Supplementary Information

Constructing donor-acceptor covalent organic frameworks with *bex* topology for efficient photocatalytic reduction of uranium

Li Wang, *[a] Lingli Zhang, [a] and Feng Luo*[a]

[a] National Key Laboratory of Uranium Resources Exploration-Mining and Nuclear Remote Sensing, East China University of Technology, Nanchang 330013, China
E-mail: wangli20040302@126.com, ecitluofeng@163.com

Materials and general methods

Uranium has low radioactivity, thus we must be careful for such experiments under special protection. X-ray powder diffraction was collected by a Bruker AXSD8 Discover or D8 ADVANCE powder diffractometer. The simulated powder patterns were calculated by Mercury 1.4. Infrared Spectra (IR) was measured by a Bruker VERTEX70 spectrometer in the 600-2000 cm^{-1} region. The gas adsorption isotherms were collected on a Belsorp-max. Ultrahigh-purity-grade (>99.999%) N_2 gases were used during the adsorption measurement. X-ray photoelectron spectroscopy (XPS) data were acquired on a Thermo Scientific ESCALAB 250xi spectrometer. Scanning electron microscopy (SEM) images were obtained using a Hitachi SU 8100 microscope. Solid-state NMR experiments were performed on Varian Infinityplus 300 solid-state NMR spectrometer (300 MHz). UV-vis spectroscopy results were recorded in diffuse reflectance (DR) mode at room temperature on aSHIMADZU UV-2700 spectrophotometer equipped with an integrating sphere attachment. Solid-state fluorescence spectra of the COFs were collected using an F7000 fluorescence spectrophotometer (HITACHI Corporation). All electrochemical measurements were performed using a CHI760 electrochemical workstation configured with a standard three-electrode system. The system employed a platinum foil and an Ag/AgCl (0.5 M Na_2SO_4) electrode as the reference electrode. Illumination was provided by a 300-W xenon arc lamp (HSW-F300) equipped with a $\lambda > 420$ nm cutoff filter. The thermogravimetric analysis (TGA) measurements were performed from 30 to 800 °C on a TA Q500 thermogravimeter.

Synthesis of Py-TAPT-COF, Py-TAPB-COF and Py-TAPA-COF

In different Pyrex tubes (25 mL), compounds of 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetrabenzaldehyde (Py, 24 mg, 0.04 mmol), and TAPT (14 mg, 0.04 mmol) or TAPB (14 mg, 0.04 mmol)) or TAPA (12 mg, 0.04 mmol) were mixed, followed by addition of 30 mg imidazole. Then, 1 mL n-butanol and 1 mL o-dichlorobenzene were added. The reaction mixture was sonicated for 5 minutes after adding 0.4 mL acetic acid, and the mixture was then subjected to another 15 minutes of sonication. The tubes were subsequently degassed via three freeze-thaw cycles using liquid nitrogen and sealed under vacuum. The sealed containers were heated at 120 °C for 3 days to afford the crude product. The obtained product was thoroughly washed with dimethyl sulfoxide (DMSO) and preheated ethanol, and then was dried in vacuum and collected. Py-TAPT-COF, Py-TAPB-COF, and Py-TAPA-COF were obtained as yellow, dark yellow, and green powdered products, with the yields of approximately 85%, 83%, and 79%, respectively.

Uranium (VI) solution adsorption experiments

The removal rate (R) of U(VI) were calculated by the following equation: $R = (C_0–C_t)/C_0 \times 100\%$, where C_0 and C_t represent the initial concentration and concentration at time t, respectively. The adsorption quantity q_e (mg/g) was calculated by the following equation: $q_e=(C_0-C_e) \times V/m$, where V (mL) is the volume of testing solution and m (mg) is the weight of sorbent.

Photocatalytic uranium reduction experiment

To evaluate the adsorption effect of different materials on uranium in the solution, 5 mg catalyst was dispersed into 45 mL U(VI)-containing solution (100 mg •L^{-1}) and added 5 mL methanol as a hole sacrificial agent. Firstly, the solutions were stirred in the dark for 60 min to reach the equilibrium state. Subsequently, the photocatalytic reduction reactions were conducted using a xenon lamp. After a certain period of time, the concentration of uranium was detected by Arsenazo-III spectrophotometric technology. For selective experiments, photocatalytic reduction experiments were performed under identical conditions to those described above, using an aqueous solution containing 10 mg L^{-1} of various metal cations: UO_2^{2+}, Na^+, K^+, Ca^{2+}, Sr^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cs^{2+}, Al^{3+}, and Cr^{3+}. Following the reaction, all samples were diluted to below 0.5 mg L^{-1} before Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis.

The removal rate and removal capacity (q_t, mg g^{-1}) were calculated using the following equation.

$$\text{Removal rate} = (C_0 - C_t)/C_0 \times 100\%$$

$$q_t = (C_0 - C_t) \times V/m$$

Where C_t is the time concentrations of U(VI) (mg L^{-1}), C_0 is the initial concentrations of U(VI) (mg L^{-1}), V is the volume of the solution (L), t is the reaction time (min), m is the COF mass (g).

Furthermore, the recyclability of the catalyst was assessed by consecutive cycling tests. Used catalyst was separated at the end of each cycle, afterwards uranium was eluted by 0.1 M HNO_3 solution, washed by water, and dried. The catalyst was then added to a fresh U(VI) solution to begin another cycle. To evaluate the roles of different reactive species in the photocatalytic extraction of U(VI), radical trapping experiments using 1 mmol of $AgNO_3$, Isopropanol (IPA), or p-benzoquinone (p-BQ) as a trapper for the photogenerated species(e^-), hydroxyl radicals (•OH), and superoxide radicals ($\bullet O_2^-$), were carried out to determine the involvement of various reactive species in the photocatalytic extraction of U(VI), besides, 5 ml of methanol was used as a hole (h^+) scavenger. In all experiments, liquid samples (~1 mL) were taken through a syringe filter (0.22 μm). The concentration of U(VI) was quantitatively determined at 652 nm using UV-Vis spectrophotometry via the Arsenazo III complexation method.

The optical and electrochemical properties measurements

The electrochemical tests were conducted using a mixture of the catalyst, isopropanol, and nafion solution. All electrochemical measurements were performed with a CHI760 electrochemical workstation equipped with a standard three-electrode system. The tests were carried out in a 0.5 M Na_2SO_4 solution, with a platinum foil as the counter electrode and an Ag/AgCl electrode as the reference electrode. For Mott-Schottky plots, electrochemical impedance spectroscopy (EIS), open-circuit potential (OCP) measurements, platinum sheet and Ag/AgCl electrode were used, with the sample coated on a platinum-carbon working electrode. Photoelectrochemical response was tested using samples coated on fluorine-doped tin oxide (FTO) glass, which was mounted with an electrode clip. Illumination was provided by a 300 W xenon arc lamp (HSW-F300) equipped with a $\lambda > 420$ nm cut-off filter.

Density Functional Theory (DFT) calculations

Density Functional Theory (DFT) calculations were performed using the VASP within the plane-wave basis set framework. The Perdew Burke Ernzerhof(PBE) functional within the generalized gradient approximation (GGA) was employed to describe the exchange-correlation energy, while the projector augmented wave (PAW) method with the GGA approximation was used to treat the electron-ion interactions. Spin-polarized calculations were considered for all computations. The wave functions were expanded in a plane-wave basis set with a kinetic energy cutoff of 500 eV. The geometric structures were fully relaxed until the residual Hellmann-Feynman forces on each atom were converged below 0.02 eV/Å.

Supplemental figures

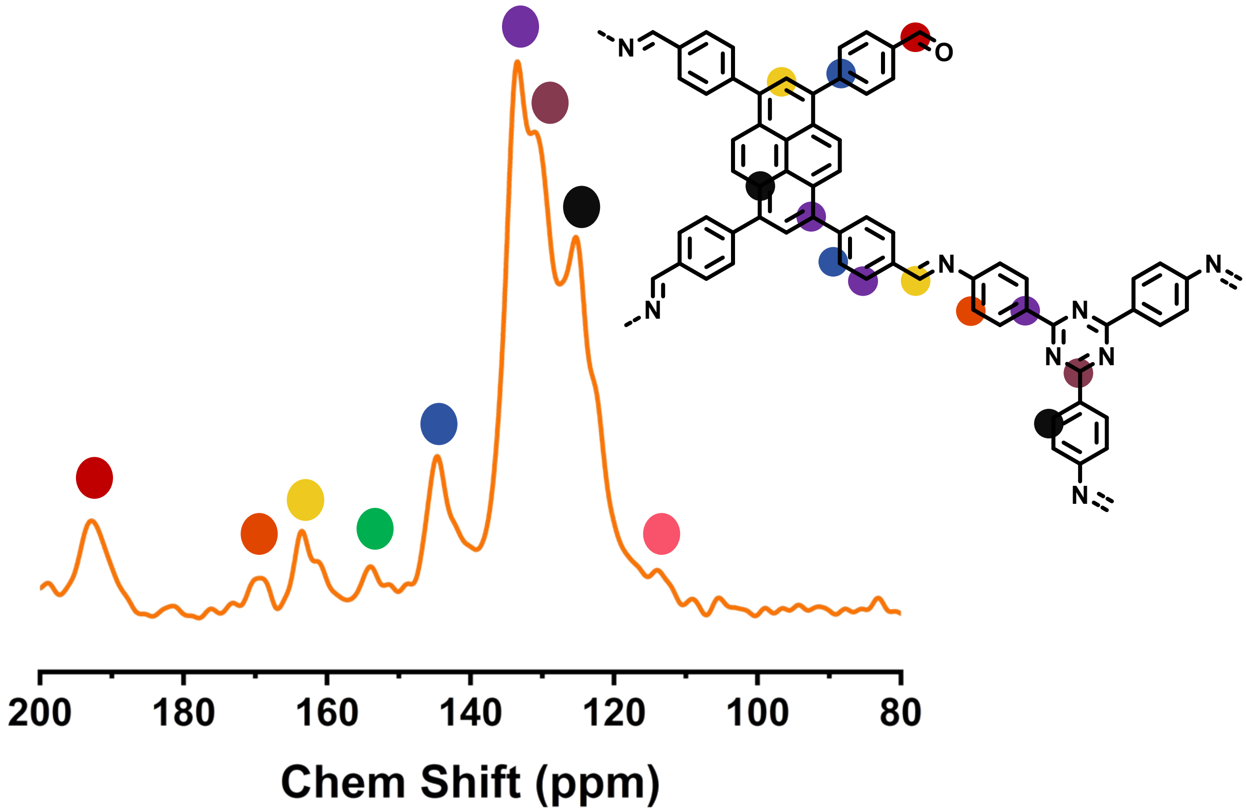


Fig. S1 CP-MAS ^{13}C NMR spectra of Py-TAPT-COF.

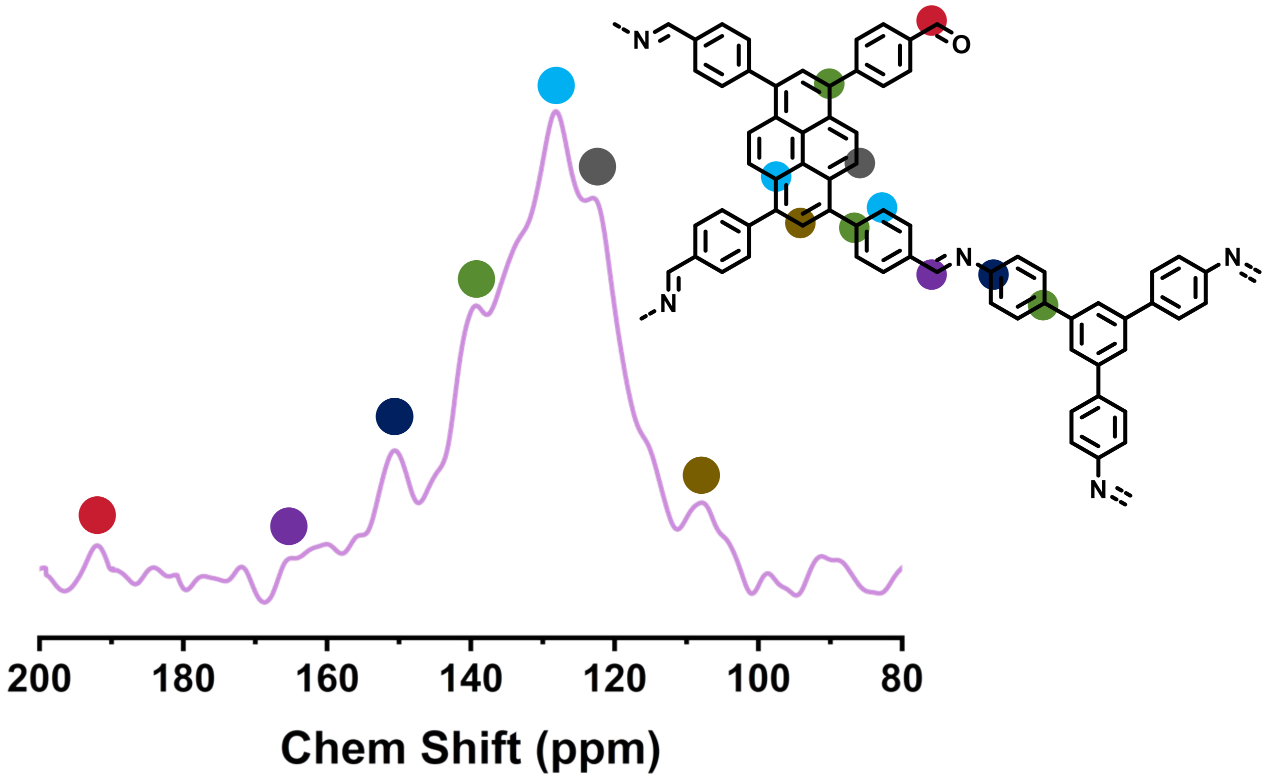


Fig. S2 CP-MAS ^{13}C NMR spectra of Py-TAPB-COF.

