Supporting Information

A facile solution-phase synthetic approach for phenol-based porous organic cages and covalent organic frameworks

Lei Zhang, [a c] Rongran Liang, [b] Cheng Hang, [a] Haiying Wang, [a] Lin Sun, [c] Lei Xu, [a] Dairong Liu, [a] Zhenyi Zhang, [d] Xingmin Zhang, [e] Feifan Chang, [a] Shengyu Zhao, [a] and Wei Huang* [a,f]

[a]*State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu Province, 210093, P. R. China. E-mail: whuang@nju.edu.cn*

[b]*Key Laboratory of Synthetic and Self-Assembly Chemistry for Organic Functional Molecules, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China*

[c]*Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224051, P. R. China*

[d]*Bruker Scientific Technology Co. Ltd, 66 Xixiaokou Road, Beijing 100081, P. R. China*

[e]*Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 239 Zhangheng Road, Pudong New Area, 201204, P. R. China*

[f] *Shenzhen Research Institute of Nanjing University, Shenzhen, Guangdong Province, 518057, P. R. China*

Table of Contents

Section S-1: Materials and Instrumentation

Materials

2,2-Bis(4-hydroxyphenyl)propane (namely Bisphenol A), 4,4'-methylenediphenol (Bisphenol F) and 1,3,5-Trihydroxywere purchased as analytical grade from Aladdin. All the other chemicals were purchased from commercial corporations and used without further purification.

General Instrumentations and Methods

Powder X-Ray Diffraction (PXRD) was carried out with a PAN alytical X'Pert Powder system using monochromated Cu/Kα (λ = 0.1542 nm). The sample was spread on the square recess of XRD sample holder as a thin layer.

Nuclear Magnetic Resonance (^{1}H, ^{13}C and ^{1}H-^{1}H COSY NMR) data were collected on a Bruker 400 spectrometer.

Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy. Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) spectra were collected on Agilent DD2 600 Solid system, equipped with a 3.2 mm HFXY MAS probe. The Hartmann-Hahn conditions of the CP experiment were obtained at a 15 kHz MAS spinning speed with a contact time of 2.0 ms. Recycle delay times are 5 s. The ^{13}C chemical shifts were externally referenced to tetramethylsilane (δ = 0.0 ppm).

Fourier Transform Infrared Spectroscopy (FT-IR) spectra were recorded as KBr pellets on a Bruker Tensor 27 FT-IR spectrometer.

Electrospray Ionization Mass Spectra (ESI-MS) were recorded by a ThermoFisher Scientific LCQ Fleet mass spectrometer in a scan range of 100-2000 amu.

Thermogravimetric Analysis (TGA) was conducted on a Mettler-Toledo (TGA/DSC) thermal analyzer under N_2 atmosphere in the temperature rang 20~600 °C with a heating rate of 10 °C/min.

Scanning Electron Microscopy (SEM) measurements were executed with scanning electron microscope (SEM, S4800, Hitachi, Japan).

Transmission Electron Microscopy (TEM) measurements were executed with transmission electron microscope (TEM, JEM-200CX, JEOL, Japan).

SFT HPR-100 Reactor. SFT HPR-100 reactor was applied to super-critical carbon dioxide (SCD) activation.

Gas Sorption Analysis. Gas sorption isotherms were collected by a volumetric method on a Micromeritics ASAP 2020 sorption analyzer. All the activated samples were degassed on the analysis port under a vacuum at 150 °C.

Single-Crystal X-ray Diffraction. The X-ray diffraction data of NC1-*S* were obtained at

beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 1.2398 Å. Single crystals of NC2-*R* and NC4-*R* were isolated from the mother liquor and mounted on the sample holder via a nylon loop imbed in Paratone-N. X-ray diffraction data of NC2-*R* and NC4-*R* were collected on a Bruker D8 Venture diffractometer outfitted with a PHOTON-100 CMOS detector using monochromatic microfocus MoK*α* radiation (*λ* = 0.71073 Å) that was operated at 50 kV and 40 mA at 123 K (or 100 K) by chilled nitrogen flow controlled by a KRYOFLEX II low temperature attachment. Unit cell determination was performed in the Bruker SMART APEX III softwar suite. The data sets were reduced and a multi-scan spherical absorption correction was implemented in the SCALE interface.[1] The structures were solved with direct methods and refined by the full-matrix least-squares method in the SHELXL-97 program package.[2] The contribution of disordered solvent molecules was treated as diffuse using *SQUEEZE* procedure implemented in PLATON.[3] Crystallographic data for **NC1-*S***, **NC2-*R*** and **NC4-*R*** described in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication.

Table S-1. Crystal data and structure refinements.

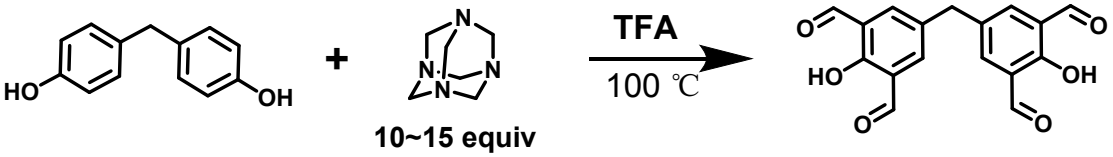
Compound	**NC1-*S***	**NC2-*R***	**NC4-*R***
Empirical formula	C_{84} H_{90} N_{12} O_6	C_{62} H_{80} N_8 O_8	C_{124} H_{144} N_{16} O_8
Formula weight	1364.69	1065.34	1986.54
Temperature / K	100	100	123
Wavelength / Å	0.7107	0.7107	0.7107
CCDC	1573819	1573820	1573821
Crystal Size (mm)	0.12×0.12×0.10	0.10×0.10×0.12	0.10×0.12×0.12
Crystal system	Tetragonal	Tetragonal	Monoclinic
Space group	$P4_32_12$	$P4_32_12$	$I2$
a / Å	24.951(3)	15.7706(4)	18.197(2)
b / Å	24.951(3)	15.7706(4)	18.1795(16)
c / Å	34.647(5)	23.9901(14)	23.1831(19)
α / °	90	90	90
β / °	90	90	100.957(6)
γ / °	90	90	90
V / Å^3	21570(6)	5966.6(4)	7529.4(12)
Z / D_{calcd} (g / cm^3)	8 / 0.840	4 / 1.186	2 / 0.876
F (000)	5808.0	2288	2128
μ / mm^{-1}	0.054	0.079	0.056
h_{min} / h_{max}	-29 / 29	-20 / 20	-16 / 23
k_{min} / k_{max}	-29 / 29	-20 / 20	-23 / 23
l_{min} / l_{max}	-41 / 41	-24 / 31	-30 / 30
Data (Uniq.) / parameters	18993 / 923	6862 / 356	17036 / 675
Final R indices [I > 2ó(I)]	R_1 = 0.1126 wR_2 = 0.2724	R_1 = 0.0474 wR_2 = 0.1117	R_1 = 0.0656 wR_2 = 0.1575
R indices (all data)	R_1 = 0.1283 wR_2 = 0.2831	R_1 = 0.0579 wR_2 = 0.1167	R_1 = 0.1025 wR_2 = 0.1698
S	1.08	1.05	1.01
Max. / min. $\triangle\rho$/e·Å^{-3}	0.39/-0.37	0.27/-0.20	0.29/-0.31

$R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma w(Fo^2)^2]^{1/2}$

Section S-2: Synthetic Procedures

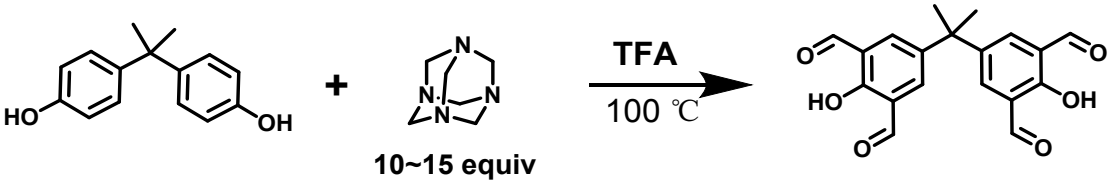
Synthesis of tetraaldehyde 1. The starting material 3,3',5,5'-tetraformyl-4,4'-biphenyldiol (**1**) was prepared according to a literature method.[4]

Synthesis of tetraaldehyde 2. 4,4'-Methylenediphenol (3.00 g, 14.98 mmol) and 10~15 equiv of hexamethylenetetramine (HMT) were mixed in a 250 mL round-bottomd flask, then trifluoroacetic acid (60~80 mL) was added. The mixture was heated at 100 °C under Ar atmosphere for 24 h via an oil bath. After being colded to room temperuture, 4 M HCl (~100 mL) was poured into the resultant red viscous solution and refluxed at 100 °C for 3 h. The mixture was then cooled to room temperuture, and the precipitated yellow product was filtered, dried under a vacuum and recrystalized from DMSO (< 20 mL) to give orange microcrystals **2** in a yield of 1.50 g (32 %). ^{1}H NMR (400 MHz, DMSO-d_6, TMS, ppm) δ 10.22 (s, CHO, 4H), 7.96 (s, ArH, 4H), 4.09 (s, CH_2, 2H); ^{13}C NMR (101 MHz, DMSO-d_6, TMS, ppm) δ:192.56, 161.38, 137.42, 133.06, 124.18, 38.22. FT-IR (KBr pellet, cm^{-1}) v 2873 (m), 1688 (vs), 1655 (vs), 1619 (w), 1596 (s), 1450 (s), 1404 (w), 1343 (w), 1320 (w), 1297 (w), 1261 (m), 1223 (s), 1158 (w), 1002 (s), 923 (s), 812 (w), 770 (m), 750 (m), 628 (m), 497(m).



Bisphenol F **10~15 equiv hexamethylenetetramine** **2**

Synthesis of tetraaldehyde 3. 2,2-Bis(4-hydroxyphenyl)propane (3.40 g, 14.89 mmol) and 10~15 equiv of hexamethylenetetramine (HMT) were dissolved in trifluoroacetic acid (60~80 ml). The mixture was heated at 100 °C under Ar atmosphere for 24 h via an oil bath. After being colded to room temperuture, 4 M HCl (~100 mL) was poured into the resultant red viscous solution and refluxed at 100 °C for 3 h. After being cooled to room temperature, the mixture was filtered and the filtrate was extracted with500 mL dichoromethane, dried over magnesium sulfate, and filtered again. The crude yellow powder or oil was afforded by rotary evaporation of the filtrate, and purified by recrystalization from EtOH/H_2O to give pale yellow powder **3** (1.80 g, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) δ 11.56 (s, OH, 2H), 10.22 (s, CHO, 4H), 7.83 (s, ArH, 4H), 1.78 (s, CH_3, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, TMS, ppm) δ 192.03, 162.11, 141.23, 135.51, 122.98, 41.99, 30.50. FT-IR (KBr pellet, cm^{-1}) v 3268 (w), 2980 (m), 2894 (m), 1687 (vs), 1662 (vs), 1601 (s), 1524 (w), 1457 (s), 1426 (w), 1396 (m), 1301 (m), 1267 (m), 1200 (s), 1120 (w), 1011 (w), 977 (s), 902 (w), 810 (w), 768 (m), 732 (m), 654 (w), 615(m), 517 (w).

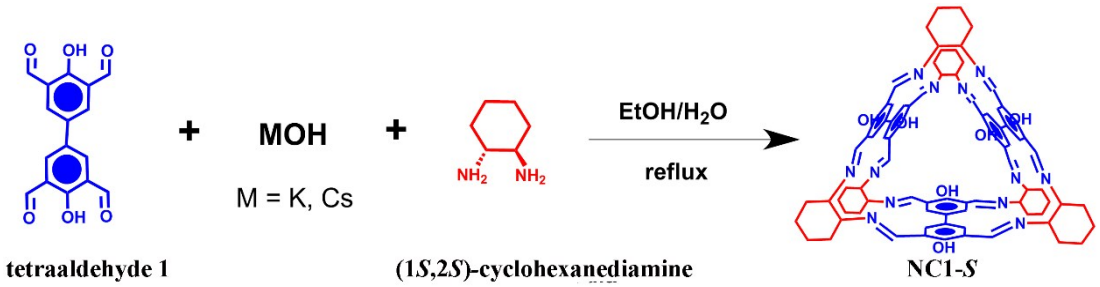


Bisphenol A **10~15 equiv hexamethylenetetramine** **3**

Synthesis of Tp. The starting material 1,3,5-triformylphloroglucinol wasprepared according to a literature method.[5]

Synthesis of NC1-*S*. Tetraaldehyde **1** (150 mg, 0.50 mmol) and 2~6 equiv KOH (or CsOH) were dissolved in a mixture of water/ethanol (20~100/100 mL, *v/v*) and refluxed for 1 h. A 50 mL ethanol solution of (1*S,2S*)-cyclohexanediamine (126 mg, 2.2 equiv relative to tetraaldehyde **1**) was added into the mixture and refluxed for additional 24 h. The resulting clear solution was filtered and the filtrate was allowed to slow evaporation to afford red crystals of NC1-*S* within 24 hours (~98 mg, 43 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) *δ*14.09 (s, OH, 6H), 8.53 (s, 6H), 8.49 (s, 6H), 8.20 (s, 6H), 7.69 (s, 6H), 3.40 (s, CHN, 6H) 3.09 (s, CHN, 6H), 1.81~0.97 (m, CH_2, 48H); ^{13}C NMR (101 MHz, $CDCl_3$, TMS, ppm) *δ* 165.25, 161.87, 157.99, 129.18, 126.51, 124.91, 123.86, 118.51, 74.65, 72.56, 32.49, 31.69, 29.69, 24.17, 24.06; FT-IR (KBr pellet, cm^{-1}) *v* 3445 (m), 2933 (m), 2863 (m), 1643(vs), 1597(s), 1531(w), 1449 (vs), 1380 (m), 1344 (w), 1288 (m), 1255 (m), 1147 (m), 1094 (m), 1012 (m), 980 (w), 939 (w), 870 (m), 844 (w), 764 (w), 678 (m), 628 (w), 591 (w), 535 (w), 481 (w), 459 (w); Positive ESI-MS in CH_3OH, *m/z* = 1364.17 ([M+H]$^+$), Calad. for $C_{84}H_{91}N_{12}O_6$: 1363.71; 1386.17 ([M+Na]$^+$), Calad. for $C_{84}H_{90}N_{12}O_6Na$: 1385.70. Anal.Calcld. For $C_{84}H_{90}N_{12}O_6$: C, 73.98; H, 6.65,; N, 12.33; found : C:74.11; H, 6.64; N, 12.61.

Scalable synthesis: The scalable synthetic protocol for **NC1-*S*** is as followed: Tetraaldehyde **1** (1 g, 3.35 mmol) and 2 equiv KOH were dissolved in a mixture of water/ethanol (100/250 mL, *v/v*) and refluxed for 0.5 h. A 300 mL ethanol solution of (1*S,2S*)-cyclohexanediamine (840 mg, 2.2 equiv relative to tetraaldehyde **1**) was added into the mixture and refluxed for additional 12 h. The resulting clear solution was filtered and the filtrate was allowed to slow evaporation to afford red crystals of **NC1-*S*** within 24 hours.



Syntheses of NC2-*R* and NC3-*R*. Tetraaldehyde **2** (150 mg, 0.48 mmol) and 2~6 equiv KOH (or NaOH, CsOH) were dissolved in a mixture of water and ethanol (50~100/80~120 mL, *v/v*) and refluxed for 1 h. A 20~50 mL ethanol solution of (1*R*,2*R*)-cyclohexanediamine (137 mg, 2.5 equiv relative to tetraaldehyde **2**) was added into the mixture, and refluxed for additional 24 h. The resulting clear solution was filtered and the filtrate was allowed to slow evaporation at higher ambient temperature (above approximate 30 ^{o}C) to afford cage crystals of **NC2-*R*** (>80 mg, 35%), whereas lower environmental temperature favors to crystallize **NC3-*R*** (> 100 mg, 44%). It is found that crystals of **NC2-*R*** and **NC3-*R*** have different growing habit and they are easy to be distinghished. Namely, the former has polyhedral morphology and the latter is needle-like.

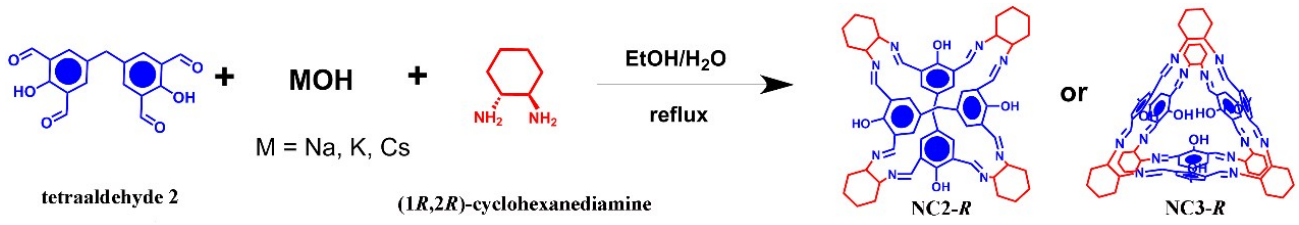
NC2-*R*: ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) *δ*14.72 (s, OH, 4H), 8.71 (s, 4H), 8.02 (s, 4H), 7.18 (d, 4H), 6.95 (d, 4H), 3.38 (m, 8H), 3.20 (d, 4H), 2.14~1.51 (m, CH_2, 32H); ^{13}C NMR (101 MHz, $CDCl_3$, TMS, ppm) *δ* 164.51, 160.49, 158.60, 132.31, 131.08, 128.96, 124.24, 117.48, 76.63, 73.40, 40.45, 32.48, 31.62, 24.67, 24.10. FT-IR (KBr pellet, cm^{-1}) *v* 3364 (w), 2936 (m),

2860 (m), 1635 (vs), 1600 (s), 1532 (w), 1453 (s), 1377 (w), 1338 (w), 1298 (w), 1253 (w), 1148 (w), 1098 (w), 1024 (w), 942 (w), 877 (w), 757 (w), 678 (w); Positive ESI-MS in CH_3OH, *m/z* = 938.00 ([M+H]$^+$). Calad for $C_{58}H_{65}N_8O_4$: 937.51. Anal. Calcld. For $C_{62}H_{80}N_8O_8$: C, 69.90; H, 7.57; N, 10.52; found: C, 69.71; H, 7.82; N, 10.40.

