Dual-Functional Two-Dimensional Covalent Organic Frameworks for Water Sensing and Harvesting

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Contents

1. Instruments and methods

The solid-state ^{13}C cross-polarization/magic-angle spinning (CP/MAS) NMR spectra were obtained using a Bruker AVANCE III 400 WB spectrometer. Powder X-ray diffraction data were recorded by a Rigaku 2550 diffractometer with Cu·Kα radiation (λ = 1.5418 Å) at 298K (scan range: 2-40°). Fourier transform infrared (FTIR) spectra were recorded on a Vertex 80V spectrometer (Germany). TGA was carried out using a TA Q500 thermogravimeter from room temperature to 800 °C under an air atmosphere at the heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Elemental analyses were performed using a Vario Micro (Elementar) spectrometer. Scanning electron microscope (SEM) images were recorded on scanning electron microscopy, JEOL JSM 6700F (Japan). Transmission electron microscope (TEM) images were recorded on a JEM-2100F instrument with an accelerating voltage of 200 kV. The sample was prepared by placing a drop of the stock solution on a 300-mesh, carbon coated copper grid and air-dried before measurement. UV-Vis spectra were recorded with a Shimadzu UV-2550 spectrophotometer (Japan). Fluorescence spectroscopy was taken with a Shimadzu RF-5301 PC spectrometer. The gas adsorption–desorption measurements at different temperatures were carried out using the Micromeritics ASAP 2020 instrument. The samples were degassed at 120 °C under vacuum for 10 h. Water adsorption was carried out by using IGAsorp dynamic moisture sorption analyzer (DVS) of Hiden company.

2. Supplementary Figures and Tables

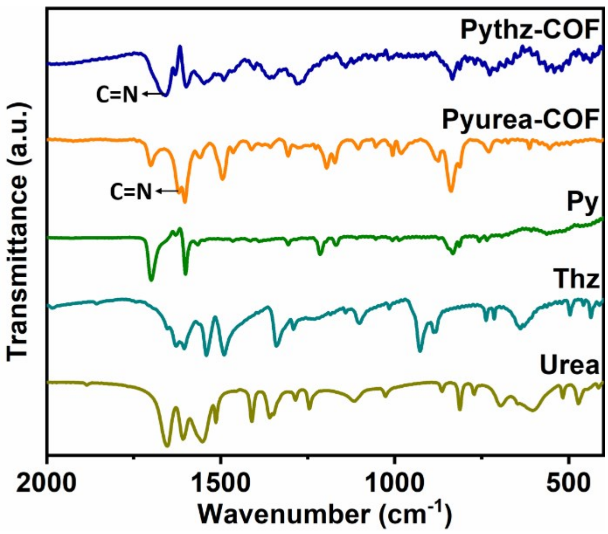

Figure S1. FTIR spectra of Py, Thz, Urea, Pythz-COF and Pyurea-COF.

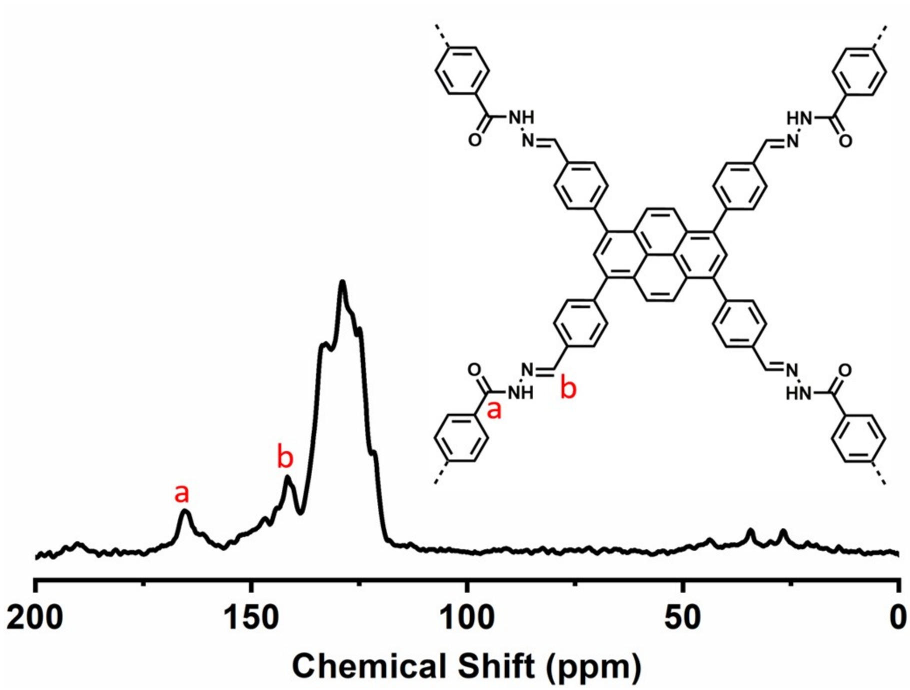

Figure S2. Solid-state ^{13}C CP/MAS NMR spectrum of Pythz-COF.

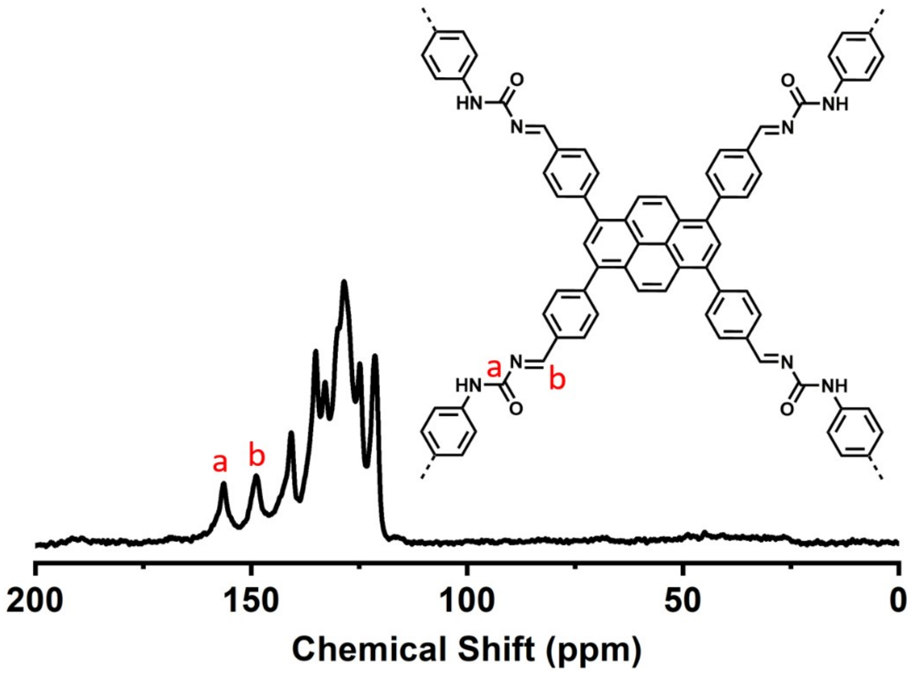

Figure S3. Solid-state ^{13}C CP/MAS NMR spectrum of Pyurea-COF.

