Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.
This journal is © the Partner Organisations 2018

Supporting Information

Coordination-supported Organic Polymers: Mesoporous Inorganic-Organic Materials with Preferred Stability

Dong Chen[a], Pengfei Zhang[a,b,*], Qianrong Fang[c], Shun Wan[b], Hui Li[c], Shize Yang[b], Caili Huang[b], Sheng Dai[b,d,*]

[a] *School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China, E-mail: chemistryzpf@sjtu.edu.cn*

[b] *Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States, E-mail: dais@ornl.gov*

[c] *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China*

[d] *Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States*

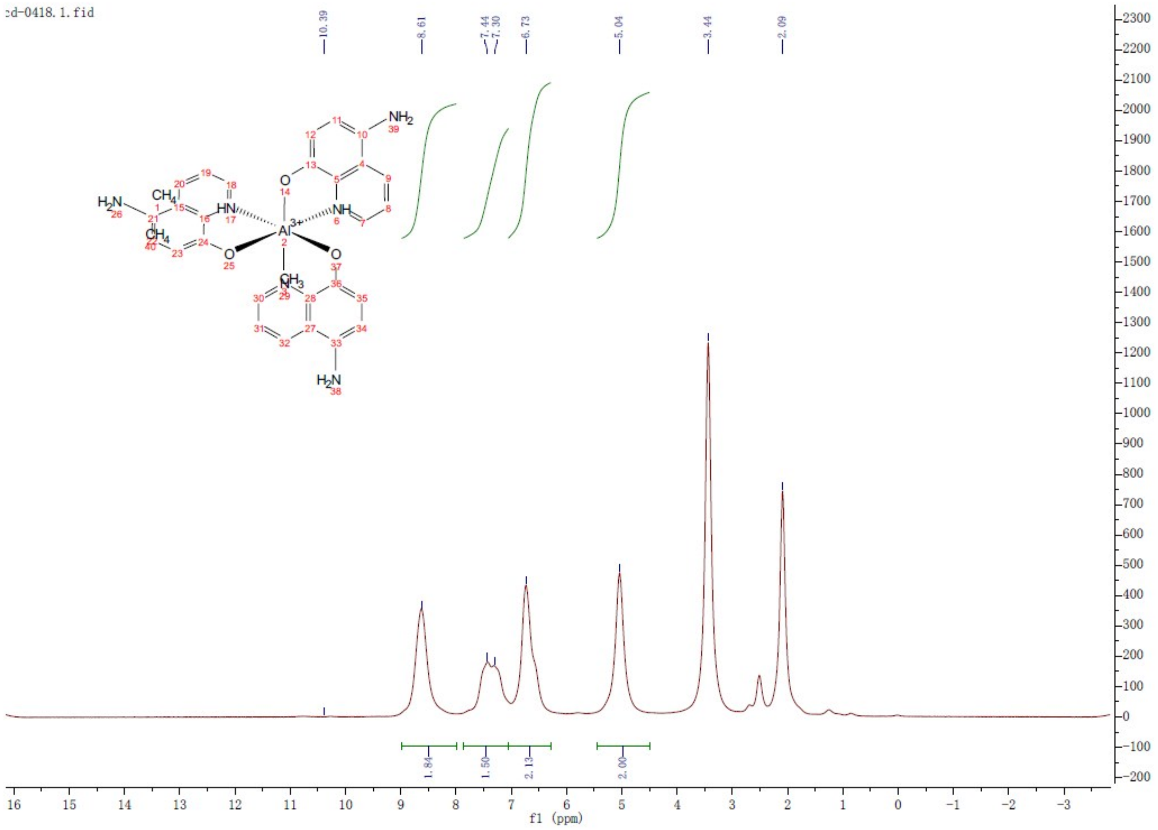
General method and characterization

N_2 sorption-desorption analysis was performed at 77 K using a TriStar (Micromeritics Instrument Corp.; Norcross, GA, USA), equipped with automated surface area and pore size analyzer. Before analysis, samples were degassed at 150 ^{o}C for 24 h. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05 to 0.20. Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) model by adsorption curve. For scanning transmission electron microscope (STEM) characterization, samples were dispersed in ethanol using an ultrasonic bath. The final suspensions were transferred to TEM grids and dried in ambient air before electron microscopy analysis. The material morphology was visualized using STEM-High angle angular dark field (HAADF) images and electron energy loss spectroscopy (EELS) on a NionUltra STEM200 microscope operated at 60 kV. Powder X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) were measured on a Bruker D8 diffractometer equipped with scintillation counter. Fourier-transform infrared spectrum was collected by PerkinElmer Frontier FTIR spectrometer.

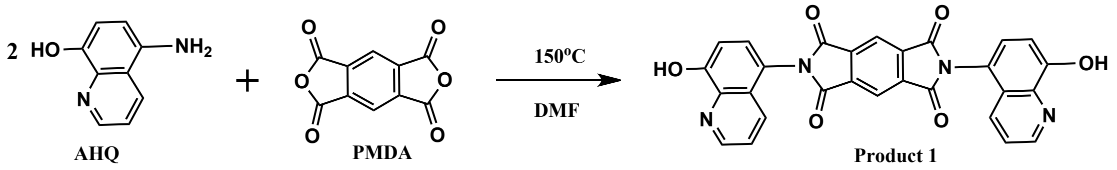
Synthetic Method

Synthesis of Al-Tri(5-amino-8-hydroxyquinoline) (Al-AHQ):