NC3-*R*: ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) *δ*13.89 (s, OH, 6H), 8.72 (s, 6H), 8.25 (s, 6H), 7.74 (d, 6H), 7.23 (d, 6H), 3.60 (s, 6H), 3.41 (m, 12H), 1.90~1.45 (m, 48H), -2.23 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$, TMS, ppm) *δ* 163.59, 160.04, 156.36, 133.54, 131.65, 128.32, 123.09, 119.44, 75.89, 72.19, 41.05, 34.40, 33.13, 24.46, 24.33. FT-IR (KBr pellet, cm^{-1}) *v* 3410 (w), 3133 (s), 2939 (m), 2856 (m), 1636 (s), 1452 (s), 1398 (vs), 1301 (w), 1252 (w), 1151 (w), 1095 (w), 1031 (w); ESI-MS in CH_3OH, *m/z* = 1406.92 ([M+H]$^+$). Calad. for $C_{87}H_{97}N_{12}O_6$: 1405.76;*m/z* = 704.08 ([M/2+H]$^+$), Calad. for $C_{43.5}H_{49}N_6O_3$: 703.38. Anal. Calcld. $C_{87}H_{96}N_{12}O_6$: C, 74.33; H, 6.88; N, 11.96; found: C, 74.11; H, 6.90; N, 11.99.

Notice: The obtaining of crystals **NC3-*R*** or **NC2-*R*** was not influenced by the reacion temperature and time as well as the ratios of solvents or MOH (M = Na, K, Cs). It is related to the ambient temperature during the solvent evaporation. Actually, it is easy to collect **NC2-*R*** crystals at higher ambient temperature, while **NC3-*R*** at lower environmental temperature.

Scalable synthesis: The scalable synthetic protocol for **NC2-*R*** and **NC2-*R*** is as followed: Tetraaldehyde **2** (1 g, 3.20 mmol) and 2 equiv KOH were dissolved in a mixture of water and ethanol (100/200 mL, *v/v*) and refluxed for 1 h. A 100 mL ethanol solution of (1*R*,2*R*)-cyclohexanediamine (802 mg, 2.2 equiv relative to tetraaldehyde **2**) was added into the mixture, and refluxed for additional 12 h. The resulting clear solution was filtered and the filtrate was allowed to slow evaporation to afford cage crystals of **NC2-*R*** or **NC3-*R***.

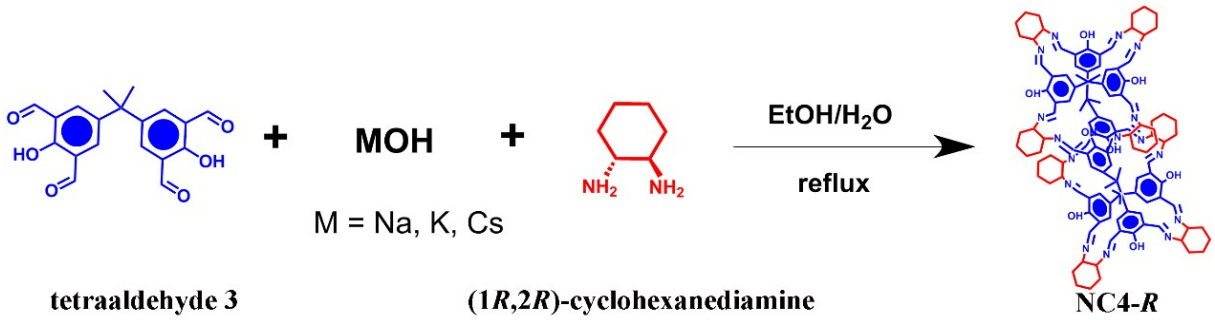


Synthesis of NC4-*R*. Tetraaldehyde **3** (100 mg, 0.29 mmol) and 2~6 equiv KOH or NaOH, CsOH were dissolved in a mixture of water and ethanol (50~100/80~120 mL, *v/v*) and refluxed for 1 h. A 20~50 mL ethanol solution of (1*R*,2*R*)-cyclohexanediamine (84 mg, 2.5 equiv relative to tetraaldehyde **3**) was added into the mixture and refluxed for additional 24 h. Theresulting clear solution was filtered and the filtrate was allowed to slow evaporation for weeks to afford yellow crystals of NC4-*R* in a yield of 43 mg (30 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm) *δ* 14.31 (s, 8H), 8.70 (s, 4H), 8.60 (s, 4H), 8.32 (s, 4H), 8.13 (s, 4H), 7.97 (s, 4H), 7.51 (s, 8H), 6.99 (s, 4H), 3.38 (m, 12H), 3.24 (m, 4H), 2.03~1.26 (m, 88H); ^{13}C NMR (101 MHz, $CDCl_3$, TMS, ppm) *δ* 164.99, 164.87, 159.47, 159.07, 155.77, 155.02, 139.13, 138.40, 133.72, 130.53, 127.60, 126.62, 124.14, 122.62, 118.63, 118.50, 76.36, 75.23, 73.62, 42.11, 40.19, 33.78, 32.89, 32.45, 29.17, 24.75, 24.49, 24.30, 24.16. FT-IR (KBr pellet, cm^{-1}) *v*3413 (w), 2935 (m), 2864 (m), 1634 (s), 1530 (w), 1457 (s), 1373 (w), 1306 (w), 1262 (w), 1196 (w), 1140 (w), 1091 (w), 1047 (w); Positive ESI-MS in CH_3OH, *m/z* = 1987.75 ([M+H]$^+$), Calad. for $C_{124}H_{145}N_{16}O_8$: 1987.15; *m/z* = 994.08 ([M/2+H]$^+$), Calad. for $C_{124}H_{144}N_{16}O_8$: 994.31. Anal.

Calcld. $C_{124}H_{144}N_{16}O_8$: C, 74.97; H, 7.31; N, 11.28; found: C, 75.22; H, 7.01; N, 10.95.

Notice: In our experiments, [4+8] cage **NC4-*R*** was isolated as block crystals (Figure S27) in a yield of ~30% via slow evaporation for several weeks, accompanied by some amorphous by-products with unknown structures (Figures S17, S20). Many attempts to avoid yielding the amorphous solid were not successful, including adjusting the solvent ratios, equiv. of NaOH (KOH) and reaction temperature. Fortunately, **NC4-*R*** could be easily purified by water or ether washing and successfully characterized by ^{1}H and ^{13}C NMR spectroscopy, FT-IR and PXRD.

Scalable synthesis: The scalable synthetic protocol for **NC4-*R*** is as followed: Tetraaldehyde **3** (1 g, 2.94 mmol) and 2 equiv KOH were dissolved in a mixture of water and ethanol (100/200 mL, *v/v*) and refluxed for 1 h. A 100 mL ethanol solution of (1*R*,2*R*)-cyclohexanediamine (737 mg, 2.2 equiv relative to tetraaldehyde **3**) was added into the mixture, and refluxed for additional 12 h. The resulting clear solution was filtered and the filtrate was allowed to slow evaporation to afford cage crystals of **NC4-*R***.



Synthesis of COF-NJU-1. Tetraaldehyde **1** (100 mg, 0.34 mmol) and 2 equiv. KOH were dissolved in water (10 mL) under ultrasonication. The red clear solution was heated at 140 °C for several minutes with constant stirring. After that, a *N*,*N*-Diethylformamide (DMF) solution (10-30 mL) of 2 equiv. benzidine was added into the red solution maintaining the temperature at 140 °Cand stirring. When the mixture was refluxed for about 1 h, the solution became opaque and red precipitate began to emergegradually. After 24 h, the precipitate was filtered and washed several times with DMF repeatedly. Ethanol and acetone were also used for washing and the powder was dried under a vacuum to yield COF-NJU-1(146 mg, 73 %). FT-IR (KBr pellet, cm^{-1})*v*3381 (w), 1623 (s), 1578 (s), 1529 (w), 1493 (s), 1448 (m), 1402 (w), 1265 (m), 1204 (m), 1173 (m), 1085 (w), 1010 (m), 820 (s), 759 (m). Anal.Calcd (%) for $C_{80}H_{26}N_4O_2$: C, 80.79; H, 4,41; N, 9.42; found: C, 80.99; H, 4.75; N, 9.71.

Scalable synthesis: The scalable synthetic protocol for **COF-NJU-1** is as followed: Tetraaldehyde **1** (1192 g, 4 mmol) and 2 equiv KOH were dissolved in water (35 mL) and refluxed for several minutes with constant stirring. After that, a *N*,*N*-Diethylformamide (DMF) solution (50 mL) of 2 equiv. benzidine was added into the red solution maintaining the temperature at 140 °C and stirring. When the mixture was refluxed for about several minutes, the solution became opaque and red precipitate began to emergegradually. After 12 h, the precipitate was filtered and washed several times with DMF repeatedly. Ethanol and acetone were also used for washing and the powder was dried under a vacuum to yield **COF-NJU-1**.

***CAUTION*:** Benzidine used in the synthesis of **COF-NJU-1** is potentially hazardous. Please

take protection measures during the process of experiment.

Synthesis of TpPa-1. 1,3,5-Triformylphloroglucinol (**Tp**) (70 mg, 0.33 mmol) and 3~5 equiv. KOH were dissolved in water (10 mL) under ultrasonication. The clear solution was heated at 140 °C for several minutes with constant stirring. After that, a DMF solution (15 mL) of 1,4-diaminobenzene (54 mg, 1.5 equiv.) was added maintaining the temperature at 140 °C and stirring. When the mixture was refluxed for about 15 minuts, the solution became opaque and dark-red precipitate emergedgradually. After 24 h, the precipitate was filtered and washed several times with DMF repeatedly. Ethanol and acetone were also used for washing and the powder was dried under a vacuum to yield **TpPa-1** (94 mg, 89 %). FT-IR (KBr pellet, cm^{-1})*v* 3446 (w), 1591 (s), 1448 (m), 1250 (s), 1120 (w), 994 (w), 820 (w). Anal. Calcld. for $C_{80}H_{48}N_{13}O_{12}$: C, 69.46; H, 3.47; N, 13.87; found: C, 68.68; H, 3.72; N, 13.46.

Scalable synthesis: The scalable synthetic protocol for **TpPa-1** is as followed: 1,3,5-Triformylphloroglucinol (**Tp**) (630 mg, 3 mmol) and 2 equiv. KOH were dissolved in water (35 mL) under ultrasonication.The clear solution was heated at 140 °C for several minutes with constant stirring. After that, a DMF solution (60 mL) of 1,4-diaminobenzene (486 mg, 1.5 equiv.) was added maintaining the temperature at 140 °C and stirring. When the mixture was refluxed for about several minuts, the solution became opaque and dark-red precipitate emergedgradually. After 12 h, the precipitate was filtered and washed several times with DMF repeatedly. Ethanol and acetone were also used for washing and the powder was dried under a vacuum to yield **TpPa-1**.

Synthesis of TpBD. The above synthetic procedure for **TpPa-1** was followed. Using 1,3,5-triformylphloroglucinol (70 mg, 0.33 mmol), KOH (3~5 equiv.), benzidine (92 mg, 0.5 mmol), H_2O (10 mL), DMF (15 mL), **TpBD** was obtained as orange precipitate (119 mg, 83 %). FT-IR (KBr pellet, cm^{-1})*v*3441 (w), 1586 (s), 1501 (w), 1452 (m), 1281 (s), 1253 (s), 1099 (w), 994 (w), 815 (w). Anal. Calcld. for C_9H_6NO: C, 74.99; H, 4.16; N, 9.72; found: C, 74.68; H, 4.56; N, 9.97.

Scalable synthesis: The scalable synthetic protocol for **TpBD** is as followed: 1,3,5-Triformylphloroglucinol (**Tp**) (630 mg, 3 mmol) and 2 equiv. KOH were dissolved in water (35 mL) under ultrasonication.The clear solution was heated at 140 °C for several minutes with constant stirring. After that, a DMF solution (50 mL) of benzidine (837 mg, 1.5 equiv.) was added maintaining the temperature at 140 °C and stirring. When the mixture was refluxed for about several minuts, the solution became opaque and orange precipitate emergedgradually. After 12 h, the precipitate was filtered and washed several times with DMF repeatedly. Ethanol and acetone were also used for washing and the powder was dried under a vacuum to yield **TpBD**.

CAUTION: Benzidine used in the **TpBD** synthesis is potentially hazardous. Please take protection measures during the process of experiment.

Synthesis of TpTph. The above synthetic procedure for **TpPa-1** was followed. Using 1,3,5-triformylphloroglucinol (75 mg, 0.33 mmol), KOH (3~5 equiv.), 4,4'-diamino-*p*-terphenyl (129 mg, 0.50 mmol), H_2O (10 mL), DMF (15 mL), **TpTph** was obtained as yellow precipitate (157

mg, 86 %). FT-IR (KBr pellet, cm^{-1}) *v* 3442 (w), 1583 (s), 1493 (w), 1449 (m), 1283 (s), 1243 (s), 1110 (w), 994 (w), 809 (w). Anal. Calcld. for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52. found: C, 70.58; H, 4.12; N, 7.20.

Scalable synthesis: The scalable synthetic protocol for **TpTph** is as followed: 1,3,5-Triformylphloroglucinol (**Tp**) (630 mg, 3 mmol) and 2 equiv. KOH were dissolved in water (50 mL) under ultrasonication.The clear solution was heated at 140 °C for several minutes with constant stirring. After that, a DMF solution (100 mL) of 4,4'-diamino-*p*-terphenyl (1170 mg, 1.5 equiv.) was added maintaining the temperature at 140 °C and stirring. When the mixture was refluxed for about several minuts, the solution became opaque and yellow precipitate emerged gradually. After 12 h, the precipitate was filtered and washed several times with DMF repeatedly. Ethanol and acetone were also used for washing and the powder was dried under a vacuum to yield **TpTph**.

Section S-3: ^{1}H and ^{13}C NMR Spectra of Tetraaldehyde Precursors and POCs as Well as ^{13}C CP-MAS Spectrum of COF-NJU-1

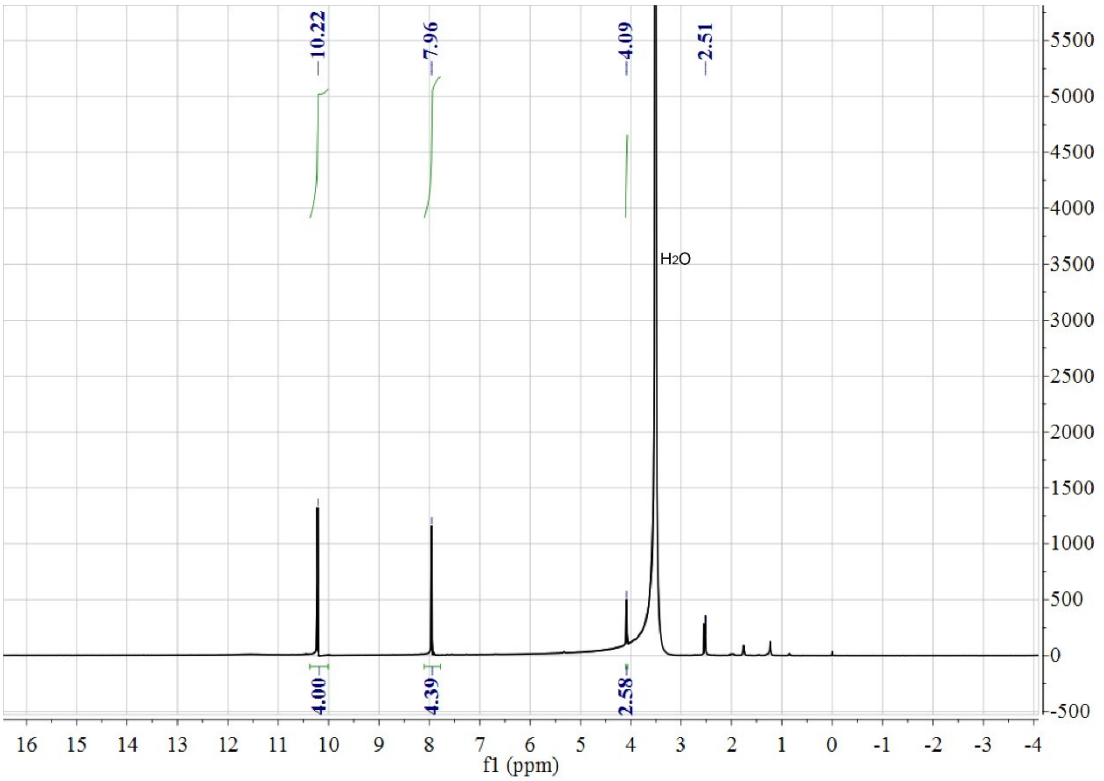


Figure S1. ^{1}H NMR spectrum (DMSO-d_6) of tetraaldehyde **2**.