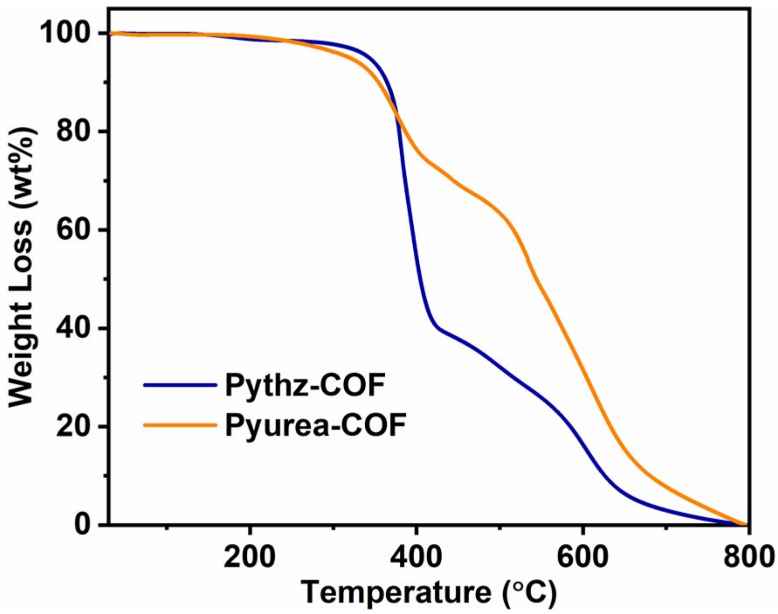

Figure S4. TGA profiles of Pythz-COF and Pyurea-COF.

Table S1. Atomic coordinates for the unit cell of Pythz-COF with AA-stacking.

Sample Name: Pythz-COF				
Space Group: CMM2 (orthorhombic)				
a = 38.4962, b = 42.6997, c = 3.7970; $\alpha = \beta = \gamma = 90^o$				
R_p= 5.63%, R_{wp}= 7.78%				
Atom	Type	x/a	y/b	z/c
C1	C	0.51803	0.44357	0.06609
C2	C	0.53696	0.47117	0.0068
C3	C	0.42626	0.47126	-0.02667
C4	C	0.40379	0.44269	-0.04239
C5	C	0.4137	0.41572	-0.22985
C6	C	0.39225	0.38935	-0.23998
C7	C	0.35969	0.38973	-0.07536
C8	C	0.34882	0.41705	0.09824
C9	C	0.37064	0.44315	0.11534
C10	C	0.33748	0.36162	-0.09007
C11	C	0.72698	0.72392	0.07244
C12	C	0.71423	0.7548	0.06881
C13	C	0.73676	0.78044	0.06496
C14	C	0.70193	0.69715	0.07694
N15	N	0.69038	0.64041	0.10206
O16	O	0.17094	0.20292	0.05824
N17	N	0.21277	0.16654	0.1129
H18	H	0.53058	0.42154	0.11938
H19	H	0.43777	0.41504	-0.37476
H20	H	0.40085	0.36879	-0.38262

H21	H	0.32368	0.41816	0.22539
H22	H	0.36175	0.46359	0.25822
H23	H	0.3447	0.34289	-0.26736
H24	H	0.68655	0.75932	0.06722
H25	H	0.72516	0.8034	0.0529
H26	H	0.23817	0.1618	0.18969
C27	C	0.48148	0.5	0.00127
C28	C	0.40923	0.5	-0.04677

Table S2. Atomic coordinates for the unit cell of Pyurea-COF with AA-stacking.

Sample Name: Pyurea-COF				
Space Group: P-1 (triclinic)				
a = b = 24.1230, c = 4.6602; α = 87.8411º, β = 92.7384º, γ = 97.5733º				
R_p= 6.27%, R_{wp}= 8.16%				
Atom	Type	x/a	y/b	z/c
C1	C	-0.18069	-0.34077	1.38504
N2	N	-0.07696	-0.42545	1.59415
C3	C	-0.03869	-0.46199	1.54398
C4	C	-0.03969	0.48784	1.70372
C5	C	0.002	-0.45055	1.33972
C6	C	0.66212	0.21187	1.47261
N7	N	0.59008	0.0798	1.34127
C8	C	0.54556	0.03947	1.4201
C9	C	0.55125	0.00104	1.6469
C10	C	0.4936	0.03765	1.27412
C11	C	0.37521	-0.2544	1.55651
C12	C	0.42172	-0.25027	1.75355
C13	C	0.3662	-0.30139	1.3828
C14	C	0.45775	-0.28989	1.77541
C15	C	0.4018	-0.34147	1.39782
C16	C	0.44967	-0.33743	1.59591
C17	C	0.48887	-0.37628	1.59943
C18	C	0.47161	-0.43524	1.59137
C19	C	0.54628	-0.35708	1.59058
C20	C	0.50931	-0.47183	1.52012
C21	C	0.41623	-0.458	1.65131
C22	C	0.58597	-0.39318	1.54449
C23	C	0.56591	-0.45073	1.48768
C24	C	0.39792	-0.51328	1.61097
C25	C	0.64334	-0.37272	1.54032
C26	C	0.68368	-0.3983	1.71918
C27	C	0.66541	-0.33108	1.3313
C28	C	0.73984	-0.38749	1.67148

C29	C	0.72195	-0.32128	1.28924
C30	C	0.76064	-0.3498	1.45181
O31	O	-0.09595	-0.39191	1.13678
O32	O	0.60299	0.12223	1.77609
N33	N	-0.14643	-0.37065	1.5219
C34	C	-0.1046	-0.39513	1.3923
N35	N	0.64469	0.16374	1.36449
C36	C	0.61238	0.12145	1.52178
H37	H	-0.16452	-0.30807	1.21553
H38	H	-0.0879	-0.41845	1.81742
H39	H	-0.07198	0.47673	1.87442
H40	H	0.00471	-0.40994	1.20482
H41	H	0.70531	0.21949	1.58531
H42	H	0.60827	0.07858	1.12761
H43	H	0.59321	0.00112	1.77038
H44	H	0.48746	0.06828	1.08656
H45	H	0.43029	-0.21316	1.90089
H46	H	0.32855	-0.30696	1.2243
H47	H	0.49474	-0.28522	1.93817
H48	H	0.39368	-0.37879	1.25172
H49	H	0.56197	-0.31092	1.62128
H50	H	0.38624	-0.43014	1.7344
H51	H	0.35291	-0.53093	1.65704
H52	H	0.66923	-0.42813	1.90433
H53	H	0.63593	-0.30589	1.19889
H54	H	0.77105	-0.40925	1.8115
H55	H	0.73878	-0.2892	1.11833