In a typical process, 0.5 mmol 5-amino-8-hydroxyquinoline•hydrogen chloride (AHQ, 116 mg) and 15 mL ethanol were added into a glass-reactor (50 mL) under stirring. After the dissolution of AHQ at room temperature, 1/6 mmol $Al(NO_3)_3$•$9H_2O$ (63 mg) was added into the solution, and the coordination process was performed at 60^{o}C for 24 h with argon flowing. Then, the solvent was removed under reduced pressure, and the solid sample was dried at 80^{o}C in vacuum. Elemental analysis, Theoretical (wt%): C (64.28), H (4.16), N (16.67), Al (5.35); Found (wt%): C (63.87), H (4.21), N (16.42).



The condensation between AHQ and pyromellitic dianhydride (PMDA):



In a typical process, 0.5 mmol 5-amino-8-hydroxyquinoline•hydrogen chloride (AHQ, 116 mg) and 5 mL DMF were added into a glass-reactor (25 mL) under stirring. After the dissolution of AHQ at room temperature, 0.25 mmol PMDA (55 mg) and 0.5 mmol K_2CO_3 were added into the solution, and the condensation was initially carried out at room temperature for 24 h with argon flowing. Then, the reaction temperature was increased to 150°C for 72 h with additional 0.5 mL acetic anhydride. After the removal of organic solvent, the solid product was thoroughly washed by D.I. water, followed by drying at 80°C in vacuum.

Synthesis of COP-1:

In a typical process, 0.5 mmol 5-amino-8-hydroxyquinoline•hydrogen chloride (AHQ, 116 mg) and 20 mL DMF were added into a glass-reactor (50 mL) under stirring. After the dissolution of

AHQ at room temperature, 1/6 mmol $Al(NO_3)_3•9H_2O$ (63 mg) and 0.5 mmol K_2CO_3 were added into the solution and the mixture was stirred for 0.5 h with argon flowing. Then, the coordination reaction was performed at 60°C for 24 h. After cooling down to room temperature, 0.125 mmol pyromellitic dianhydride (56 mg) was added into the mixture under argon flowing. The reaction temperature was increased to 100°C for 40 minutes, then to 160°C for 4 h and finally carried out 170°C for 48 h with another 20 mL 1-methyl-2-pyrrolidinone (NMP) as co-solvent. After cooling down to room temperature, the solid product was filtered and washed with DMF, D.I. water and ethanol, followed by soxhlet extracting in ethanol for 24 h. Final product (COP-1) was dried and got as a red powder. Elemental analysis, Theoretical (wt%): C (76.27), H (4.23), N (5.93); Found (wt%): C (76.92), H (3.93), N (5.53).

