Supporting Information

Pore Size Engineering in Covalent Organic Frameworks for High-Performance Anion Exchange Membranes

Man Cai[1], Hengyi Wang[1], Tianyi Chen[1], Cheng Lian*[1], Fuzhen Xuan*[2], Bin Zhang*[1,2]

[1]Key Laboratory for Advanced Materials, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China

[2]Shanghai Key Laboratory of Intelligent Sensing and Detection, Institute of Intelligent Sensing and Instruments, East China University of Science and Technology, Shanghai 200237, China

Materials and Methods

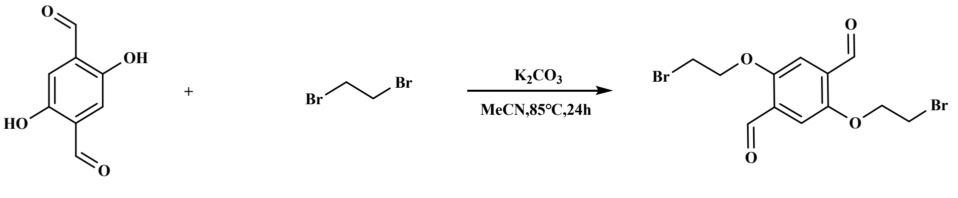
Reagents

(Most chemical reagents were of analytical grade and were purchased from Shanghai Macklin Biochemical Technology Co., Ltd., including triethylamine, acetic acid, N,N-dimethylformamide, ethanol, methanol, acetonitrile, acetone, ethyl acetate, n-hexane, sodium chloride, potassium carbonate, sodium carbonate, sodium bicarbonate, potassium chromate, and 1-methylpiperidine. Silver nitrate was obtained from Sinopharm Chemical Reagent Co., Ltd. 1,2-Dibromoethane were purchased from Shanghai Titan Scientific Co., Ltd. 2,5-Dihydroxyterephthalaldehyde was purchased from Shanghai Kewel Chemical Technology Co., Ltd. 1,3,5-Tris(4-aminophenyl) benzene (TAPB) was purchased from Anhui Zesheng Technology Co., Ltd. 1,3,5-Trimethyl-[4'-amino-(1,1-biphenyl-4-yl)] (TABB) was purchased from Shanghai Dibai Chemical Technology Co., Ltd.) 1,3,5-Trimethylenephenyl (TAB) was purchased from Shanghai Yinghan Chemical Technology Co., LTD

Synthesis of 1-Methylpiperidine-functionalized quaternary ammonium monomer

Synthesis of 2,5-Bis(2-bromoethoxy) terephthalaldehyde[1]: Under anhydrous and oxygen-free conditions, 2,5-dihydroxy-1,4-benzenedicarboxaldehyde (1.6 g, 10 mmol) and K$_2$CO$_3$ (5.3 g, 39 mmol) were added to a 250 mL round-bottom flask, followed by the addition of acetonitrile (anhydrous, 100 mL) and 1,2-dibromoethane (5.1 mL, 58 mmol). The mixture was heated under reflux and stirred overnight. The reaction gradually changed from reddish-brown to a bright yellow. Upon completion, the mixture was cooled to room temperature, concentrated under reduced pressure, dissolved in dichloromethane, and washed with an aqueous Na$_2$CO$_3$ solution. The resulting organic phase was dried over anhydrous MgSO$_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography using DCM: hexane (2:1) as the eluent. After concentration under reduced pressure, the product was obtained as a bright yellow crystalline solid.

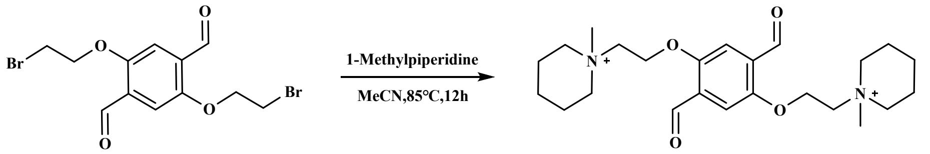
1H NMR (400 MHz, Chloroform-d) δ 10.56 (s, 2H), 7.45 (s, 2H), 4.46 (t, J = 5.8 Hz, 4H), 3.71 (t, J = 5.8 Hz, 4H).



Synthesis of 2,5-Bis[2-(1-methylpiperidin-1-ium-1-yl)ethoxy]terephthalaldehyde (2p)[2]: 0.12 mmol of 1-methylpiperidine (14.5 μL) was dissolved in 50 mL of acetonitrile, followed by the addition of 0.06 mmol of 2,5-bis(2-bromoethoxy)terephthalaldehyde (22.9 mg) to the solution. The mixture was refluxed at 83 °C overnight. The crude product was then dissolved in water, extracted with chloroform, and subsequently evaporated under rotary conditions. The resulting hydrated orange monomer was dried overnight in a vacuum oven at 100 °C to completely remove moisture, yielding a dry, bright yellow solid product.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 2H), 7.58 (s, 2H), 4.64 (t, 4H), 3.97 (t, 4H), 3.50

(t, $J = 6.9$ Hz, 8H), 3.18 (s, $J = 4.4$ Hz, 6H), 1.85 (q, $J = 6.0$ Hz, 8H), 1.57 (q, $J = 6.9$ Hz, 4H).



Preparation of COF-Pips powder

Synthesis of COF-Pip-S2: Keep in an oxygen-free environment in the glove box, 1,3,5-Trimethylenephenyl (**TAB**, 12 mg, 0.10 mmol) and the previously synthesized **2p** (62.7 mg, 0.15 mmol) were added to a 20 mL vial. Then, a pre-mixed solution of 1,4-dioxane/mesitylene (4:1 v/v, 4.0 mL) was added. The mixture was sonicated at room temperature until the monomers were completely dissolved. Scandium trifluoromethanesulfonate (3.0 mg, 6.0 µmol) was added to the dissolved mixture, followed by another brief period of sonication. The vial was then sealed with a plastic cap and kept for 10 minutes. Finally, while keeping the resulting powder in a moist state, it was activated by Soxhlet extraction with methanol for 12 hours[3]. Subsequently, the powder was dried by heating from 50 to 100 °C at a rate of 1 °C/min under a nitrogen flow until completely dry, yielding a gray purple dry powder[4].

