Supporting Information

A Novel 3D Covalent Organic Framework Membrane Grown on a Porous α-Al_2O_3 Substrate under Solvothermal Conditions

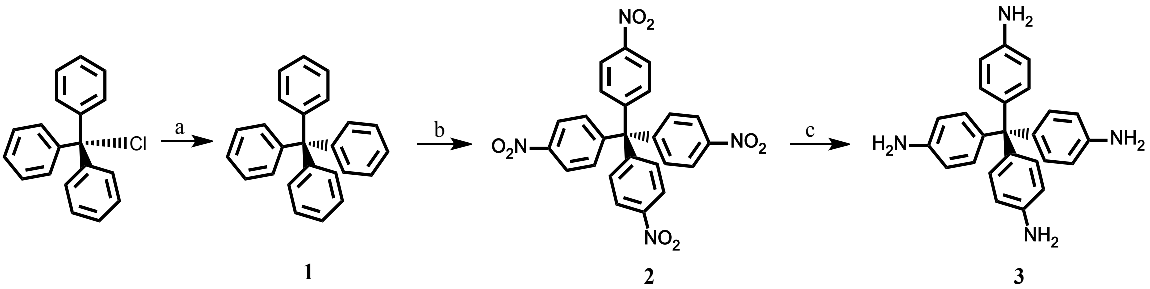
*Hui Lu, Chang Wang, Juanjuan Chen, Rile Ge, Wenguang Leng, Bin Dong, Jun Huang, and Yanan Gao**

1. Synthesis of tetra-(4-anilyl)-methane (TAM)

Tetra-(4-anilyl)-methane was synthesized according to the literature[S1]. Typically, a mixture of triphenylmethylchloride (9.18 g, 33 mmol) and aniline (8.4 g, 89 mmol) was heated to 200 °C for 5 minutes and cooled to 90 °C. And then, 100 mL of (2 mol/L) HCl solution and 45 mL of methanol were added to the reaction system. The reaction was refluxed briefly. The gray solid was obtained and filtered. The solid was then dissolved in a mixture of 65 mL of ethanol and 10 mL of concentrated sulfuric acid. The mixture was cooled to -10 °C and 8 mL of isoamylnitrite was then added. The mixture was stirred for about 30 minutes, and 15 mL of 50% hypophosphorous acid was added at -10 °C and heated to reflux. A light green solid was filtered and washed with a solution of ethanol/dioxane (4:1, v:v) to get compound **1**.

To compound **1** (7.5 g, 23.4 mmol), 40 mL of fuming nitric was added dropwise at -10°C with vigorous stirring. To this mixture, 12 mL of acetic anhydride and 25 mL of acetic acid was slowly added and stirred for 15 minutes. After that, the mixture was diluted with 50 mL of acetic acid and filtered off. The resulting yellow solid was washed with methanol thoroughly. The crude product was recrystallized with DMF to get yellow crystals of compound **2.**

To compound **2** (0.75 g, 1.55 mmol) in 50 mL of THF, 1.00 g (excess) of hydrazine monohydrate and about 10 g of Raney-nickel were added and refluxed for 3 hours. The mixture was filtered carefully and washed with ethanol. The filter was collected and solvent was removed by rotary evaporator. The residue was washed with ethanol thoroughly and dried to get compound **3.**



Scheme S1. *a*. Treated with aniline at 200 °C, reflux with 2mol/L HCl/MeOH at 90 °C, -10 °C, H_2SO_4/EtOH, isoamylnitrite, reflux with hypophosphorous acid; *b*. treated with fuming HNO_3, acetic anhydride/acetic acid at -10 °C; *c*. Hydrazine monohydrate, THF, Raney-nickel.