Synthesis of COP-2:

In a typical process, 0.5 mmol 5-amino-8-hydroxyquinoline•hydrogen chloride (AHQ, 116 mg) and 20 mL DMF were added into a glass-reactor (50 mL) under stirring. After the dissolution of AHQ at room temperature, 1/6 mmol $Al(NO_3)_3•9H_2O$ (63 mg) and 0.5 mmol K_2CO_3 were added into the solution and the mixture was stirred for 0.5 h with argon flowing. Then, the coordination reaction was performed at 60°C for 24 h. After cooling down to room temperature, 0.25 mmol pyromellitic dianhydride (55 mg) was added into the mixture under argon flowing. The reaction temperature was increased to 100°C for 40 minutes, then to 160°C for 4 h and finally carried out 170°C for 48 h with another 20 mL 1-methyl-2-pyrrolidinone (NMP) as co-solvent. After cooling down to room temperature, the solid product was filtered and washed with DMF, D.I. water and ethanol, followed by soxhlet extracting in ethanol for 24 h. Final product (COP-2) was dried and got as a brown yellow powder. Elemental analysis, Theoretical (wt%): C (64.86), H (2.31), N (10.81); Found (wt%): C (64.82), H (2.33), N (10.50)

Supporting Figures

Figure S1. FTIR profiles of COP-1 and tetrakis(4-formylphenyl)-silane (TFS).

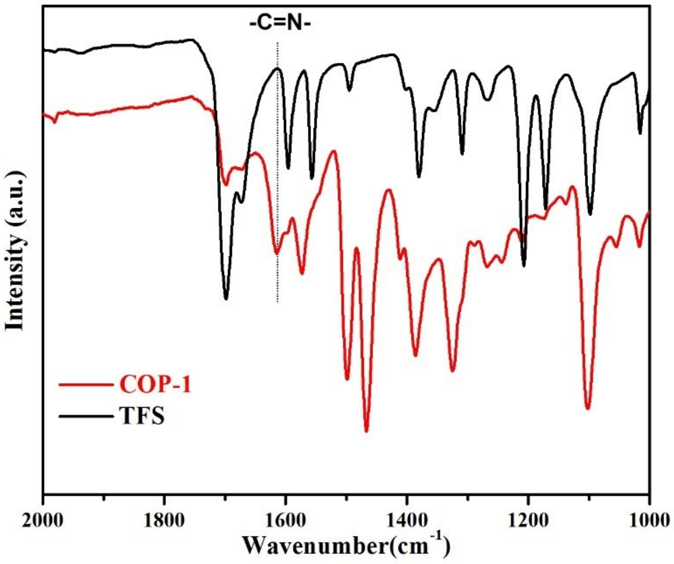


Figure S2. FTIR profiles of COP-2 and poly(BDI-PMDA). Poly(BDI-PMDA) is a typical aromatic polyamide, and it is introduced as the standard sample. BDI: benzidine, PMDA: pyromellitic dianhydride.