Synthesis of COF-Pip-2: 1,3,5-Tris(4-aminophenyl)benzene (TAPB, 36 mg, 0.10 mmol) and the previously synthesized 2p (62.7 mg, 0.15 mmol) were added to a 20 mL vial. Then, 1,4-dioxane/mesitylene (4:1 v/v, 4.0 mL) was added. The mixture was sonicated at room temperature until the monomers were completely dissolved. Scandium trifluoromethanesulfonate (3.0 mg, 6.0 µmol) was added to the dissolved mixture, followed by brief period of sonication. Let it stand for 10 minutes. Finally, it was activated by Soxhlet extraction with methanol for 12 hours[3]. Subsequently, the powder was dried by heating from 50 to 100 °C at a rate of 1 °C/min under a nitrogen flow until completely dry, yielding a yellow dry powder[4].

Synthesis of COF-Pip-B2: 1,3,5-Trimethyl-[4’-amino-(1,1-biphenyl-4-yl)] (TABB, 58 mg, 0.10 mmol) and the previously synthesized 2p (62.7 mg, 0.15 mmol) were added to a 20 mL vial. Then, a pre-mixed solution of 1,4-dioxane/mesitylene (4:1 v/v, 4.0 mL) was added. The mixture was sonicated at room temperature. Scandium trifluoromethanesulfonate (3.0 mg, 6.0 µmol) was added to the dissolved mixture, followed by brief period of sonication. Let it stand for 10 minutes. Finally, it was activated by Soxhlet extraction with methanol for 12 hours[3]. Subsequently, the powder was dried by heating from 50 to 100 °C at a rate of 1 °C/min under a nitrogen flow until completely dry, yielding a faint yellow dry powder[4].

Preparation of COF-Pip Membranes

Synthesis of Amorphous COF-Pip-S2, COF-Pip-2, and COF-Pip-B2 membranes[5]: Following the membranes synthesis method described in the literature. The dissolution step of COF-Pip-S2 was carried out in a vacuum glovebox. For COF-Pip-S2 and COF-Pip-2, **2p** (62.7mg, 0.15 mmol) and **TAB** or **TAPB** (12 mg or 36 mg, respectively, each 0.10 mmol) were individually dissolved in 500 µL of a pre-prepared solution of trifluoroacetic acid/water (90:10 v/v) with sonication until complete dissolution. The solutions were then mixed, resulting in the immediate formation of a yellow oligomeric powder, which gradually aggregated. For COF-Pip-B2, **TABB** (57.9 mg, 0.10 mmol) and **2p** (62.7 mg, 0.15 mmol) were dissolved respectively in 1200 µL and 400 µL of the previously prepared trifluoroacetic acid: water (95:5 v) solution. The solutions were then ultrasonicated until the monomers were completely dissolved, and the solutions were mixed. Subsequently, 150 µL of the oligomeric solution was pipetted onto a preheated (40 °C) square silicon wafer substrate (side length 1.5 cm) or glass slide placed on a leveled petri dish. After the polymer deposited from the solution, a complementary petri dish was immediately placed on top as a cover. The assembly was left undisturbed for 4 hours, allowing solvent evaporation and the formation of a dark red amorphous membranes on the silicon surface. The silicon wafer with the membranes was then rapidly submerged in methanol, causing the membranes to detach from the substrate. The detached membrane was soaked in a triethylamine/methanol (1:9 v/v) solution, where the trifluoroacetate ions in the membranes were neutralized by triethylamine, causing the membranes to rapidly change from reddish-brown to bright yellow. The membranes were subjected to Soxhlet extraction with tetrahydrofuran for 12 hours to remove residual oligomers. After extraction, the membranes were washed three times each with tetrahydrofuran and n-pentane. They were then wrapped in filter paper to prevent deformation during drying and dried overnight in a vacuum oven at 50 °C, yielding opaque, orange-yellow membranes with a yield of 95%. Notably, Since the solubility of TABB in the trifluoroacetic acid/water system is poorer compared to TAPB and TAB, more solvents need to be added for dissolution. Less solvent will cause the evaporation rate of the mixed solution on the substrate to be too fast.

Solvothermal Annealing of COF-Pip-S2, COF-Pip-2, and COF-Pip-B2 membranes[5]: According to the method provided in the literature, the membranes were placed in 5 mL vials with 0.4 mL of acetonitrile and 0.04 mL of 10 mol/L acetic acid as a catalyst. The vials were sealed with caps and placed in an oven at 100 °C for 48 hours for thermal annealing of the amorphous membranes. After cooling, the membranes were washed with acetonitrile and methanol, followed by Soxhlet extraction with tetrahydrofuran to remove oligomers. The solvents were then exchanged three times each with tetrahydrofuran and n-pentane, resulting in opaque membranes.

Characterization

The ^{1}H (^{1}H, 400M) and ^{13}C NMR spectra (^{13}C, 400M) spectra by Bruker AVANCE III (Switzerland), The Fourier Transform Infrared Spectroscopy (FTIR) by Thermo Fisher Scientific Nicolet iS5 (America), X-ray Powder Diffraction (PXRD) by Rigaku SmartLab SE (Japan), Scanning Electron Microscopy (SEM) by ZEISS GeminiSEM 300 (German), Atomic Force Microscopy (AFM) by Bruker Dimension Icon (German), Electrochemical Workstation by CHI600E, Fully Automatic Surface Area and Porosity Analyzer (BET) by Micromeritics ASAP 2460 (American), Thermogravimetric Analysis (TG) by TA Q50 (American).

