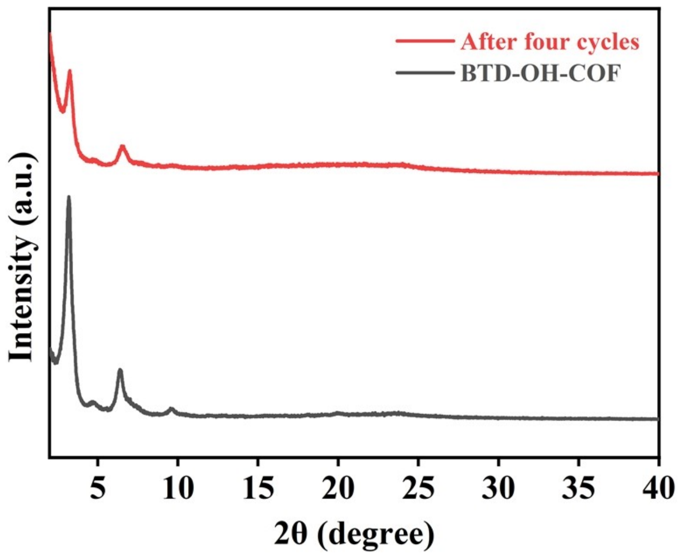


Fig. S23. The PXRD pattern of BTD-OH-COF that undergoes four cycles

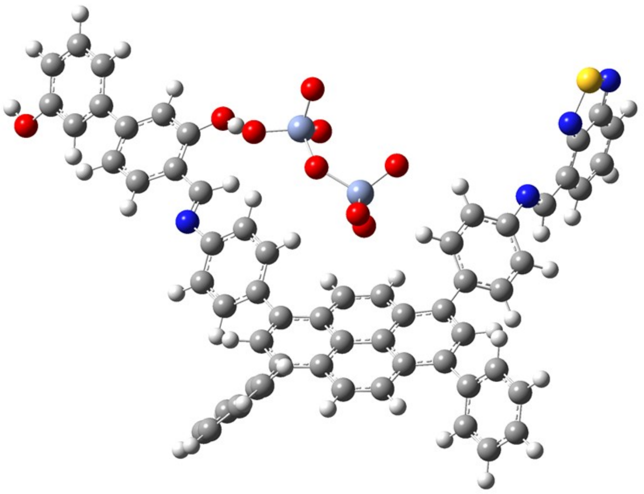


Fig. S24 Optimized structures of BTD-OH-COF and $Cr_2O_7^{2-}$

Tables

Table S1. Fractional atomic coordinates for the unit cell of BTD-COF.

BTD-COF: Space group: P1			
a = 36.4257 Å, b = 33.3084 Å, c = 7.8057 Å			
α = 90.4052º, β = 110.7749º, γ = 89.9766º			
C1	0.07488	0.46348	0.72417
C2	0.01708	0.42731	0.74787
C3	0.97952	0.42725	0.75686
C4	0.95961	0.46309	0.76296
C5	0.9209	0.46329	0.76958
C6	0.09914	0.42722	0.72627
C7	0.89673	0.42691	0.7642
C8	0.13605	0.42756	0.83007
C9	0.16013	0.39496	0.82916
C10	0.14782	0.361	0.72353
C11	0.11119	0.3606	0.62014
C12	0.08737	0.39353	0.61901
C13	0.90799	0.39407	0.87503
C14	0.88435	0.36101	0.87193
C15	0.84815	0.36065	0.76438
C16	0.83622	0.39372	0.65498
C17	0.86035	0.42636	0.65482
N18	0.82475	0.32637	0.77312
N19	0.17133	0.32664	0.71512
C20	0.78913	0.3223	0.70269
C21	0.76885	0.28488	0.726
C22	0.78644	0.25189	0.82315
C23	0.7664	0.21745	0.84143
C24	0.72786	0.21406	0.76416
C25	0.70998	0.24681	0.66675
C26	0.73026	0.28172	0.64805
C27	0.03653	0.46318	0.73668
C28	0.70694	0.17697	0.78453
N29	0.82159	0.25093	0.90132
S30	0.83349	0.20447	1.01055
N31	0.78578	0.18952	0.93379
H32	0.0303	0.39837	0.75086
H33	0.96659	0.39823	0.75639
H34	0.14618	0.45304	0.91431
H35	0.18786	0.39661	0.91387
H36	0.10136	0.33497	0.5364