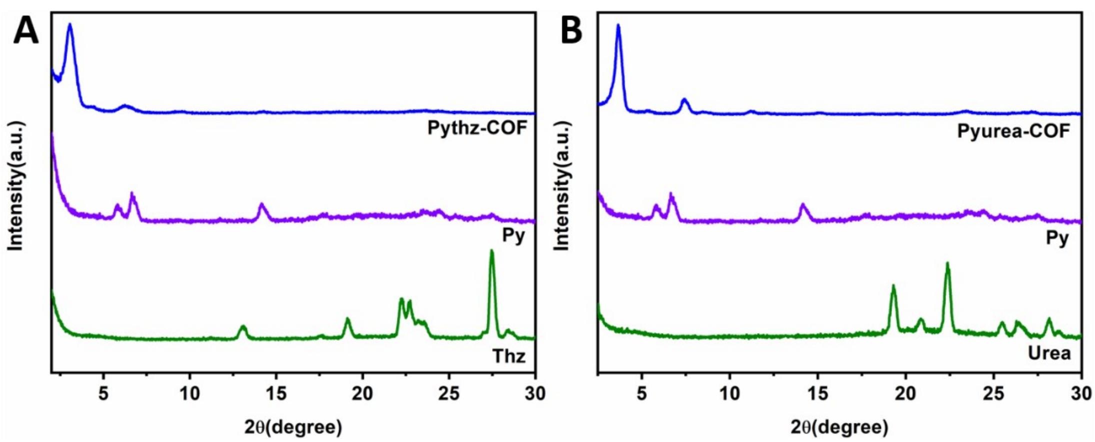

Figure S5. A) PXRD patterns of Pythz-COF, Py and Thz. B) PXRD patterns of Pyurea-COF, Py and Urea.

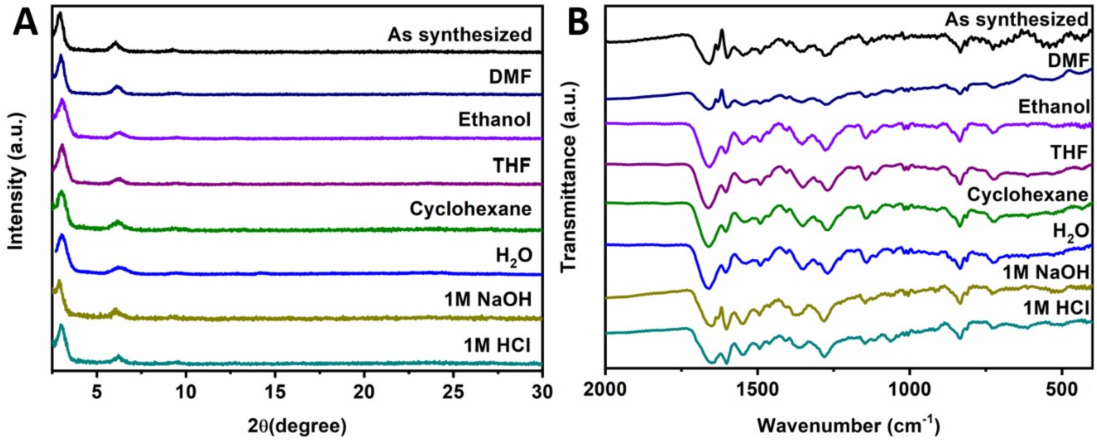

Figure S6. A) PXRD patterns and B) FT-IR spectra of Pythz-COF upon treatment in different solvents.

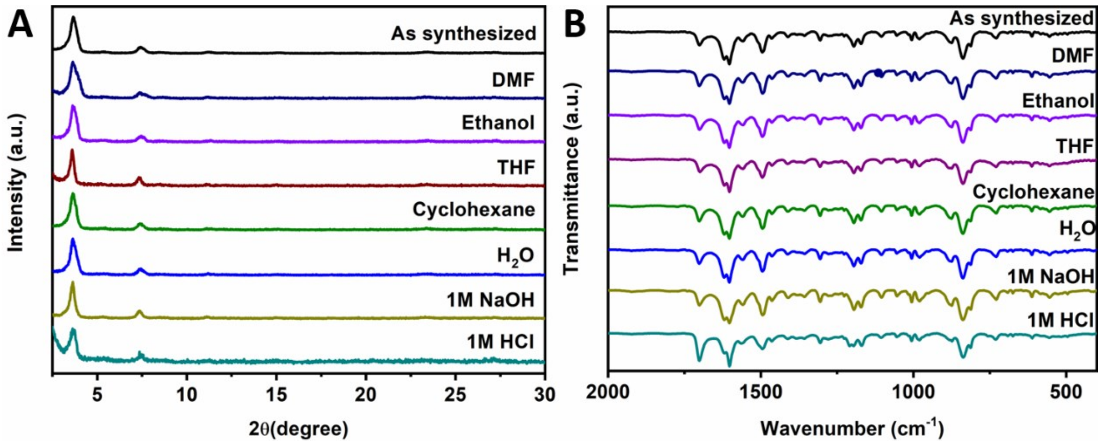

Figure S7. A) PXRD patterns and B) FT-IR spectra of Pyurea-COF upon treatment in different solvents.

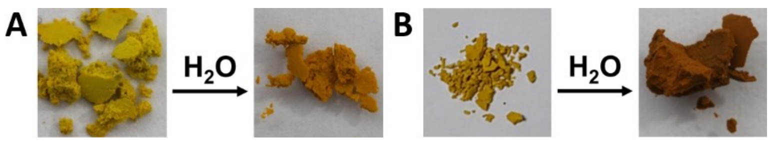

Figure S8. A) Photographs of the dry and wet Pythz-COF. B) Photographs of the dry and wet Pyurea-COF.

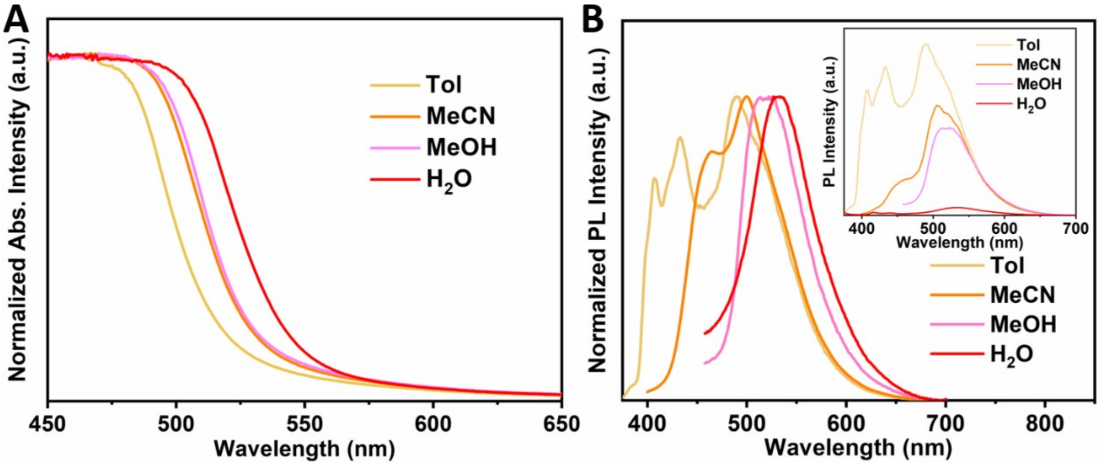

Figure S9. A) Solid-state UV-Vis absorption spectra of Pythz-COF soaked by various polarity solvents. B) PL spectra of Pythz-COF in various polarity solvents (0.1mg/ml).