2. Modification of α-Al_2O_3 ceramic supports

Porous α-Al_2O_3 ceramic supports were immersed in 50 mL of hydrochloric acid solution (1 mol/L) for 5 h, then washed with water and dried, and then treated with APTES (98.29 mg in 20 mL toluene) at 100℃ for 3 h under argon, leading to APTES monolayer deposited on the surface of α-Al_2O_3 ceramic supports. The α-Al_2O_3 support was washed with ethanol for several times, then immersed in a solution of 20 mL ethanol and 4,4′-biphenyldicarboxaldehyde (BPDA). The reaction was heated at 50 ℃ for 1 hour and the α-Al_2O_3 supports were washed with ethanol thoroughly to provide the surface modified α-Al_2O_3 ceramic supports.

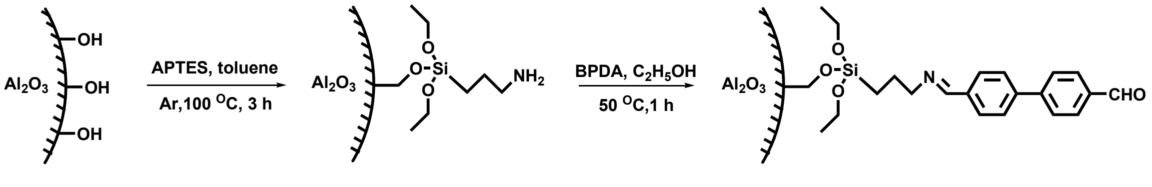


Figure S1. The surface APTES modification of the porous α-Al_2O_3 support and the imine linkage reaction for the 3D COF-320 membrane formation along with the as-modified α-Al_2O_3 ceramic substrates.

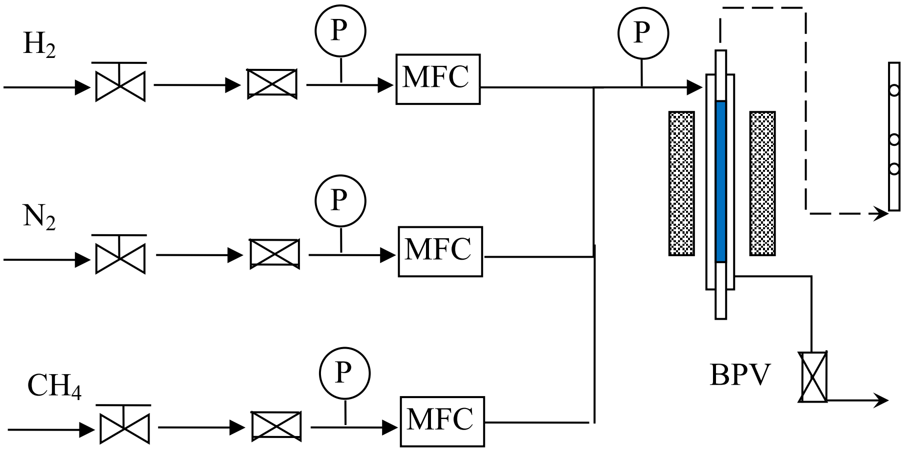
3. Fabrication of COF-320 membrane

The COF-320 membrane was prepared as following: 4,4′-biphenyldicarboxaldehyde (BPDA, 20 mg, 0.095 mmol) and tetra-(4-anilyl)-methane (TAM, 20 mg, 0.053 mmol) were dissolved in 1.0 mL of anhydrous dioxane within a 5 mL ampoule bottle under sonication. Then, 0.2 mL of aqueous acetic acid (3 mol/L) and modified α-Al_2O_3 supports were added into the bottle. After quick freezing the mixture with liquid N_2, the reaction system was degassed by freeze-pump-thaw cycle for 3 times. The frozen bottle was vacuumed under 10 Pa and then quickly sealed with a torch. After heating at 120 ºC for 72 h, the yellow COF-320 membrane was formed on the modified α-Al_2O_3 supports. The COF-320 membrane on α-Al_2O_3 supports was washed with anhydrous THF thoroughly and immersed in anhydrous THF overnight. The solvent was then exchanged with fresh THF for several times. The COF-320 membrane was dried under vacuum at 100 ºC for 24 hours.