H37	0.0599	0.39259	0.53278
H38	0.9348	0.39412	0.96682
H39	0.8938	0.33603	0.95858
H40	0.80878	0.39452	0.56732
H41	0.85062	0.45124	0.56795
H42	0.77337	0.34634	0.62822
H43	0.68035	0.2455	0.60426
H44	0.71569	0.30631	0.57177
H45	0.7224	0.15222	0.85435
C46	0.57488	0.96348	0.72417
C47	0.51708	0.92731	0.74787
C48	0.47952	0.92725	0.75686
C49	0.45961	0.96309	0.76296
C50	0.4209	0.96329	0.76958
C51	0.59914	0.92722	0.72627
C52	0.39673	0.92691	0.7642
C53	0.63605	0.92756	0.83007
C54	0.66013	0.89496	0.82916
C55	0.64782	0.861	0.72353
C56	0.61119	0.8606	0.62014
C57	0.58737	0.89353	0.61901
C58	0.40799	0.89407	0.87503
C59	0.38435	0.86101	0.87193
C60	0.34815	0.86065	0.76438
C61	0.33622	0.89372	0.65498
C62	0.36035	0.92636	0.65482
N63	0.32475	0.82637	0.77312
N64	0.67133	0.82664	0.71512
C65	0.28913	0.8223	0.70269
C66	0.26885	0.78488	0.726
C67	0.28644	0.75189	0.82315
C68	0.2664	0.71745	0.84143
C69	0.22786	0.71406	0.76416
C70	0.20998	0.74681	0.66675
C71	0.23026	0.78172	0.64805
C72	0.53653	0.96318	0.73668
C73	0.20694	0.67697	0.78453
N74	0.32159	0.75093	0.90132
S75	0.33349	0.70447	1.01055
N76	0.28578	0.68952	0.93379
H77	0.5303	0.89837	0.75086
H78	0.46659	0.89823	0.75639
H79	0.64618	0.95304	0.91431

H80	0.68786	0.89661	0.91387
H81	0.60136	0.83497	0.5364
H82	0.5599	0.89259	0.53278
H83	0.4348	0.89412	0.96682
H84	0.3938	0.83603	0.95858
H85	0.30878	0.89452	0.56732
H86	0.35062	0.95124	0.56795
H87	0.27337	0.84634	0.62822
H88	0.18035	0.7455	0.60426
H89	0.21569	0.80631	0.57177
H90	0.2224	0.65222	0.85435
C91	0.9252	0.46297	0.27501
C92	0.98309	0.42695	0.25013
C93	0.02064	0.42701	0.24099
C94	0.04047	0.46291	0.23594
C95	0.07917	0.46323	0.22929
C96	0.90101	0.42664	0.27233
C97	0.10339	0.42693	0.23373
C98	0.86402	0.42674	0.16937
C99	0.83999	0.39411	0.16999
C100	0.85242	0.36036	0.27455
C101	0.88915	0.36017	0.37696
C102	0.91292	0.39313	0.37834
C103	0.09225	0.39394	0.1215
C104	0.11593	0.3609	0.12407
C105	0.15202	0.36071	0.23263
C106	0.16384	0.39396	0.34325
C107	0.13969	0.42659	0.34381
N108	0.1754	0.32635	0.22396
N109	0.82892	0.32604	0.28304
C110	0.21088	0.32222	0.29652
C111	0.23113	0.28468	0.27329
C112	0.21362	0.25159	0.17425
C113	0.23362	0.21703	0.15616
C114	0.27203	0.21361	0.23551
C115	0.28982	0.24645	0.3349
C116	0.26959	0.28149	0.35341
C117	0.96356	0.46277	0.2624
C118	0.29293	0.17642	0.21512
N119	0.17859	0.25064	0.09411
S120	0.16676	0.20403	-0.01702
N121	0.21433	0.18901	0.06197
H122	0.96992	0.39796	0.2461

H123	0.03363	0.39803	0.24034
H124	0.85378	0.45206	0.086
H125	0.8122	0.39556	0.0859
H126	0.89907	0.33471	0.45989
H127	0.94045	0.39237	0.46394
H128	0.0655	0.39382	0.02924
H129	0.10656	0.33578	0.03647
H130	0.19121	0.39494	0.43156
H131	0.14932	0.45161	0.43165
H132	0.22656	0.34628	0.37304
H133	0.31936	0.24512	0.39905
H134	0.28408	0.30614	0.43122
H135	0.27755	0.15166	0.14311
C136	0.4252	0.96297	0.27501
C137	0.48309	0.92695	0.25013
C138	0.52064	0.92701	0.24099
C139	0.54047	0.96291	0.23594
C140	0.57917	0.96323	0.22929
C141	0.40101	0.92664	0.27233
C142	0.60339	0.92693	0.23373
C143	0.36402	0.92674	0.16937
C144	0.33999	0.89411	0.16999
C145	0.35242	0.86036	0.27455
C146	0.38915	0.86017	0.37696
C147	0.41292	0.89313	0.37834
C148	0.59225	0.89394	0.1215
C149	0.61593	0.8609	0.12407
C150	0.65202	0.86071	0.23263
C151	0.66384	0.89396	0.34325
C152	0.63969	0.92659	0.34381
N153	0.6754	0.82635	0.22396
N154	0.32892	0.82604	0.28304
C155	0.71088	0.82222	0.29652
C156	0.73113	0.78468	0.27329
C157	0.71362	0.75159	0.17425
C158	0.73362	0.71703	0.15616
C159	0.77203	0.71361	0.23551
C160	0.78982	0.74645	0.3349
C161	0.76959	0.78149	0.35341
C162	0.46356	0.96277	0.2624
C163	0.79293	0.67642	0.21512
N164	0.67859	0.75064	0.09411
S165	0.66676	0.70403	-0.01701