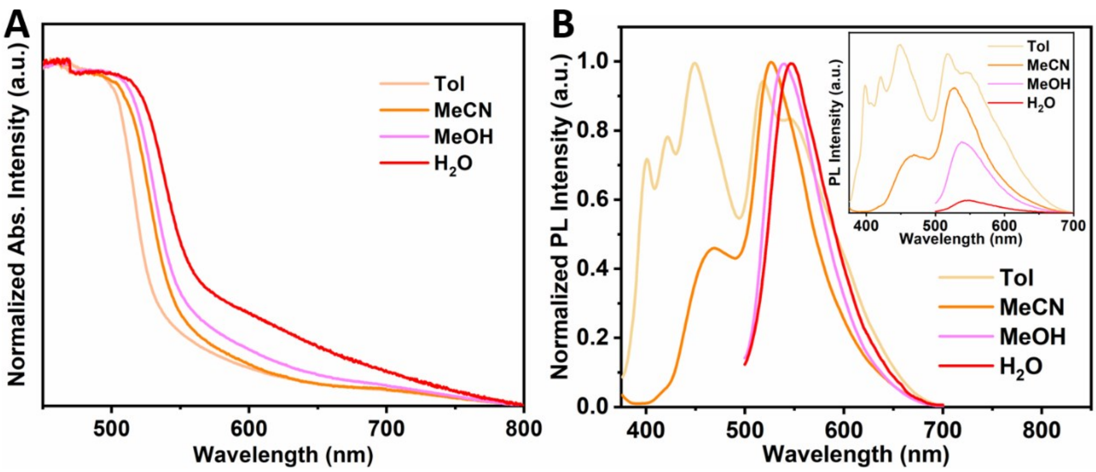

Figure S10. A) Solid-state UV-Vis absorption spectra of Pyurea-COF soaked by various polarity solvents. B) PL spectra of Pyurea-COF in various polarity solvents (0.1mg/ml).

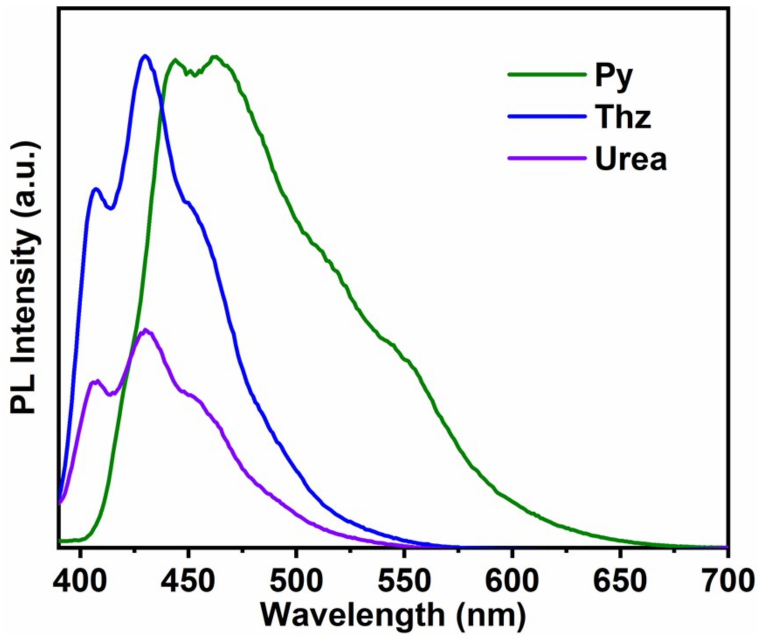

Figure S11. The PL spectra of the monomers (Py, Thz and Urea) in acetonitrile (10^{-5} mol/L).

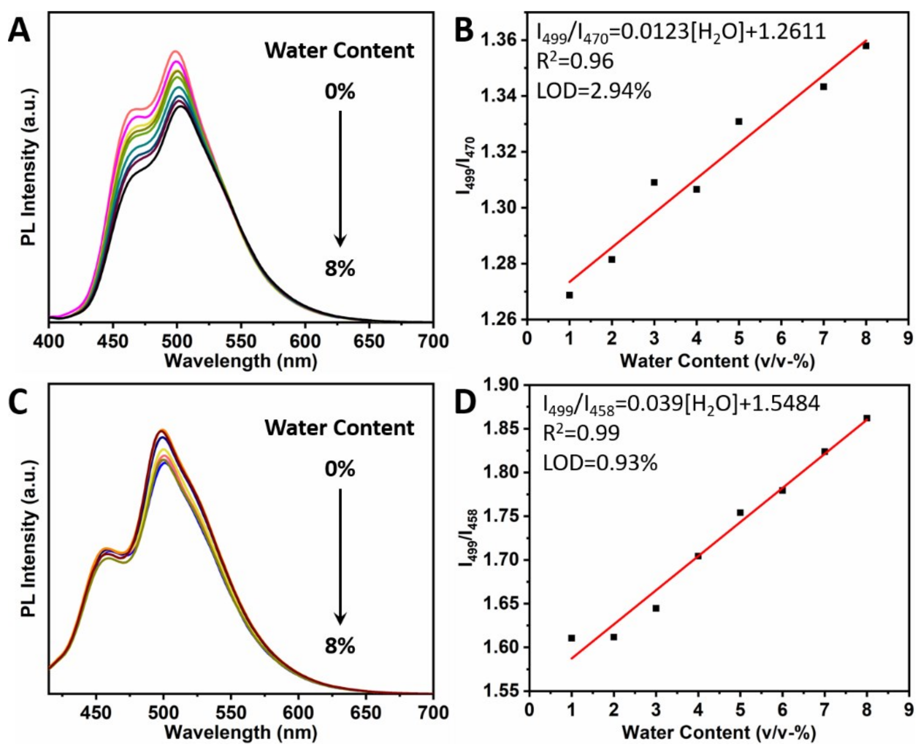

Figure S12. A) PL spectra of Pythz-COF in N,N-Dimethylformamide with trace content of water. B) The linear correlation between the fluorescence of Pythz-COF and different water contents in N,N-Dimethylformamide. C) PL spectra of Pythz-COF in tetrahydrofuran with trace content of water. D) The linear correlation between the fluorescence of Pythz-COF and different water contents in tetrahydrofuran.