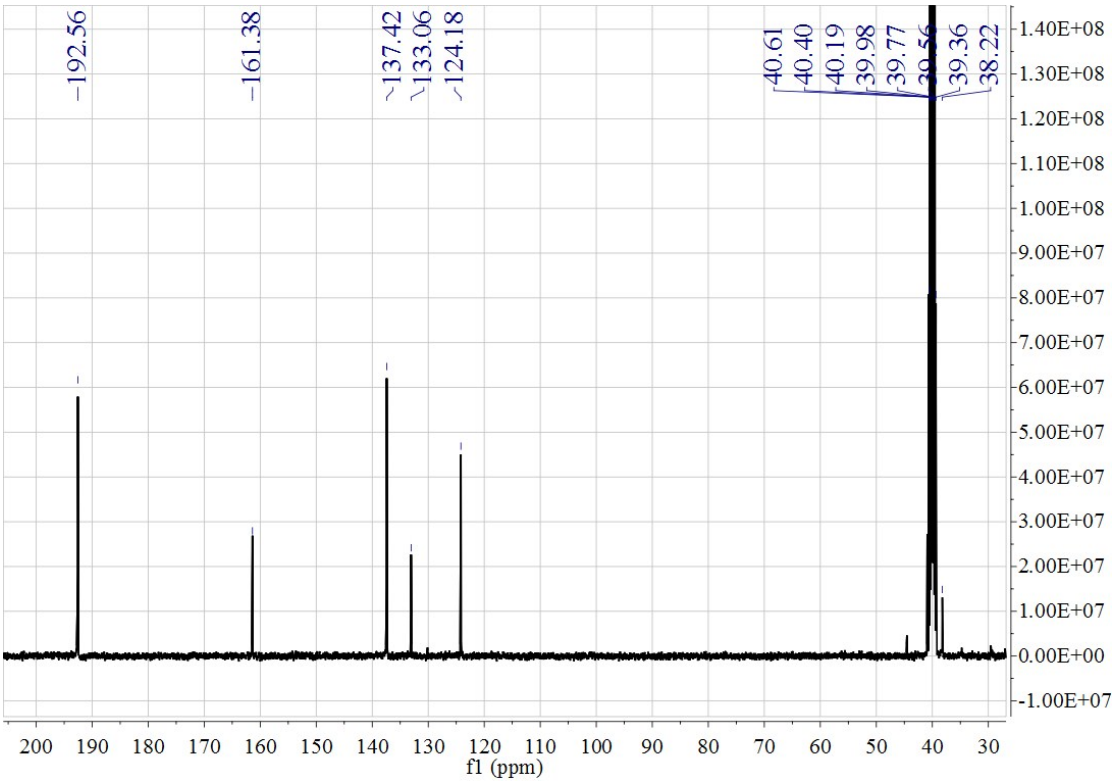


Figure S2. ^{13}C NMR spectrum (DMSO-d_6) of tetraaldehyde **2**.

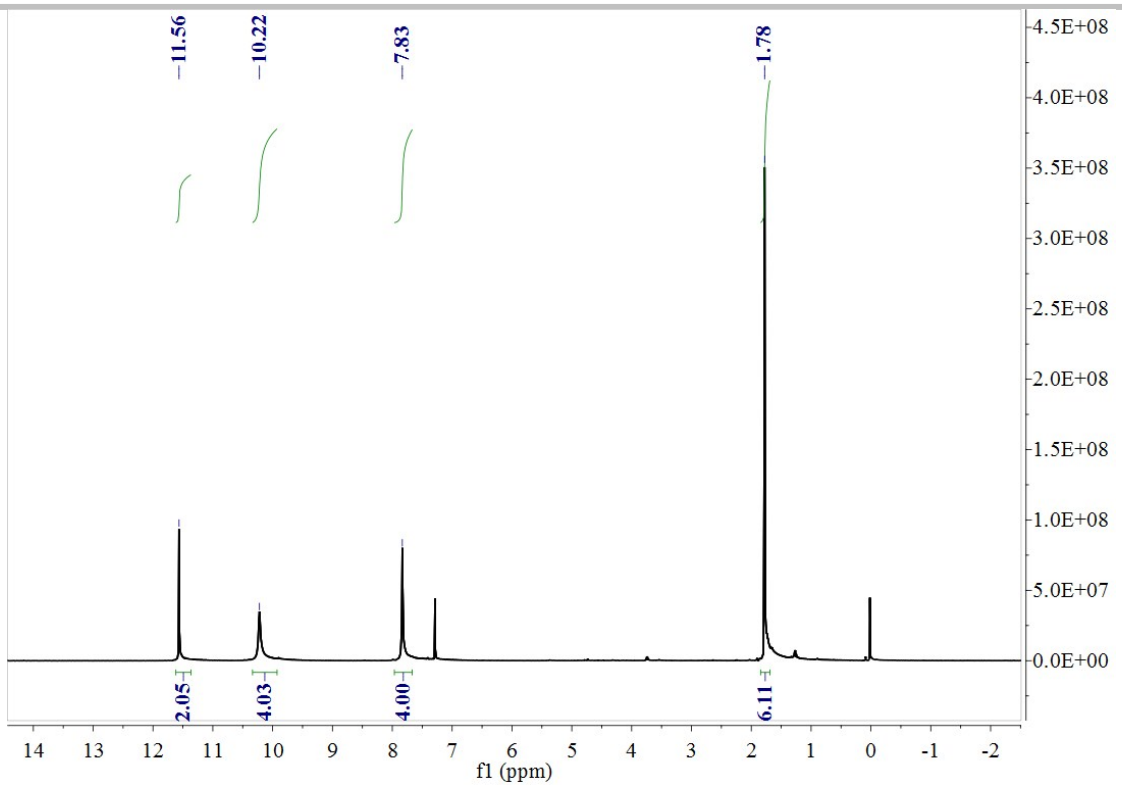


Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of tetraaldehyde **3**.

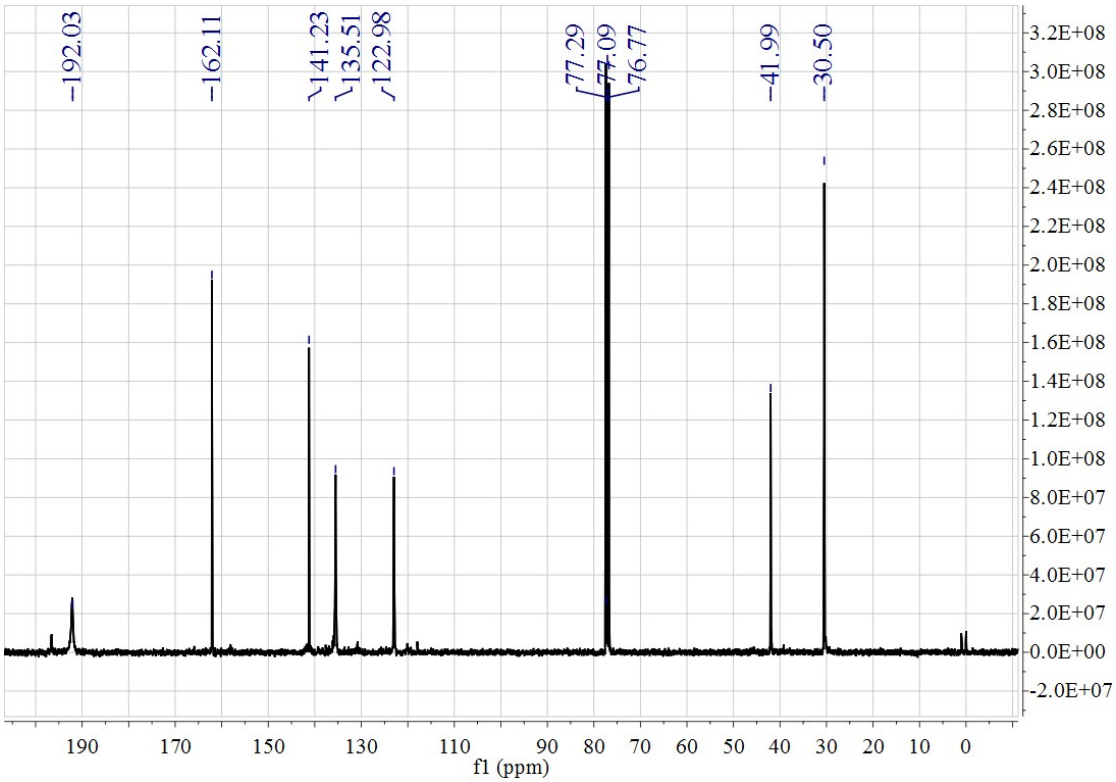


Figure S4. ^{13}C NMR spectrum ($CDCl_3$) of tetraaldehyde **3**.

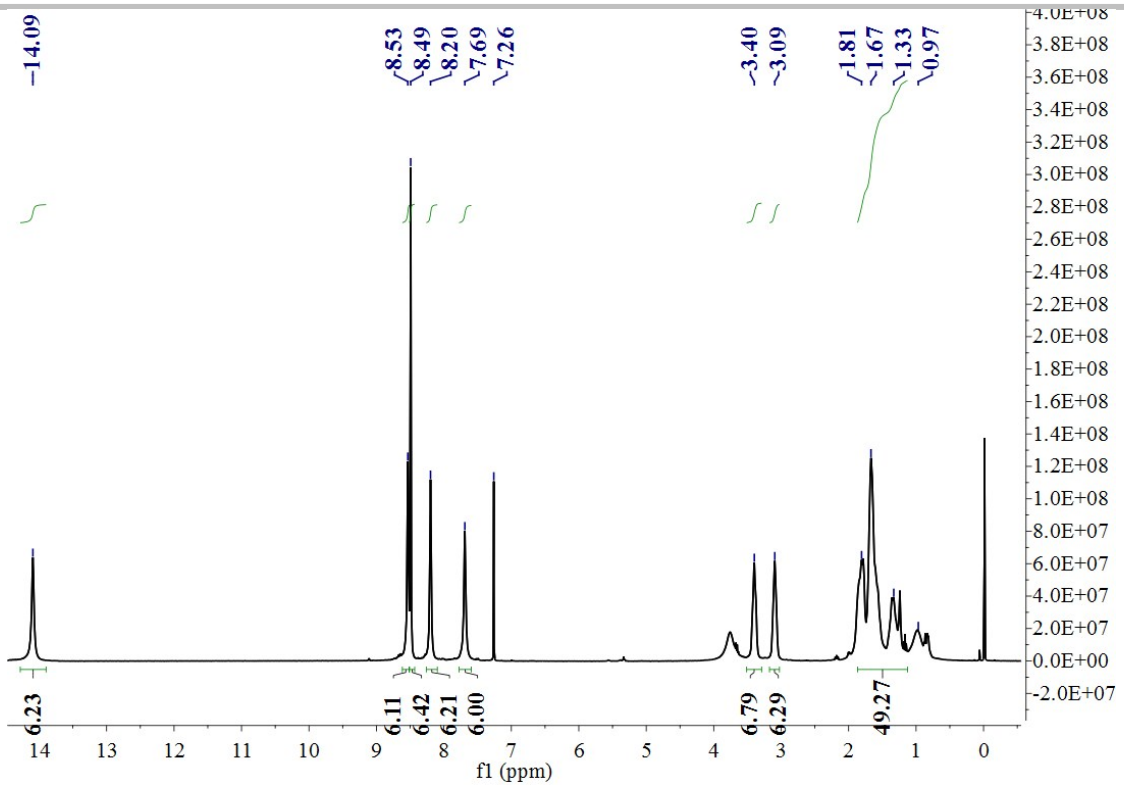


Figure S5. ^{1}H NMR spectrum ($CDCl_3$) of **NC1-*S***.

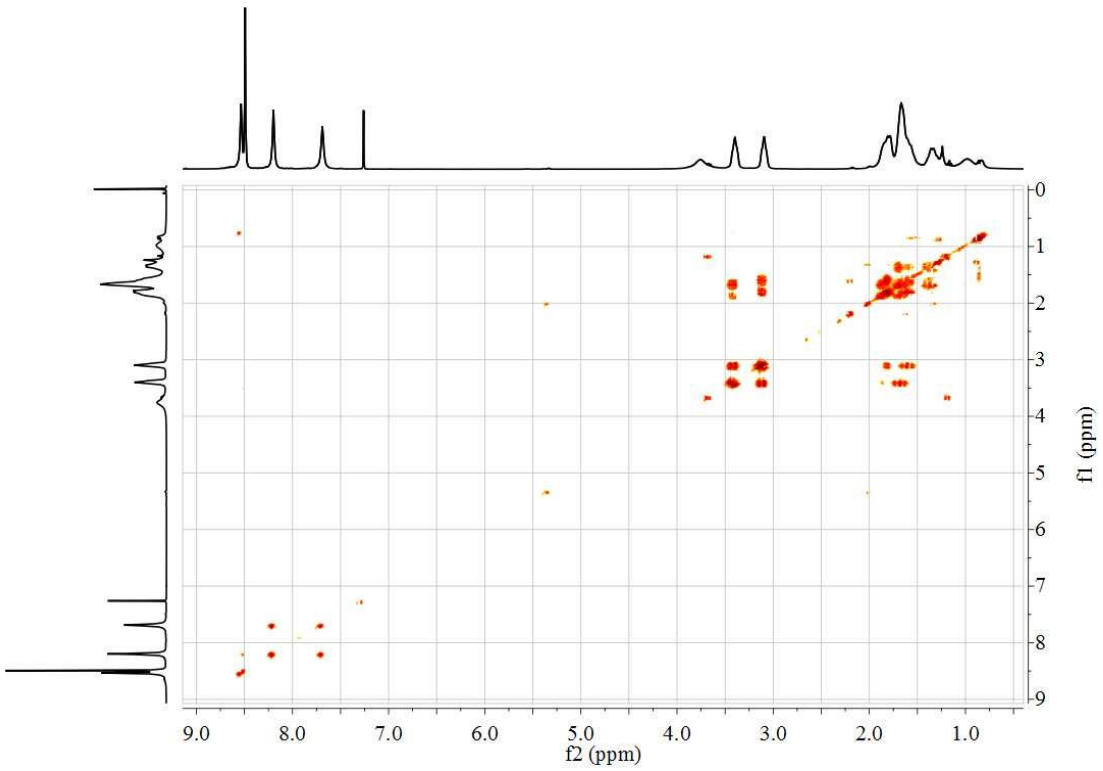


Figure S6.^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$) of **NC1-S**.

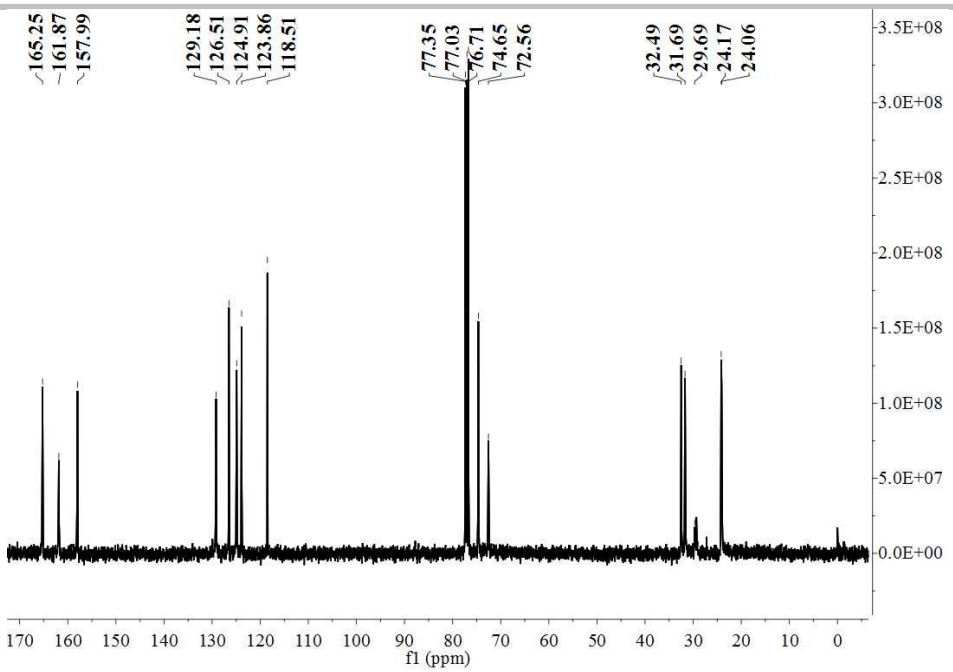


Figure S7. ^{13}C NMR spectrum ($CDCl_3$) of **NC1-*S***.

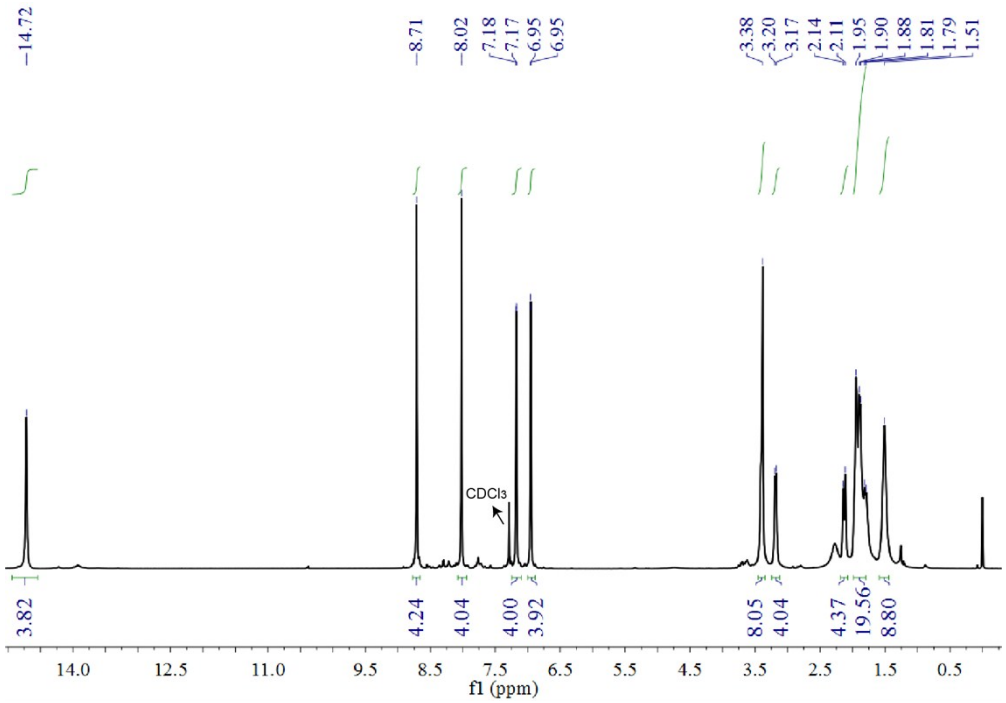


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of **NC2-*R***.