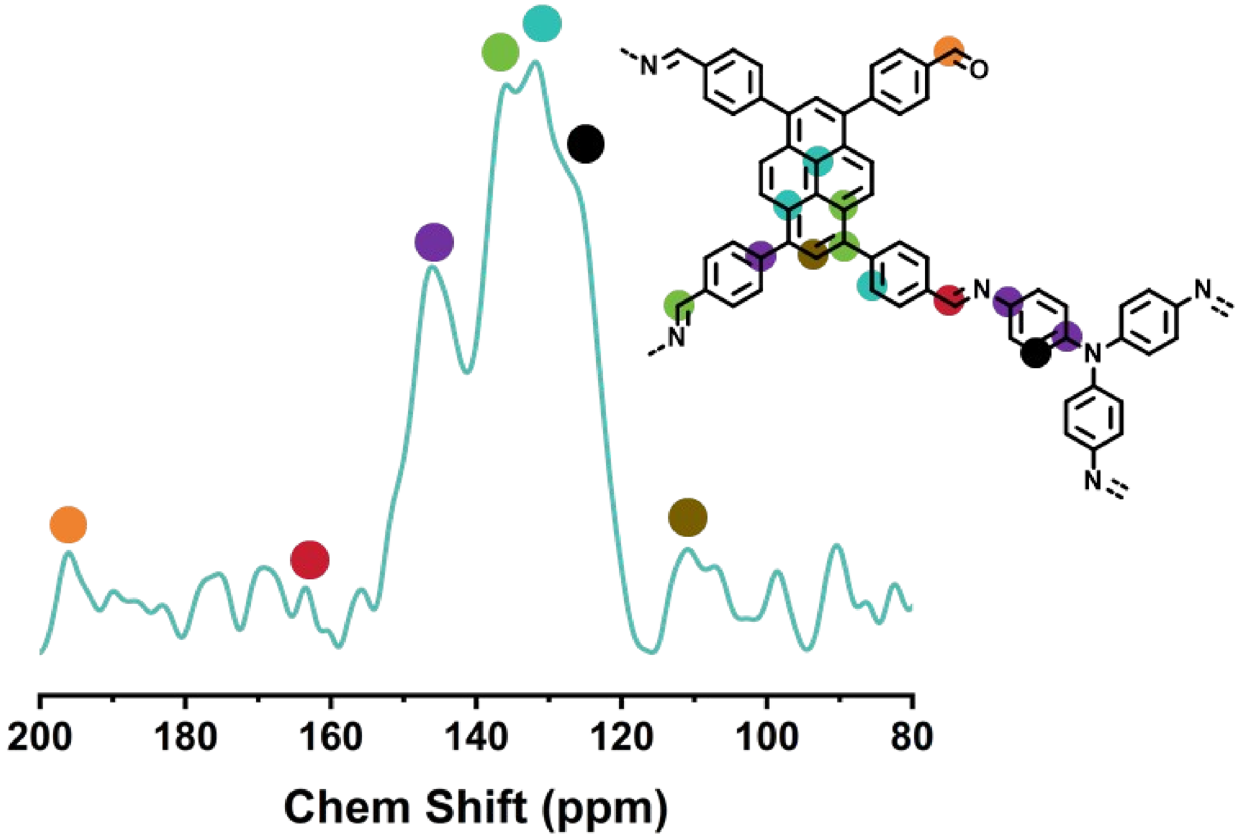


Fig. S3 CP-MAS ^{13}C NMR spectra of Py-TAPA-COF.

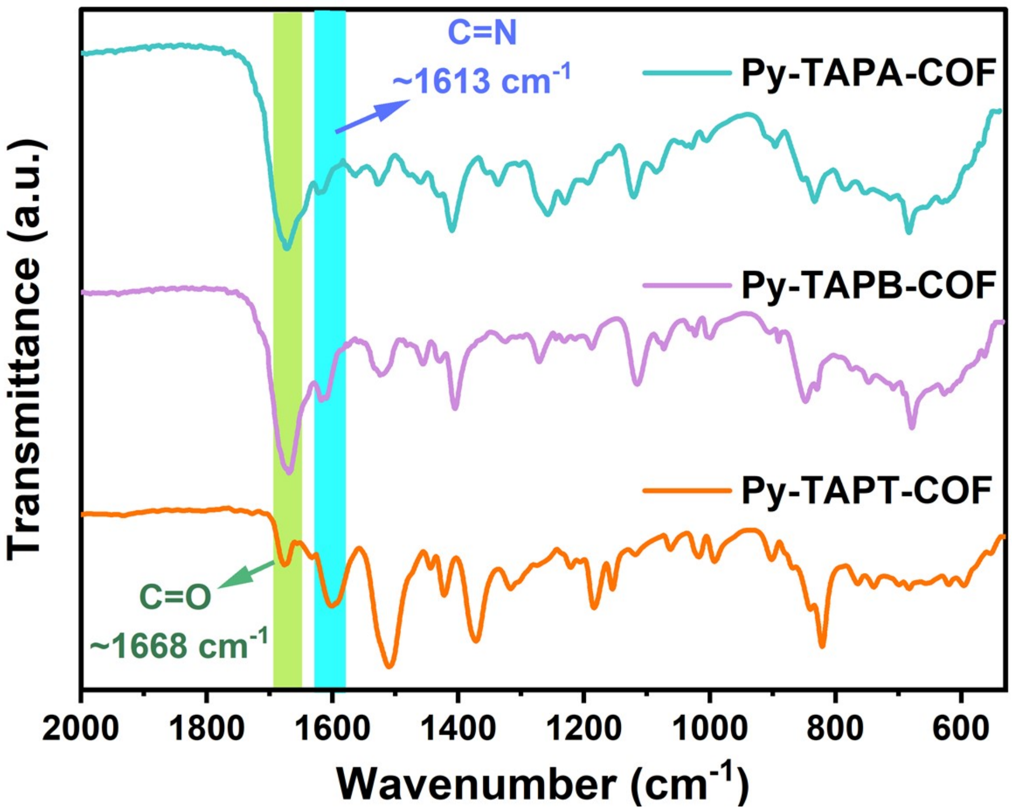


Fig. S4 Fourier-transform infrared (FT-IR) spectra of the three COFs.

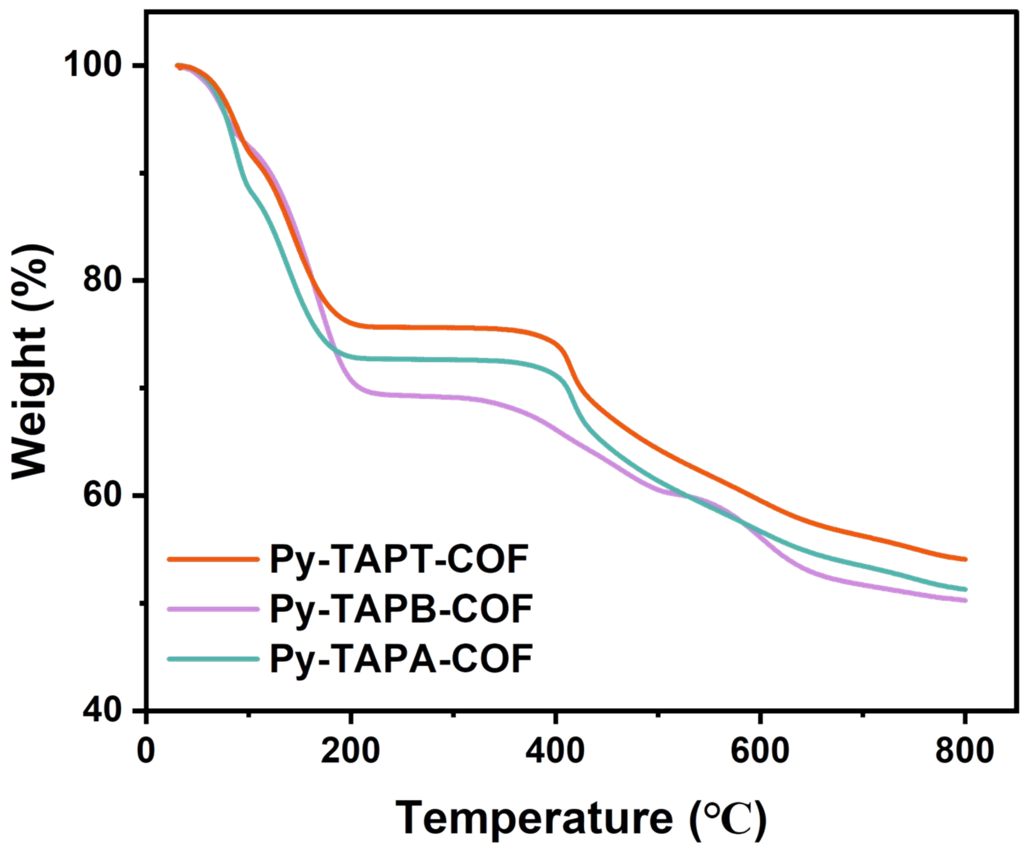


Fig. S5 TGA curves of each COFs.

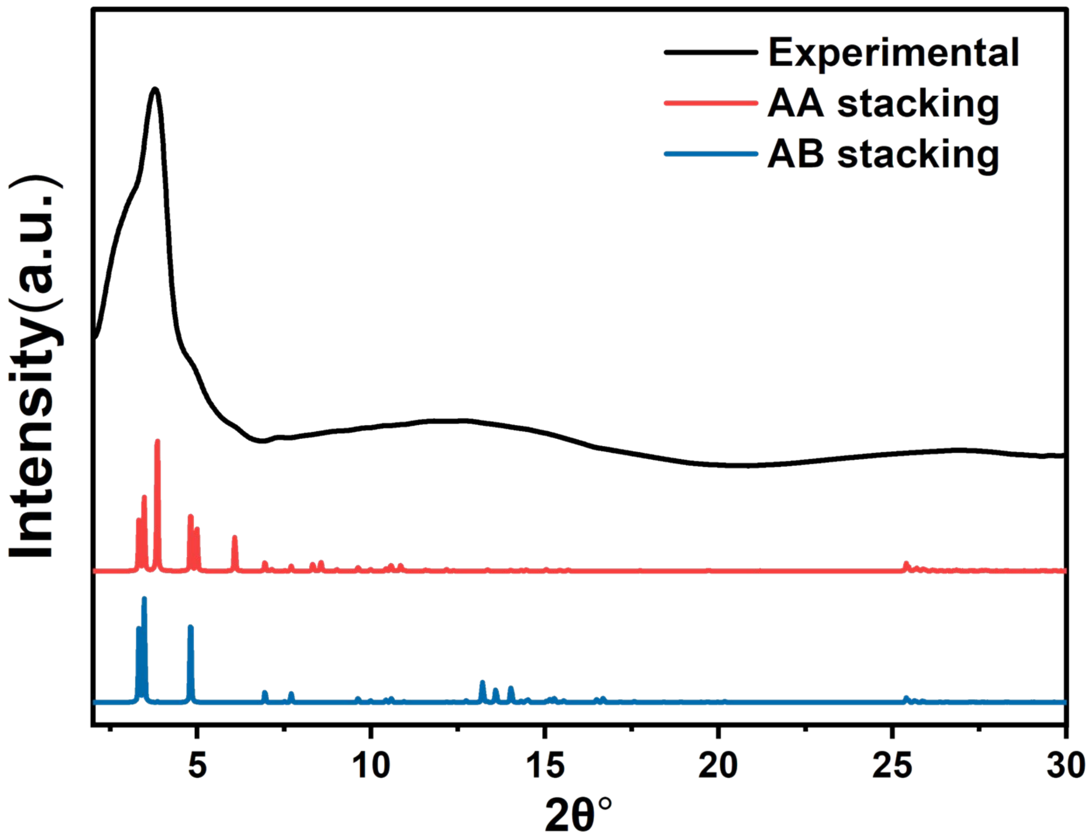


Fig. S6 Simulated PXRD patterns for AA stacking, AB stacking and experimental PXRD patterns of Py-TAPT-COF.