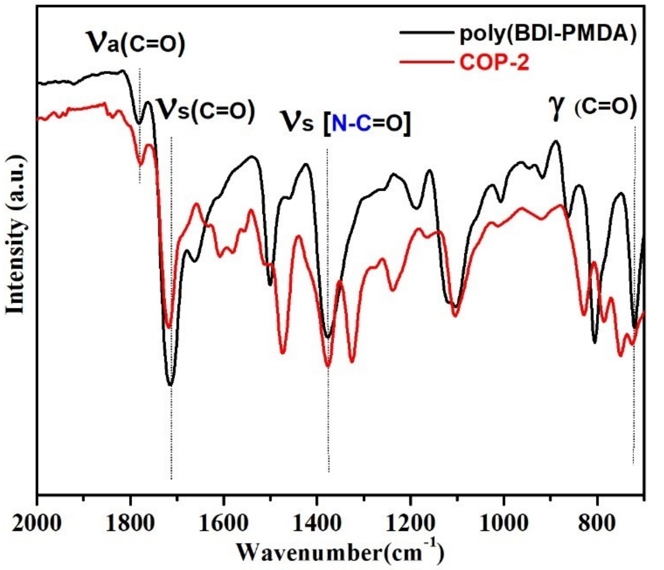


Figure S3. Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectrum of COP-2.

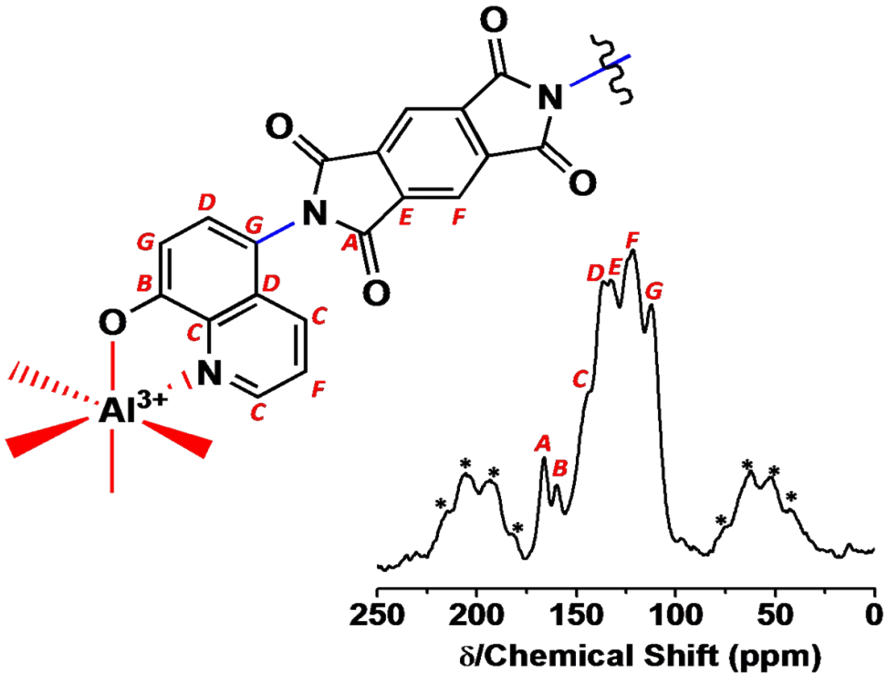


Figure S4. PXRD patterns of COP-1.

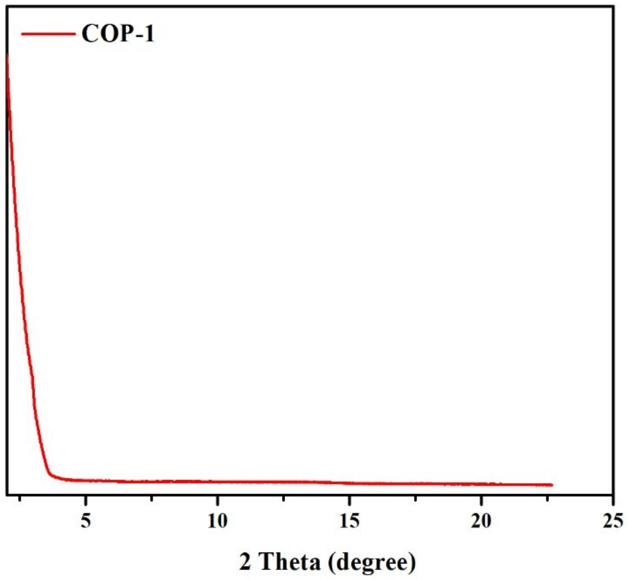


Figure S5. PXRD patterns of starting molecules and Al-AHQ.