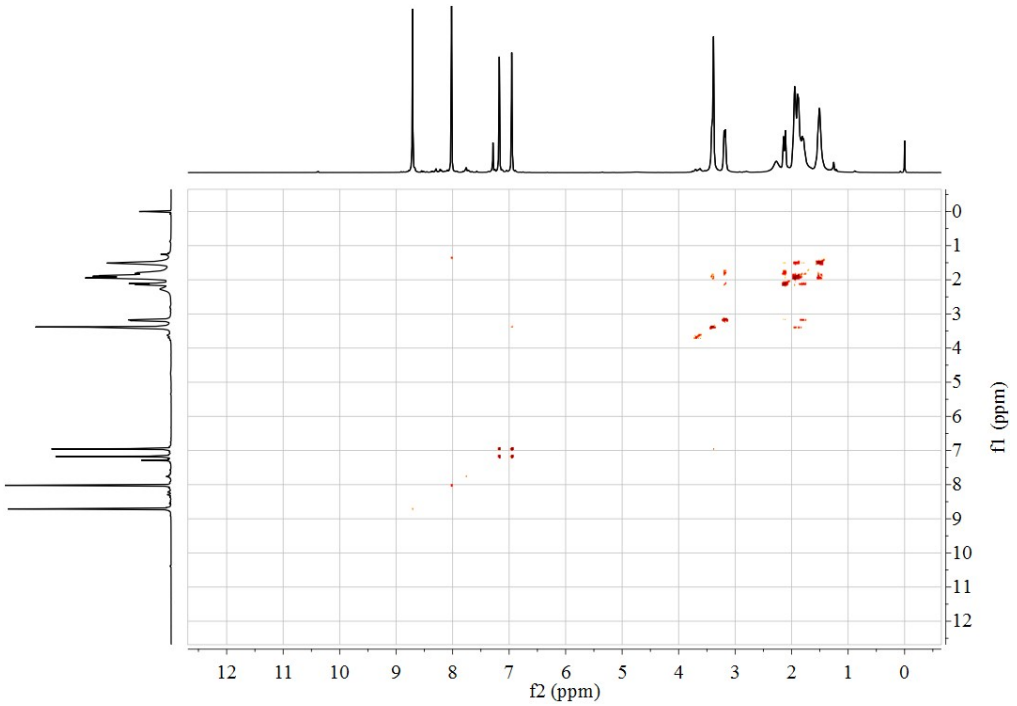


Figure S9. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$) of **NC2-*R***.

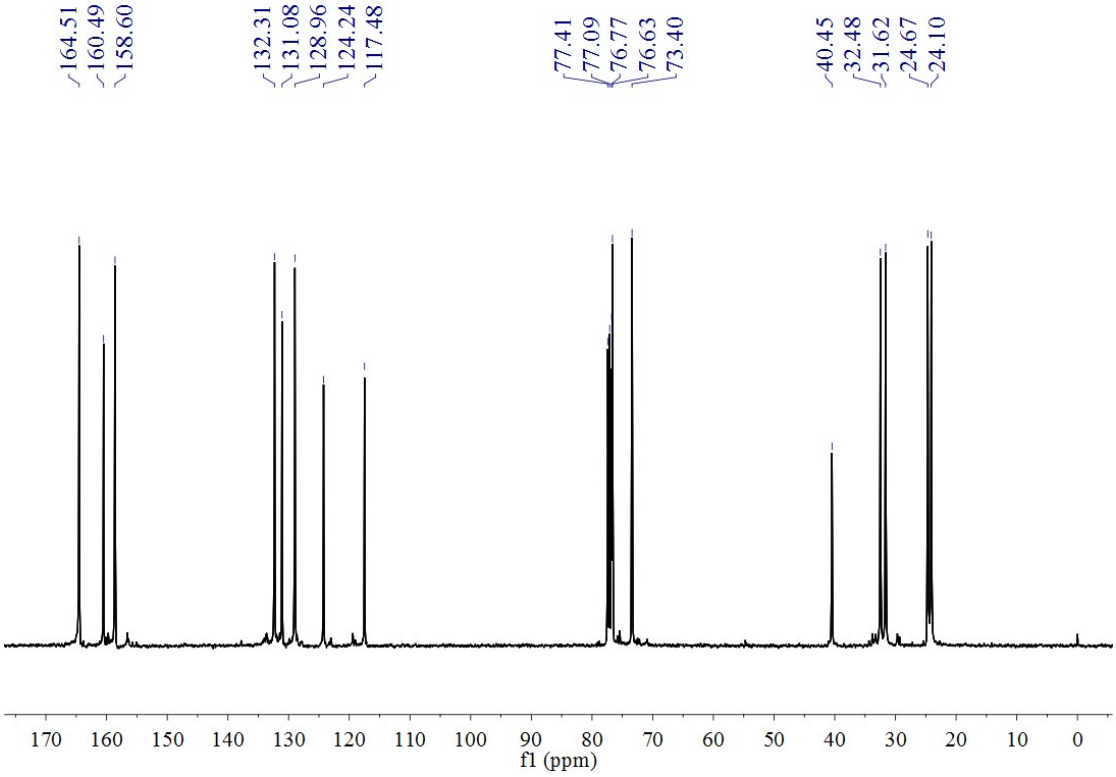


Figure S10. ^{13}C NMR spectrum ($CDCl_3$) of **NC2-*R***.

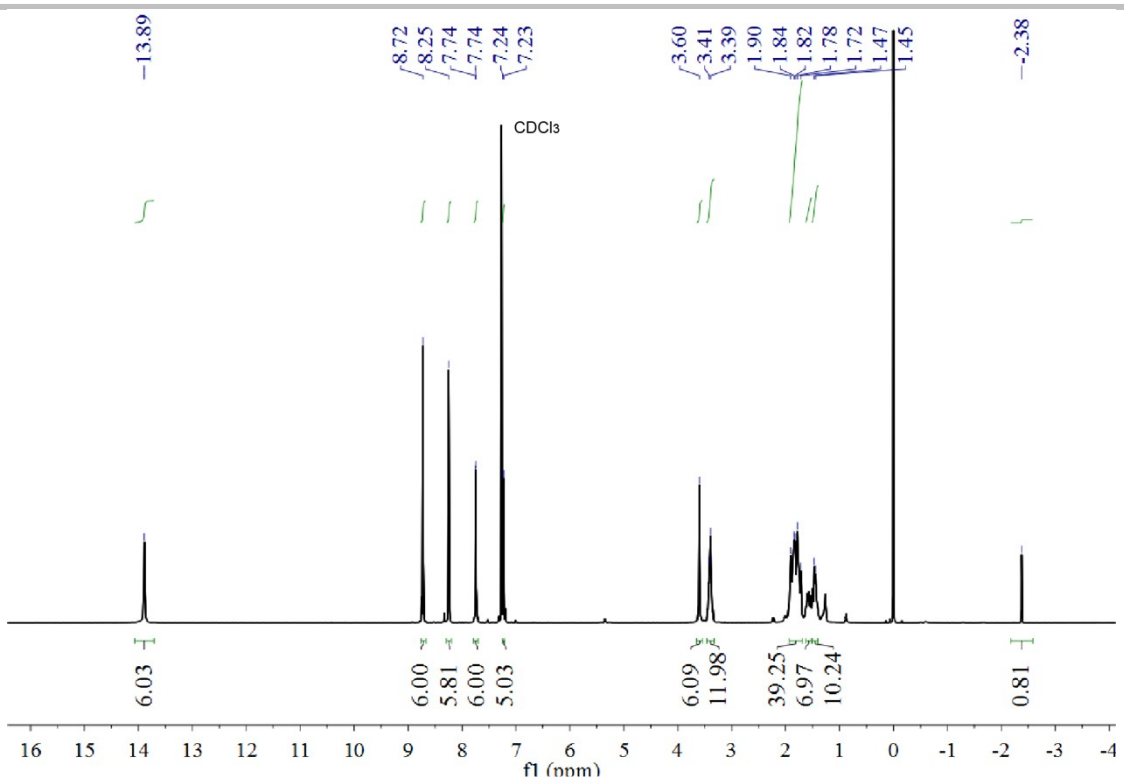


Figure S11. ^{1}H NMR spectrum ($CDCl_3$) of **NC3-*R***.

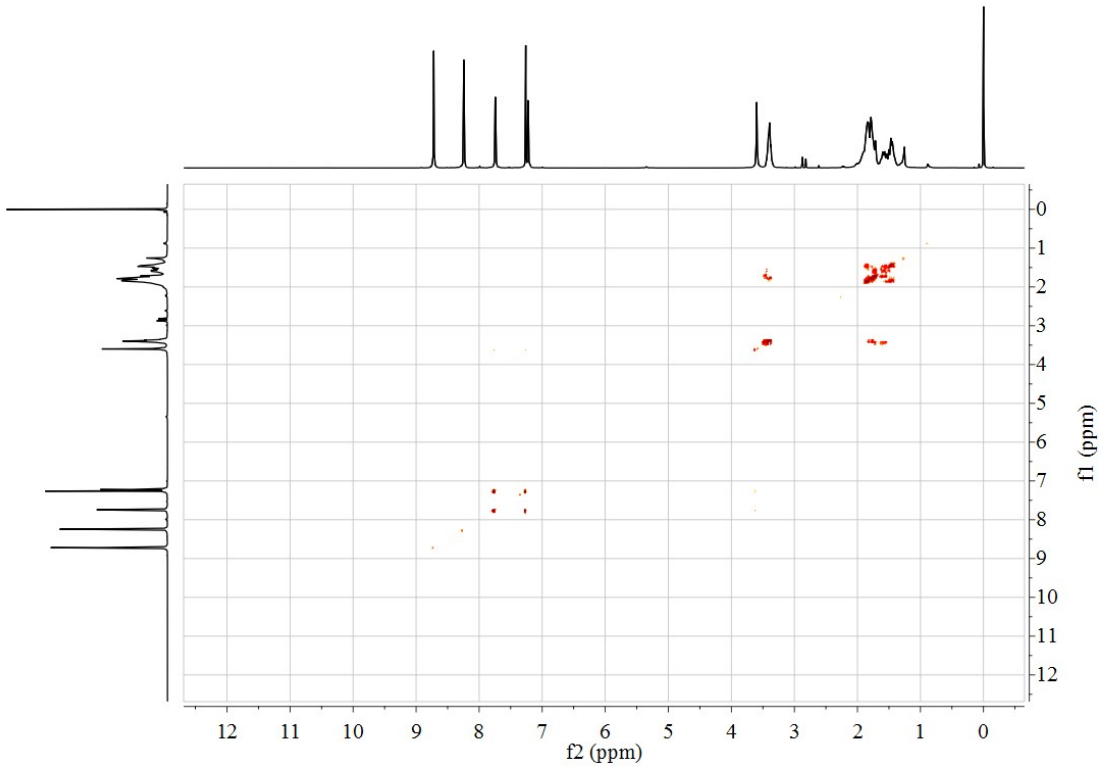


Figure S12. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$) of **NC3-*R***.

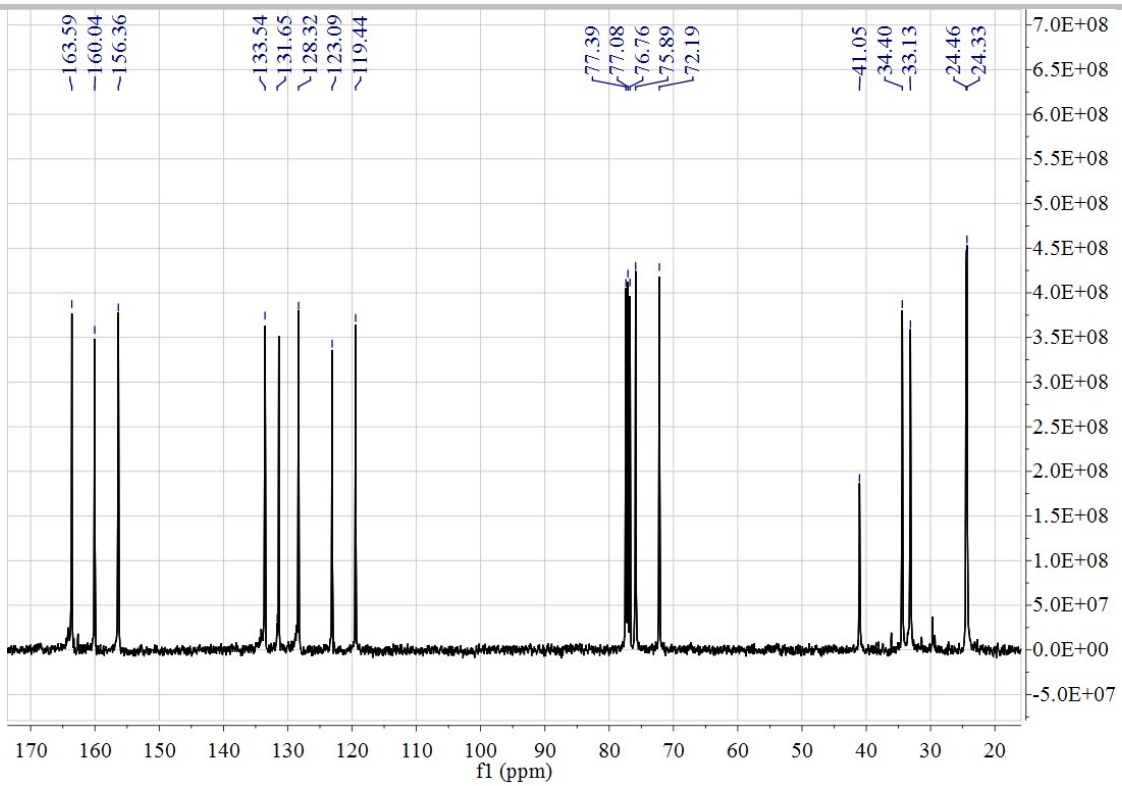


Figure S13. ^{13}C NMR spectrum ($CDCl_3$) of **NC3-*R***.

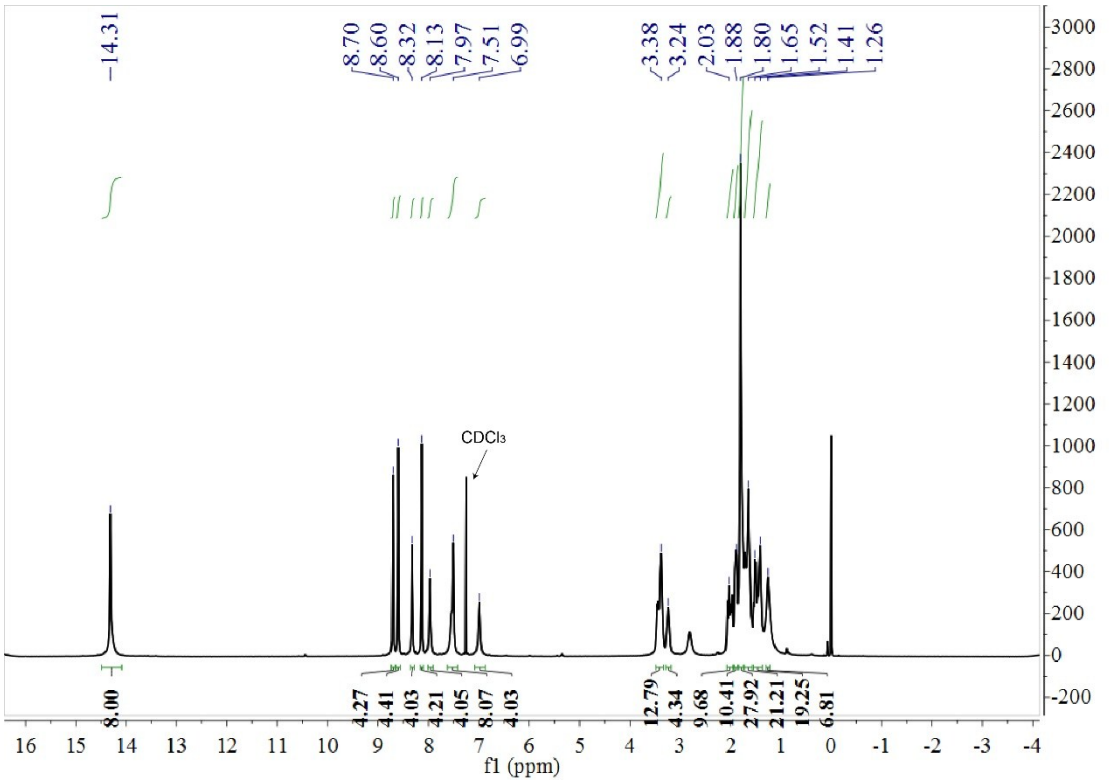


Figure S14.^{1}H NMR spectrum ($CDCl_3$) of **NC4-*R***.

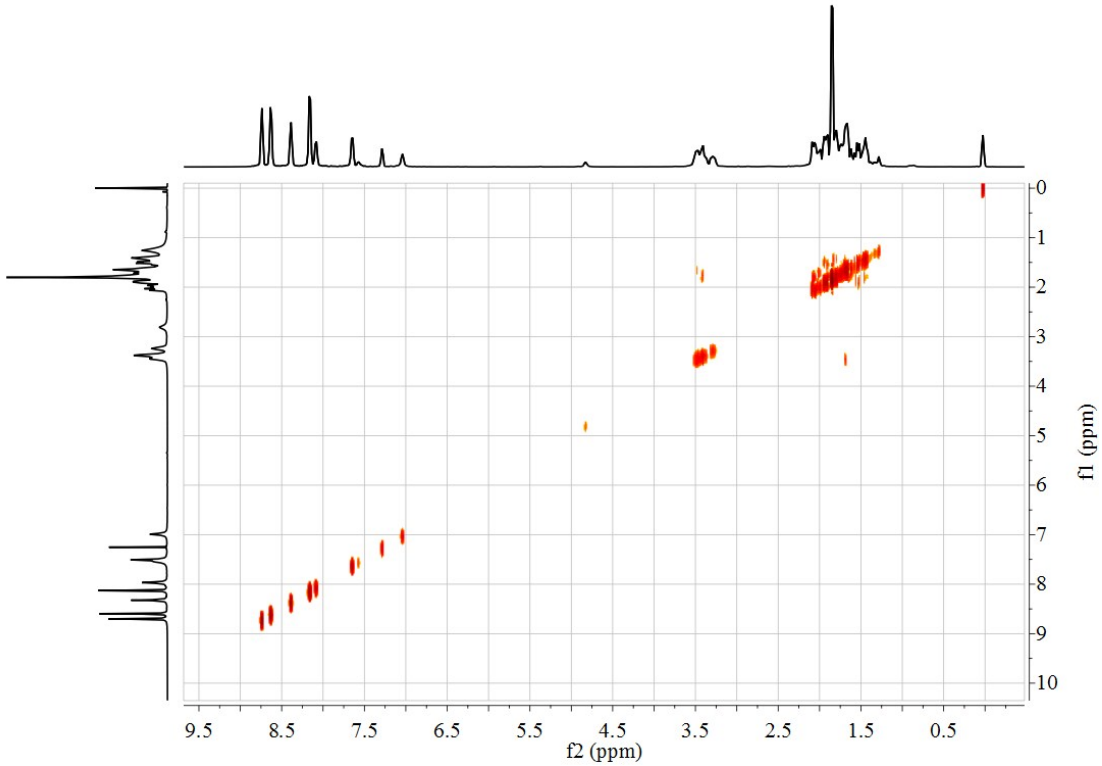


Figure S15. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$) of **NC4-*R***.