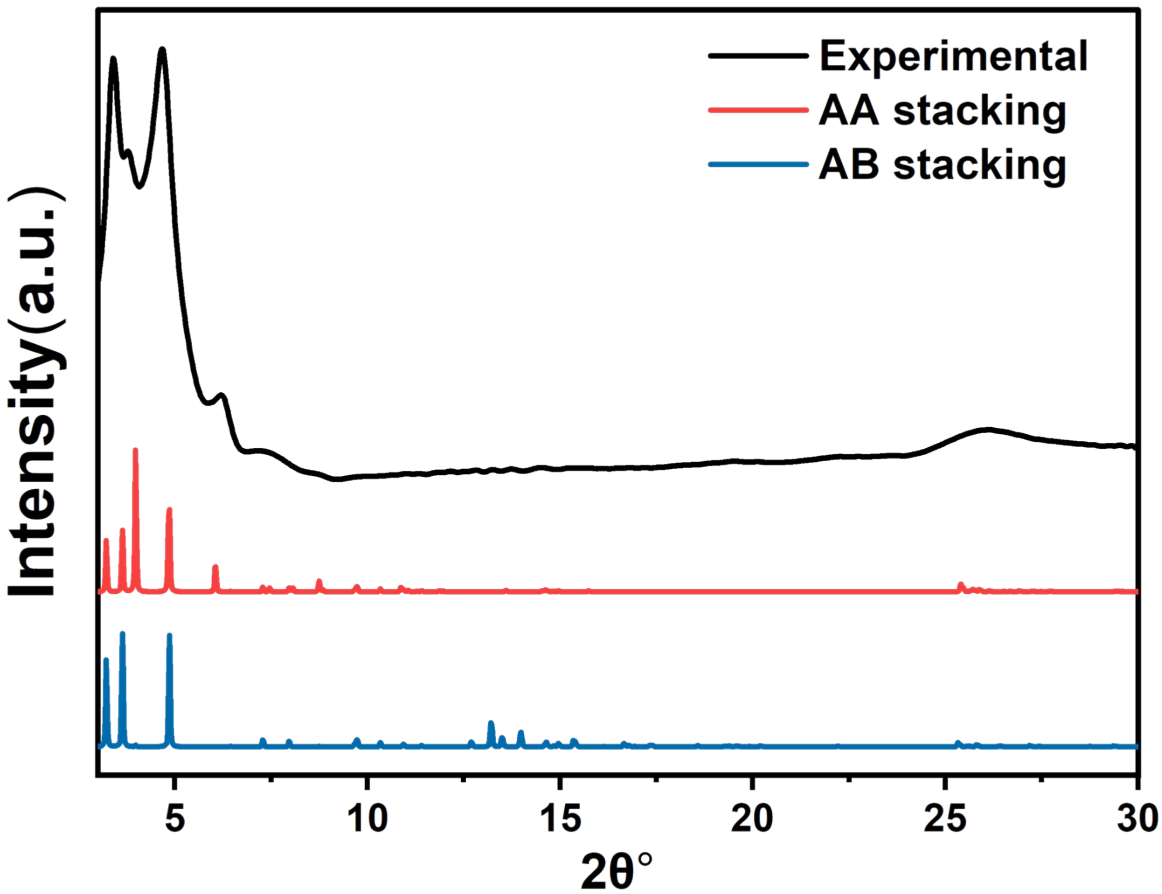


Fig. S7 Simulated PXRD patterns for AA stacking, AB stacking and experimental PXRD patterns of Py-TAPB-COF.

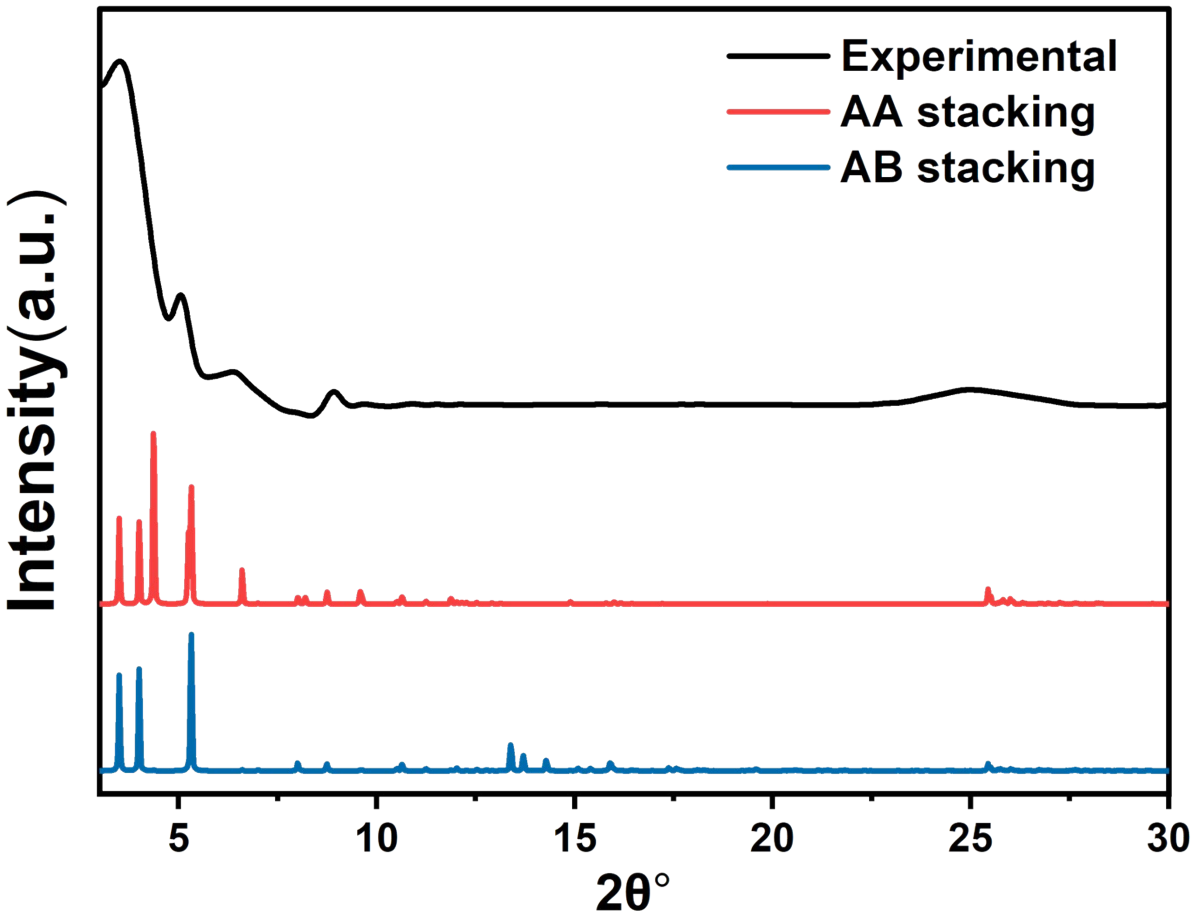


Fig. S8 Simulated PXRD patterns for AA stacking, AB stacking and experimental PXRD patterns of Py-TAPA-COF.

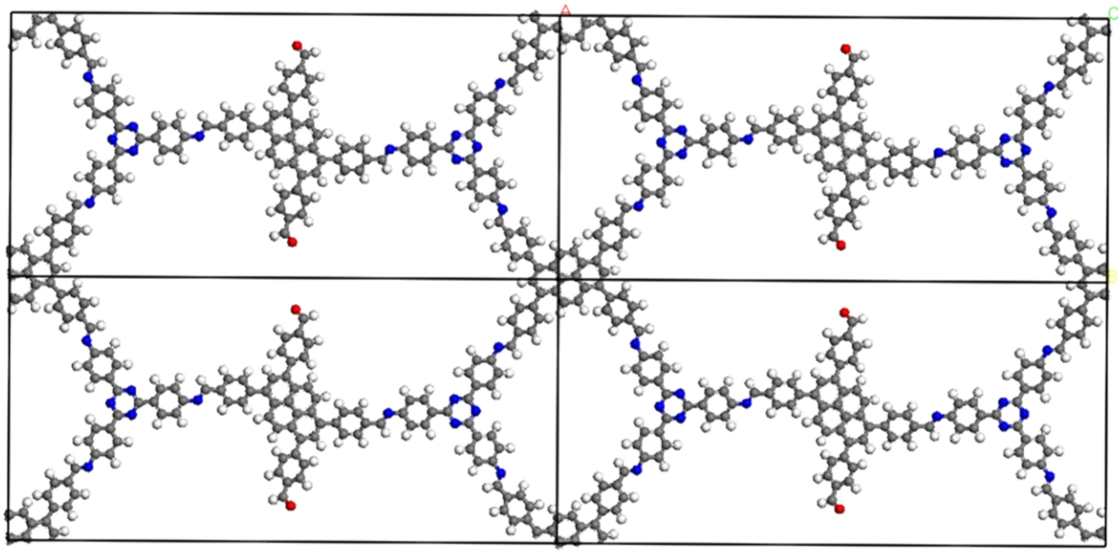


Fig. S9 The AA stacking model of Py-TAPT-COF.

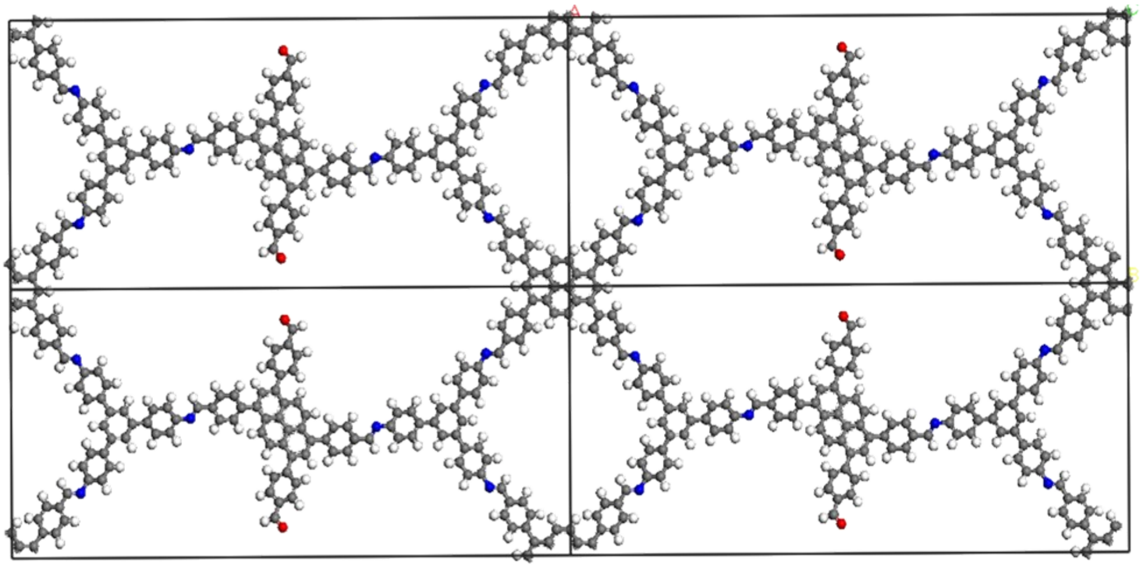


Fig. S10 The AA stacking model of Py-TAPB-COF.