N166	0.71433	0.68901	0.06197
H167	0.46992	0.89796	0.2461
H168	0.53363	0.89803	0.24034
H169	0.35378	0.95206	0.086
H170	0.3122	0.89556	0.0859
H171	0.39907	0.83471	0.45989
H172	0.44045	0.89237	0.46394
H173	0.5655	0.89382	0.02924
H174	0.60656	0.83578	0.03647
H175	0.69121	0.89494	0.43156
H176	0.64932	0.95161	0.43165
H177	0.72656	0.84628	0.37304
H178	0.81936	0.74512	0.39905
H179	0.78408	0.80614	0.43122
H180	0.77755	0.65166	0.14311
C181	0.92512	0.53652	0.27583
C182	0.98292	0.57269	0.25213
C183	0.02048	0.57275	0.24314
C184	0.04039	0.53691	0.23704
C185	0.0791	0.53671	0.23042
C186	0.90086	0.57278	0.27373
C187	0.10327	0.57309	0.2358
C188	0.86395	0.57244	0.16993
C189	0.83987	0.60504	0.17084
C190	0.85218	0.639	0.27647
C191	0.88881	0.6394	0.37986
C192	0.91263	0.60647	0.38099
C193	0.09201	0.60593	0.12497
C194	0.11565	0.63899	0.12807
C195	0.15185	0.63935	0.23562
C196	0.16378	0.60628	0.34502
C197	0.13965	0.57364	0.34518
N198	0.17525	0.67363	0.22688
N199	0.82867	0.67336	0.28488
C200	0.21087	0.6777	0.29731
C201	0.23115	0.71512	0.274
C202	0.21356	0.74811	0.17685
C203	0.2336	0.78255	0.15857
C204	0.27214	0.78594	0.23584
C205	0.29002	0.75319	0.33325
C206	0.26974	0.71828	0.35195
C207	0.96347	0.53682	0.26332
C208	0.29306	0.82303	0.21547

N209	0.17841	0.74907	0.09868
S210	0.16651	0.79553	-0.01055
N211	0.21422	0.81048	0.06621
H212	0.9697	0.60163	0.24914
H213	0.03341	0.60177	0.24361
H214	0.85382	0.54696	0.08569
H215	0.81214	0.60339	0.08613
H216	0.89864	0.66503	0.4636
H217	0.9401	0.60741	0.46722
H218	0.0652	0.60588	0.03318
H219	0.1062	0.66397	0.04142
H220	0.19122	0.60548	0.43268
H221	0.14938	0.54876	0.43205
H222	0.22663	0.65366	0.37178
H223	0.31965	0.7545	0.39574
H224	0.28431	0.69369	0.42823
H225	0.2776	0.84778	0.14564
C226	0.42512	0.03652	0.27583
C227	0.48292	0.07269	0.25213
C228	0.52048	0.07275	0.24314
C229	0.54039	0.03691	0.23704
C230	0.5791	0.03671	0.23042
C231	0.40086	0.07278	0.27373
C232	0.60327	0.07309	0.2358
C233	0.36395	0.07244	0.16993
C234	0.33987	0.10504	0.17084
C235	0.35218	0.139	0.27647
C236	0.38881	0.1394	0.37986
C237	0.41263	0.10647	0.38099
C238	0.59201	0.10593	0.12497
C239	0.61565	0.13899	0.12807
C240	0.65185	0.13935	0.23562
C241	0.66378	0.10628	0.34502
C242	0.63965	0.07364	0.34518
N243	0.67525	0.17363	0.22689
N244	0.32867	0.17336	0.28488
C245	0.71087	0.1777	0.29731
C246	0.73115	0.21512	0.274
C247	0.71356	0.24811	0.17685
C248	0.7336	0.28255	0.15857
C249	0.77214	0.28594	0.23584
C250	0.79002	0.25319	0.33325
C251	0.76974	0.21828	0.35195