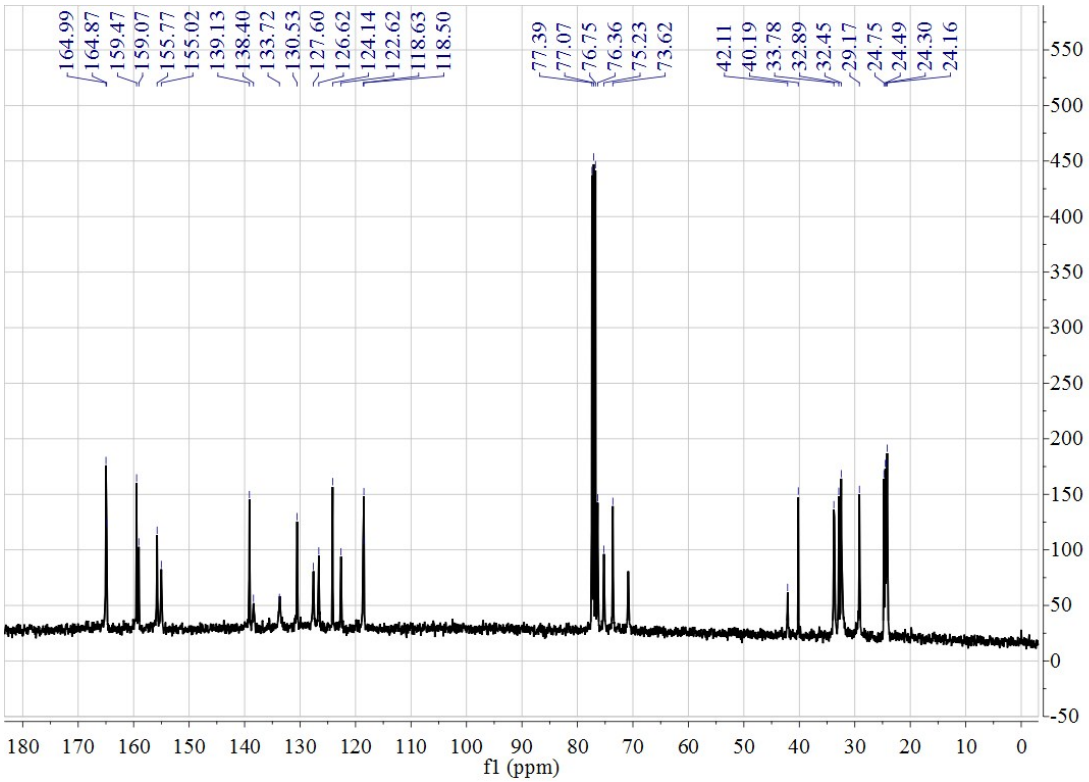


Figure S16. ^{13}C NMR spectrum ($CDCl_3$) of **NC4-*R***.

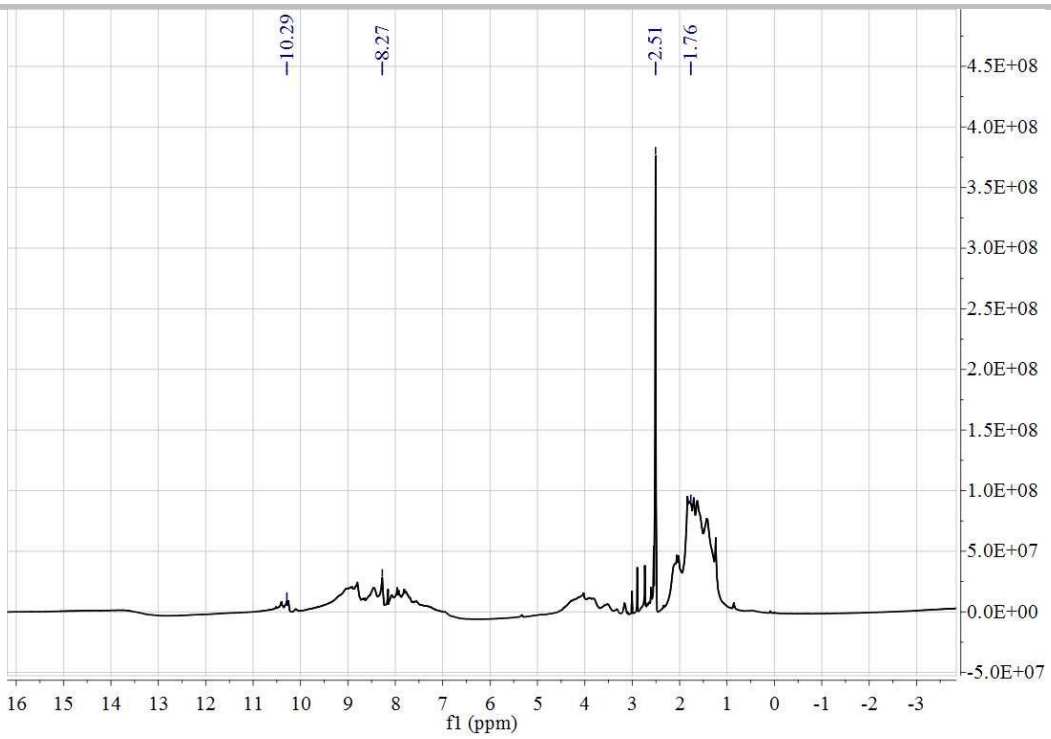


Figure S17. ^{13}C NMR spectrum ($CDCl_3$) of byproduct accompanied with **NC4-*R***.

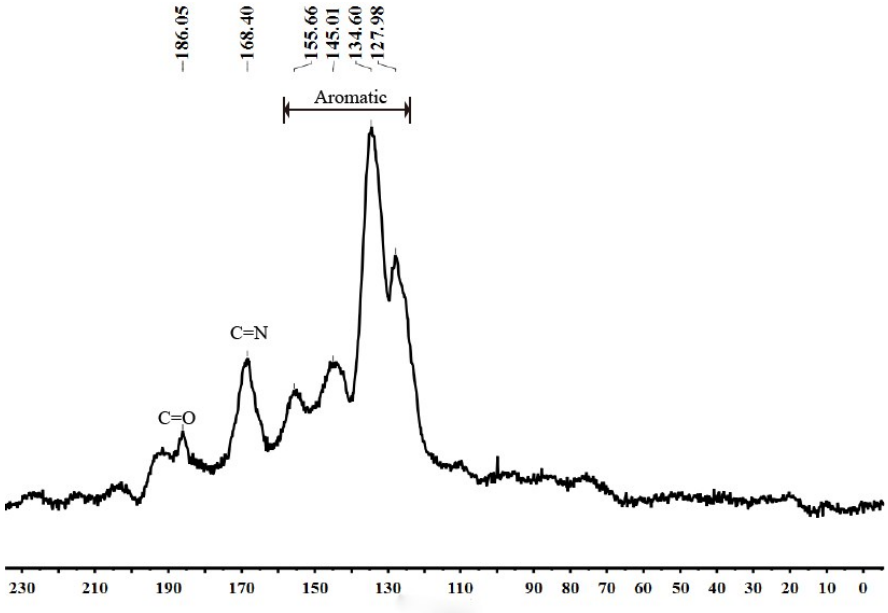


Figure S18. Solid-state ^{13}C CP/MAS NMR spectrum of **COF-NJU-1**.

Section S-4. PXRD and ESI-MS Spectra for POCs

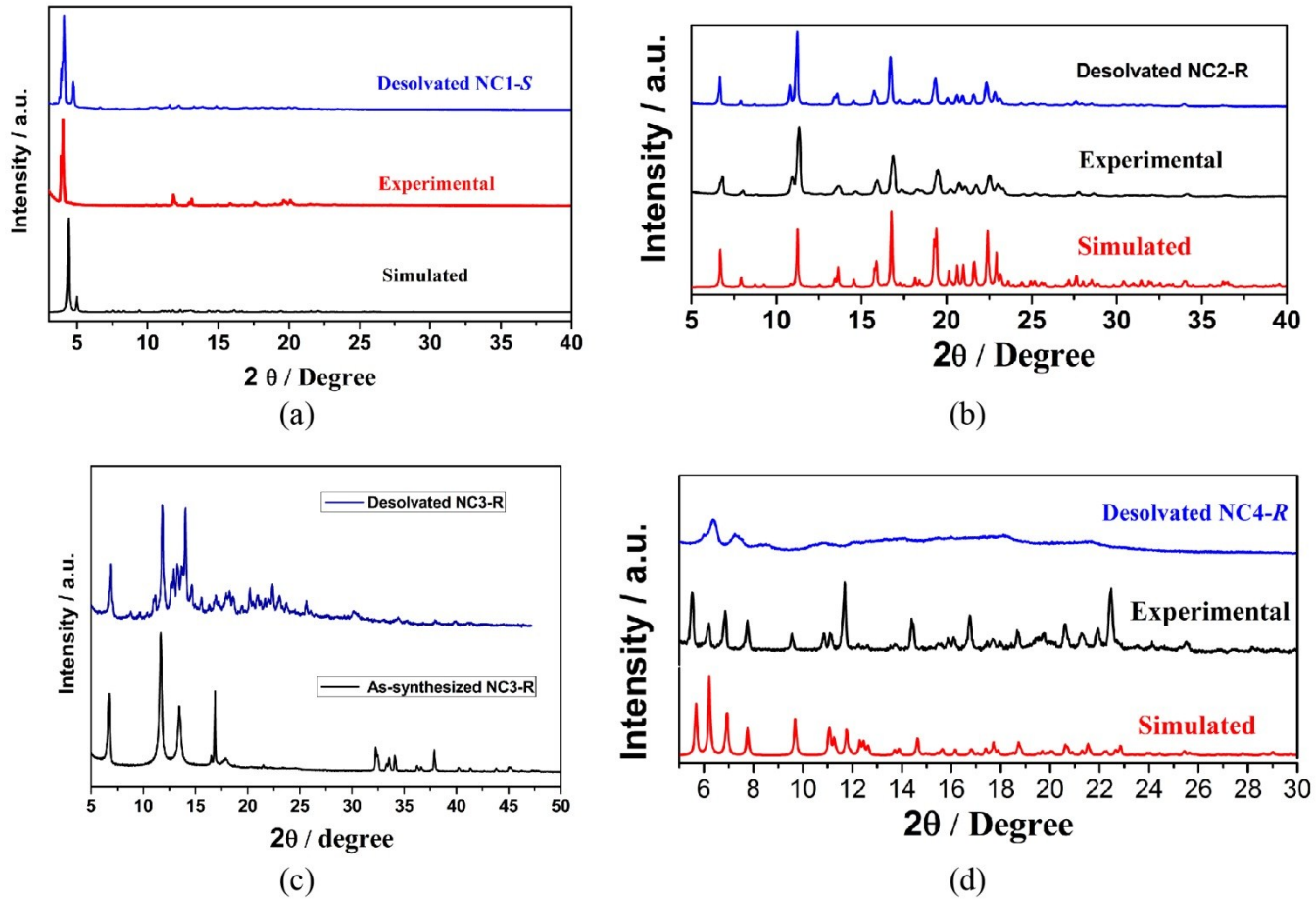


Figure S19. PXRD patterns for simulated (red line), experimental (black line), and desolvated form (blue line): (a) **NC1-*S***; (b) **NC2-*R***; (c) **NC3-*R***; (d) **NC4-*R***.

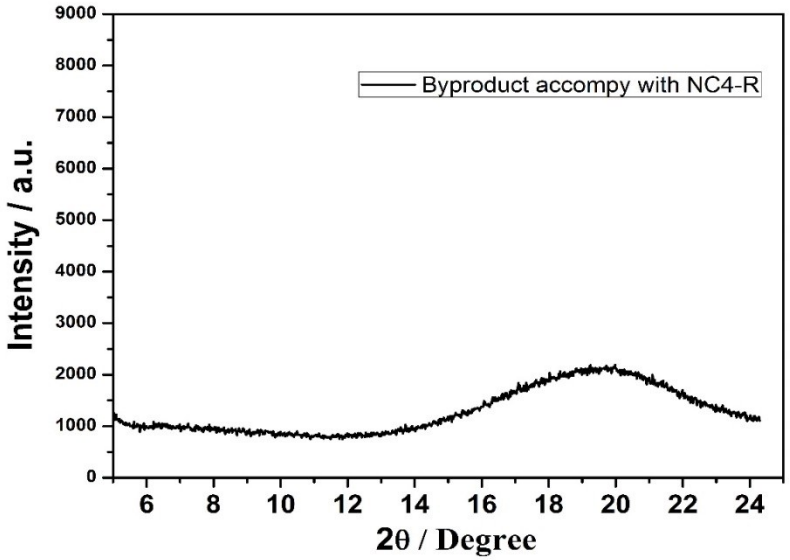


Figure S20. PXRD patterns for amorphous byproduct during the synthesis of **NC4-*R***.

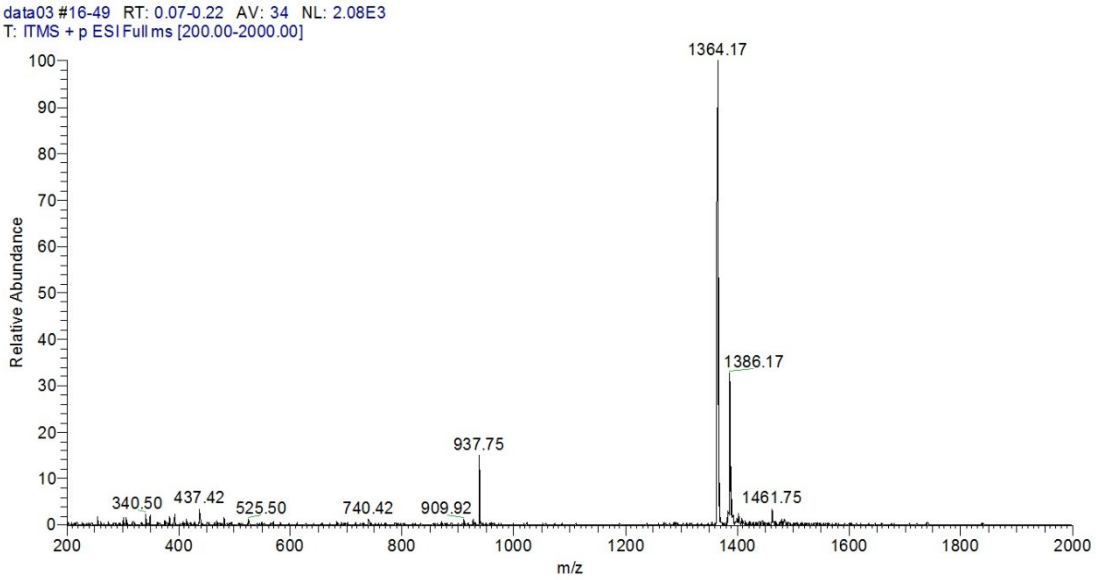


Figure S21. Positive ESI-MS of **NC1-*S***.

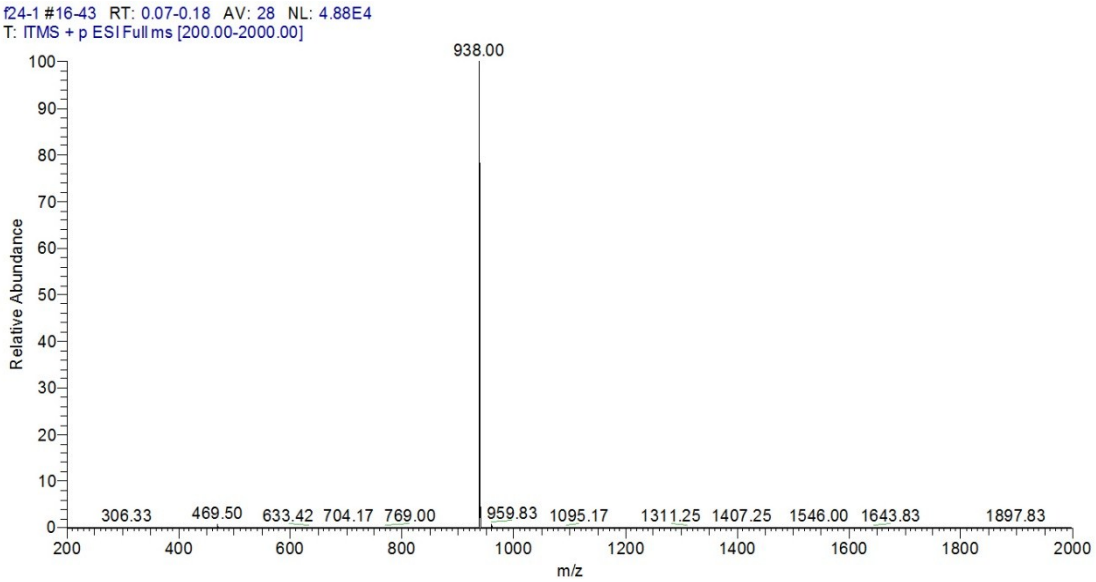


Figure S22. Positive ESI-MS of **NC2-*R***.