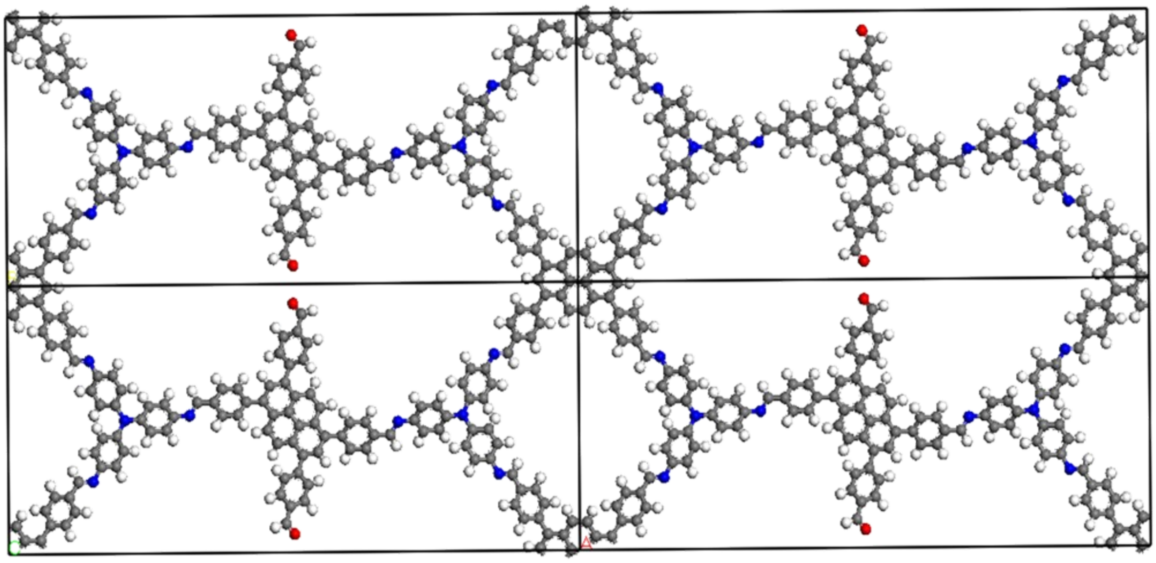


Fig. S11 The AA stacking model of Py-TAPA-COF.

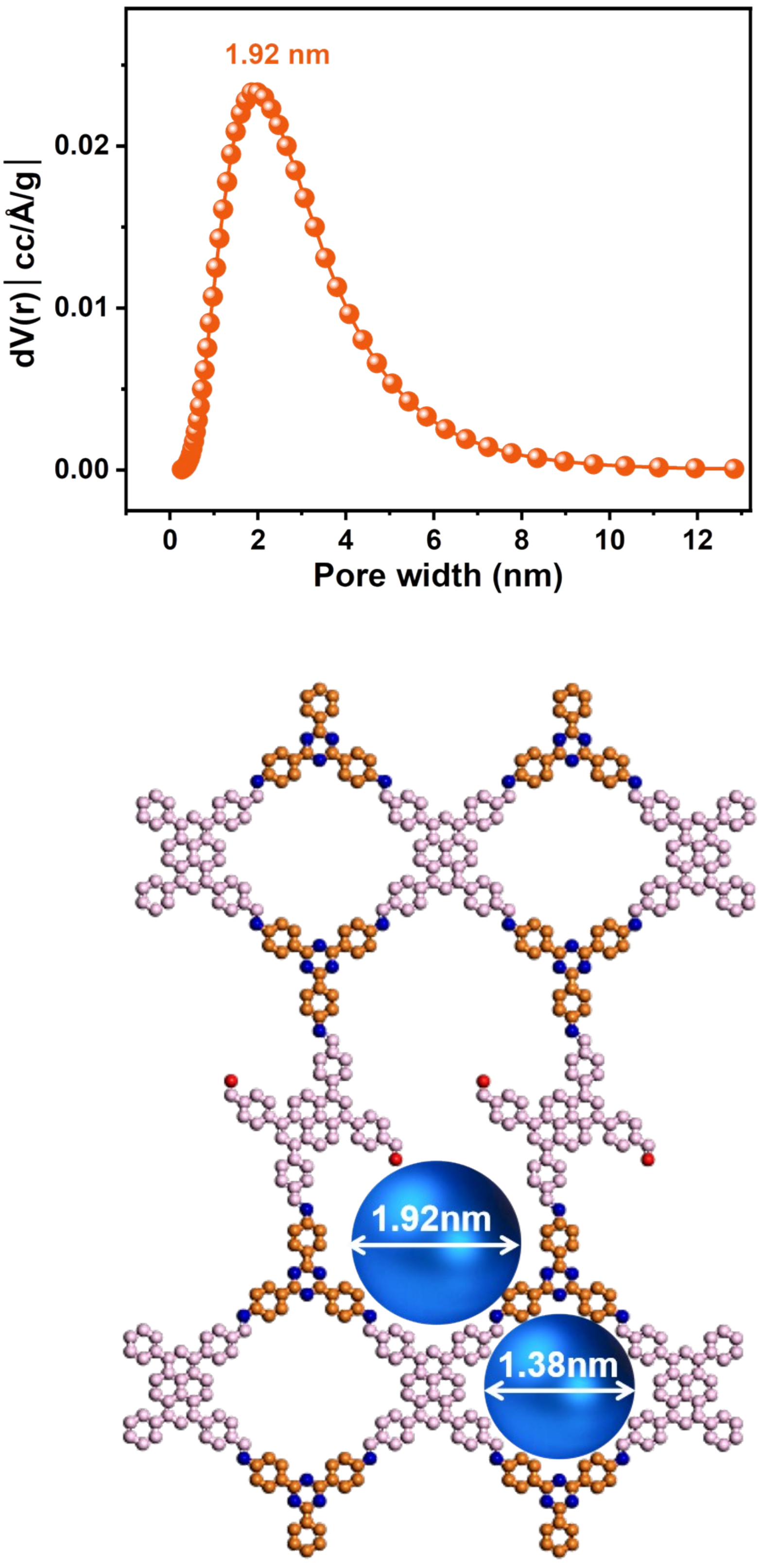
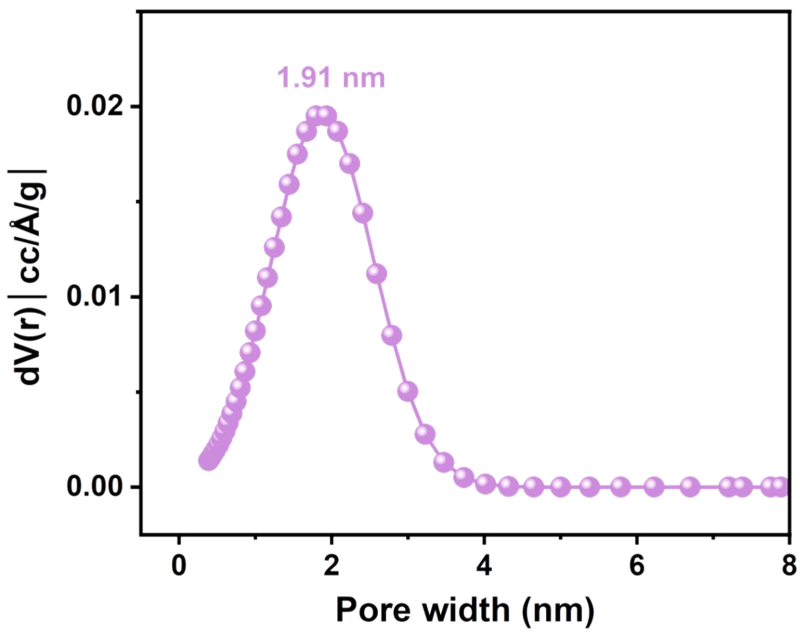


Fig. S12 The micropore sizes of simulated AA stacking model and the experimental micropore sizes of Py-TAPT-COF.



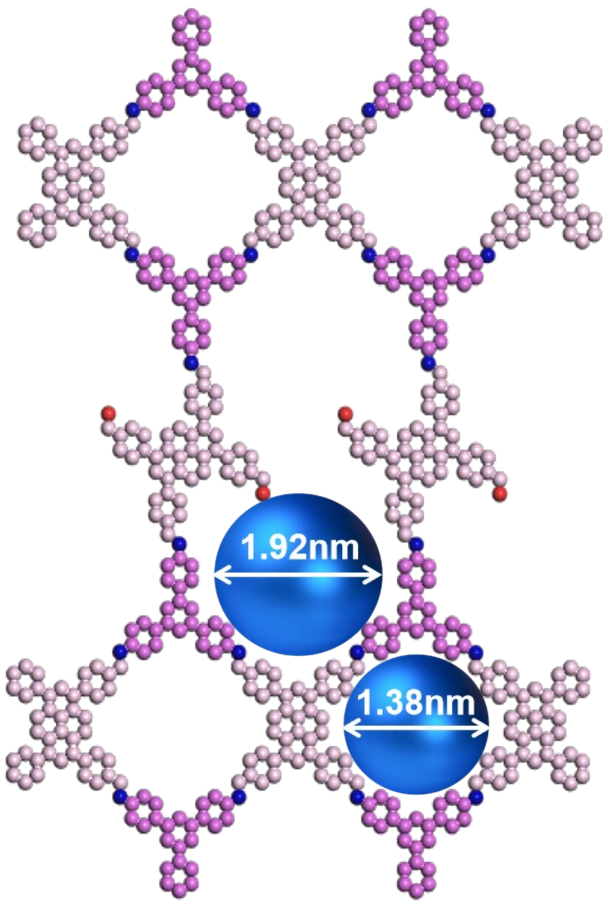


Fig. S13 The micropore sizes of simulated AA stacking model and the experimental micropore sizes of Py-TAPB-COF.

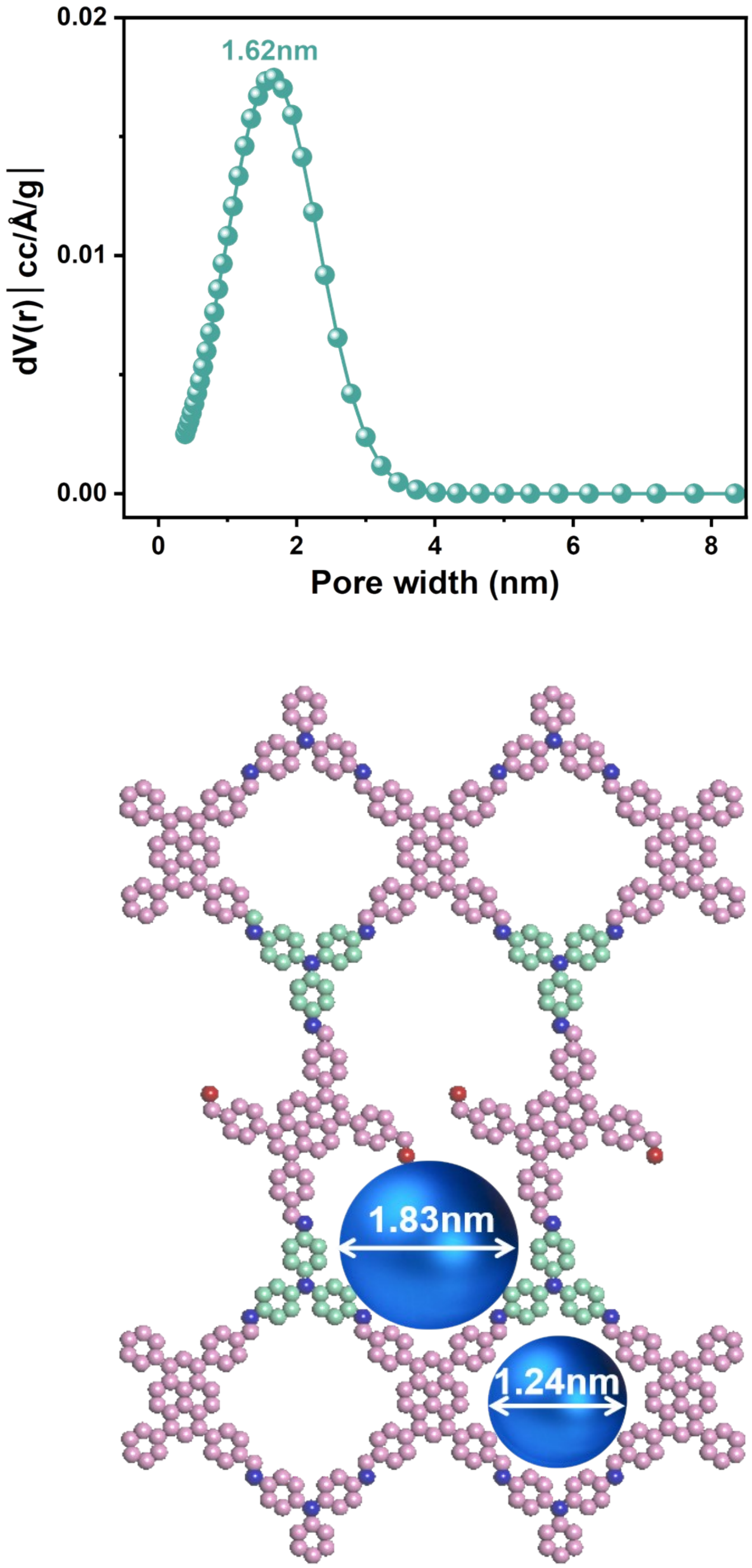


Fig. S14 The micropore sizes of simulated AA stacking model and the experimental micropore sizes of Py-TAPA-COF.