The yellow COF-320 powder was also obtained on the bottom of the bottle. The 3D COF-320 powder was isolated by filtration, washed with THF and immersed in anhydrous THF overnight. The solvent was then exchanged with fresh THF for several times. The sample was dried under vacuum at 100 ºC for 24 hours, yielding COF-320 light-yellow powder.

4. Permeation experiments

Scheme S2 represents a schematic of the experimental setup. The membrane module was composed of the membrane tube and stainless steel permeation cell. The tubular COF-320 membranes were placed and fitted in the module using the silicon-rubber sealants and O-type rings. The feeding flow rates and inside chamber pressure were regulated by the mass flow controllers (MFC) and a back pressure valve (BPV), respectively. The permeation flow rates of the various feeding gases through the membranes were measured by the soap bubble flow meter.



Scheme S2. Gas permeation setup for the 3D COF-320 membranes.

5. Characterizations

Scanning electron microscopy (SEM) micrographs were taken on a QUANTA 200 FEG with a cold field emission gun operating at 20 kV. The X-ray diffraction (XRD) patterns were recorded at room temperature with a D/MAX-2500/PC X-ray diffractometer with Cu Ka radiation at 20 kV and 40 mA. The COF-320 powders were characterized by a transmission mode by FT-IR spectrophotometer using a compressed KBr disc. The 3D COF-320 membrane on the surface-modified α-Al_2O_3 substrate was scanned by a reflection mode by a Bruker Optics HYPERION 3000 FT-IR spectrophotometer. TG experiments were carried out on a TA Instruments Netzsch STA 449 F3 series thermal gravimetric analyzer under nitrogen atmosphere.

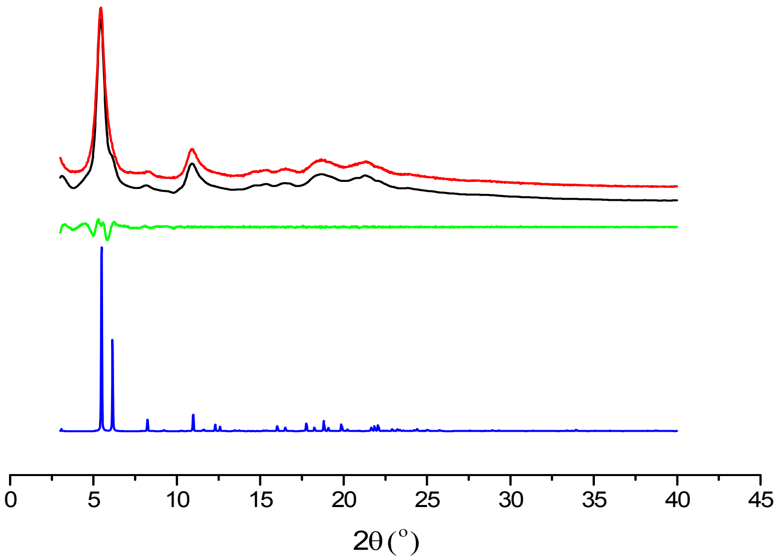


Figure S2. XRD patterns of the 3D COF-320. The red curve is the experimentally observed pattern, the black curve is Pawley refinement and the green curve is their difference. The blue curve is the calculated XRD pattern. Rwp=4.68%, Rp=3.05%, a=28.7744, b=32.2361 and c=7.888.