C252	0.46347	0.03682	0.26332
C253	0.79306	0.32303	0.21547
N254	0.67841	0.24907	0.09868
S255	0.66651	0.29553	-0.01055
N256	0.71422	0.31048	0.06621
H257	0.4697	0.10163	0.24914
H258	0.53341	0.10177	0.24361
H259	0.35382	0.04696	0.08569
H260	0.31214	0.10339	0.08613
H261	0.39864	0.16503	0.4636
H262	0.4401	0.10741	0.46722
H263	0.5652	0.10588	0.03318
H264	0.6062	0.16397	0.04142
H265	0.69122	0.10548	0.43268
H266	0.64938	0.04876	0.43205
H267	0.72663	0.15366	0.37178
H268	0.81965	0.2545	0.39574
H269	0.78431	0.19369	0.42823
H270	0.7776	0.34778	0.14564
C271	0.0748	0.53703	0.72499
C272	0.01691	0.57305	0.74987
C273	0.97936	0.57299	0.75901
C274	0.95953	0.53709	0.76406
C275	0.92083	0.53677	0.77071
C276	0.09899	0.57336	0.72767
C277	0.89661	0.57307	0.76627
C278	0.13598	0.57326	0.83063
C279	0.16001	0.60589	0.83001
C280	0.14758	0.63964	0.72545
C281	0.11085	0.63983	0.62304
C282	0.08708	0.60687	0.62166
C283	0.90775	0.60606	0.8785
C284	0.88407	0.6391	0.87593
C285	0.84798	0.63929	0.76737
C286	0.83616	0.60604	0.65675
C287	0.86031	0.57341	0.65619
N288	0.8246	0.67365	0.77604
N289	0.17108	0.67396	0.71696
C290	0.78912	0.67778	0.70348
C291	0.76887	0.71532	0.72671
C292	0.78638	0.74841	0.82575
C293	0.76638	0.78297	0.84384
C294	0.72797	0.78639	0.76449

C295	0.71018	0.75355	0.6651
C296	0.73041	0.71851	0.64659
C297	0.03644	0.53723	0.7376
C298	0.70707	0.82358	0.78488
N299	0.82141	0.74936	0.90589
S300	0.83324	0.79597	1.01701
N301	0.78567	0.81099	0.93803
H302	0.03008	0.60204	0.7539
H303	0.96637	0.60197	0.75966
H304	0.14622	0.54794	0.914
H305	0.1878	0.60444	0.9141
H306	0.10093	0.66529	0.54011
H307	0.05955	0.60763	0.53606
H308	0.9345	0.60618	0.97076
H309	0.89344	0.66422	0.96353
H310	0.80879	0.60506	0.56844
H311	0.85068	0.54839	0.56835
H312	0.77344	0.65372	0.62696
H313	0.68064	0.75488	0.60095
H314	0.71592	0.69386	0.56878
H315	0.72245	0.84834	0.85689
C316	0.5748	0.03703	0.72499
C317	0.51691	0.07305	0.74987
C318	0.47936	0.07299	0.75901
C319	0.45953	0.03709	0.76406
C320	0.42083	0.03677	0.77071
C321	0.59899	0.07336	0.72767
C322	0.39661	0.07307	0.76627
C323	0.63598	0.07326	0.83063
C324	0.66001	0.10589	0.83001
C325	0.64758	0.13964	0.72545
C326	0.61085	0.13983	0.62304
C327	0.58708	0.10687	0.62166
C328	0.40775	0.10606	0.8785
C329	0.38407	0.1391	0.87593
C330	0.34798	0.13929	0.76737
C331	0.33616	0.10604	0.65675
C332	0.36031	0.07341	0.65619
N333	0.3246	0.17365	0.77604
N334	0.67108	0.17396	0.71696
C335	0.28912	0.17778	0.70348
C336	0.26887	0.21532	0.72671
C337	0.28638	0.24841	0.82575

C338	0.26638	0.28297	0.84384
C339	0.22797	0.28639	0.76449
C340	0.21018	0.25355	0.6651
C341	0.23041	0.21851	0.64659
C342	0.53644	0.03723	0.7376
C343	0.20707	0.32358	0.78488
N344	0.32141	0.24936	0.90589
S345	0.33324	0.29597	1.01701
N346	0.28567	0.31099	0.93803
H347	0.53008	0.10204	0.7539
H348	0.46637	0.10197	0.75966
H349	0.64622	0.04794	0.914
H350	0.6878	0.10444	0.9141
H351	0.60093	0.16529	0.54011
H352	0.55955	0.10763	0.53606
H353	0.4345	0.10618	0.97076
H354	0.39344	0.16422	0.96353
H355	0.30879	0.10506	0.56844
H356	0.35068	0.04839	0.56835
H357	0.27344	0.15372	0.62696
H358	0.18064	0.25488	0.60095
H359	0.21592	0.19386	0.56878
H360	0.22245	0.34834	0.85689
C361	0.90286	0.50001	0.77304
C362	0.97883	0.50012	0.75789
C363	0.9074	0.49973	0.28169
C364	0.98275	0.49983	0.25704
C365	0.40286	0.00001	0.77304
C366	0.47883	0.00012	0.75789
C367	0.4074	-0.00027	0.28169
C368	0.48275	-0.00017	0.25704
C369	0.09714	0.49999	0.22696
C370	0.02117	0.49988	0.24211
C371	0.0926	0.50027	0.71831
C372	0.01725	0.50017	0.74296
C373	0.59714	-0.00001	0.22696
C374	0.52117	-0.00012	0.24211
C375	0.5926	0.00027	0.71831
C376	0.51725	0.00017	0.74296