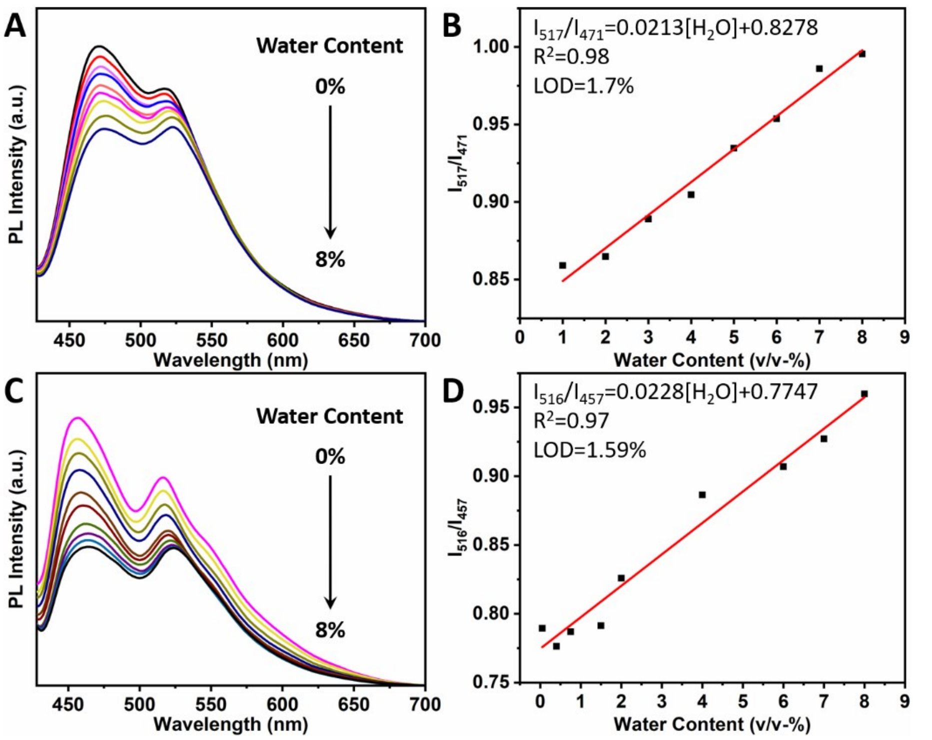

Figure S13. A) PL spectra of Pyurea-COF in N,N-Dimethylformamide with trace content of water. B) The linear correlation between the fluorescence of Pyurea-COF and different water contents in N,N-Dimethylformamide. C) PL spectra of Pyurea-COF in tetrahydrofuran with trace content of water. D) The linear correlation between the fluorescence of Pyurea-COF and different water contents in tetrahydrofuran.

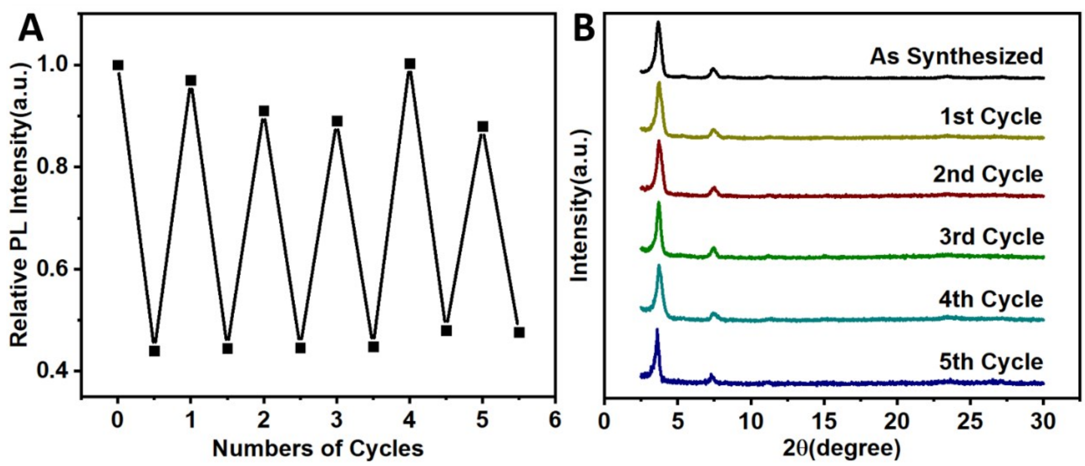

Figure S14. A) Reversible switching of relative PL intensity of Pyurea-COF with or without being added water (7%), em: 527nm. B) PXRD patterns of Pyurea-COF after different cycles of trace water sensing (7%).

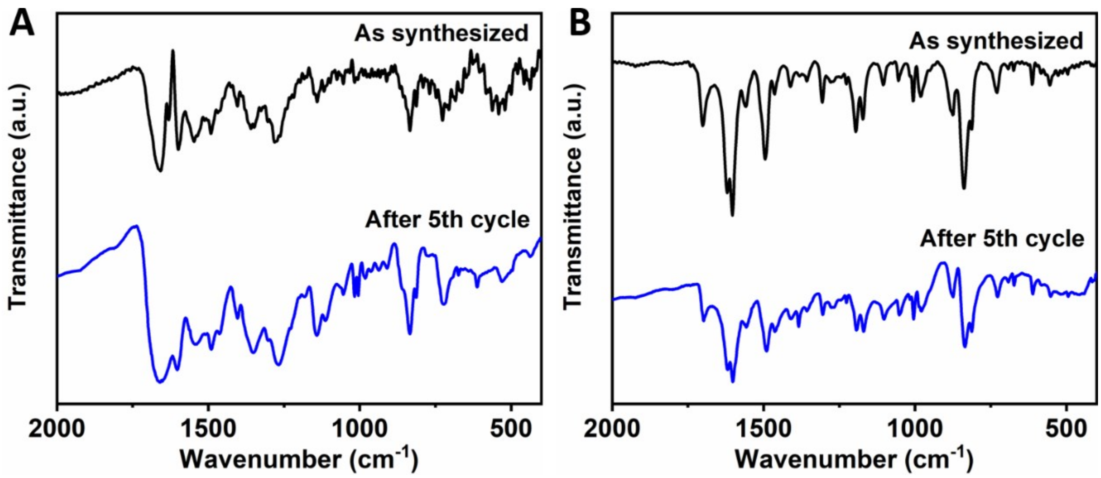

Figure S15. FTIR spectra of A) Pythz-COF and B) Pyurea-COF before and after 5 cycles of trace water sensing.