Water Uptake and Dimensional Swelling Measurement

For the determination of Water uptake and Dimensional swelling, the dry ion-exchange membrane was weighed and the obtained mass $\mathbf{m_0}$ (mg), area $\mathbf{A_0}$ (cm^2), and thickness $\mathbf{d_0}$ (μm) were measured. The weighed and dried membrane was then immersed in deionized water for 12 hours, and the new mass $\mathbf{m_1}$ (mg), area $\mathbf{A_1}$ (cm^2), and thickness $\mathbf{d_1}$ (μm) were obtained. According to the formula, the results can be calculated as follows:

$$\text{Water uptake (wt\%)} = (\boldsymbol{m_1} - \boldsymbol{m_0}) / \boldsymbol{m_0} \times 100\%$$

$$\text{Area swelling (\%)} = (\boldsymbol{A_1} - \boldsymbol{A_0}) / \boldsymbol{A_0} \times 100\%,$$

$$\text{Through-plane swelling (\%)} = (\boldsymbol{d_1} - \boldsymbol{d_0}) / \boldsymbol{d_0} \times 100\%$$

IEC Determination

Before the IEC test, the mass (W_0, g) of the sample dry anion exchange membrane was weighed. The dried ion exchange membrane was immersed in a 1M sodium chloride solution at 60°C for 24 hours to ensure that the Cl^- ions in the membrane were fully exchanged. Then, it was immersed in a 1M sodium sulfate solution at 60°C for three days, using potassium chromate as the indicator. The chloride ions displaced in the solution were titrated with a standard silver nitrate solution (c, mol·L^{-1}) until a brick-red precipitate was formed. The volume of the titration (V, mL) was recorded. The ion exchange capacity was calculated using the formula

$$\text{IEC} = \boldsymbol{cV / W_0}.$$

HCO_3^- and OH^- Conductivity Measurement

Before the test, the dried membranes were respectively immersed in 80°C, 1.5M $NaHCO_3$ and

NaOH solutions for 24 hours. The Br^- form of the membrane ions were completely exchanged for HCO_3 and OH. Using an electrochemical workstation, the anion conductivity of the membrane in the form of HCO_3 and OH was measured at 100% humidity by the AC impedance spectroscopy method. The anion conductivity (σ, $mS \cdot cm^{-1}$) was calculated according to the following formula:

$$\boldsymbol{\sigma = I / AR}$$

where I (cm) and A (cm^2) represent the distance between the electrodes on both sides of the membrane and the cross-sectional area of the sample. R (Ω) represents the membrane resistance obtained from the impedance spectroscopy method.

Alkaline stability Measurement

The prepared membranes were thoroughly immersed in a pre-prepared 1M KOH solution at 60°C. The 1M KOH solution was replaced every 24 hours to maintain a constant pH, and the OH^- ion conductivity was measured once every 24 hours.

Morphology characterizations of membranes

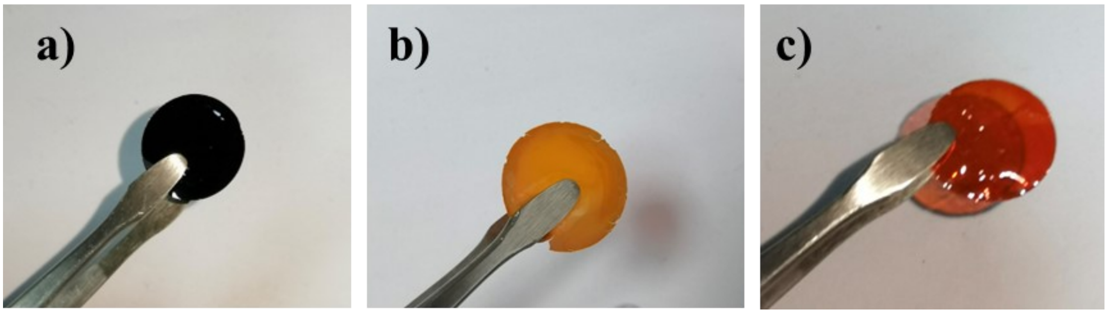


Figure S1. Photos of (a) COF-Pip-S2, (b) COF-Pip-2, (c) COF-Pip-B2 membranes.