Table S2. Fractional atomic coordinates for the unit cell of OH-COF.

OH-COF: Space group: C2/M			
a = 41.2119 Å, b = 41.1111 Å, c = 7.3933 Å			
α = 90º, β = 118.1641º,γ = 90º			
C1	1.06877	1.46971	0.74068
C2	1.01671	1.43993	0.74801
C3	0.98314	1.43994	0.75042
C4	0.96555	1.4695	0.7555
C5	0.9311	1.46971	0.75826
C6	1.09039	1.43978	0.74831
C7	0.90963	1.4397	0.75194
C8	1.12315	1.43955	0.8612
C9	1.14469	1.41269	0.86406
C10	1.13386	1.38534	0.75369
C11	1.10122	1.38527	0.64309
C12	1.08004	1.41249	0.6372
C13	0.92021	1.4126	0.864
C14	0.89932	1.38518	0.85871
C15	0.86676	1.38477	0.74723
C16	0.85565	1.41203	0.63638
C17	0.87689	1.43914	0.63903
N18	0.84609	1.35623	0.75049
N19	1.15495	1.35711	0.75158
C20	1.03431	1.4695	0.74311
C21	0.69046	-0.19983	0.68229
C22	0.7077	-0.22874	0.66368
C23	0.74148	-0.23341	0.75769
C24	0.75734	-0.20784	0.87071
C25	0.74061	-0.17829	0.88696
C26	0.70653	-0.17406	0.79192
C27	0.76002	-0.26463	0.73816
C28	0.74251	-0.29418	0.6784
C29	0.75974	-0.32338	0.65863
C30	0.79515	-0.32384	0.70608
C31	0.81274	-0.29455	0.76623
C32	0.79548	-0.26532	0.77912
C33	0.68768	-0.1431	0.80032
C34	0.8135	-0.35483	0.69268
O35	0.75883	-0.15439	1.00156
O36	0.74183	-0.35223	0.59567
H37	1.02842	1.41604	0.75193
H38	0.97142	1.41605	0.74649

H39	1.13201	1.46014	0.94898
H40	1.16934	1.41317	0.95558
H41	1.09258	1.36447	0.55662
H42	1.05572	1.41222	0.5441
H43	0.94453	1.41261	0.95707
H44	0.90817	1.36452	0.94592
H45	0.83105	1.41232	0.54452
H46	0.86785	1.45962	0.55079
H47	0.66462	-0.19726	0.60531
H48	0.69435	-0.2469	0.57109
H49	0.78277	-0.21069	0.95167
H50	0.7154	-0.29523	0.65045
H51	0.84	-0.29401	0.80058
H52	0.81031	-0.24324	0.81862
H53	0.70122	-0.12032	0.8397
H54	0.79923	-0.37668	0.64037
H55	0.74522	-0.13561	1.0322
H56	0.71647	-0.34945	0.56535
C57	0.91506	1.5	0.75944
C58	0.98275	1.5	1.75318
C59	0.91522	1.5	0.26051
C60	0.9829	1.5	0.25469

Table S3. Fractional atomic coordinates for the unit cell of BTD-OH-COF.