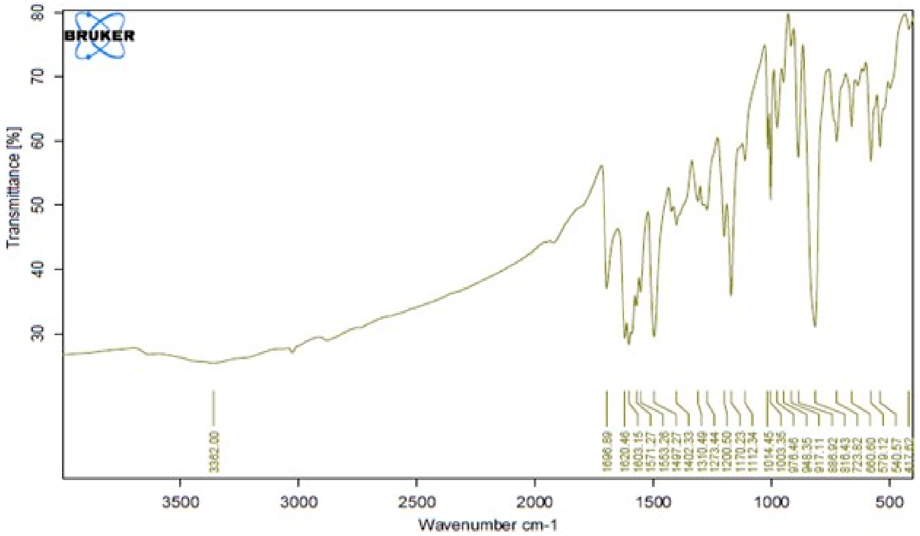


Figure S3. FI-TR spectrum of COF-320 powder collected from the same reaction tube, in which the supported COF-320 membrane was simultaneously formed. The peak at 1620.46 cm^{-1} can be ascribed to the stretching of the formed –C=N–.

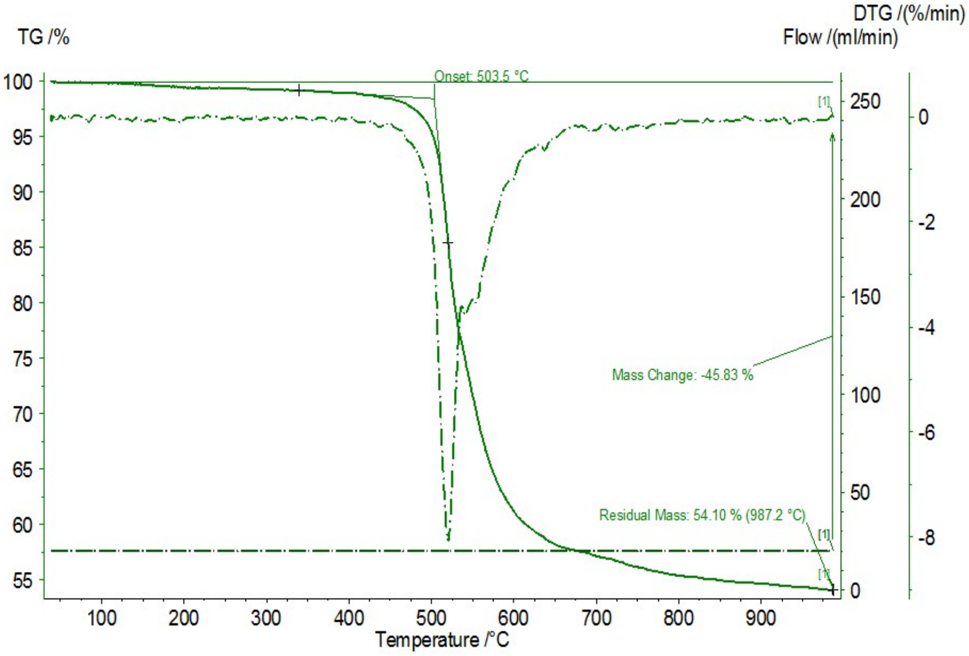


Figure S4. TG of COF-320 powder collected from the same reaction tube, in which the supported COF-320 membrane was simultaneously formed.

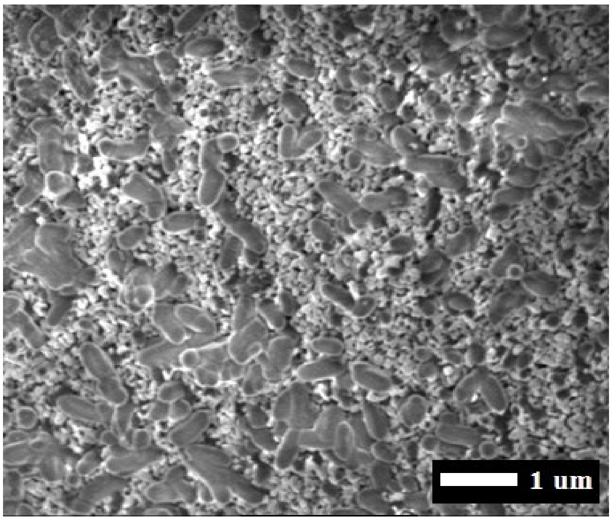


Figure S5. Top view micrograph of the 3D COF-320 membrane grown on the porous α-Al_2O_3 without surface modification and grafting.