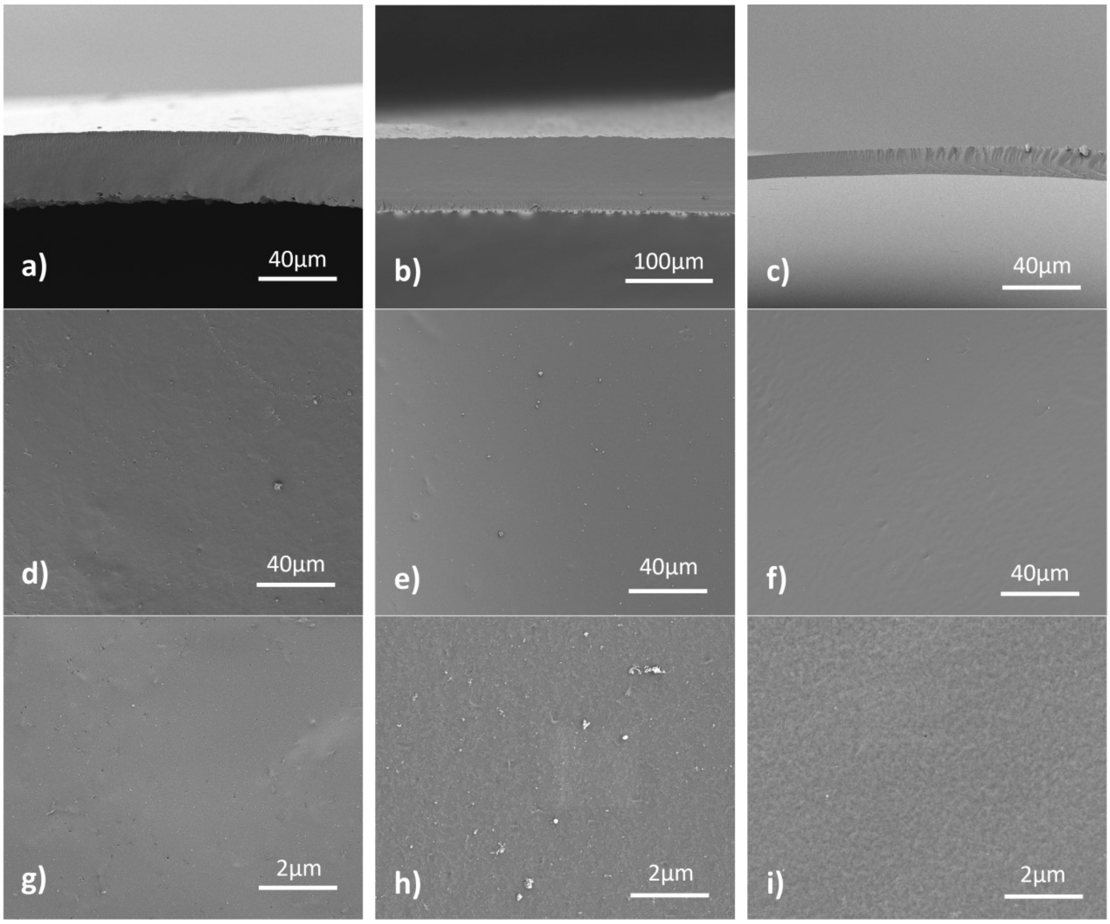


Figure S2. Synthesized COF-Pip membranes using the face-on orientation method **(a)** Cross-sectional SEM image of COF-Pip-S2, **(b)** COF-Pip-2, and **(c)** COF-Pip-B2. **(d)** Top-view images of COF-Pip-S2, **(e)** COF-Pip-2, and **(f)** COF-Pip-B2 at low magnification along with **(g)** top-view images of COF-Pip-S2, **(h)** COF-Pip-2, and **(i)** COF-Pip-B2 at high magnification.

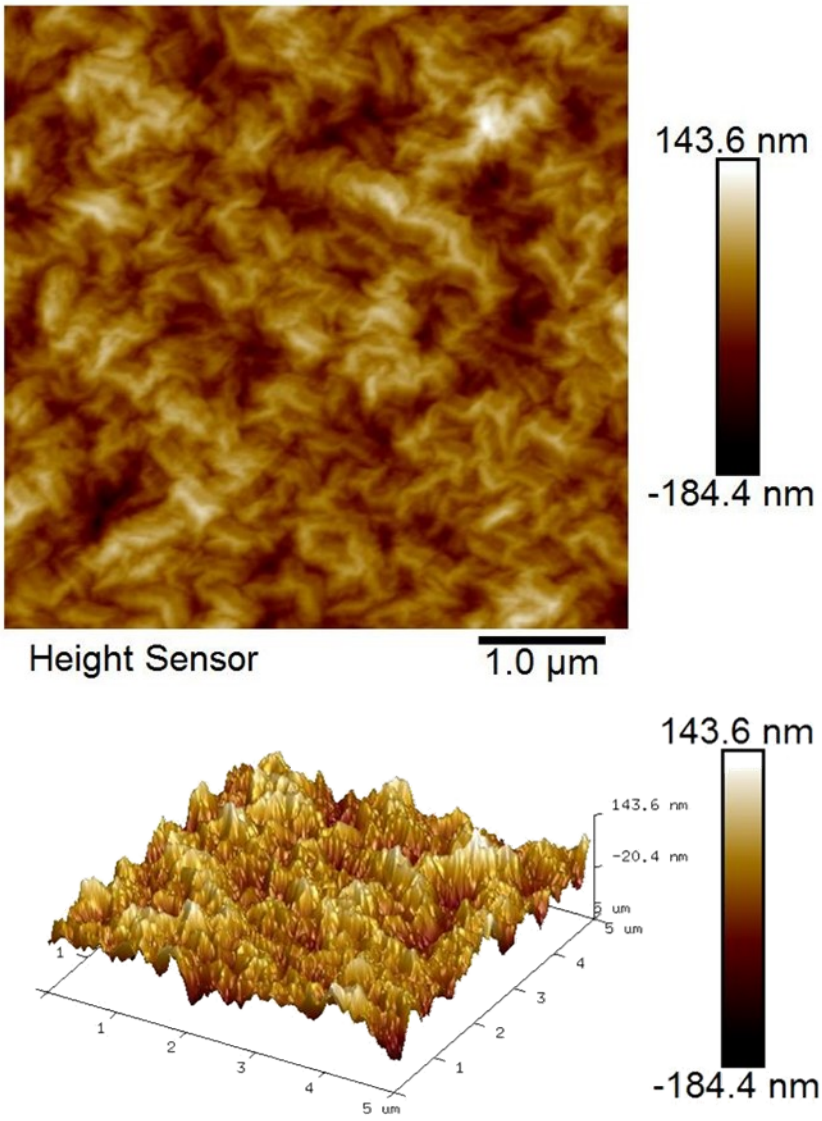


Figure S3. **(a)** Top view AFM images and **(b)** 3D AFM image of COF-Pip-2.