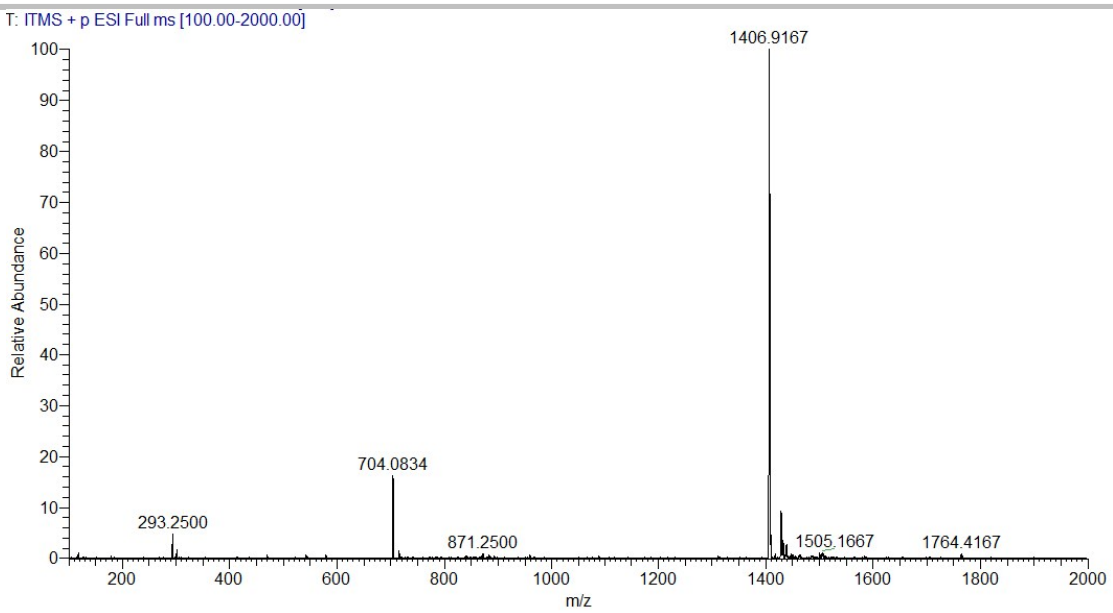


Figure S23. Positive ESI-MS of **NC3-*R***.

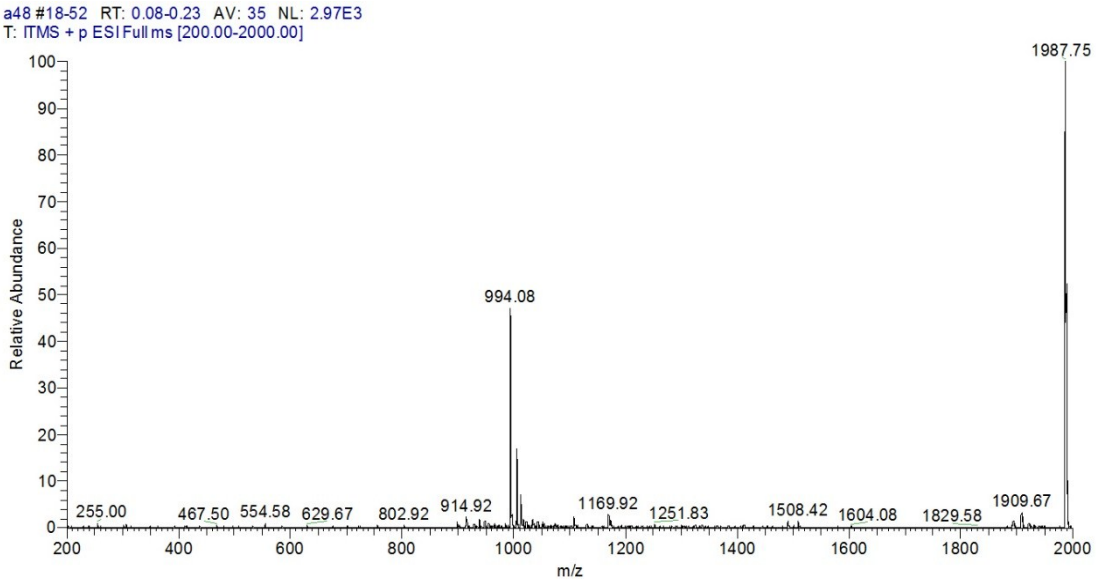


Figure S24. Positive ESI-MS of **NC4-*S***.

Section S-X Solvent Stability of POCs and COF-NJU-1

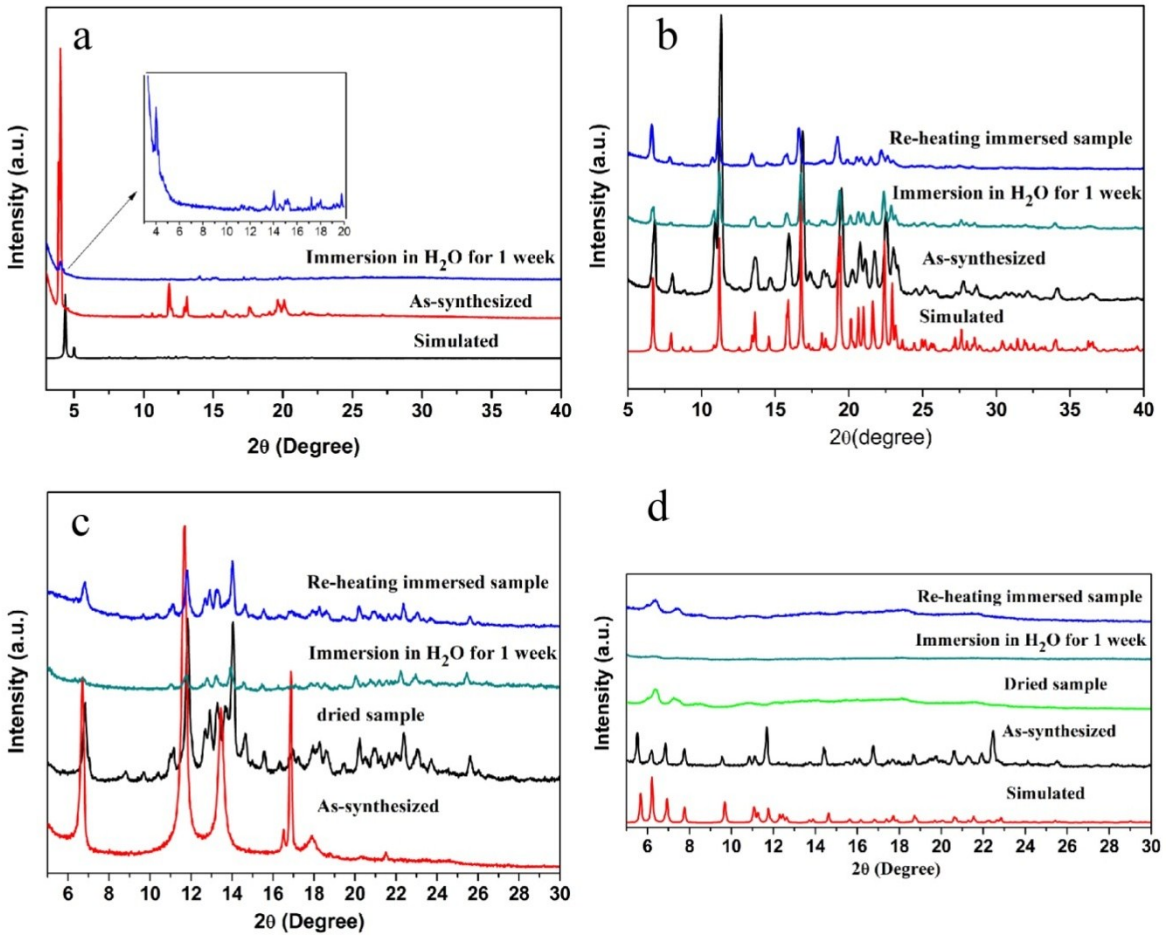


Figure S25.PXRD patterns for four POC samples immersed into water for one week: (**a**), **NC1-S**; (**b**), **NC2-R**; (**c**), **NC3-R**; (**d**), **NC4-R**.

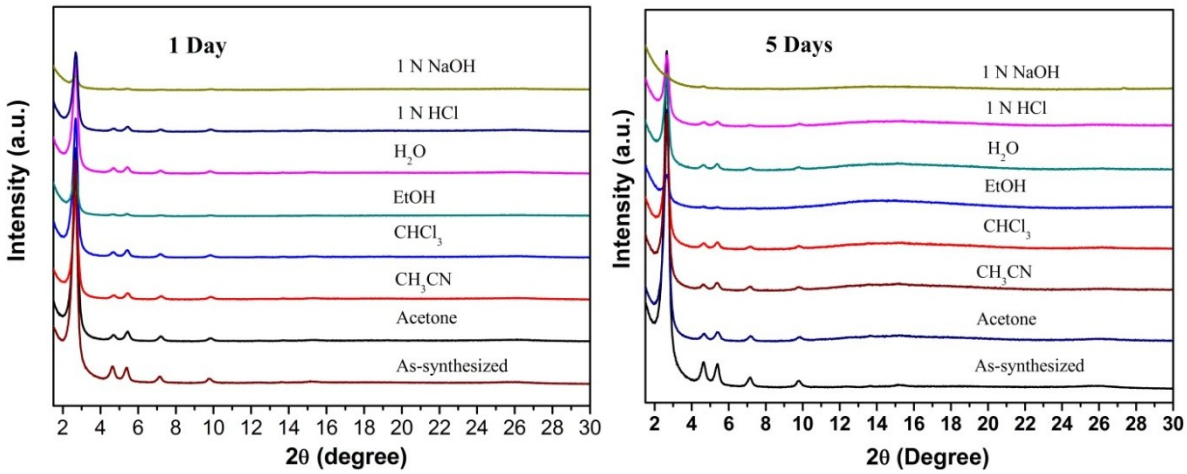


Figure S26 PXRD patterns showing solvent stability for **COF-NJU-1** by immersing powder samples in various solvents for 1 day and 5 days.

Section S-5. Optical Microscope Photographs and Crystal packing for the POCs and SEM, TEM images of COF Crystals

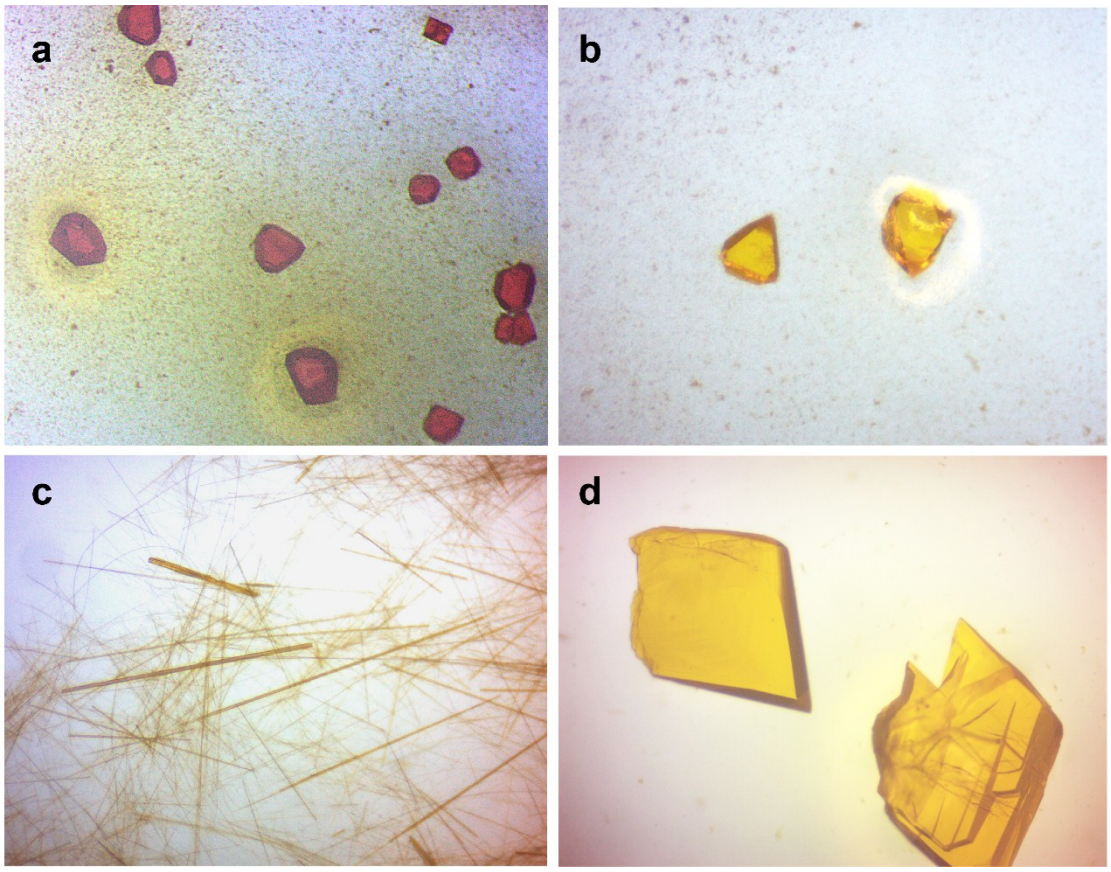


Figure S27. Optical microscope images for four single-crystals of POCs: (**a**) **NC1-*S***; (**b**) **NC2-*R***; (**c**) **NC3-*R***; (**d**) **NC4-*R***.

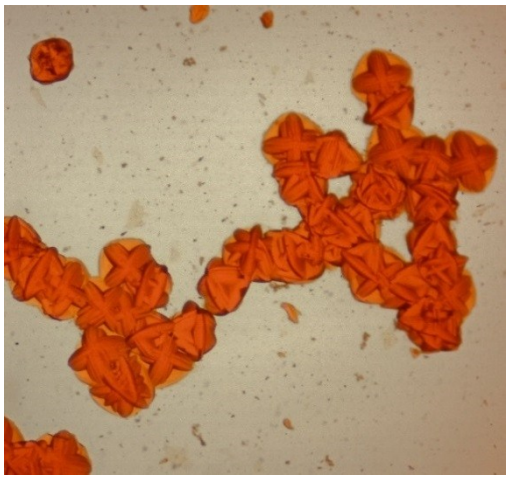


Figure S28. Optical microscope images for [3+6]-*S* cage crystallized form the mixture of DMF/EtOH via the traditional synthesis (organic solvent/acid catalysis).

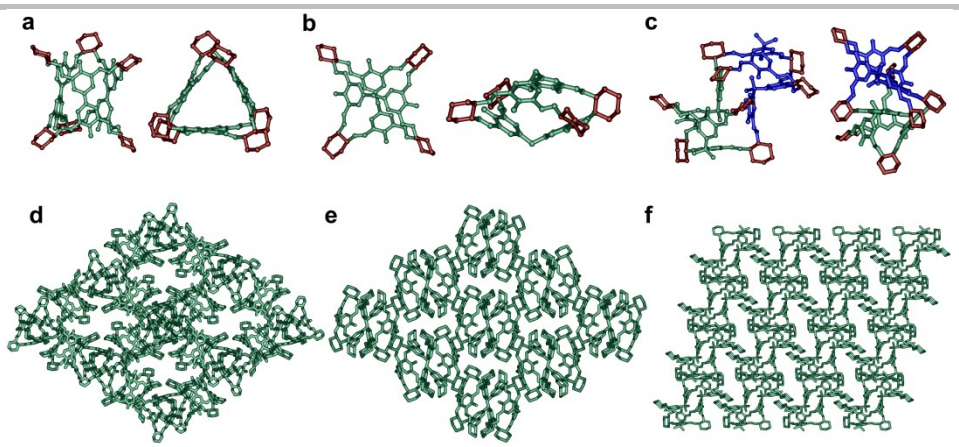


Figure S29. Structures for POCs determined by X-ray crystallography and their extended crystal packing. Solvents and hydrogen atoms are omitted for clarity. (**a**)-(**c**) Front and side representation for POCs: (**a**) **NC1-*S***; (b) **NC2-*R***; (c) **NC4-*R***. (**d**)-(**f**), Crystal packing representation for POCs: (**d**) **NC1-*S*** along *b* axis; (**e**) **NC2-*R*** along *b* axis; (**f**) **NC4-*R*** along *b* axis.

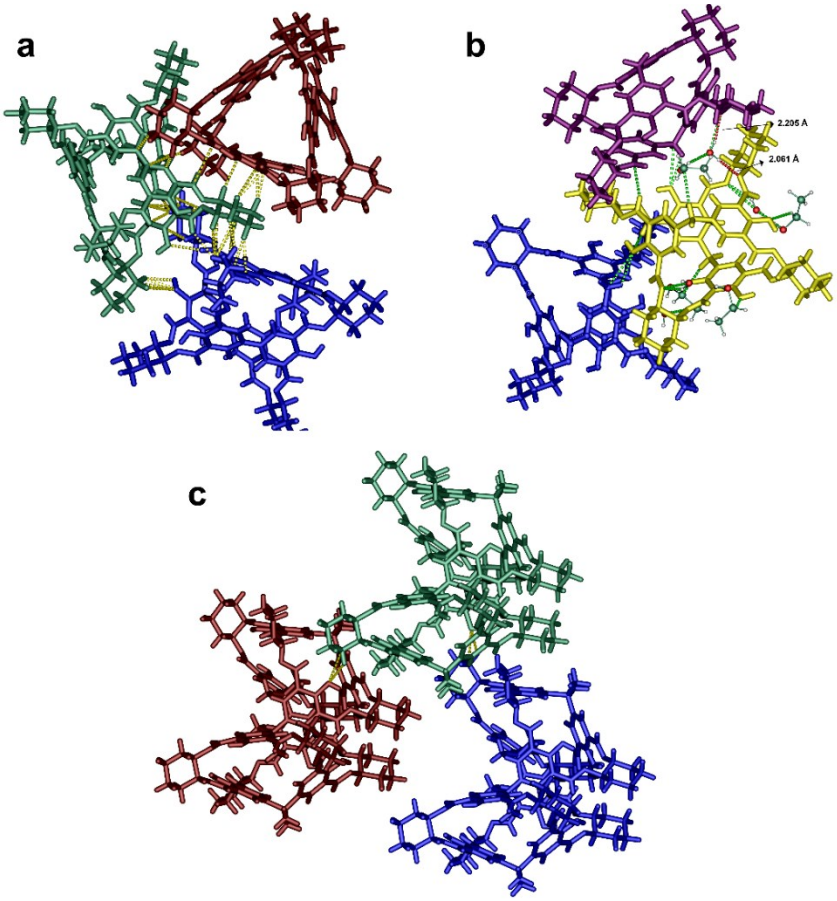


Figure S30. Intermolecular interactions existed in the crystal packing of three cages: (**a**) **NC1-*S***; (**b**) **NC2-*R***; (**c**) **NC4-*R***. Dotted lines represent weak interactions between adjacent molecules.