BTD-OH-COF: Space group: P1			
a = 37.1037Å, b = 39.0998 Å, c = 3.7156 Å			
α = 86.7172º, β = 102.1214º,γ = 88.868º			
C1	0.08601	0.45701	0.73177
C2	0.03105	0.43019	0.7564
C3	0.99421	0.43343	0.76682
C4	0.97218	0.46707	0.78326
C5	0.93386	0.4706	0.78877
C6	0.1116	0.42183	0.74167
C7	0.91401	0.44132	0.78463
C8	0.14762	0.41701	0.96688
C9	0.1721	0.38459	0.97013
C10	0.1609	0.35607	0.7551
C11	0.12542	0.36118	0.52267
C12	0.10151	0.39376	0.51363
C13	0.92889	0.41022	0.9977
C14	0.90843	0.38247	0.99725
C15	0.87195	0.38544	0.79458
C16	0.85647	0.41627	0.58073
C17	0.87717	0.44377	0.57677
N18	0.8517	0.35672	0.81507
N19	0.18658	0.32307	0.76364
C20	0.04811	0.46038	0.74561
C21	0.70442	0.7599	0.6592
C22	0.69375	0.72864	0.48433
C23	0.7194	0.69813	0.47507
C24	0.75735	0.697	0.63892
C25	0.76844	0.72819	0.81104
C26	0.74231	0.75921	0.82137
C27	0.6768	0.79248	0.67184
C28	0.7847	0.66401	0.63451
C29	0.91368	0.50541	0.78892
C30	0.98855	0.49844	0.77012
N31	0.65843	0.724	0.30026
S32	0.65613	0.68236	0.11817
N33	0.70296	0.671	0.28526
C34	0.58601	0.95752	0.71816
C35	0.53133	0.93059	0.75126
C36	0.49481	0.93382	0.77342
C37	0.47308	0.96749	0.79122
C38	0.43553	0.97087	0.81554

C39	0.61168	0.92237	0.73007
C40	0.41456	0.94005	0.7989
C41	0.64767	0.91773	0.95591
C42	0.6722	0.88529	0.96202
C43	0.66107	0.8566	0.74921
C44	0.62563	0.86154	0.51616
C45	0.60165	0.89411	0.50456
C46	0.42855	0.90927	1.01626
C47	0.40791	0.88149	1.00411
C48	0.37196	0.88453	0.78797
C49	0.35745	0.91529	0.57008
C50	0.37864	0.94258	0.57451
N51	0.35126	0.85601	0.80114
N52	0.68676	0.82358	0.7601
C53	0.54827	0.96083	0.73685
C54	0.20445	0.25952	0.65826
C55	0.19398	0.22823	0.48253
C56	0.21972	0.1977	0.4768
C57	0.25756	0.19659	0.64523
C58	0.26845	0.22784	0.81747
C59	0.24224	0.25888	0.82425
C60	0.1767	0.29205	0.66931
C61	0.28498	0.16354	0.64611
C62	0.41559	0.00531	0.83529
C63	0.48924	-0.00115	0.77681
N64	0.15879	0.22354	0.29494
S65	0.15674	0.18184	0.11368
N66	0.20348	0.17052	0.28595
C67	0.0809	0.52279	0.72867
C68	0.02077	0.56013	0.74541
C69	0.98356	0.56344	0.74515
C70	0.96677	0.53319	0.76344
C71	0.92876	0.53657	0.76798
C72	0.10183	0.55362	0.7451
C73	0.90238	0.57143	0.73447
C74	0.13738	0.55142	0.97523
C75	0.15837	0.57894	0.98441
C76	0.14402	0.60968	0.76538
C77	0.10859	0.61211	0.53924
C78	0.08817	0.58407	0.52245
C79	0.91002	0.60097	0.95332
C80	0.8834	0.63205	0.93352
C81	0.84793	0.63351	0.70928

C82	0.84028	0.6043	0.48595
C83	0.86722	0.57383	0.4974
N84	0.82022	0.66459	0.71723
N85	0.16418	0.63887	0.76094
C86	0.04291	0.52636	0.74021
C87	0.69593	0.20187	0.68338
C88	0.71201	0.23229	0.66069
C89	0.7493	0.23285	0.83147
C90	0.77027	0.20227	1.02449
C91	0.75424	0.1716	1.05036
C92	0.71676	0.17127	0.87822
C93	0.76624	0.26535	0.80957
C94	0.74649	0.2998	0.84194
C95	0.76229	0.3307	0.82735
C96	0.79854	0.3273	0.77014
C97	0.81821	0.29269	0.73942
C98	0.80235	0.26212	0.76051
C99	0.69963	0.13907	0.9033
C100	0.81579	0.35908	0.73247
O101	0.7752	0.14155	1.24909
O102	0.74151	0.3638	0.88359
C103	0.1011	0.48827	0.71592
C104	0.02655	0.49505	0.75071
C105	0.58088	0.02332	0.71702
C106	0.52105	0.06062	0.74622
C107	0.4842	0.06385	0.76068
C108	0.46766	0.03352	0.78266
C109	0.43011	0.03665	0.80464
C110	0.60188	0.05411	0.73594
C111	0.40339	0.07124	0.76852
C112	0.63748	0.05164	0.96562
C113	0.65862	0.07905	0.9764
C114	0.64438	0.10994	0.75923
C115	0.60889	0.11266	0.53392
C116	0.58827	0.08476	0.51613
C117	0.41074	0.10118	0.98208
C118	0.38379	0.13206	0.95815
C119	0.34841	0.13301	0.73346
C120	0.34111	0.10339	0.51481
C121	0.3683	0.07304	0.53165
N122	0.3205	0.16408	0.73508
N123	0.66469	0.13906	0.7571
C124	0.54308	0.02686	0.7347