Crystalline structures of COF-Pip membranes

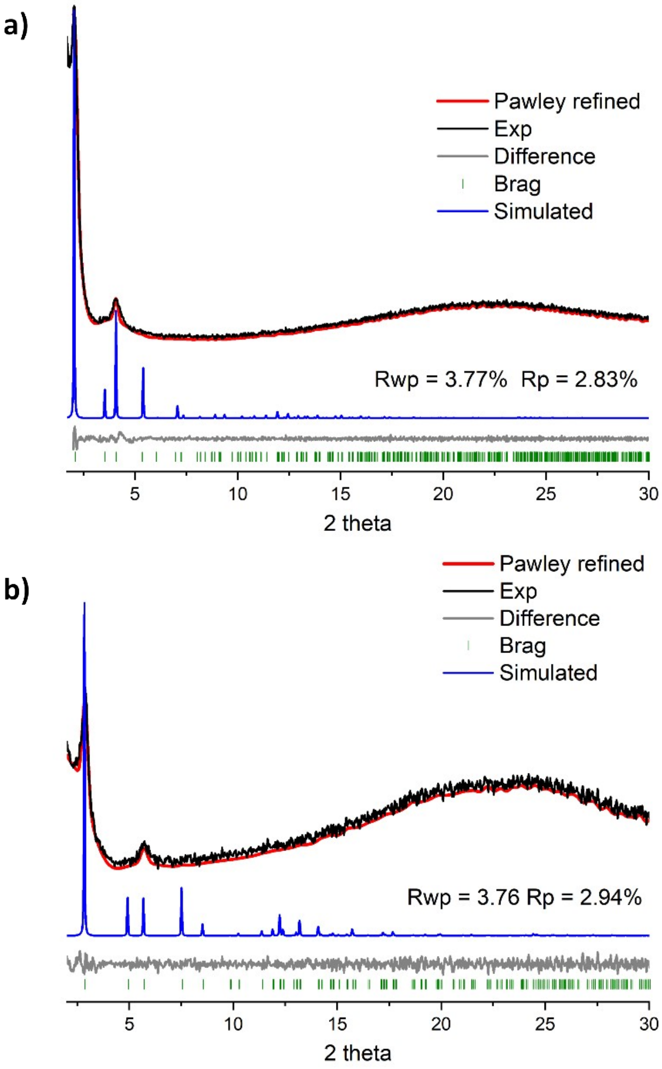


Figure S4. **(a)** PXRD pattern of COF-Pip-B2, including the Pawley refined (red), experimental (black), simulated curves (blue), Bragg positions (green), and difference plot (grey). **(b)** PXRD pattern of COF-Pip-2, including the Pawley refined (red), experimental (black), simulated curves (blue), Bragg positions (green), and difference plot (grey).

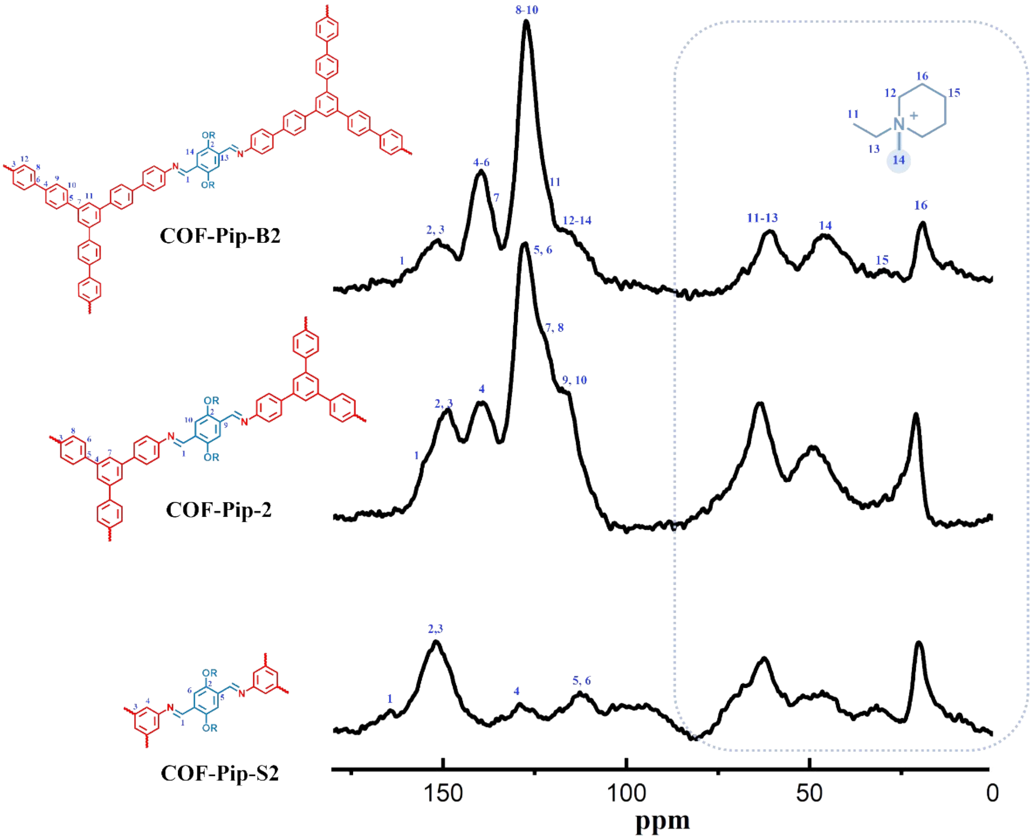


Figure S5. ^{13}C solid-state NMR of COF-Pip membranes.

Thermal stability of COF-Pip membranes

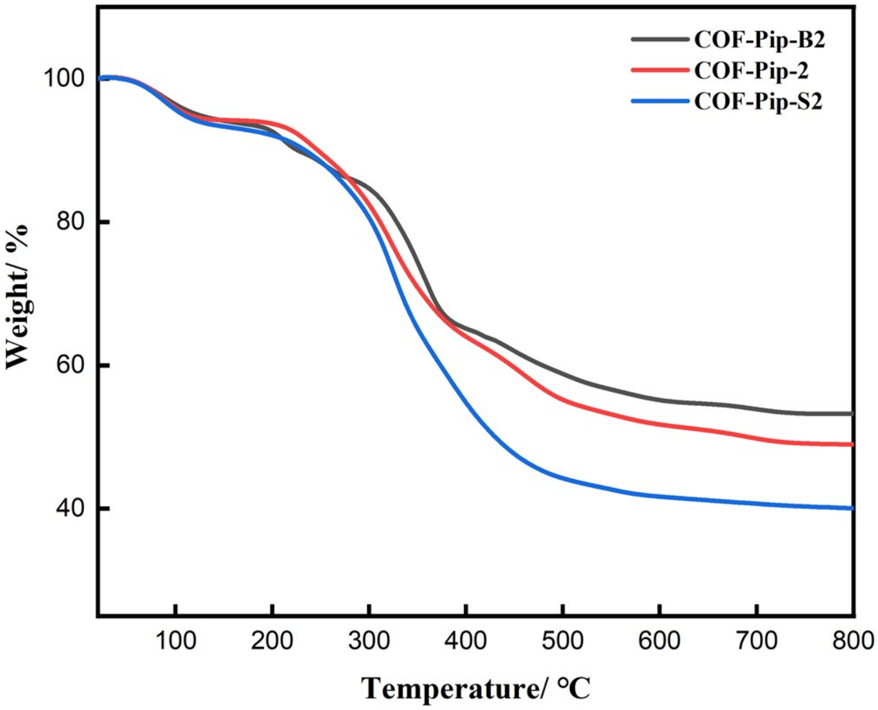


Figure S6. TGA curves of the COF-Pip membranes.