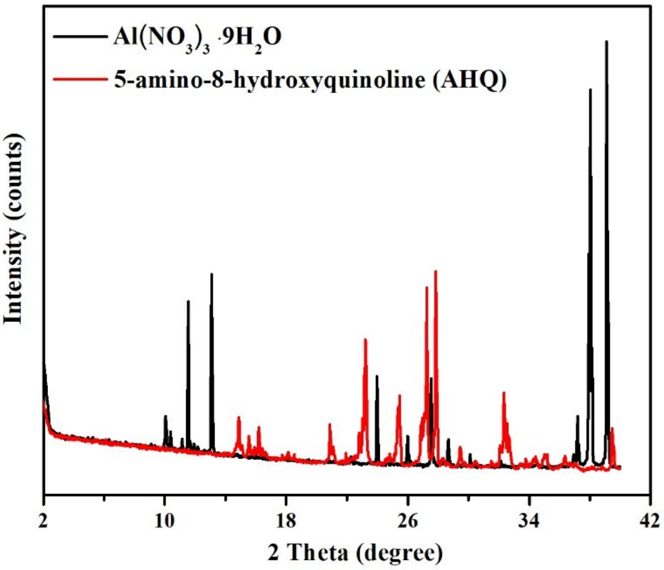


Figure S6. PXRD patterns of Al-AHQ.

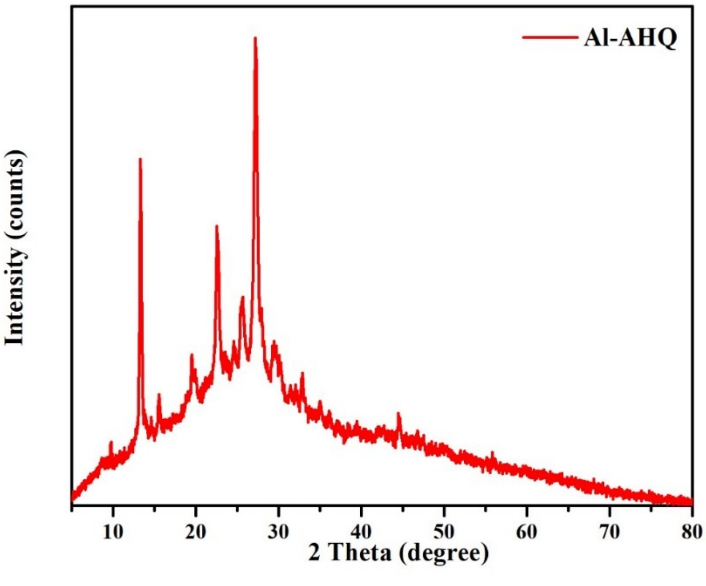


Figure S7. The experimental PXRD pattern of COP-2, and the calculated PXRD pattern by the simulated structure (*P*63 topology of staggered packing model).