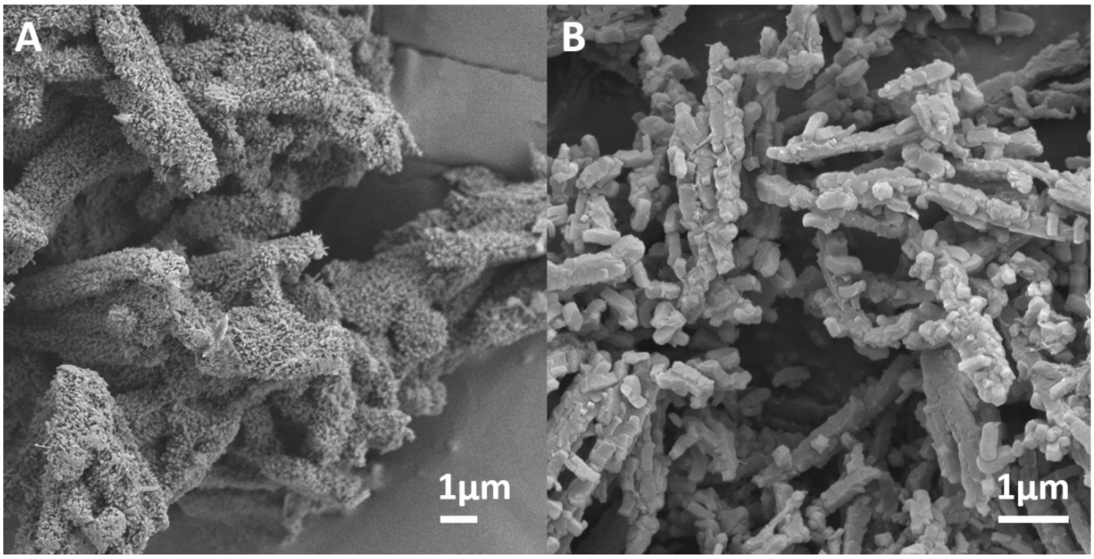

Figure S16. SEM images of A) Pythz-COF and B) Pyurea-COF after 5 cycles of trace water sensing.

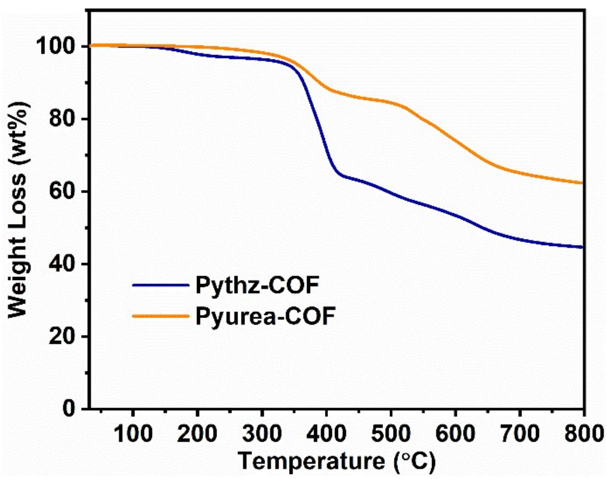

Figure S17. TGA profiles of Pythz-COF and Pyurea-COF after 5 cycles of trace water sensing.

Table S3. Comparison of the sensing performance of various materials toward water.

Materials	Type	Solvents	LOD	Ref.
Pythz-COF Pyurea-COF	COF	acetonitrile	0.09 (v/v-%) 0.02 (v/v-%)	This work
COFs	COF	methanol	0.042 (v/v-%)	1
TzDa	COF	EtAC	0.006 (wt-%)	2
COF-4-OH	COF	ethanol	0.03 (v/v-%)	3
TAPT-BMTA-COF	COF	acetonitrile	0.12 (v/v-%)	4
$Tb_{97.11}Eu_{2.89}$-L1	MOF	acetonitrile	0.04 (v/v-%)	5
AEMOF-1'	MOF	THF	0.05 (v/v-%)	6
PPQ-CDs	carbon dots	DMSO	0.023 (v/v-%)	7
RCDs	carbon dots	acetone	0.082% (v/v-%)	8
MOF@superparamagnetic	complex material	hexane	0.3 (wt-%)	9

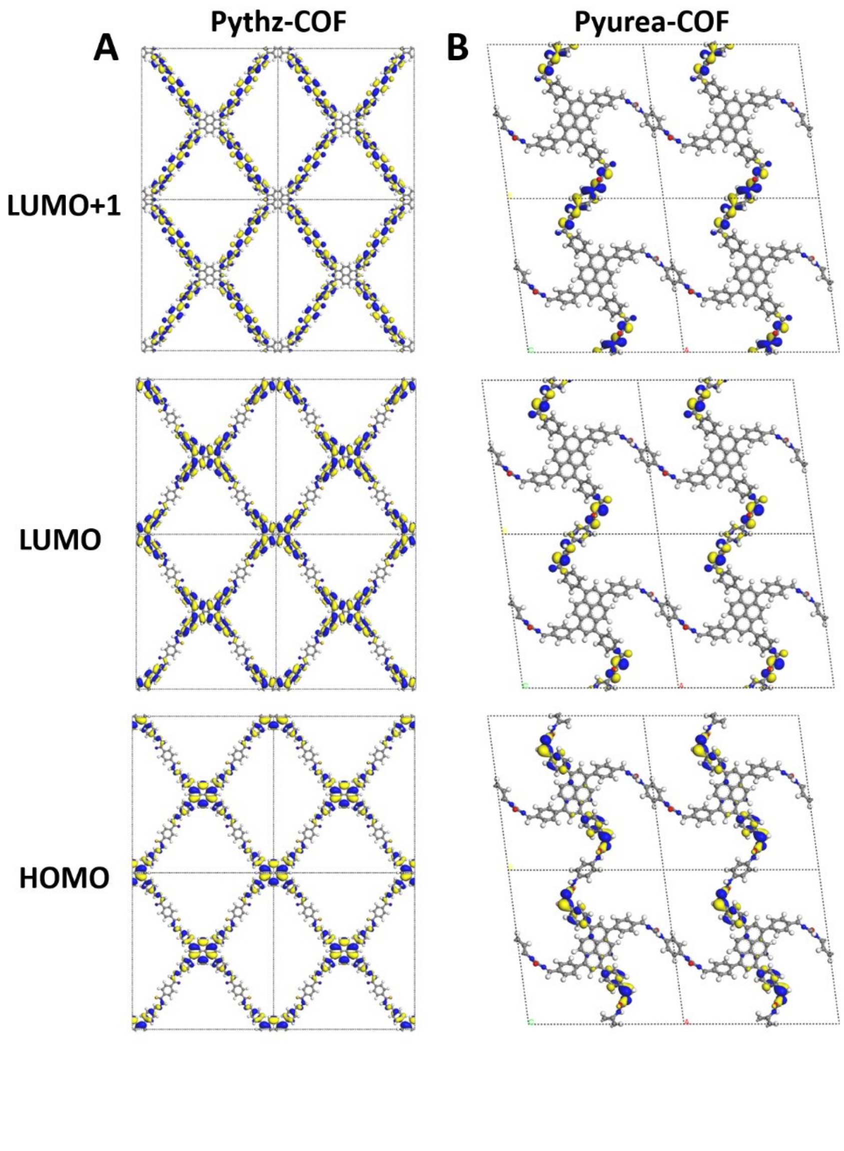

Figure S18. The frontier orbital contribution of the single-layer molecular structure of A) Pythz-COF and B) Pyurea-COF by DFT calculations.