Ion conductivity performance of COF-Pip membranes

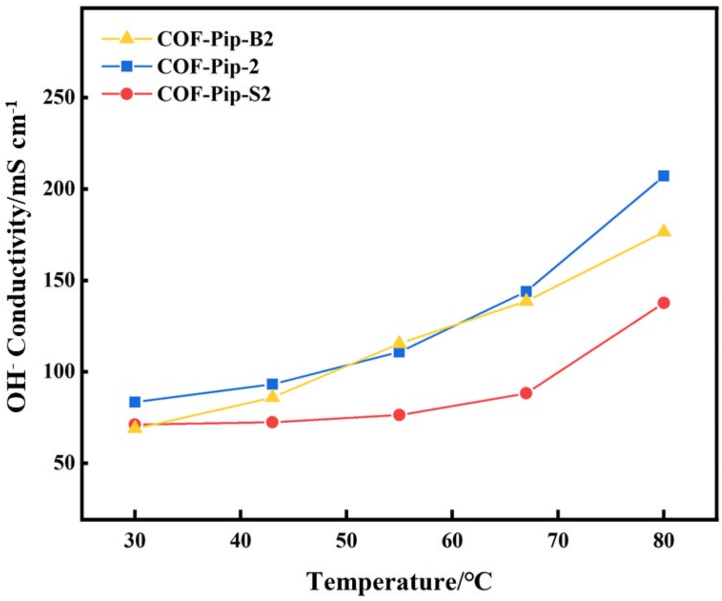


Figure S7. The comparison curve of OH^- Conductivity of the COF-Pips membrane under temperature gradient ranging from 30 to 80 °C (100% RH).

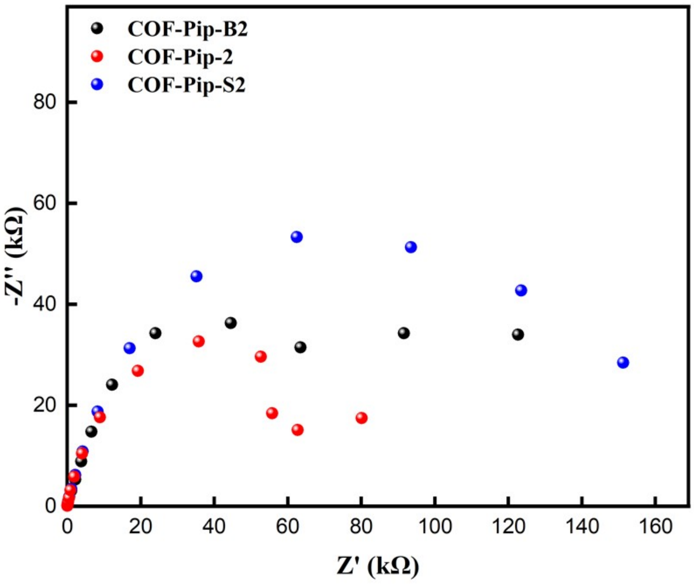


Figure S8. EIS curve of COF-Pip membranes after 1.5M NaOH treatment under 80 °C and 100% RH.

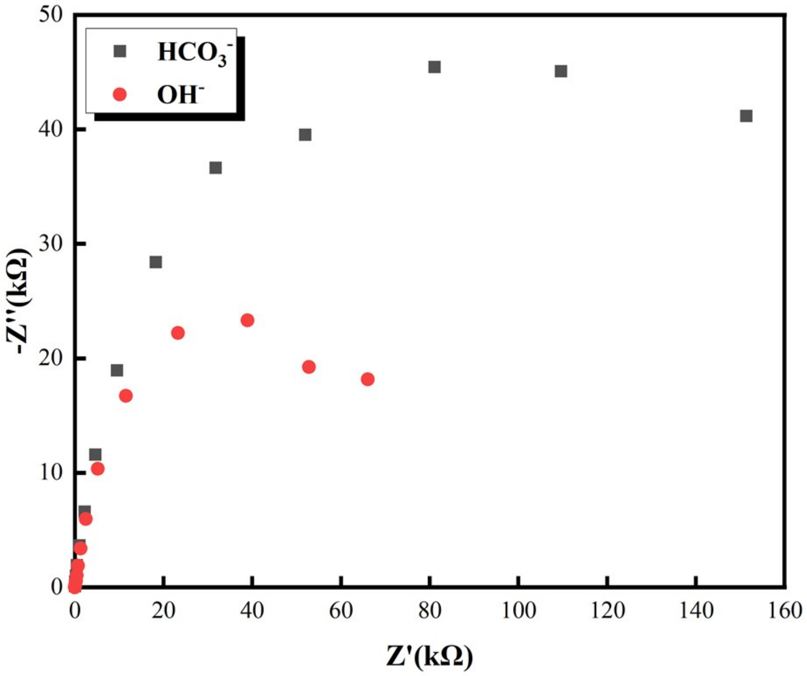


Figure S9. EIS curve of COF-Pip-2 membranes after 1.5M NaOH (red) and $NaHCO_3$ (black) treatment under 80 °C and 100% RH.