Table S1. FT-IR data analysis of the 3D COF-320 membrane on the surface modified and grafted α-Al_2O_3 porous substrate.

Peak (cm^{-1})	**Assignment and notes**
3380.8 (br)	N-H stretching from the groups present at the surface of the crystallites and incompletely reacted groups at defects in the material and unreacted starting material.
3207.6 (br)	O-H stretching vibration from surface modified α-Al_2O_3
3079. 7 (w)	C-H stretching from alkanes of surface modified α-Al_2O_3
3029.8 (s)	Aromatic C-H stretching from phenyl rings in tetraphenylmethane.
2951.6 (s)	Stretching from surface modified α-Al_2O_3
2921.8 (s)	stretching from surface modified α-Al_2O_3
2852.2 (s)	stretching from surface modified α-Al_2O_3
2727.7 (w)	C-H stretch from the –CHO groups present at the surface of the crystallites and incompletely reacted groups at defects in the material and unreacted starting material.
1914.6 (m)	Aromatic C=C ring stretching from incompletely reacted groups at defects in the material and unreacted starting material.
1779.8 (w)	Aromatic C=C ring stretching from incompletely reacted groups at defects in the material and unreacted starting material.
1701.6 (m)	Aromatic C=C ring stretching from phenyl rings in tetraphenylmethane or biphenyl
1624.6 (vs)	Imine C=N stretching.
1606.9 (m)	Aromatic C=C ring stretching from phenyl rings in tetraphenylmethane
1593.1 (m)	Aromatic ring stretching from phenyl rings in tetraphenyladanmantane.
1571.6 (m)	N-H bending vibrations
1554.0 (m)	Aromatic ring stretching from phenyl rings in tetraphenyladanmantane.
1515.6 (m)	Aromatic C=C ring stretching from phenyl rings in tetraphenyl adanmantane.
1501.5 (s)	Aromatic C-C ring stretching from phenylene-dimethylidene ring.
1459.9 (m)	Aromatic C-C ring stretching tetraphenyladanmantane
1402.9 (w)	Aromatic C-C ring stretching tetraphenyladanmantane
1373.6 (w)	Aromatic ring bending.
1318.2 (w)	Aromatic ring stretching from phenylene-dimethylidene ring.
1201.4 (w)	Imine C-C=N-C stretching.
1172.1 (m)	C-Ph breathing. C-C stretching, characteristic of biphenyl.
1115.0 (m)	C-Ph breathing. Tetrahedral C-C stretching, characteristic of tetraphenyladanmantane.
1015.0 (w)	Aromatic C-H in plane bending from tetraphenyladanmantane.
1006.1 (w)	Aromatic C-H in plane bending from biphenyl.
979.0 (w)	Aromatic ring stretching from tetraphenyladanmantane.

952.3 (vw)	Aromatic C-H out of plane vibration from tetraphenylmethane.
883.9 (vw)	Aromatic C-H phenyl ring substitution bands from biphenyl.
836.0 (w)	Si-O stretching vibration
820.7 (w)	Aromatic ring stretching from tetraphenyladanmantane.
660.8 (vw)	C-Ph tetrahedral stretching, characteristic of tetraphenyladanmantane.
629.3 (w)	Si-C stretching from surface modified α-Al_2O_3

Reference

[S1] Plietzsch, O.; Schilling, C. I.; Tolev, M.; Nieger, M.; Richert, C.; Muller, T.; Brase, S. *Org. Biomol. Chem*. **2009**, *7*, 4734.