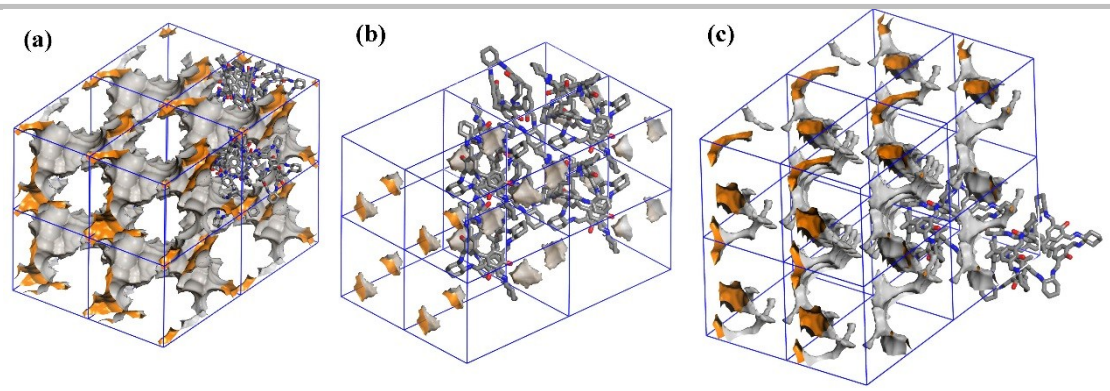


Figure S31. Solvent-accessible surface diagrams of supercell 2×2×2: (**a**) **NC1-*S***, probe radius 1.82 Å, (**b**) **NC2-*R***, probe radius 1.45 Å and (**c**) **NC4-*R***, probe radius 1.82 Å.

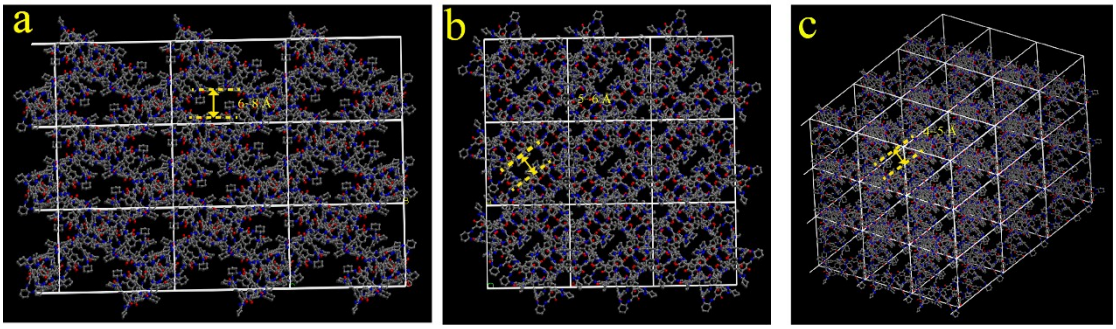
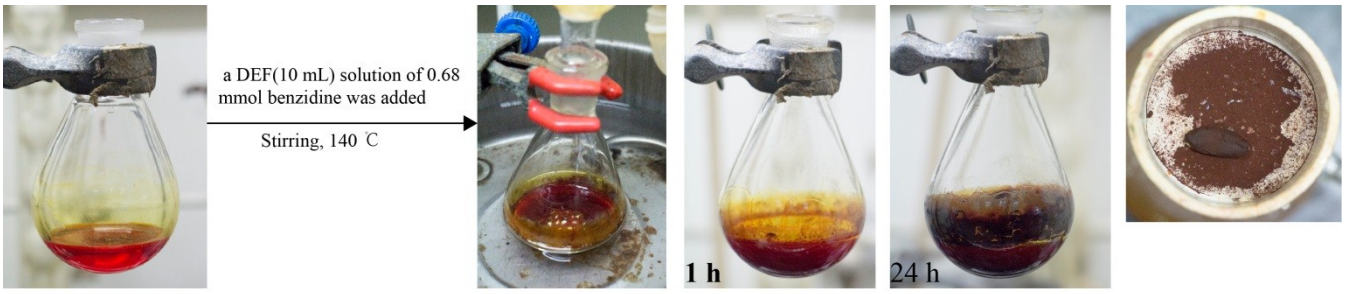
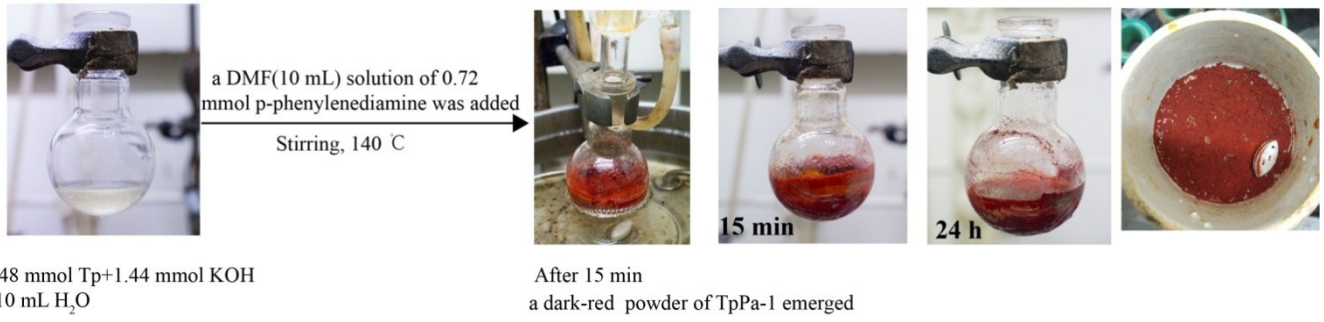


Figure S32. Three interconnected pores in different sizes measured from the 2×2×2 supercell of **NC1-*S***: (**a**) along *a* axis; (**b**) along *c* axis; (**c**) along [111] plane.





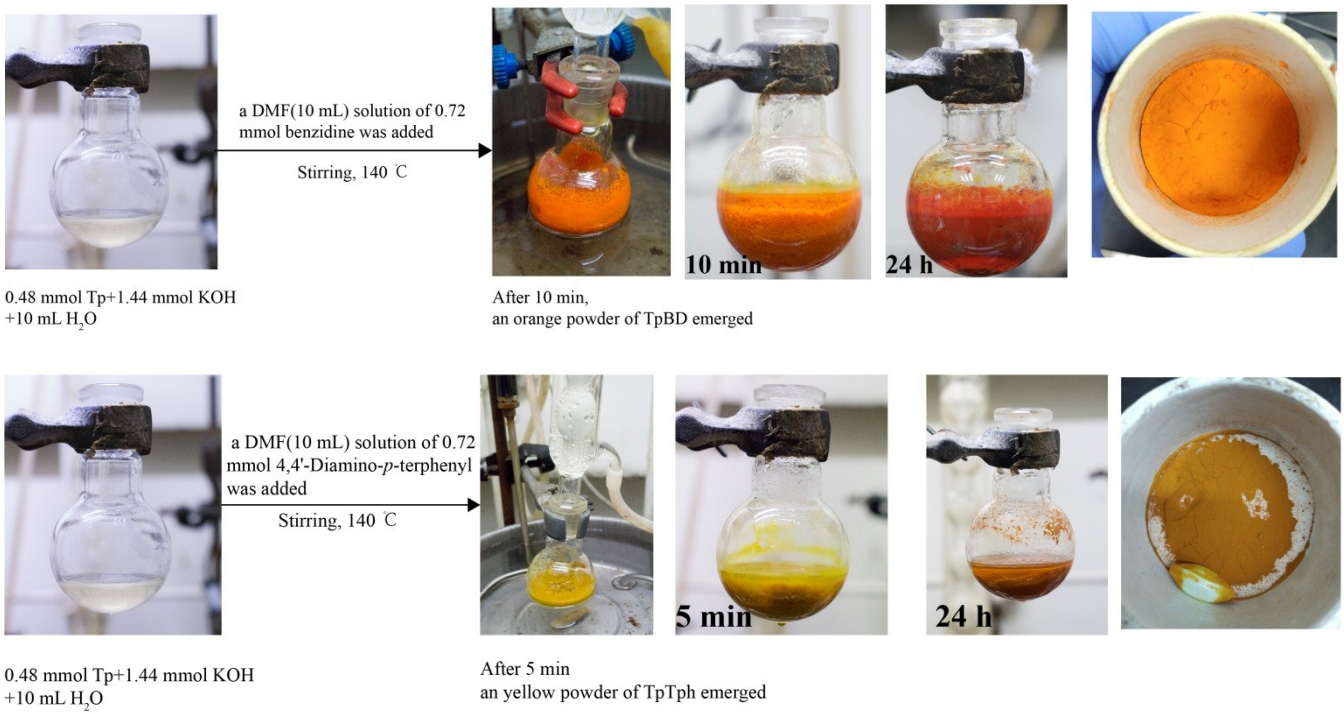


Figure S33. Digital images of the reaction process for four COFs.

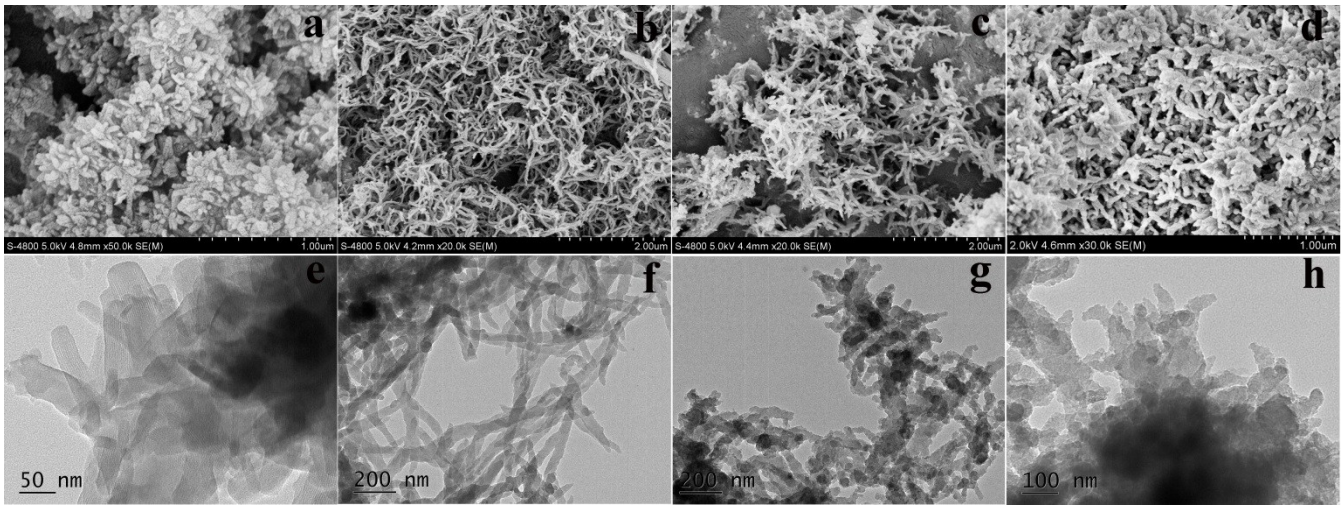


Figure S34. SEM (**a**-**d**) and TEM (**e**-**h**) images of four COFs: (**a**, **e**) **COF-NJU-1**; (**b**, **f**) **TpPa-1**; (**c**, **g**) **TpBD**; (**d**, **h**) **TpTph**.

Section S-6. FT-IR and TGA Profiles of the POCs and COFs

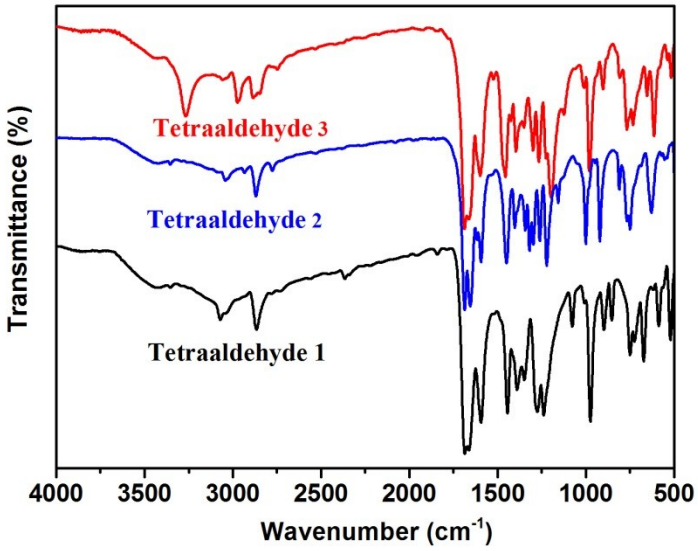


Figure S35. FT-IR spectra of tetraaldehydes (**1**, **2** and **3**) and K-tetraaldegyde **1**.

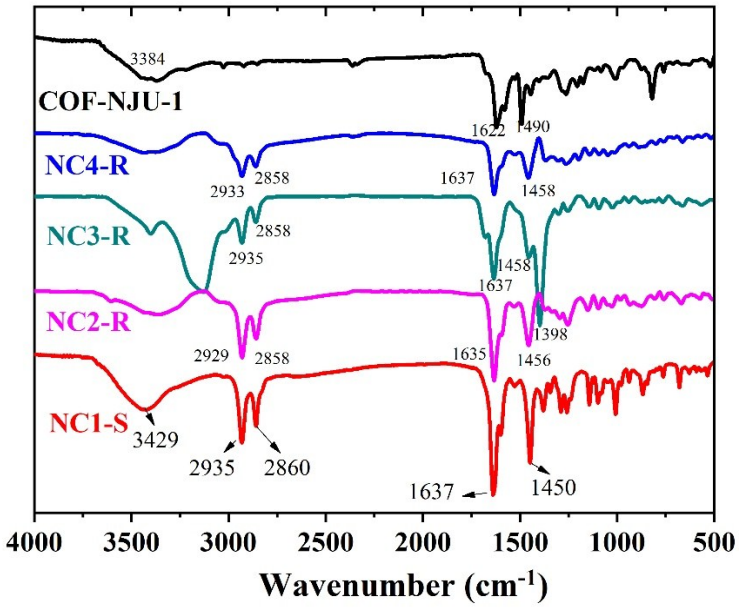


Figure S36. FT-IR spectra of the POCs and **COF-NJU-1** synthesized in this work.

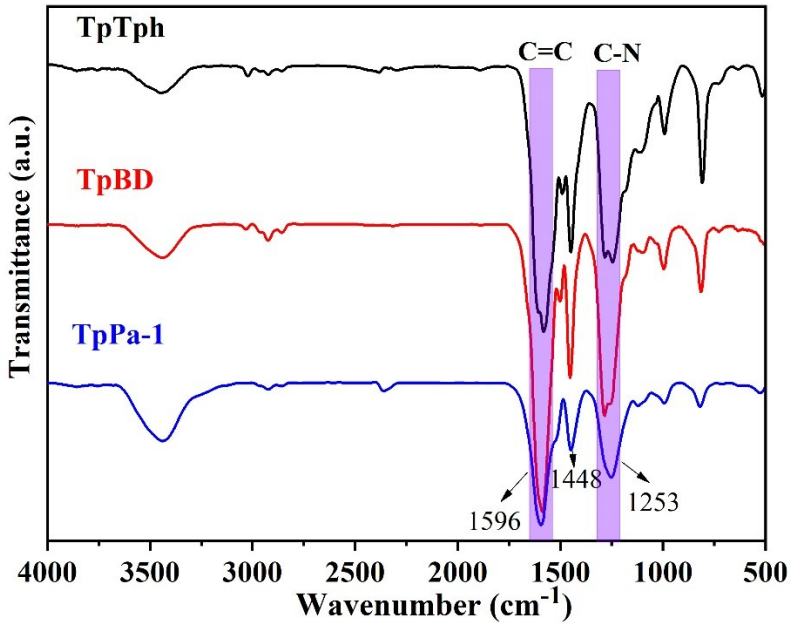


Figure S37. FT-IR spectra of the **Tp** series COFs synthesized in this work.

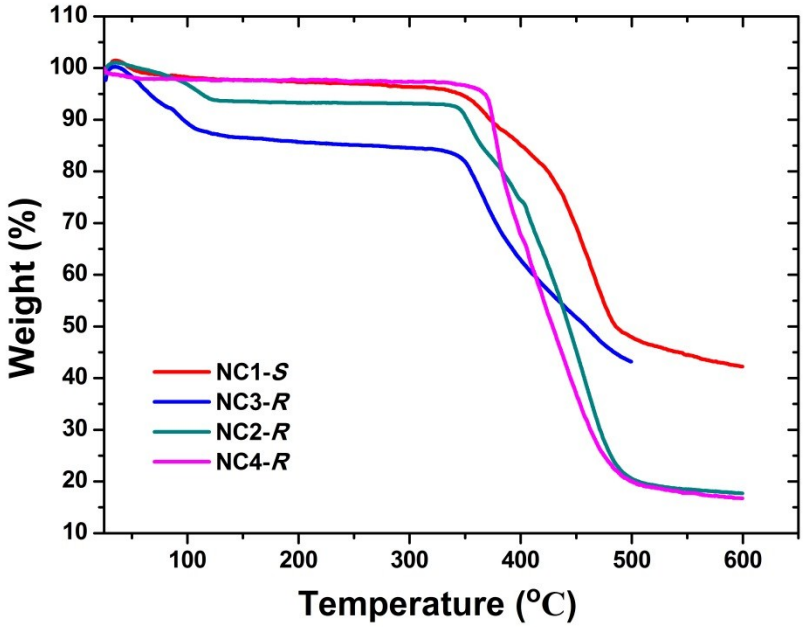


Figure S38. TGA diagrams of activated POCs (N_2 flow with a heating rate of 10 °C/min).