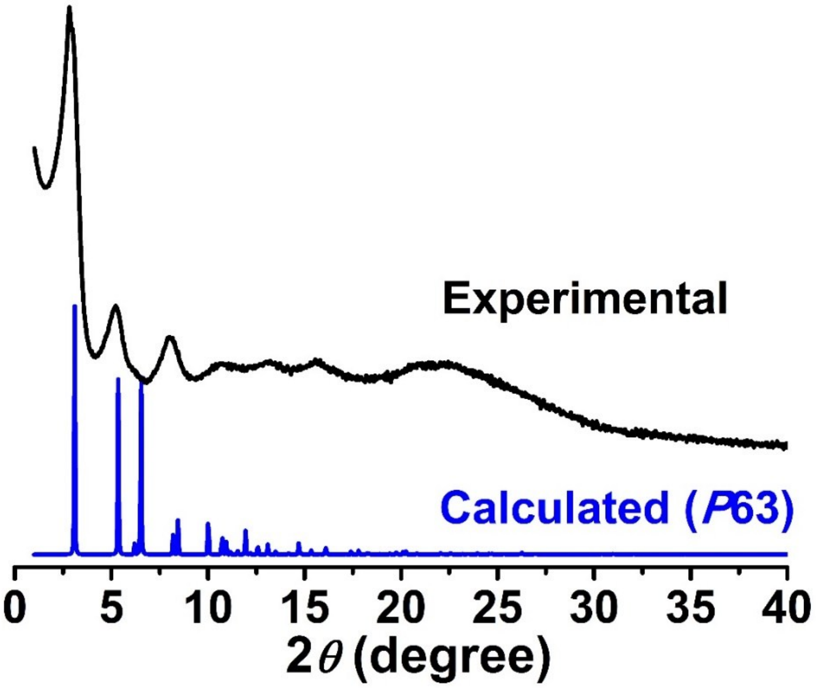


Figure S8. CO_2 adsorption isotherms (298K) of COP samples.

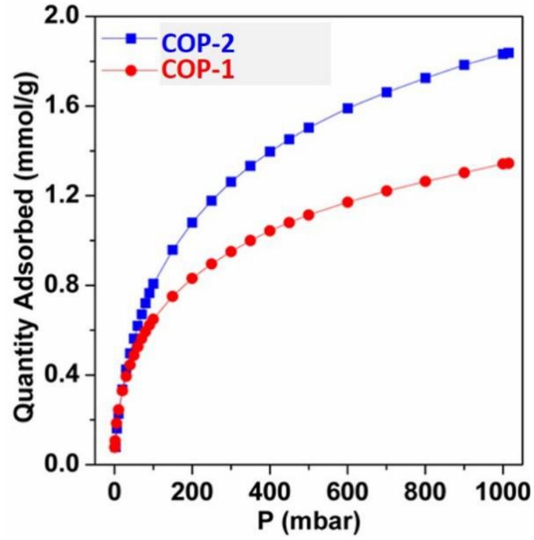


Figure S9. FTIR spectra of COP-1 sample before and after the water treatment.

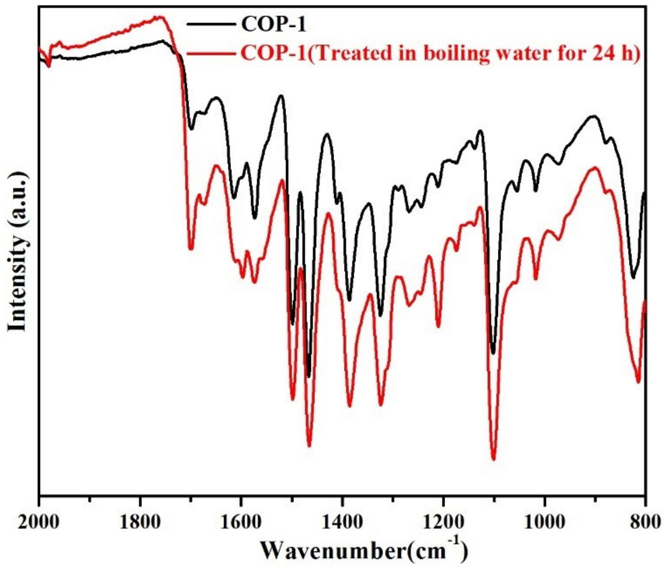


Figure S10. FTIR spectra of COP-2 sample before and after the water treatment.