Table S1. Fractional atomic coordinates for the unit cell of COF-Pip-B2

COF-Pip-B2: Space group symmetry P3

$a = b = 50.0000$ Å, $c = 7.5256$ Å, $\alpha = \beta = 90$ °, $\gamma = 120$ °

C1	0.35243	0.65344	1.22176	C56	0.38203	1.02283	1.58168
C2	0.63678	0.32899	0.63128	C57	0.41973	1.07342	1.69368
C3	0.65751	0.3857	0.66241	H58	0.61364	0.32559	0.63899
C4	0.67396	0.40715	0.79725	H59	0.39034	0.70033	1.22161
C5	0.66635	0.42951	0.84502	H60	0.57798	0.5704	1.41321
C6	0.64223	0.43095	0.75839	H61	0.60824	0.59404	1.26354
C7	0.62695	0.41064	0.61667	H62	0.45586	0.4233	1.3576
C8	0.63444	0.38811	0.56965	H63	0.4257	0.42942	1.43456
N9	0.58389	0.49627	1.02051	H64	0.52279	0.94856	1.56283
C10	0.56213	0.48291	1.13848	H65	0.54235	0.9673	1.76473
C11	0.54182	0.49539	1.18228	H66	0.49727	0.94206	1.93873
C12	0.51043	0.47459	1.21265	H67	0.49262	0.91261	1.78522
C13	0.48974	0.48529	1.24478	H68	0.44394	0.91473	1.8184
C14	0.50029	0.5171	1.2351	H69	0.45853	0.92304	1.59604
C15	0.53185	0.53791	1.21053	H70	0.45056	0.96352	1.86025
C16	0.55298	0.52733	1.19393	H71	0.45109	0.96468	1.62247
C17	0.47824	0.52839	1.25191	H72	0.50483	0.99604	1.88514
O18	0.585	0.54812	1.19173	H73	0.49484	1.0116	1.69836
O19	0.45833	0.46482	1.27904	H74	0.56356	1.02051	1.69349
N20	0.48689	0.55718	1.22165	H75	0.54195	1.0338	1.57096
C21	0.36545	0.68564	1.22188	H76	0.45838	1.06778	1.46957
C22	0.6623	0.35908	0.633	H77	0.42634	1.06682	1.3598
C23	0.37249	0.63953	1.22049	H78	0.4468	1.02622	1.67896
C24	0.3663	0.61519	1.1039	H79	0.44288	1.04728	1.85109
C25	0.38509	0.60191	1.10309	H80	0.41613	0.99492	1.94471
C26	0.41036	0.61259	1.21963	H81	0.39682	0.98097	1.73698
C27	0.4166	0.63704	1.33582	H82	0.38674	1.02206	2.004
C28	0.39787	0.65043	1.33591	H83	0.36113	0.98167	1.96698
H29	0.6916	0.40558	0.87238	H84	0.35699	1.02944	1.8
H30	0.67862	0.44502	0.95384	H85	0.3399	0.99082	1.71984
H31	0.60806	0.41105	0.54882	H86	0.37239	1.03381	1.49312
H32	0.62154	0.3719	0.46475	H87	0.37821	1.00157	1.51244
H33	0.55583	0.46009	1.18766	H88	0.4095	1.06976	1.82878
H34	0.50189	0.45	1.20681	H89	0.40866	1.08352	1.60961
H35	0.54015	0.56246	1.20658	H90	0.44462	1.09115	1.70715
H36	0.45464	0.51211	1.28841	C91	0.40196	0.83188	0.221
C37	0.59653	0.57112	1.3287	C92	0.43414	0.85057	0.20512
C38	0.45097	0.44119	1.40961	C93	0.44795	0.88269	0.20548
H39	0.34713	0.60674	1.01173	C94	0.42978	0.89679	0.22394
H40	0.38005	0.5835	1.00974	C95	0.39771	0.8782	0.23763
H41	0.4356	0.64543	1.42901	C96	0.38385	0.84603	0.23703

H42	0.40285	0.66894	1.42851	H97	0.38342	0.88873	0.24893
N43	0.51729	0.98612	1.6378	H98	0.35895	0.83218	0.24626
C44	0.52084	0.95965	1.68645	C99	0.82033	1.36918	-0.1722
C45	0.4936	0.93524	1.7965	C100	0.84533	1.37749	-0.28799
C46	0.46304	0.93204	1.73423	C101	0.87551	1.39157	-0.22182
C47	0.46342	0.96302	1.74114	C102	0.88113	1.3981	-0.04033
C48	0.49619	0.99128	1.74655	C103	0.8561	1.38858	0.07661
C49	0.5459	1.01395	1.58716	C104	0.82596	1.37419	0.0112
C50	0.43316	1.05282	1.44364	H105	0.85994	1.393	0.21773
N51	0.41577	1.0442	1.61614	H106	0.80713	1.36829	0.10313
C52	0.42938	1.03072	1.743	H107	0.4487	0.84032	0.19354
C53	0.40527	1.00048	1.83273	H108	0.47267	0.89614	0.18814
C54	0.3782	1.00361	1.90168	H109	0.84149	1.37372	-0.42968
C55	0.36242	1.01163	1.7525	H110	0.89467	1.39898	-0.31294