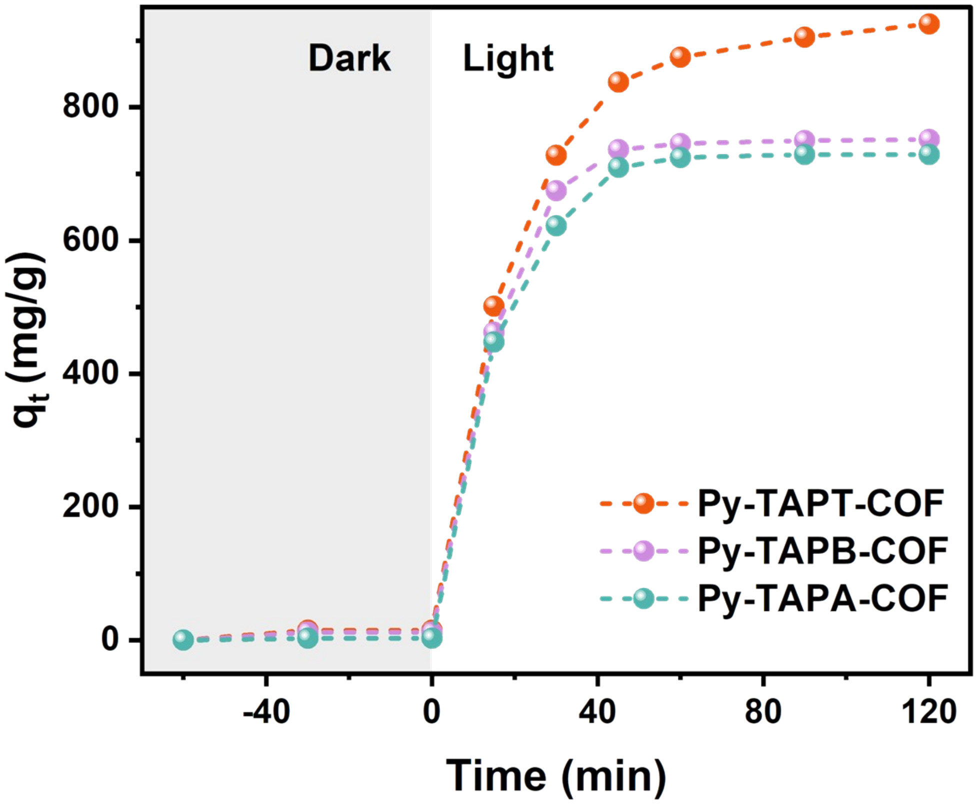


Fig. S15 Uranium extraction capacity via dark adsorption and photocatalysis.

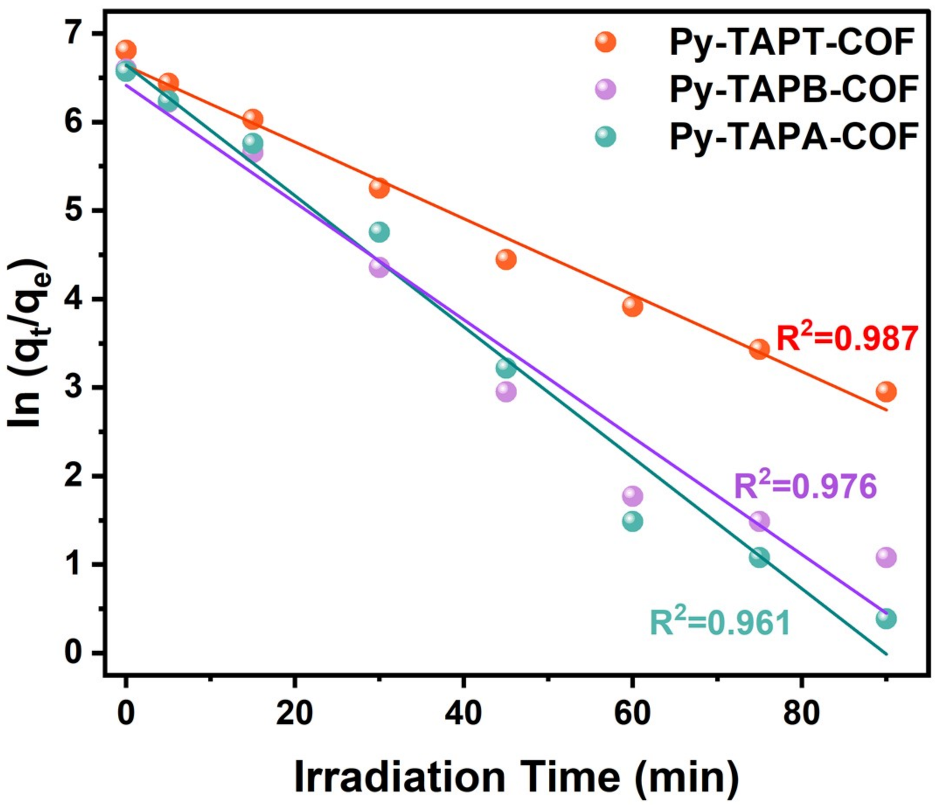


Fig. S16 Pseudo-first-order kinetic fit for the photocatalytic process.

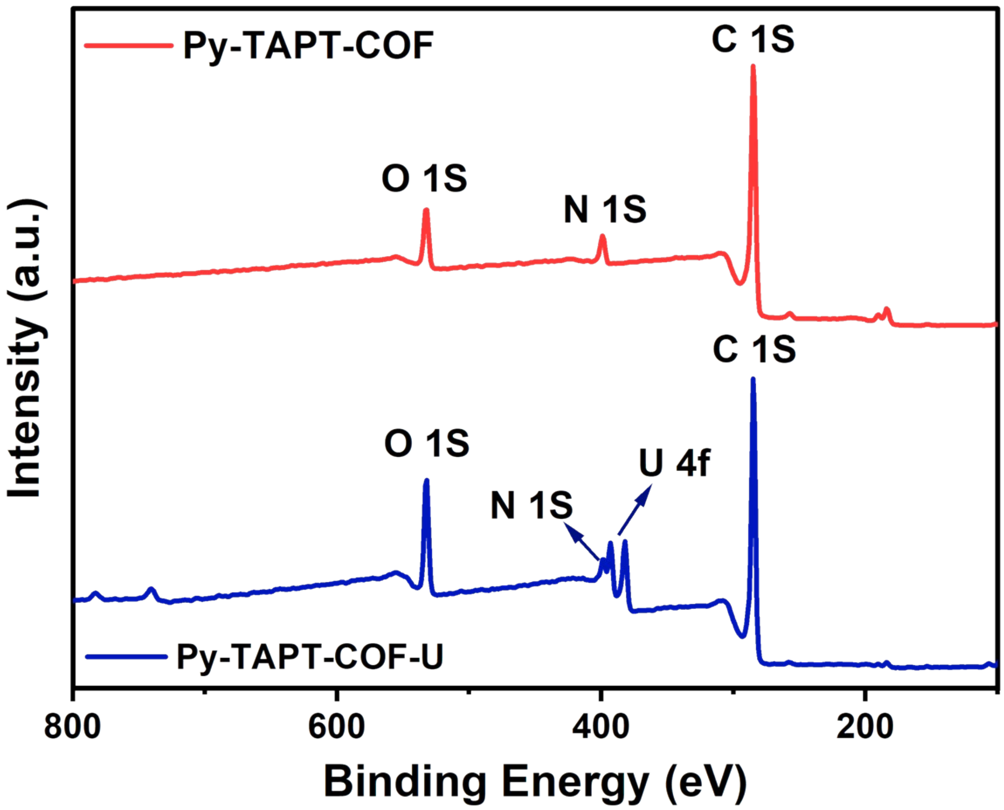


Fig. S17 The XPS spectra of Py-TAPT-COF and Py-TAPT-COF-U.

(a) (b)

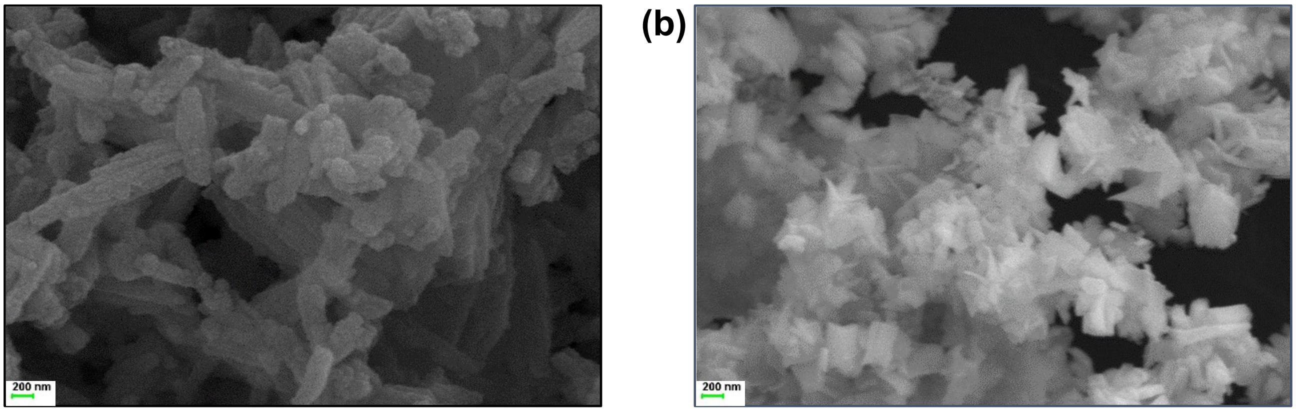


Fig. S18 scanning electron microscopy (SEM) images of the material (a) before and (b) after photocatalytic uranium reduction.

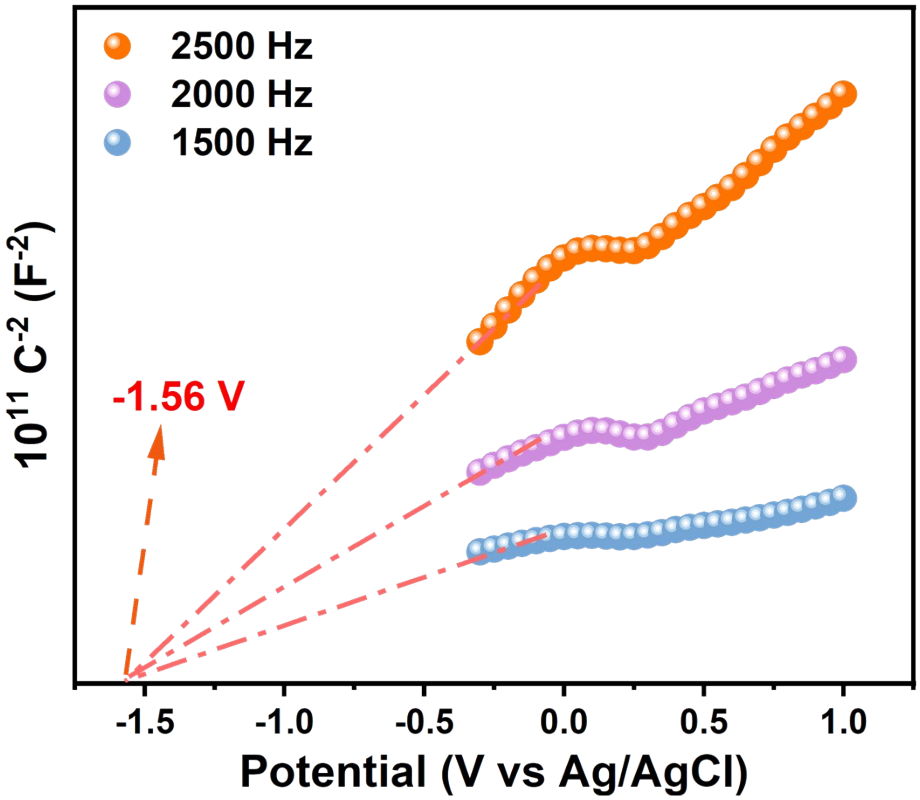


Fig. S19 Mott-Schottky plots of Py-TAPT-COF.