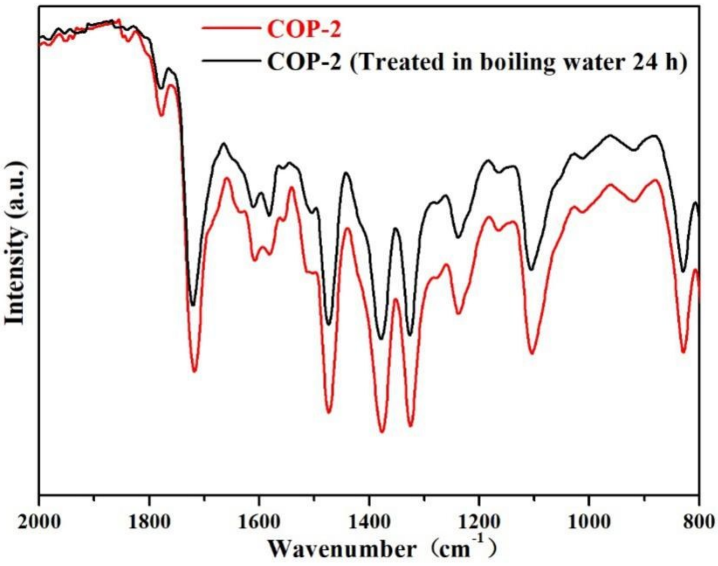
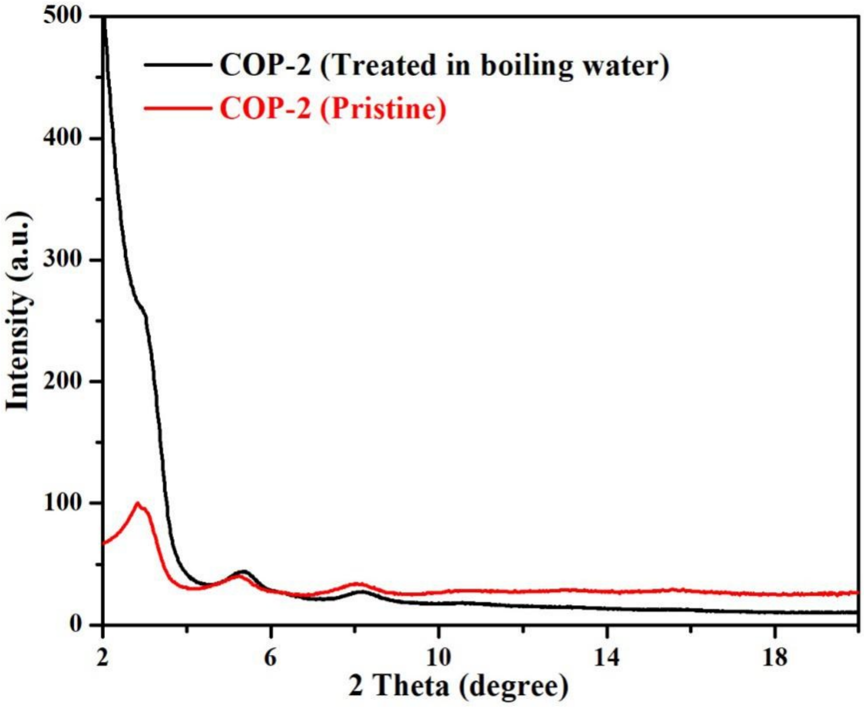
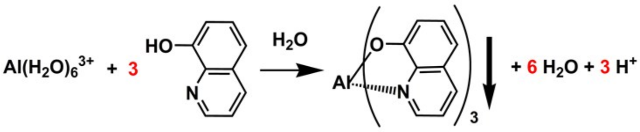


Figure S11. PXRD patterns of COP-2 before and after the water treatment.



Supporting Equation S1. The coordination by 8-hydroxyquinoline.