C125	0.19508	0.70177	0.68196
C126	0.21111	0.73211	0.65362
C127	0.24849	0.73277	0.82066
C128	0.26957	0.70236	1.016
C129	0.2536	0.67178	1.04759
C130	0.21606	0.67135	0.87879
C131	0.26541	0.76515	0.79222
C132	0.24562	0.79975	0.81796
C133	0.26145	0.83054	0.79814
C134	0.29779	0.82686	0.74304
C135	0.31747	0.79213	0.7181
C136	0.30157	0.76169	0.74389
C137	0.19903	0.63919	0.90872
C138	0.31537	0.85842	0.70567
O139	0.27471	0.64192	1.24831
O140	0.24061	0.86382	0.84822
C141	0.60098	-0.01119	0.69996
C142	0.52687	-0.00448	0.74715
H143	0.04554	0.4031	0.75739
H144	0.98361	0.4085	0.75111
H145	0.15666	0.4382	1.14431
H146	0.19957	0.38141	1.14644
H147	0.11644	0.34069	0.33681
H148	0.07503	0.39691	0.32632
H149	0.95591	0.40758	1.17582
H150	0.92064	0.35904	1.16641
H151	0.82884	0.41899	0.40941
H152	0.86457	0.46658	0.40013
H153	0.79726	0.7285	0.94251
H154	0.75177	0.78252	0.96023
H155	0.64773	0.79014	0.60497
H156	0.77469	0.63883	0.56868
H157	0.88522	0.5086	0.81345
H158	0.54575	0.9035	0.74977
H159	0.48426	0.90899	0.77266
H160	0.65663	0.93906	1.13169
H161	0.69963	0.88223	1.13883
H162	0.61672	0.84087	0.33219
H163	0.57516	0.89707	0.31782
H164	0.45534	0.90662	1.19857
H165	0.41942	0.85805	1.1747
H166	0.33026	0.9181	0.39032
H167	0.36701	0.9657	0.39963

H168	0.29718	0.22818	0.95215
H169	0.25155	0.28221	0.96376
H170	0.14764	0.2897	0.5979
H171	0.27499	0.13836	0.57928
H172	0.38736	0.00786	0.86526
H173	0.03144	0.58496	0.75052
H174	0.96846	0.59044	0.73007
H175	0.14881	0.52846	1.15257
H176	0.1852	0.57614	1.16961
H177	0.09726	0.63538	0.36591
H178	0.06187	0.58619	0.33193
H179	0.9361	0.59976	1.14719
H180	0.88977	0.65429	1.10741
H181	0.81379	0.60506	0.2973
H182	0.8605	0.55187	0.32061
H183	0.66715	0.20229	0.54596
H184	0.69539	0.25524	0.50459
H185	0.79897	0.20244	1.16069
H186	0.71899	0.30277	0.89049
H187	0.8458	0.28924	0.69236
H188	0.81812	0.23591	0.73149
H189	0.71687	0.11543	1.04042
H190	0.79828	0.38447	0.64477
H191	0.80162	0.14468	1.3671
H192	0.7558	0.38458	0.93527
H193	0.12959	0.48563	0.69313
H194	0.53161	0.08546	0.74734
H195	0.46923	0.09083	0.75591
H196	0.64885	0.02853	1.14107
H197	0.68548	0.07606	1.16129
H198	0.59762	0.13608	0.36249
H199	0.56184	0.08717	0.32734
H200	0.43686	0.10049	1.174
H201	0.38992	0.15465	1.12791
H202	0.31474	0.10371	0.32547
H203	0.36184	0.05073	0.3588
H204	0.16625	0.70212	0.54718
H205	0.19438	0.75489	0.49573
H206	0.29834	0.70257	1.14943
H207	0.21808	0.80296	0.86583
H208	0.34515	0.78848	0.67291
H209	0.31739	0.73539	0.7198
H210	0.21632	0.61578	1.04987

H211	0.29812	0.88374	0.61053
H212	0.30117	0.64511	1.36359
H213	0.25482	0.8847	0.89354
H214	0.62937	-0.0138	0.67428

Table S4. Comparison of this work with previously reported fluorescence methods for detecting Cr(VI)

Materials	Linear Range (μmol/L)	LOD (μmol/L)	Response time (min)	Ref.
CDs@Eu-MOF	2-100	0.21	5	[1]
g-C_3N_4 nanosheet	0.6-300	0.15	10	[2]
Si QDs	1.25-40	0.65	30s	[3]
Imi-TPP-COF-Br-AR	0.5-220	0.041	3.5	[4]
Gold nanoparticles	0.5-50	0.28	10	[5]
CDs	5-100	0.589	-	[6]
SQDs@UiO-66-NH_2	0-200	0.61	10s	[7]
BTD-OH-COF	0.2-300	0.068	3s	This work

Table S5. Determination results of Cr (VI) in real samples (n = 3).