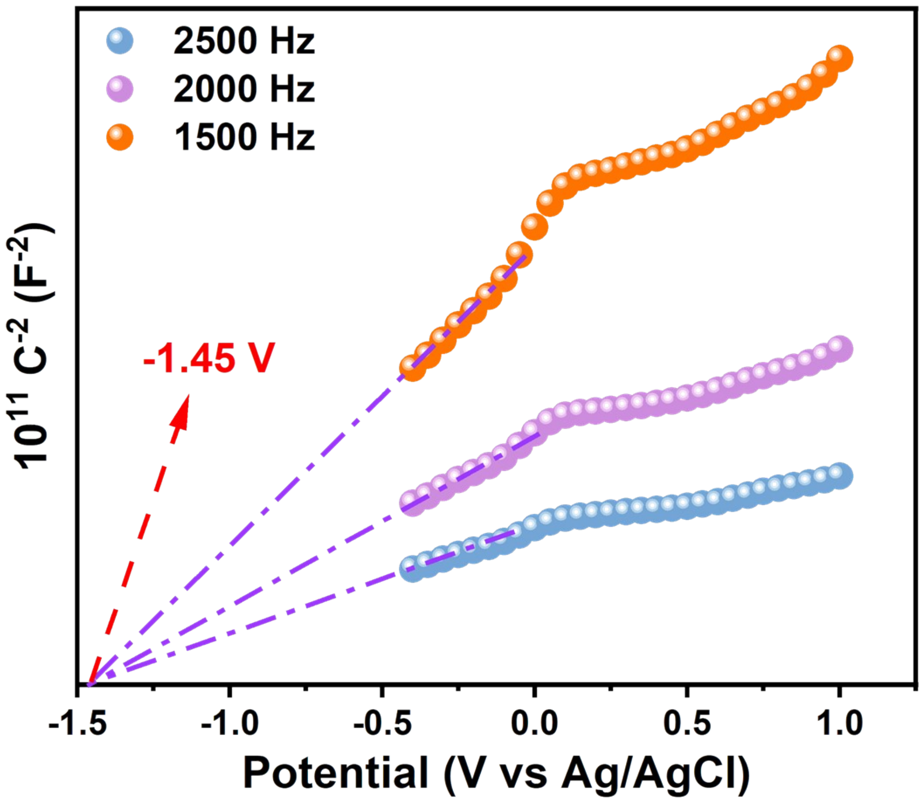


Fig. S20 Mott-Schottky plots of Py-TAPB-COF.

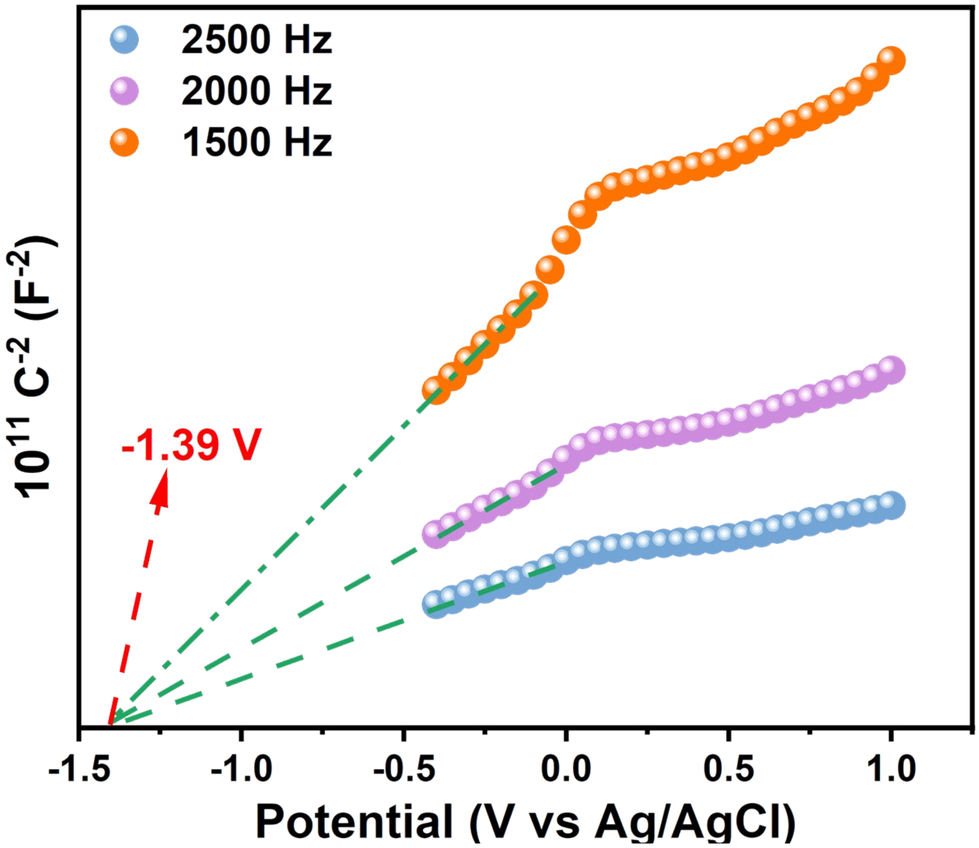


Fig. S21 Mott-Schottky plots of Py-TAPA-COF.

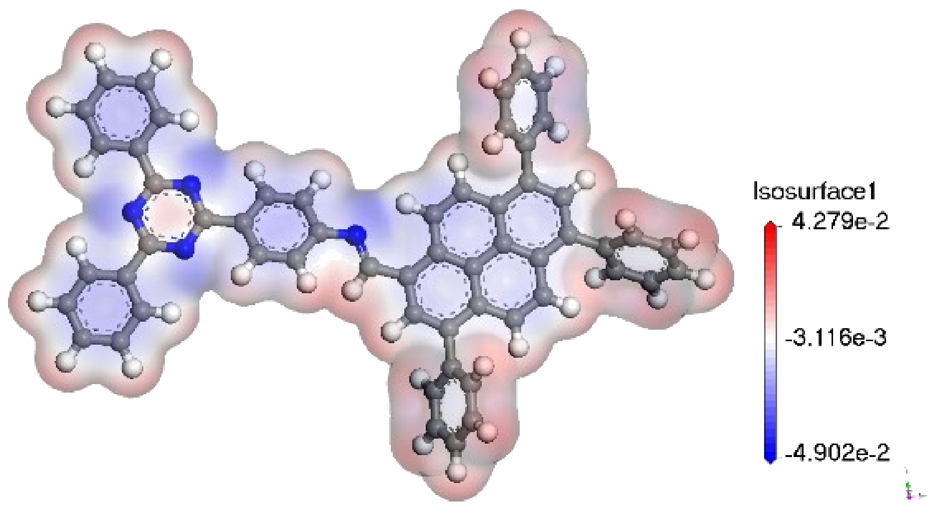


Fig. S22 Electrostatic potential (ESP) calculation of Py-TAPT-COF units:

Supplemental table

Table S1 The unit cell information and CIF atomic coordinates of Py-TAPT-COF.

Space-group	P 1 (1) - triclinic						
Cell	a=53.1100 Å b=25.4426 Å c=3.5042 Å α=90.0000° β=90.0000° γ=90.0000°						
Atom	x	y	z	Atom	z	y	z
C1	0.03658	0.95602	0.64447	C111	0.89096	0.77866	0.46572
C2	0.05479	0.91023	0.67357	C112	0.91581	0.78128	0.33472
C3	0.04939	0.86084	0.50952	C113	0.92872	0.82896	0.32686
C4	0.0664	0.81911	0.53127	C114	0.87804	0.72717	0.46136
C5	0.09032	0.82632	0.69195	C115	0.64175	0.42545	0.66203
C6	0.09654	0.87574	0.84053	C116	0.61396	0.4273	0.68504
C7	0.07889	0.91665	0.83998	C117	0.60095	0.46964	0.84946
C8	0.10888	0.78297	0.7034	C118	0.57453	0.46978	0.86087
C143	-0.00209	0.90328	0.72395	C119	0.56035	0.43019	0.67725
C10	0.11808	0.68992	0.57986	C120	0.5739	0.38742	0.52086
C11	0.10624	0.64146	0.52353	C121	0.60012	0.38544	0.53374
C12	0.12026	0.59517	0.5009	C122	0.53187	0.4306	0.64421
C13	0.14665	0.59641	0.53064	C123	0.51651	0.47576	0.57342
C14	0.15862	0.64517	0.58429	C124	0.49033	0.46943	0.49597
C15	0.14451	0.69158	0.60873	C125	0.48003	0.41817	0.45501
C16	0.16142	0.54704	0.50499	C126	0.49496	0.37334	0.54299
C142	0.97245	0.89594	0.66023	C127	0.51991	0.38144	0.65929
C18	0.16255	0.45429	0.47062	C128	0.52613	0.52707	0.57388
C141	0.04671	1.00675	0.6071	C129	0.51045	0.57052	0.56359
C20	0.20051	0.50287	0.47173	C130	0.48625	0.3171	0.50877
C140	0.00986	0.95067	0.63346	H176	0.525	0.74876	0.19475
C22	0.14878	0.40351	0.46056	H219	0.9654	0.85772	0.7249
C23	0.22846	0.50507	0.45739	H218	0.06682	1.01145	0.62274
C24	0.12238	0.40311	0.42868	H217	0.44532	1.14311	0.54266
C25	0.10904	0.35586	0.42908	H216	0.52154	1.28906	0.26821
C26	0.12175	0.30761	0.46542	H215	0.50942	1.19707	0.24658
C27	0.1481	0.30774	0.48631	H214	0.43648	1.23639	0.70259
C28	0.16154	0.35519	0.48532	H213	0.44898	0.32738	0.75211
C29	0.24295	0.45885	0.44093	H212	0.51939	0.60753	0.61874
C30	0.26928	0.46147	0.42521	H211	0.54583	0.53574	0.58191
C31	0.28166	0.5101	0.42079	H210	0.5307	0.34781	0.75314
C32	0.26722	0.55636	0.44421	H209	0.60965	0.35207	0.40699
C33	0.24097	0.55381	0.46074	H208	0.56433	0.35587	0.37311
C139	-0.00562	0.99447	0.54259	H207	0.56553	0.49999	1.02753
C138	0.00533	1.04525	0.50839	H145	0.03234	0.85418	0.35151
C36	0.04548	1.10429	0.54906	H146	0.06115	0.78178	0.40612
C37	0.07001	1.10879	0.39363	H147	0.11482	0.88229	0.96846
C38	0.08343	1.15618	0.41168	H148	0.08419	0.95286	0.97976
C39	0.07228	1.20118	0.56998	H149	0.12751	0.79074	0.8143

C40	0.04799	1.19728	0.72211	H150	0.08595	0.63963	0.49666
C41	0.03529	1.14927	0.72531	H151	0.11036	0.55846	0.45669
C42	0.08522	1.25261	0.58046	H152	0.17892	0.64751	0.60723
C43	0.32227	0.55065	0.28802	H153	0.15444	0.72831	0.64401
C44	0.35012	0.54866	0.28875	H154	0.11191	0.43942	0.40117
C45	0.36341	0.50623	0.4463	H155	0.08883	0.35739	0.39495
C46	0.38974	0.50713	0.46336	H156	0.15824	0.27098	0.50955
C47	0.40377	0.5487	0.30076	H157	0.18185	0.35402	0.5077
C48	0.39001	0.5903	0.1327	H158	0.23398	0.42063	0.43955
C49	0.36371	0.59081	0.13542	H159	0.28007	0.42541	0.41165
C50	0.4322	0.55211	0.33751	H160	0.27603	0.59461	0.45616
C51	0.44865	0.50794	0.34869	H161	0.2305	0.59026	0.47732
C52	0.47451	0.51457	0.44348	H162	0.0788	1.07603	0.24895
C53	0.48463	0.56593	0.4862	H163	0.10214	1.158	0.28975
C54	0.46864	0.61066	0.44755	H164	0.03916	1.23108	0.85424
C55	0.44286	0.60218	0.38374	H165	0.01777	1.14756	0.87798
C56	0.44038	0.45738	0.25414	H166	0.07488	1.28584	0.693
C57	0.45542	0.41372	0.31398	H167	0.31332	0.58579	0.17892
C58	0.47731	0.6671	0.47232	H168	0.35345	0.47358	0.57477
C59	0.49989	0.68447	0.30246	H169	0.39882	0.47604	0.62007
C60	0.50735	0.73705	0.32401	H170	0.3994	0.62263	-0.00785
C61	0.49151	0.77468	0.48875	H171	0.35395	0.62389	0.00874
C62	0.46838	0.75862	0.64222	H172	0.4307	0.63597	0.37038
C63	0.46163	0.70555	0.64099	H173	0.42221	0.45047	0.12784
C64	0.49926	0.83031	0.49385	H174	0.44724	0.3767	0.24164
C65	0.93098	0.92822	0.43999	H175	0.51155	0.65812	0.13929
C66	0.95697	0.93642	0.5247	H220	0.0079	0.87081	0.84874
C67	0.96775	0.98736	0.48841	H177	0.45582	0.78679	0.77418
C68	0.95197	1.0314	0.41328	H178	0.44421	0.69478	0.78045
C69	0.91653	0.9719	0.33194	H179	0.51751	0.84151	0.38308
C70	-0.01087	1.08754	0.43468	H180	0.89731	0.9653	0.24144
C71	0.96326	1.08127	0.41819	H181	-0.00426	1.12681	0.38861
C137	0.03191	1.0519	0.55268	H182	0.95281	1.11719	0.41234
C73	0.92565	1.02376	0.34197	H183	0.92821	1.12061	-0.05338
C74	0.9063	1.06721	0.29738	H184	0.89924	1.19379	-0.01154
C75	0.9113	1.11515	0.11032	H185	0.84573	1.09462	0.56614
C76	0.89415	1.15687	0.12147	H186	0.87663	1.02471	0.59695
C77	0.87035	1.15022	0.28802	H187	0.83358	1.18567	0.42665
C78	0.86401	1.10091	0.43714	H188	0.87666	0.33956	0.27432
C79	0.88183	1.06046	0.44958	H189	0.85304	0.4211	0.36937
C80	0.85226	1.1942	0.3208	H190	0.78398	0.33176	0.43061
C136	0.46418	1.15418	0.45743	H191	0.80748	0.2511	0.33081
C82	0.8442	0.28898	0.30365	H192	0.85198	0.53984	0.6201
C83	0.85642	0.33772	0.30852	H193	0.87482	0.62214	0.63753
C84	0.84286	0.38424	0.36339	H194	0.80506	0.70801	0.54894
C85	0.81659	0.38302	0.41256	H195	0.78174	0.62463	0.54084