Table S2. Fractional atomic coordinates for the unit cell of COF-Pip-2

COF-Pip-2: Space group symmetry P3

$a = b = 35.9459$ Å, $c = 7.4393$ Å, $\alpha = \beta = 90$ °, $\gamma = 120$ °

C1	0.34357	0.63366	1.44561	C48	0.58546	0.85734	1.66538
C2	0.62297	0.30257	1.04331	C49	0.59961	0.9005	1.57012
C3	0.60324	0.36007	1.04997	C50	0.62982	0.9458	1.83374
C4	0.56964	0.3419	1.17644	C51	0.44987	1.03896	1.1263
C5	0.54022	0.3564	1.18893	N52	0.45507	1.07446	1.24984
C6	0.54364	0.38896	1.07282	C53	0.50155	1.10751	1.27697
C7	0.57678	0.40656	0.94548	C54	0.51992	1.10258	1.45718
C8	0.60643	0.39239	0.93379	C55	0.49576	1.10781	1.61724
N9	0.51666	0.4076	1.09089	C56	0.4477	1.08972	1.57869
C10	0.47876	0.38921	1.16347	C57	0.43161	1.05643	1.42484
C11	0.45473	0.41241	1.18607	C58	0.43424	1.09599	1.15569
C12	0.4099	0.38772	1.2075	H59	0.58913	0.27876	1.04512
C13	0.38477	0.40721	1.23465	H60	0.40954	0.6848	1.44288
C14	0.40528	0.45214	1.24265	H61	0.53659	0.53723	1.31952
C15	0.44996	0.47687	1.22344	H62	0.52623	0.54062	1.08476
C16	0.47537	0.45783	1.19155	H63	0.32898	0.32103	1.28188
C17	0.38044	0.47405	1.27269	H64	0.28391	0.32691	1.29997
O18	0.52041	0.48253	1.16402	H65	0.62868	0.98874	1.56517
O19	0.33948	0.38362	1.24362	H66	0.68315	1.0035	1.59553
N20	0.39848	0.51069	1.35612	H67	0.68482	0.9248	1.51459
C21	0.37627	0.67686	1.44613	H68	0.7033	0.95381	1.72071
C22	0.6357	0.34633	1.04357	H69	0.65913	0.887	1.89674
C23	0.35452	0.59915	1.4341	H70	0.68971	0.87829	1.73078
C24	0.33291	0.56501	1.31177	H71	0.61243	0.81804	1.75018
C25	0.34585	0.53458	1.2888	H72	0.62874	0.84104	1.52853
C26	0.38057	0.5378	1.38897	H73	0.57369	0.85695	1.80452
C27	0.40131	0.57114	1.51401	H74	0.55798	0.83139	1.58986
C28	0.38837	0.60149	1.5373	H75	0.57237	0.9069	1.57332
H29	0.56705	0.31747	1.26958	H76	0.60491	0.89527	1.42653
H30	0.51596	0.34314	1.29324	H77	0.65836	0.97404	1.89388
H31	0.57965	0.43157	0.8561	H78	0.62076	0.9187	1.92801
H32	0.63185	0.40657	0.83412	H79	0.60276	0.95252	1.83575
H33	0.46345	0.35588	1.20457	H80	0.41504	1.01533	1.109
H34	0.3949	0.35327	1.19637	H81	0.46203	1.05182	0.98884
H35	0.46431	0.5113	1.23078	H82	0.52153	1.10751	1.16304
H36	0.34733	0.45895	1.22917	H83	0.50674	1.1408	1.27718
C37	0.54123	0.52827	1.18148	H84	0.55456	1.12716	1.46622
C38	0.31837	0.34302	1.3352	H85	0.51753	1.07067	1.46506
H39	0.30726	0.563	1.228	H86	0.51051	1.14243	1.65177
H40	0.32993	0.51005	1.18713	H87	0.49975	1.09134	1.7363

H41	0.4283	0.57414	1.59072	H88	0.44188	1.1164	1.54375
H42	0.40526	0.62724	1.63381	H89	0.42892	1.07449	1.7034
C43	0.65191	0.97723	1.5432	H90	0.39635	1.04292	1.40846
N44	0.63882	0.93707	1.6482	H91	0.4351	1.02925	1.47385
C45	0.67445	0.92746	1.65292	H92	0.43466	1.12184	1.23974
C46	0.66283	0.88486	1.74869	H93	0.40004	1.07294	1.12232
C47	0.62211	0.84746	1.66864	H94	0.45105	1.11114	1.02678

Table S3. The Water Uptake, Area Swelling, and Ion Exchange Capacity of the COF-Pip membranes in this work are compared with recently reported anion exchange membranes, including hydrazone-linked COFs (abbreviated as COFs), cross-linked polymers, and block polymers.

Membrane	Category	Water uptake %	Area swelling %	IEC (mmol g^{-1})	reference
COF-Pip-2	COFs	141.35	6.40	3.0	This work
COF-Pip-B2	COFs	110.56	2.17	2.4	
COF-Pip-S2	COFs	153.21	7.11	4.0	
COF-QA-2	COFs	80	18	2.24	**1**
COF-SDQA	COFs	77.7	11.71	2.73	**2**
QA@COF-LZU1/PPO-5	COFs	45.6	12.6	2.91	**3**
Im@PI-2/PPO-5.0	COFs	45.6	14.7	2.76	**4**
IL-COF/GPPO-5	COFs	45.37	17	2.88	**5**
TJU-1	COFs	18.1	6.7	2.99	**6**
COF-3OH	COFs	125.3	5.0	2.05	**7**
COF-QA-TFB(P)	COFs	83	16	2.38	**8**
OHPTP-10TBB	cross-linked	63.1 ± 4.4	30.1 ± 5.2	1.97	**9**
x-PDB-0-F5-SEBS	cross-linked	111.1 ± 2.4	32.3 ± 1.9	1.86	**10**
QPBP-PX-15%	cross-linked	40.3	9.7	2.81	**11**
CQP(Vpip-St-AN)2-QPDTP1	cross-linked	73.4	19.04	1.49	**12**
PFTP-13	block	45	16	2.81	**13**
b-N5-QPTP	block	97.53	26.67	2.65	**14**
qPTOCB-10	block	76	29	2.87	**15**
pQP50-mTP	block	85	88	2.41	**16**

Table S4. The OH^- Conductivity, and Ion Exchange Capacity of the COF-Pip-2 in this work are compared with recently reported anion exchange membranes, including hydrazone-linked COFs (abbreviated as COFs), cross-linked polymers, and block polymers.

Membrane	Category	OH^- Conductivity	IEC (mmol g^{-1})	reference
COF-Pip-2	COFs	207.1	3.0	**This work**
COF-QA-2	COFs	212	2.24	**1**
COF-SDQA	COFs	329.4	2.73	**2**
QA@COF-LZU1/PPO-5	COFs	168	2.91	**3**
Im@PI-2/PPO-5.0	COFs	147	2.76	**4**
IL-COF/GPPO-5	COFs	89.93	2.88	**5**
TJU-1	COFs	187	2.99	**6**
COF-3OH	COFs	263.14	2.05	**7**
COF-QA-TFB(P)	COFs	200	2.38	**8**
OHPTP-10TBB	cross-linked	136	1.97	**9**
x-PDB-0-F5-SEBS	cross-linked	135.11	1.86	**10**
QPBP-PX-15%	cross-linked	163	2.81	**11**
CQP(Vpip-St-AN)2-QPDTP1	cross-linked	148	1.49	**12**
PFTP-13	block	208	2.81	**13**
b-N5-QPTP	block	157.68	2.65	**14**
qPTOCB-10	block	155	2.87	**15**
pQP50-mTP	block	197	2.41	**16**

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