Sample	Added (μmol/L)	Found (μmol/L)	Recovery[a](%)	RSD[b](%)
Lake water	0.50	0.48	94.94	3.3
	1.00	1.06	106.39	4.5
	5.00	5.24	104.72	1.3
Tap water	0.50	0.47	94.71	7.4
	1.00	0.96	95.98	2.3
	5.00	4.71	94.29	1.6
Wei River water	0.50	0.49	97.95	4.4
	1.00	0.97	97.12	2.9
	5.00	4.98	99.65	1.5

a:Recovery (%) = 100 × (cmeasured/cadded).
b:RSD means the relative standard deviation.

Table S6. Comparison of various catalysts for Cr (VI) reduction under visible-light irradiation.

Photocatalyst	Dose (mg)	Volume (mL) /pH	Time (min)	Concentration (mg/L)	Reduction efficiency (%)	Ref.
COF-PDZ	15	60/7	100	5	95	[8]
COF-Au@C_2	10	30/2.3	120	9	98.2	[9]
BiOBr/TzDa-COF	10	50/2.1	100	10	98	[10]
HDU-108	10	50/3	120	10	99.9	[11]
TPB-TP-COF	10	10/7	105	10	80	[12]
MIL-68(In)-NH_2	10	40/2	180	20	97	[13]
NNU-37(Co)	24.8	40/2	110	10	91.8	[14]
BTD-OH-COF	5	50/3	120	15	99.9	This work

References

[1] Y. Y. Wang, J. He, M. D. Zheng, M. D. Qin, W. Wei, *Talanta* 2019, **191**, 519-525.

[2] M. C. Rong, L. P. Lin, X. H. Song, Y. R. Wang, Y. X. Zhong, J. W. Yan, Y. F. Feng, X. Y. Zeng, X. Chen, *Biosens Bioelectron*., 2015, **68**, 210-217.

[3] L. M. T. Phan, S. H. Baek, T. P. Nguyen, K. Y. Park, S. Haa, R. Rafique, S. K. Kailasaa, T. J. Park, *Mater. Sci. Eng. C*, 2018, **93**, 429-436.

[4] R. Ding, J. J. Liu, Q. G. Meng, T. Wang, X. M. Zhang, *Sep Purif Technol*., 2025, **359**, 130544.

[5] J. F. Guo, D. Q. Huo, M. Yang, C. J. Hou, J. J. Li, H. B. Fa, H. B. Luo, P. Yan, *Talanta*, 2016, **161**, 819-825.

[6] N. Liu, Y. Q. Zhang, J. Y. Huang, S. C. Liu, T. P. Qing, P. Zhang, B. Feng, *J Ind Eng Chem*., 2024, **130**, 297-305.

[7] Y. Q. Zhang, J. X. Liu, X. H. Wu, W. Q. Tao, Z. Li, *Anal Chim Acta*., 2020, **1131**, 68-79.

[8] F. Y. Liu, Z. Y. Ma, Y. C. Deng, M. Wang, P. Zhou, W. Liu, S. J. Guo, M. P. Tong, D. Ma, *Environ Sci Technol*., 2021, **55**, 5371-5381.

[9] W. Y. Geng, F. Y. Chen, Y. H. Luo, Z. Y. Liu, S. F. Guo, Y. Y. Zhang, D. E. Zhang, X. Y. Yu, *Micropor Mesopor Mat*., 2023, **351**, 112479.

[10] Y. Zhang, Z. Chen, Z. X. Shi, T. T. Lu, D. L. Chen, Q. Wang, Z. L. Zhan, *Sep Purif Technol*., 2021, **275**, 119216.

[11] C. Wang, W. Lu, W. H. Song, Z. X. Zhang, C. D. Xie, Y. Li, J. J. Wang, *Appl Catal B*., 2025, **361**, 124583.

[12] W. B. Chen, Z. F. Yang, Z. Xie, Y. S. Li, F. L. Lu, L. Chen, *J Mater Chem*., 2019, **7**, 998-1004.

[13] R. W. Liang, L. J. Shen, F. F. Jing, W. M. Wu, N. Qin, R. Lin, L. Wu, *Appl Catal B*., 2015, **162**, 245-251.

[14] T. L. Andualem, E. A. Tesema, R. P. DM, *Sci Rep*., 2025, **15**, 27091.