C86	0.80422	0.33416	0.39837	H196	0.72987	0.55747	0.64967
C87	0.81782	0.28761	0.34388	H197	0.68397	0.5518	0.72012
C88	0.80221	0.4323	0.47937	H198	0.68915	0.3826	0.73753
C135	0.50297	1.27847	0.36878	H199	0.73432	0.38794	0.65892
C90	0.80133	0.52461	0.55721	H200	0.88309	0.9072	0.70409
C134	0.49603	1.22554	0.35417	H201	0.86018	0.82399	0.7013
C92	0.76353	0.47577	0.58948	H202	0.9252	0.74632	0.23006
C133	0.47197	1.20976	0.47222	H203	0.94742	0.82839	0.21306
C94	0.81501	0.57547	0.57388	H204	0.88846	0.69392	0.35101
C95	0.73579	0.47314	0.64259	H205	0.65017	0.39029	0.54444
C96	0.8414	0.57612	0.60116	H206	0.61116	0.50156	0.98296
C97	0.85459	0.62358	0.60698	N107	0.65571	0.46568	0.75069
C98	0.84171	0.6718	0.57963	N9	0.1025	0.7361	0.59171
C99	0.81534	0.67134	0.5647	N17	0.14944	0.5	0.49216
C100	0.80207	0.62369	0.56058	N19	0.18817	0.45596	0.46106
C101	0.72114	0.51909	0.66661	N21	0.18697	0.54815	0.49433
C102	0.69493	0.51596	0.7073	N34	0.1085	1.25819	0.47157
C103	0.6828	0.4671	0.72282	N35	0.30877	0.51104	0.40341
C104	0.69753	0.4211	0.71102	N93	0.77686	0.43093	0.52748
C105	0.72365	0.42417	0.66934	N81	0.85932	1.24239	0.25852
C132	0.45512	1.24767	0.60789	N89	0.81429	0.47928	0.49618
C131	0.46234	0.30033	0.63314	N91	0.7759	0.5226	0.60227
C108	0.91762	0.87571	0.46082	N106	0.85481	0.72144	0.57197
C109	0.89255	0.87263	0.59553	O72	0.48536	0.8643	0.61859
C110	0.87934	0.82485	0.59581	O144	0.4787	1.12008	0.35202

Table S2 The unit cell information and CIF atomic coordinates of Py-TAPB-COF.

Space-group	P 1 (1) - triclinic						
Cell	a=54.8644 Å b=24.2670 Å c=3.5143 Å α=90.0000° β=90.0000° γ=90.0000°						
Atom	x	y	z	Atom	z	y	z
C1	0.00059	0.00331	0.52647	C114	0.15471	0.34841	0.42847
C2	0.98705	0.95355	0.53842	C115	0.16414	0.29827	0.56522
C3	0.94998	1.00602	0.43488	C116	0.1882	0.29713	0.70062
C4	0.9612	0.95473	0.48973	C117	0.20215	0.34564	0.71718
C5	0.94496	0.90457	0.48658	C138	0.04026	0.05161	0.53421
C6	0.92101	0.90712	0.63605	C137	0.07733	-0.00095	0.43416
C7	0.90576	0.86075	0.63385	C120	0.12318	0.74942	0.4005
C8	0.91449	0.81027	0.49641	C121	0.10903	0.80071	0.42532
C9	0.93796	0.80762	0.34323	C122	0.12639	0.247	0.52059
C10	0.95248	0.85446	0.32428	C123	0.11249	0.19537	0.49394
C11	0.90028	0.75903	0.51657	C124	0.11853	0.84914	0.58487
C142	0.00215	0.10188	0.60011	C125	0.10405	0.8965	0.60961
C13	0.86232	0.70868	0.53585	C126	0.07997	0.89705	0.46549
C14	0.83832	0.70938	0.67379	C127	0.0713	0.84861	0.29317
C15	0.82454	0.66065	0.69033	C128	0.08528	0.80088	0.28253
C16	0.83452	0.61038	0.5633	C129	0.08912	0.19761	0.33674
C17	0.85803	0.61098	0.40354	C130	0.07477	0.15053	0.31557
C18	0.87168	0.65905	0.38989	C131	0.08233	0.10058	0.4796
C19	0.82109	0.55699	0.58859	C132	0.10624	0.09832	0.63067
C20	0.79556	0.55373	0.56171	C133	0.12134	0.14495	0.63092
C21	0.78382	0.50206	0.53769	C134	0.06491	0.94896	0.48069
C22	0.79826	0.45421	0.51262	C135	0.0661	0.05039	0.48518
C23	0.82351	0.45645	0.56534	C136	0.03911	0.95058	0.53247
C24	0.83442	0.50788	0.62325	H182	0.03613	0.13862	0.67074
C25	0.83873	0.40568	0.55095	H225	0.03312	0.86396	0.66396
C26	0.7567	0.497	0.54694	H224	-0.00884	0.86677	0.68112
C27	0.82953	0.35428	0.66902	H223	0.09642	-0.00191	0.35749
C28	0.8442	0.30717	0.65598	H222	0.13936	0.14226	0.75515
C29	0.86837	0.31038	0.53012	H221	0.11309	0.06102	0.76102
C30	0.87766	0.36189	0.41585	H220	0.05771	0.15393	0.16919
C31	0.86292	0.40849	0.42022	H219	0.08214	0.23578	0.21969
C32	0.74137	0.53992	0.42252	H145	0.93088	1.00689	0.35814
C33	0.71603	0.53454	0.44373	H146	0.9142	0.94453	0.76554
C34	0.70539	0.48616	0.58308	H147	0.88768	0.86372	0.75555
C35	0.72059	0.44294	0.70365	H148	0.94486	0.76934	0.22649
C36	0.74581	0.44868	0.69064	H149	0.9696	0.85078	0.17981
C141	0.02517	0.90337	0.60714	H150	0.91053	0.72104	0.50475
C140	-0.00004	0.90492	0.61406	H151	0.8306	0.74738	0.78094
C39	0.66633	0.44238	0.72997	H152	0.80654	0.66221	0.81503
C40	0.63954	0.44376	0.71042	H153	0.86589	0.57434	0.2781
C41	0.62718	0.489	0.55518	H154	0.88929	0.65694	0.2534

C42	0.60188	0.4882	0.52063	H155	0.78498	0.59121	0.55931
C43	0.58803	0.44341	0.65654	H156	0.78984	0.41502	0.44852
C44	0.6007	0.39875	0.82144	H157	0.85363	0.50988	0.69041
C45	0.6261	0.39867	0.84327	H158	0.81123	0.35048	0.78051
C46	0.90458	0.25636	0.38658	H159	0.83685	0.2681	0.75043
C47	0.91855	0.20483	0.41304	H160	0.89621	0.36731	0.32206
C48	0.9089	0.1566	0.57336	H161	0.87055	0.44665	0.31493
C49	0.92327	0.10907	0.60033	H162	0.74875	0.57726	0.30073
C50	0.94738	0.10813	0.45743	H163	0.70458	0.56797	0.34546
C51	0.95615	0.15633	0.28321	H164	0.71343	0.40478	0.81412
C52	0.94231	0.20423	0.27078	H165	0.75667	0.41535	0.80455
C53	0.561	0.44003	0.58853	H166	0.67477	0.40692	0.86016
C54	0.9624	0.05618	0.47711	H167	0.6371	0.52422	0.44644
C55	0.54503	0.48609	0.60492	H168	0.59343	0.52231	0.3765
C56	0.52061	0.48086	0.47717	H169	0.59107	0.36357	0.93539
C57	0.51176	0.4288	0.35401	H170	0.63525	0.36338	0.96657
C58	0.52687	0.38134	0.37901	H171	0.91312	0.29032	0.24009
C59	0.55128	0.38864	0.48607	H172	0.89054	0.15598	0.68651
C60	0.55245	0.53687	0.75584	H173	0.91558	0.07345	0.74141
C61	0.53725	0.58245	0.75272	H174	0.97362	0.15755	0.14922
C62	0.51375	0.57998	0.5975	H175	0.95002	0.24065	0.13919
C63	0.50495	0.52797	0.47253	H176	0.56311	0.35318	0.48861
C64	0.48055	0.5227	0.34404	H177	0.56987	0.54202	0.89003
C65	0.47321	0.47197	0.19167	H178	0.54411	0.61913	0.88618
C66	0.48831	0.42633	0.19809	H179	0.45586	0.46678	0.05553
C67	0.49853	0.62734	0.57507	H180	0.4814	0.38956	0.06704
C68	0.4741	0.61993	0.46728	H181	0.46218	0.65522	0.46663
C69	0.46448	0.56855	0.36234	H226	-0.00576	0.14139	0.65435
C70	0.50713	0.68537	0.65013	H183	0.54248	0.67681	0.37738
C71	0.43742	0.5647	0.29512	H184	0.55524	0.77125	0.47752
C72	0.51812	0.32327	0.30945	H185	0.48559	0.80854	0.98133
C73	0.9882	0.05457	0.5289	H186	0.47355	0.71283	0.92055
C74	0.02735	0.10033	0.6066	H187	0.43385	0.64496	0.02371
C75	0.53011	0.70393	0.52421	H188	0.38956	0.64365	-0.00621
C76	0.53738	0.75859	0.57559	H189	0.38897	0.48158	0.49547
C77	0.52142	0.79709	0.73587	H190	0.43247	0.48518	0.56942
C78	0.49825	0.77969	0.85418	H191	0.48275	0.33281	0.57992
C79	0.49133	0.72455	0.81616	H192	0.46998	0.23815	0.4968
C80	0.42445	0.60921	0.13382	H193	0.53946	0.19913	-0.00673
C81	0.39901	0.60841	0.1121	H194	0.55157	0.29498	0.03932
C82	0.38593	0.56237	0.23814	H195	0.54736	0.86711	0.69072
C83	0.39863	0.51731	0.38871	H196	0.34977	0.60104	0.16546
C84	0.42386	0.5192	0.42665	H197	0.47793	0.14141	0.30355
C85	0.49512	0.30521	0.43801	H198	0.31651	0.5975	0.5706
C86	0.48782	0.25043	0.39566	H199	0.27313	0.58965	0.66572
C87	0.50374	0.21139	0.2406	H200	0.27494	0.42465	0.19355

C88	0.52685	0.22839	0.11709	H201	0.31909	0.43189	0.13453
C89	0.53382	0.28361	0.14674	H202	0.23663	0.59003	0.40772
C90	0.52919	0.85496	0.77632	H203	0.17433	0.49674	0.75012
C91	0.35912	0.5628	0.22914	H204	0.24144	0.41358	0.52336
C92	0.49601	0.15335	0.21192	H205	0.21679	0.65539	0.77973
C139	0.02671	0.00183	0.5263	H206	0.19117	0.73808	0.75274
C94	0.32091	0.51564	0.33476	H207	0.13071	0.6381	0.37323
C95	0.3075	0.56005	0.4804	H208	0.15627	0.55841	0.36408
C96	0.28243	0.55544	0.53239	H209	0.16058	0.4334	0.32604
C97	0.26991	0.50685	0.43014	H210	0.137	0.35127	0.29631
C98	0.28359	0.46244	0.28397	H211	0.19596	0.25883	0.80197
C99	0.30887	0.46662	0.24387	H212	0.22035	0.34378	0.835
C100	0.24297	0.5028	0.48817	H213	0.11494	0.7155	0.24905
C101	0.22867	0.55104	0.4891	H214	0.11595	0.28461	0.50201
C102	0.20387	0.54933	0.58131	H215	0.13687	0.85008	0.6985
C103	0.19316	0.4983	0.65991	H216	0.11164	0.93234	0.7493
C104	0.20603	0.44896	0.60934	H217	0.05383	0.84709	0.15887
C105	0.23124	0.4515	0.54081	H218	0.07767	0.76426	0.15213
C106	0.18865	0.6	0.57432	N118	0.14468	0.74482	0.55221
C107	0.19221	0.39613	0.59505	N12	0.87661	0.75851	0.541
C108	0.19819	0.65158	0.68065	N37	0.88291	0.26104	0.53182
C109	0.18355	0.69877	0.66871	N38	0.67925	0.48262	0.5924
C110	0.15916	0.69541	0.55379	N93	0.34688	0.51816	0.30033
C111	0.14952	0.64362	0.45396	N119	0.14997	0.24819	0.56045
C112	0.16418	0.59692	0.45805	O143	0.51541	0.8898	0.90323
C113	0.16847	0.39629	0.44431	O144	0.50972	0.11816	0.08822

Table S3 The unit cell information and CIF atomic coordinates of Py-TAPA-COF.