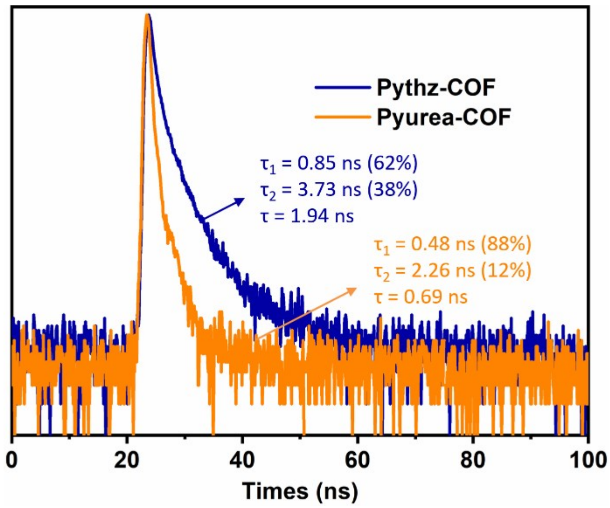

Figure S19. Fluorescence decay profiles of two COFs in solid state.

Table S4. Summary of textural properties of various materials along with their water uptake performance.

Materials	Type	BET surface area (m^2 /g)	Total pore volume (cm^3/g)	H_2O adsorption (mmol/g)[b]	H_2O adsorption (wt%)[b]	Temperatur e (K)	Ref.
Pythz-COF Pyurea-COF	COF	1571 1016	1.01 0.53	46.2 35.8	83.2 64.5	298	This work
COF-432	COF	895	0.43	16.7	30	298	10
AB-COF ATFG-COF	COF	1125 520	0.47 0.5	22.9 13.6	41 25	288	11
DhaTab	COF	N/A[a]	N/A	31.7	57	298	12
TpPa-1 TpAzo	COF	1432 3038	N/A	28.9 22.7	52 41	298	13
Trzn-COF	COF	408.5	N/A	2	4	298	14
2D ep-POP 3D ep-POP	POP	852 779	0.18 0.17	22.9 22.9	41.1 41.1	298	15
KFUPM-1	POP	305	N/A	18.7	33.5	298	16
UiO-66 UiO-66-NH_2	MOF	1160 1040	0.52 0.57	20.5 20.5	37 37	298	17
UiO-67 H_2N-MIL-125	MOF	2064 1220	0.97 0.55	10 20.5	18 37	293	18

[a] N/A: Not available

[b] Condensation effects observed at higher humidity levels.

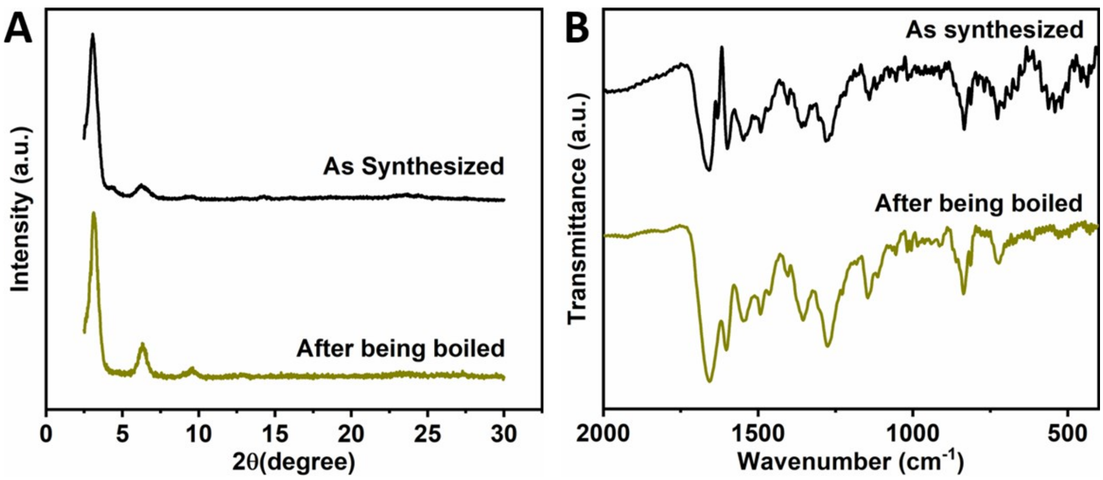

Figure S20. A) PXRD patterns and B) FTIR spectra of Pythz-COF before and after being boiled in hot water (80 ºC) for 8 hours.

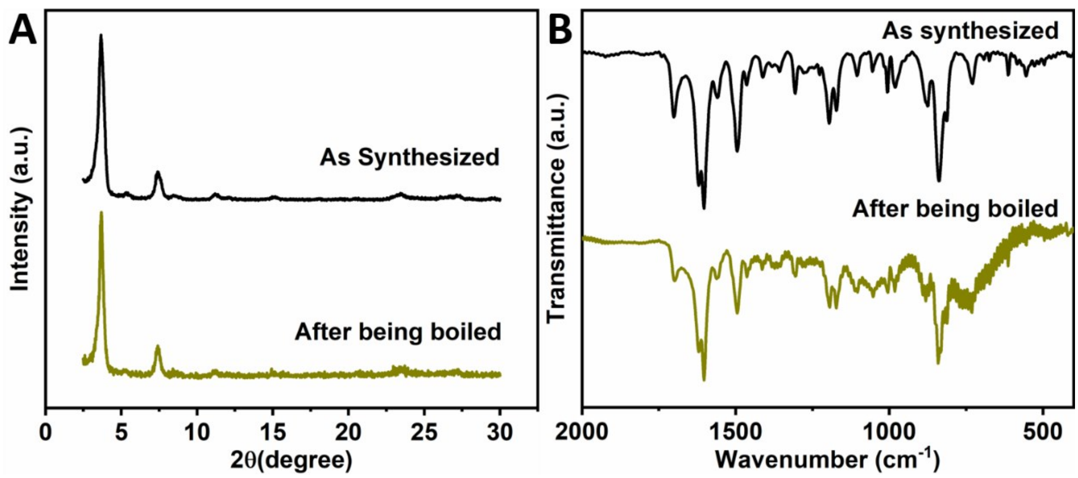

Figure S21. A) PXRD patterns and B) FTIR spectra of Pyurea-COF before and after being boiled in hot water (80 ºC) for 8 hours.