Supporting Tables

Table S1. Unit cell parameters and fractional atomic coordinates for COP-2 calculated based *P*6 symmetry.[a]

Atoms	x	y	z
C1	0.45203	0.45887	-0.04017
C2	0.46156	0.50569	-0.04432
C3	0.43134	0.5234	-0.05941
C4	0.45528	0.63431	-0.25589
C5	0.43614	0.66348	-0.30035
O6	0.38806	0.49912	-0.08485
C7	0.49305	0.45538	-0.03819
C8	0.49837	0.41625	-0.03571
C9	0.60006	0.40494	0.07901
C10	0.61782	0.37425	0.03217
O11	0.46561	0.37497	-0.02281
N12	0.45577	0.57067	-0.05255
C13	0.39877	0.65763	-0.15455
C14	0.43731	0.5995	-0.07088
O15	0.30583	0.62766	-0.17085
C16	0.37709	0.56277	0.26982
C17	0.33939	0.56148	0.39927
C18	0.32485	0.59392	0.33551
N19	0.34654	0.6254	0.15395
H20	0.41438	0.42887	-0.03877
H21	0.48576	0.63813	-0.36834
H22	0.45097	0.69053	-0.44983
H23	0.38988	0.53753	0.3174
H24	0.32176	0.53498	0.54928
H25	0.29483	0.59392	0.43577
Al26	0.33333	0.66667	0.06054

[a]calculated unit cell: a=b=33.0756Å, c=5.5855 Å; α=β=90.000, γ=120.000

Table S2. Unit cell parameters and fractional atomic coordinates for COP-2 calculated based *P*63 symmetry. a)

Atoms	x	y	z
O1	0.00943	0.04847	1.04348
C2	0.9277	0.10244	0.94235
N3	0.90045	0.12156	0.90708
C4	0.9833	0.06792	1.01214
N5	0.77826	0.22277	0.75085
C6	0.68969	0.26991	0.64716
C7	0.74931	0.23997	0.71576
O8	0.66085	0.28655	0.61748
C9	0.98451	0.10699	1.04991
C10	0.95661	0.12409	1.01524
C11	0.90532	0.14105	0.8263
C12	0.81449	0.16218	0.90875
C13	0.80629	0.1847	0.83912
C14	0.77373	0.20234	0.83058
C15	0.87298	0.15875	0.81618
C16	0.74639	0.27706	0.75604
C17	0.71593	0.29092	0.72033
O18	0.85437	0.11339	1.02463
O19	0.74517	0.1983	0.88538
C20	0.77303	0.30176	0.82912
C21	0.76773	0.33793	0.86487
C22	0.73614	0.34947	0.82721
N23	0.71099	0.32556	0.75565
N24	0.95725	0.01011	0.90667
C25	0.92987	0.9856	0.83766
C26	0.89924	-0.0013	0.80114
C27	0.89778	0.03753	0.83432
C28	0.0445	0.95314	0.44051
C29	0.07324	0.93719	0.40469
C30	0.13306	0.8734	0.45018
C31	0.13512	0.81874	0.24648
C32	0.16936	0.80612	0.26079
C33	0.187	0.78269	0.20499
C34	0.15125	0.85038	0.39441
C35	0.27726	0.78093	0.14004
C36	0.3071	0.76606	0.10579
O37	0.06644	0.85616	0.27191
O38	0.17425	0.76925	0.13074
H39	1.00724	0.12432	1.10479
H40	0.9579	0.15464	1.04432
H41	0.79564	0.15503	0.96973
H42	0.79811	0.29379	0.85821
H43	0.78807	0.35698	0.92125

H44	0.73224	0.37734	0.85549
H45	0.93098	0.95584	0.811
H46	0.87652	-0.0214	0.74803
H47	0.87368	0.047	0.80569
H48	0.11614	0.81153	0.18563
H49	0.27532	0.80927	0.10842
H50	0.32763	0.78251	0.04801
Al51	0.33333	0.66667	0.19016
Al52	0	0	0.97197

a)calculated unit cell: a=b=32.9708Å, c=15.3424 Å; α=β=90.000, γ=120.000

Note S1. When the polycondensation of Al-AHQ and TFS was performed in DMF with 4 mol/L acetic acid, no solid products were observed. The reaction solution turned into black during the heating process to 120°C. Hence, we consider the decomposing of Al-AHQ happen under such acid condition.