Space-group	P 1 (1) - triclinic						
Cell	a=50.5032 Å b=22.0847 Å c=3.4987 Å α=90.0000° β=90.0000° γ=90.0000°						
Atom	x	y	z	Atom	z	y	z
C1	0.98507	1.00182	0.45127	C106	0.49189	0.52274	0.48696
C2	0.97029	0.94828	0.37527	C107	0.50243	0.58236	0.48119
C3	0.9842	0.8933	0.37858	C108	0.48526	0.63288	0.53306
C4	0.93054	1.00942	0.3064	C109	0.45823	0.62133	0.58753
C5	0.94233	0.95194	0.30547	C110	0.45485	0.45539	0.39321
C6	0.05484	0.94035	0.51854	C111	0.47169	0.40584	0.39577
C7	0.02676	0.94282	0.47181	C112	0.49373	0.69839	0.52939
C8	0.01149	0.89112	0.40005	C113	0.48333	0.27581	0.68323
C9	0.92817	0.11954	0.44	C114	0.47617	0.21471	0.67214
C10	0.93792	0.17498	0.30168	C115	0.4935	0.17148	0.52053
C11	0.92304	0.22771	0.32514	C116	0.51792	0.19051	0.37286
C12	0.89737	0.22644	0.47212	C117	0.52453	0.2519	0.36814
C13	0.88678	0.17133	0.60027	C118	0.48591	0.10702	0.52094
C14	0.9021	0.11853	0.58646	C126	0.06498	0.16206	0.41469
C15	0.88248	0.28351	0.48492	C125	0.08095	0.2133	0.40613
C134	0.15151	0.37616	0.74138	C121	0.07345	0.10775	0.58708
C17	0.84412	0.34234	0.65639	C122	0.09967	0.10659	0.7328
C18	0.85629	0.39902	0.64945	C123	0.11636	0.15711	0.70202
C19	0.84124	0.45173	0.63751	C124	0.10688	0.21118	0.5434
C20	0.81298	0.45149	0.62635	H168	0.80168	0.7218	0.52298
C21	0.80169	0.39285	0.68755	H209	0.53066	0.68775	0.8391
C22	0.81683	0.33986	0.69399	H208	0.13206	0.37528	0.87113
C23	0.76743	0.5023	0.58105	H207	0.15512	0.46785	0.8496
C24	0.75116	0.54359	0.78138	H206	0.22088	0.38137	0.29435
C25	0.72346	0.53954	0.76841	H205	0.19782	0.286	0.33541
C26	0.71118	0.48959	0.59833	H204	0.11257	0.30847	0.45246
C27	0.72708	0.44643	0.41529	H203	0.04619	0.16561	0.27485
C28	0.75429	0.45499	0.39045	H202	0.07326	0.25434	0.27755
C133	0.16524	0.43053	0.73317	H201	0.13627	0.15459	0.81589
C30	0.66938	0.43562	0.53794	H135	0.97486	0.84986	0.37073
C31	0.64026	0.43538	0.54716	H136	0.91003	1.01344	0.2213
C32	0.62584	0.48429	0.69369	H137	0.01987	0.84712	0.35893
C33	0.59822	0.48227	0.70317	H138	0.95714	0.17865	0.17534
C34	0.58414	0.43339	0.54284	H139	0.93155	0.26962	0.22103
C35	0.59902	0.38457	0.39496	H140	0.86692	0.16915	0.7157
C36	0.62662	0.38503	0.40512	H141	0.89359	0.07704	0.69549
C37	0.55431	0.43025	0.53995	H142	0.8916	0.32287	0.35595
C38	0.5371	0.48058	0.48417	H143	0.87761	0.40333	0.6569
C39	0.50928	0.47171	0.48821	H144	0.85331	0.49153	0.64316
C40	0.49874	0.41211	0.47711	H145	0.78112	0.38435	0.72845

C41	0.51585	0.36154	0.53073	H146	0.80708	0.29641	0.72243
C42	0.54283	0.37298	0.59237	H147	0.75945	0.57582	0.97832
C43	0.54641	0.53921	0.40776	H148	0.71163	0.57259	0.92048
C44	0.52955	0.58871	0.40664	H149	0.71875	0.40823	0.26504
C45	0.50734	0.29606	0.52293	H150	0.76506	0.4241	0.21634
C46	0.51764	0.71849	0.69343	H151	0.67918	0.39388	0.46147
C47	0.52487	0.77954	0.68389	H152	0.63588	0.52327	0.8129
C48	0.50769	0.8229	0.53039	H153	0.5882	0.51891	0.8428
C49	0.48333	0.80406	0.37987	H154	0.58941	0.34607	0.26327
C50	0.47666	0.74269	0.3736	H155	0.63736	0.3467	0.28979
C51	0.51537	0.8873	0.53196	H156	0.55544	0.33561	0.67461
C132	0.19047	0.43662	0.56676	H157	0.56674	0.54864	0.34434
C131	0.20182	0.38218	0.42551	H158	0.53848	0.63157	0.34269
C54	0.92409	0.89844	0.23931	H159	0.54354	0.79319	0.8097
C55	0.89769	0.89908	0.3778	H160	0.46971	0.83653	0.25693
C56	0.88118	0.84829	0.34009	H161	0.45821	0.72997	0.23852
C57	0.891	0.79485	0.17635	H162	0.53459	0.9006	0.64026
C58	0.91662	0.79474	0.02547	H163	0.89003	0.93765	0.53297
C59	0.93229	0.84642	0.04144	H164	0.86136	0.84979	0.45749
C60	0.87588	0.7378	0.16607	H165	0.9244	0.75481	-0.11511
C130	0.18854	0.32637	0.4484	H166	0.95069	0.84521	-0.10967
C62	0.83672	0.67772	0.31396	H167	0.88632	0.69886	0.05801
C63	0.81084	0.67885	0.45366	H210	0.47015	0.30646	0.82677
C64	0.79662	0.62482	0.51147	H169	0.77665	0.63216	0.59545
C65	0.80834	0.56675	0.44932	H170	0.84086	0.52957	0.14183
C66	0.83256	0.569	0.25552	H171	0.86596	0.61705	0.06191
C67	0.84699	0.62176	0.19965	H172	0.02273	0.14474	0.78213
C68	0.0133	-0.001	0.50137	H173	0.0899	-0.00674	0.58045
C69	0.02787	0.05252	0.58234	H174	0.97762	0.15025	0.68809
C70	0.0135	0.10477	0.67065	H175	0.04304	0.82933	0.85463
C71	0.06866	-0.00497	0.56318	H176	0.06817	0.73695	0.84591
C72	0.05612	0.05157	0.58624	H177	0.13227	0.82947	0.28158
C73	0.94409	0.06208	0.41383	H178	0.10514	0.91976	0.22562
C74	0.97172	0.058	0.49095	H179	0.10695	0.6786	0.66898
C75	0.98642	0.1077	0.62049	H180	0.1263	0.60575	0.29429
C76	0.07094	0.88273	0.52612	H181	0.15071	0.51582	0.32559
C77	0.0616	0.82995	0.70647	H182	0.21834	0.61624	0.74325
C78	0.07641	0.77688	0.71104	H183	0.19279	0.70629	0.71574
C79	0.10209	0.7761	0.56359	H184	0.24136	0.41436	0.82483
C80	0.11251	0.82905	0.4016	H185	0.28886	0.42132	0.8059
C81	0.09692	0.88123	0.37481	H186	0.28246	0.59285	0.22911
C82	0.11723	0.71937	0.58105	H187	0.23613	0.58268	0.21541
C129	0.16283	0.32349	0.59372	H188	0.32244	0.60348	0.41328
C84	0.15753	0.6629	0.51208	H189	0.36452	0.47256	0.77081
C85	0.1465	0.60795	0.397	H190	0.41226	0.476	0.81883
C86	0.16141	0.55499	0.4062	H191	0.41263	0.64843	0.23374

C87	0.18808	0.5534	0.53252	H192	0.36467	0.64864	0.24025
C88	0.19854	0.61042	0.64693	H193	0.44548	0.65856	0.66828
C89	0.18381	0.66395	0.62877	H194	0.43458	0.44624	0.32279
C90	0.23314	0.49889	0.52872	H195	0.46283	0.36301	0.32908
C91	0.24947	0.45328	0.68811	H196	0.45743	0.20091	0.79497
C92	0.27715	0.45722	0.68002	H197	0.53166	0.15812	0.25185
C93	0.28964	0.50837	0.5311	H198	0.54306	0.26478	0.2361
C94	0.27395	0.55364	0.36623	H199	0.46668	0.09351	0.62764
C95	0.24654	0.54771	0.35687	H200	0.10737	0.06742	0.88049
C127	0.1228	0.26689	0.52596	N16	0.85899	0.28702	0.63399
C97	0.33187	0.56102	0.48354	N29	0.68282	0.48434	0.61536
C98	0.36097	0.5603	0.50015	N96	0.31804	0.51249	0.54952
C99	0.37494	0.51114	0.65324	N53	0.79648	0.50756	0.56589
C100	0.40255	0.51263	0.67336	N61	0.85172	0.73331	0.29309
C101	0.41705	0.56123	0.51724	N83	0.14244	0.71787	0.50962
C102	0.40263	0.61018	0.36212	N128	0.1482	0.26765	0.58736
C103	0.37503	0.61022	0.36131	N120	0.20387	0.49629	0.54213
C104	0.44684	0.56418	0.52735	O119	0.50102	0.06821	0.4039
C105	0.46409	0.5139	0.47448	O52	0.50035	0.92625	0.41456

Table S4 Kinetic parameters of pseudo-first-order and pseudo-second-order models for U(Ⅳ) removal upon three COFs

PFO model

$$\ln\left(q_e - q_t\right) = \ln\left(q_e\right) - \left(\frac{k_1}{2.303} * t\right)$$

q_e: removal capacities at equilibrium (mg g^{-1});

q_t: removal capacities at time t (mg g^{-1}); k_1: pseudo-first-order rate constant for the kinetic model (mg g^{-1} min);

PSO model

$$\frac{t}{q_t} = \frac{1}{{q_e}^2 * k_2} + \frac{1}{q_e} * t$$

k_2: pseudo-second-order rate constant of adsorption (mg g^{-1} min);

Adsorbent		pseudo-first-order			pseudo-second-order		
	$q_{e,\,exp}$ (mg·g^{-1})	$q_{e,cal}$ (mg·g^{-1})	k_1 (min^{-1})	R^2	$q_{e,\,cal}$ (mg·g^{-1})	k_2 (g·mg^{-1}·min^{-1})	R^2
Py-TAPT-COF	905.882	762.506	0.09954	0.987	1016.850	0.000075735	0.998
Py-TAPB-COF	732.353	768.715	0.17038	0.976	806.452	0.00013176	0.995
Py-TAPA-COF	713.235	611.687	0.15269	0.961	806.152	0.00010389	0.993