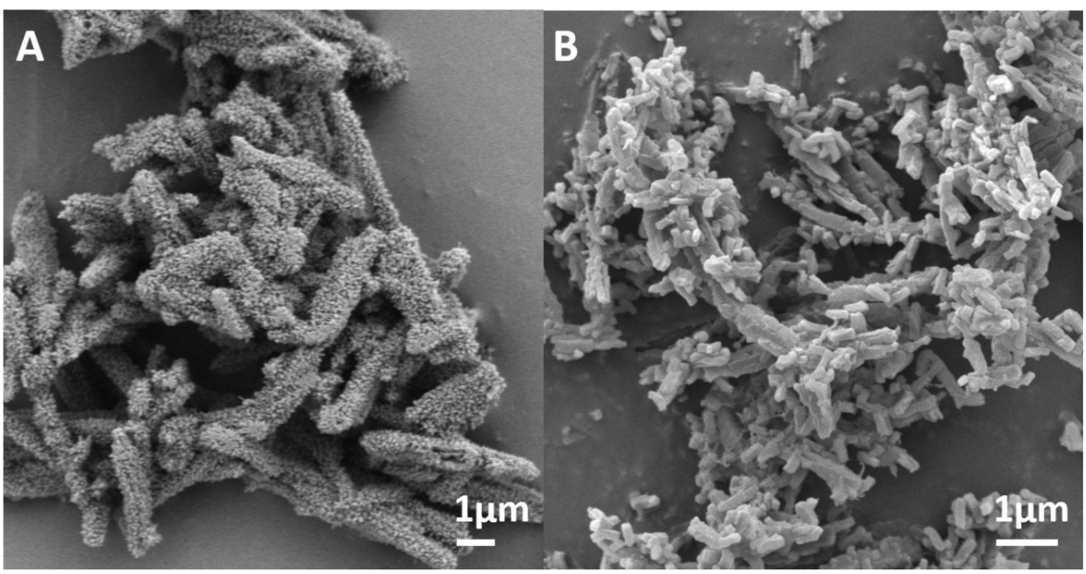

Figure S22. SEM images of A) Pythz-COF and B) Pyurea-COF after being boiled in hot water (80 ºC) for 8 hours.

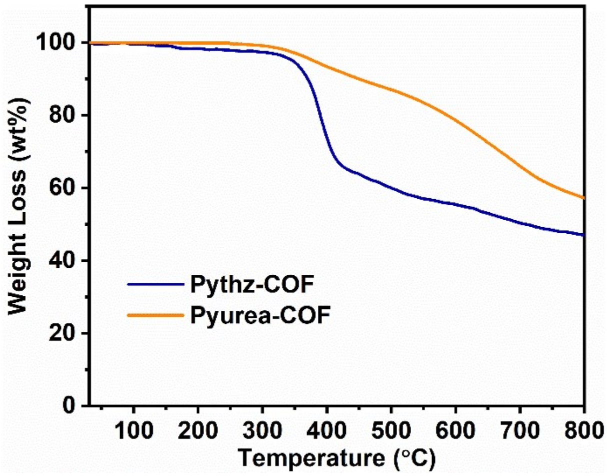

Figure S23. TGA profiles of Pythz-COF and Pyurea-COF after being boiled in hot water (80 ºC) for 8 hours.

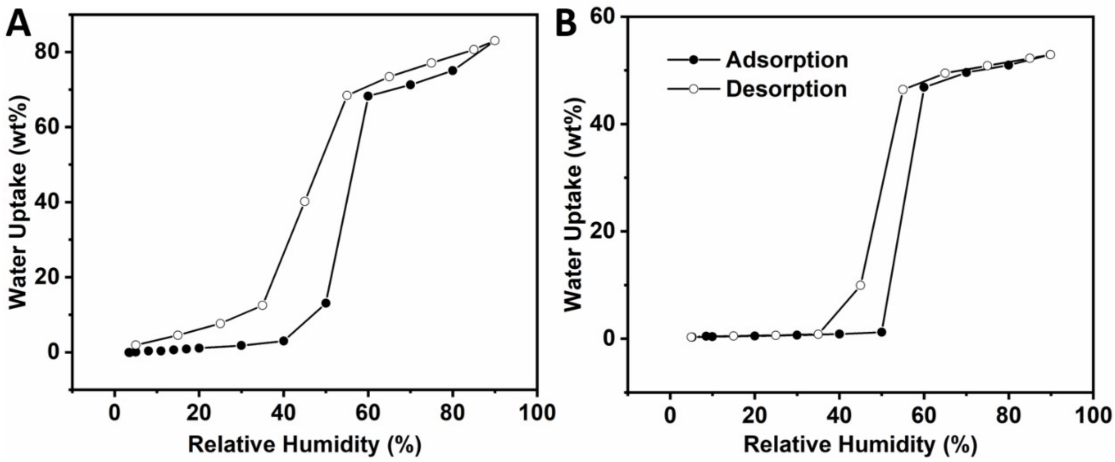

Figure S24. Water sorption analysis on A) Pythz-COF and B) Pyurea-COF after being boiled in hot water (80 ºC) for 8 hours in the relative humidity range between 0% and 90% measured at 298K.

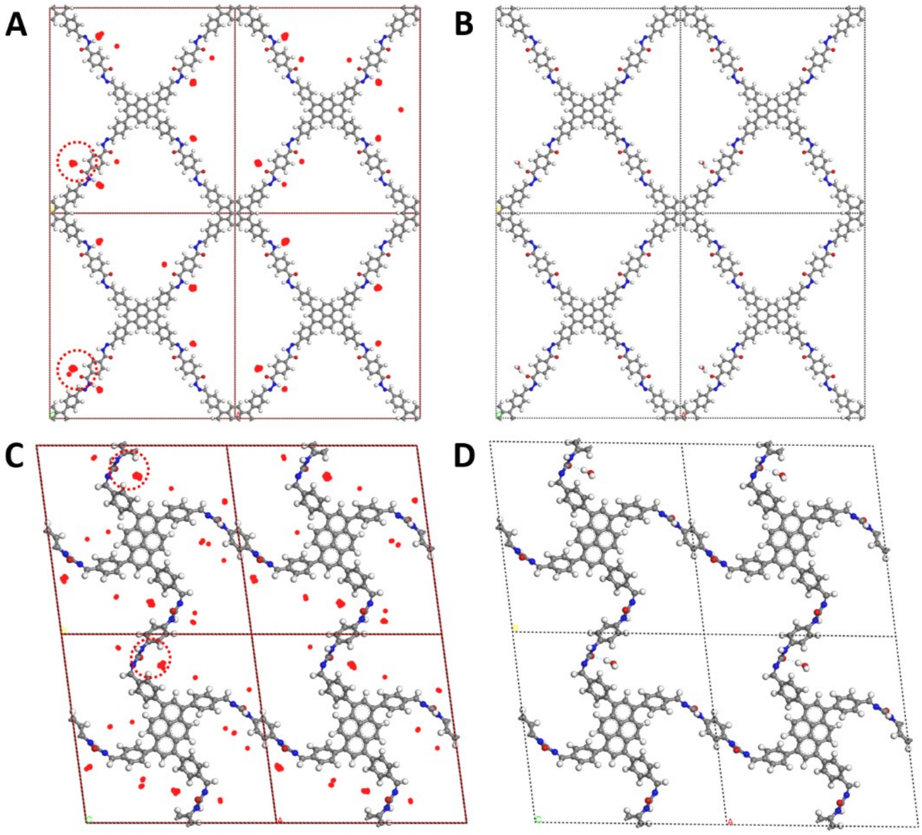

Figure S25. Simulated adsorption location of H_2O in A) Pythz-COF and C) Pyurea-COF and H_2O is most likely to occur in the red circle (The area of red dots is proportional to the probability of H_2O occurrence); Theoretical calculation on hydrogen bonds between B) Pythz-COF and D) Pyurea-COF (grey: C, blue: N, white: H, red: O).

3. Reference

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