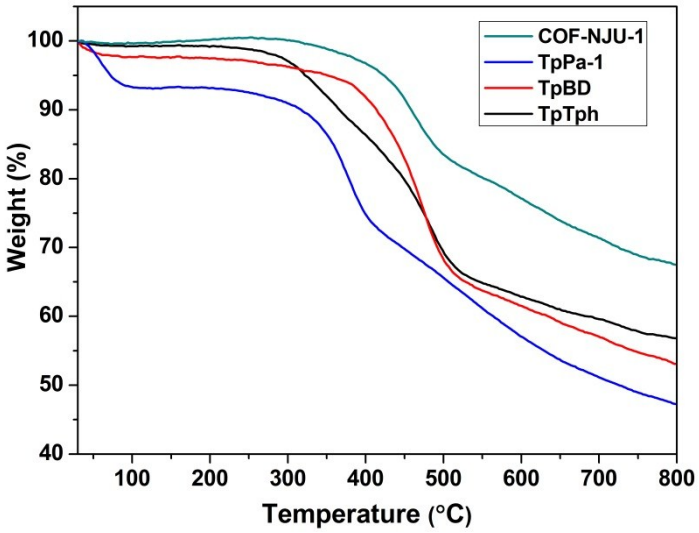


Figure S39. TGA diagrams of activated COFs (N_2 flow with a heating rate of 10 °C / min).

Table S-2. Screened solvent compositions for the syntheses of **NC2-*R***, **NC3-*R*** and **NC4-*R*** via the traditional method.

Solvents	**NC2-*R***	**NC3-*R***	**NC4-*R***
DMF	—	—	—
DMF/MeOH	—	—	—
DMF/EtOH	—	—	—
DMF/$CHCl_3$	—	—	—
DMF/1,4-dioxane	—	—	—
DMF/CH_3CN	—	—	—
$CHCl_3$	—	—	—
$CHCl_3$/MeOH	—	—	—
$CHCl_3$/CH_3CN	—	—	—
EtOH/CH_3CN	—	—	—
$CHCl_3$/cyclohexane	—	—	—
$CHCl_2$	—	—	—
$CHCl_2$/MeOH	—	—	—
$CHCl_2$/methylbenzene	—	—	—
THF	—	—	—
THF/MeOH	—	—	—
THF/cyclohexane	—	—	—
CH_3CN	—	—	—
$CHCl_3$/petroleum ether	—	—	—
$CHCl_3$/ether	—	—	—

Note: '—' represents the formation of amorphous powder under the given solvent combination via slow evaporation in air at room temperature.

Section S-7. Pore Size Distribution and Gas Sorption Measurements

Before gas sorption measurements for POCs, super-critical carbon dioxide (SCD) activation was used to remove the solvent molecules. The samples were transferred into an SFT HPR-100 reactor. The pressure and temperature gradually rose up to 1400 psi and 40 °C, respectively, and were maintained for 4 h. The pressure was then released slowly over a period of 1 h while the temperature was still kept at 40 °C. Such procedure was repeated three times. The desolvated POCs were degassed on the analysis port under a vacuum over 6 h at 150 °C. The as-prepared COFs samples were activated by soxhlet extraction in DMF for overnight and dried in a vacuum at 120 °C for 24 h. The desolvated COFs were degassed on the analysis port under a vacuum over 20 h at 180 °C.

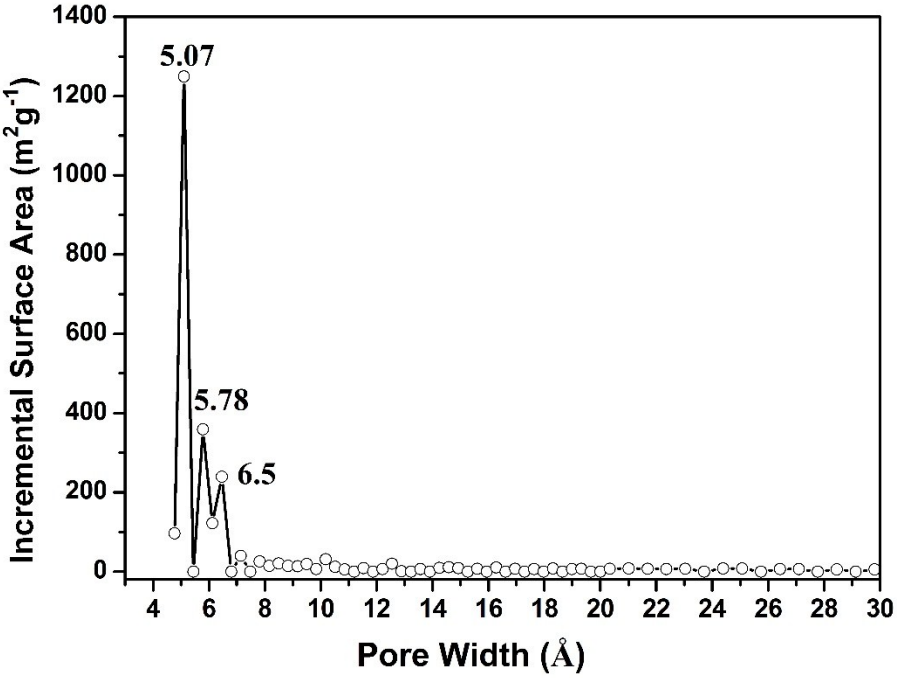


Figure S40. Pore size distribution of **NC1-*S*** from Ar isotherm.

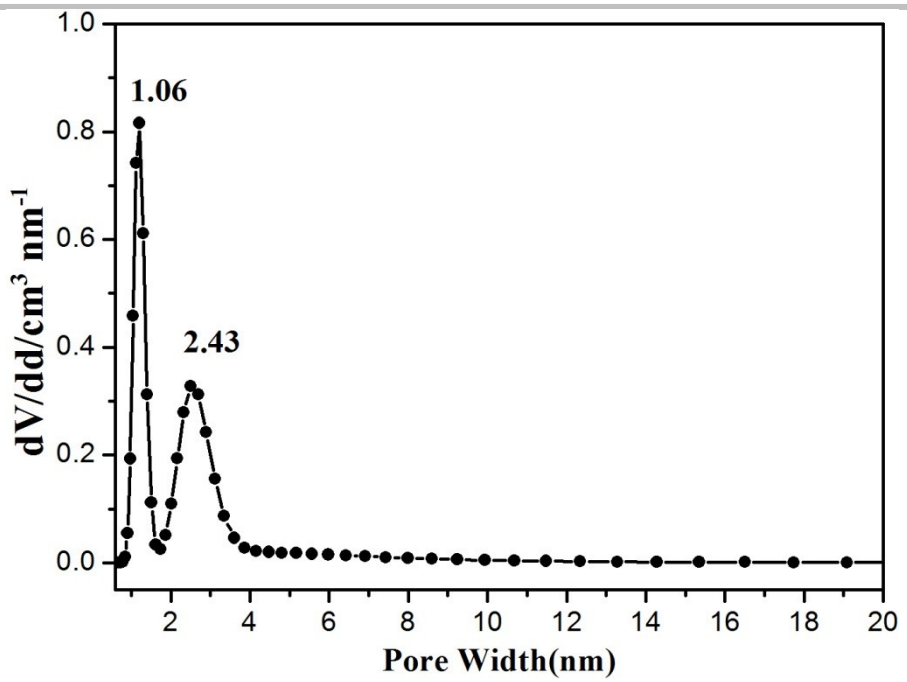


Figure S41. Pore size distribution of **COF-NJU-1** from HK theory based on N_2 isotherm at 77 K.

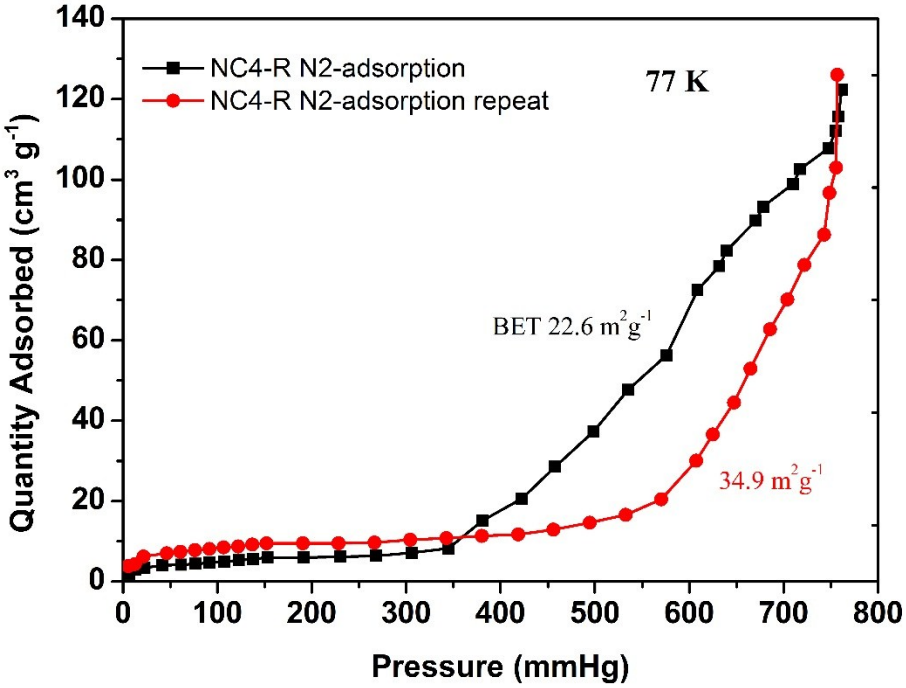


Figure S42. N_2 adsorption isotherms of **NC4-*R*** at 77 K.

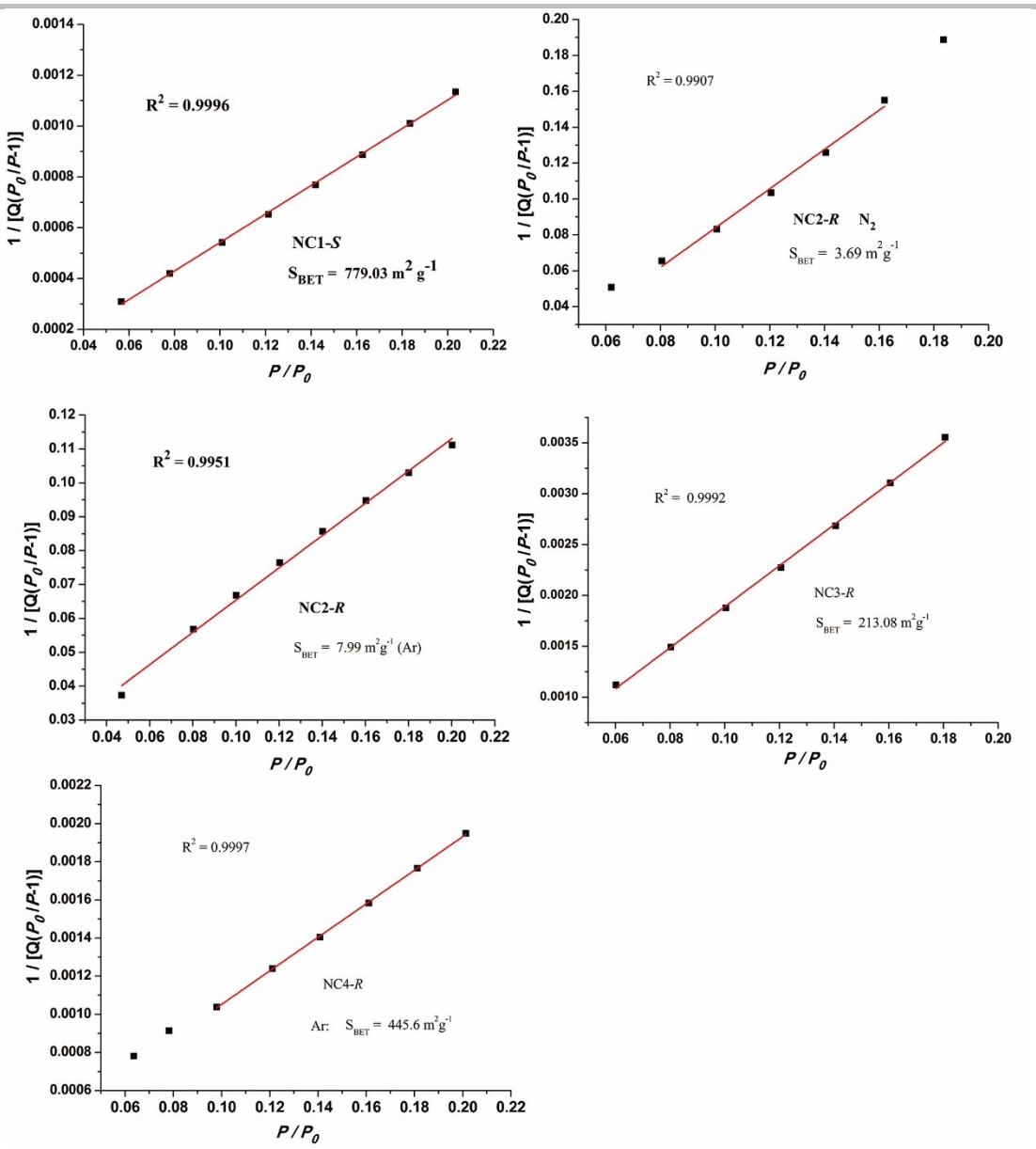


Figure S43. BET surface area plot for four POCs calculated from the isotherm.

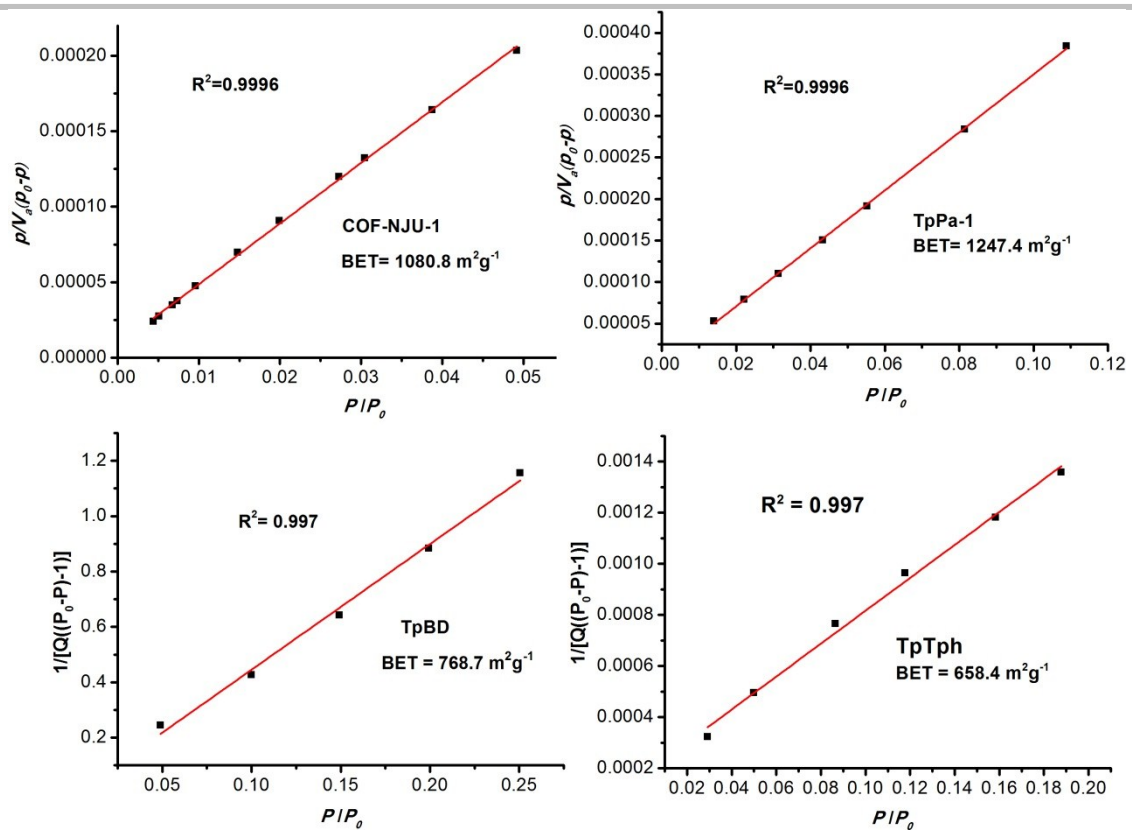


Figure S44. BET surface area plot for four COFs calculated from the isotherm.

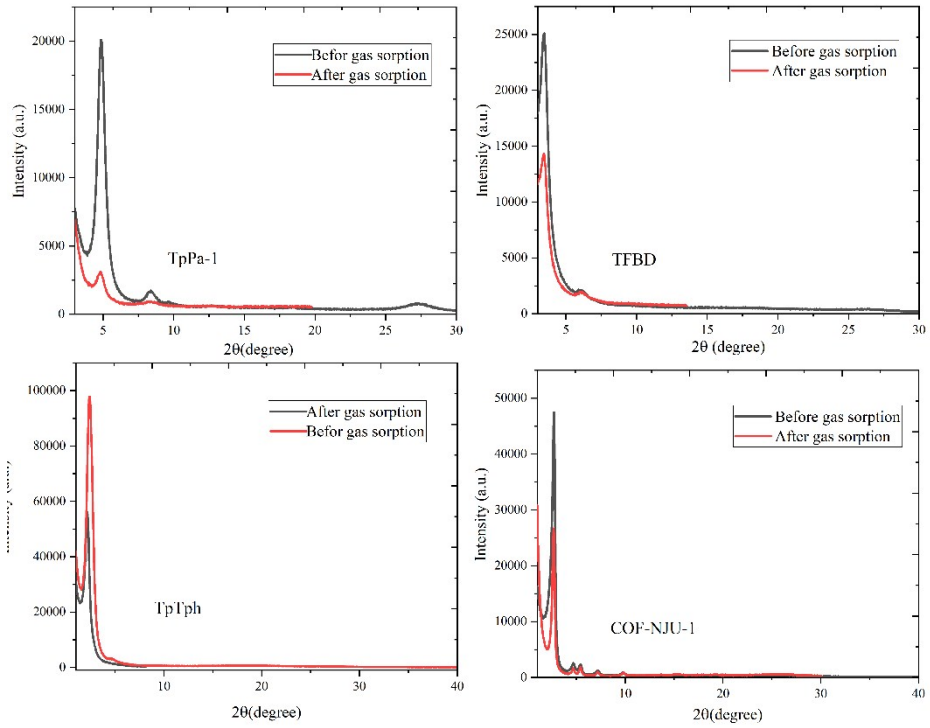
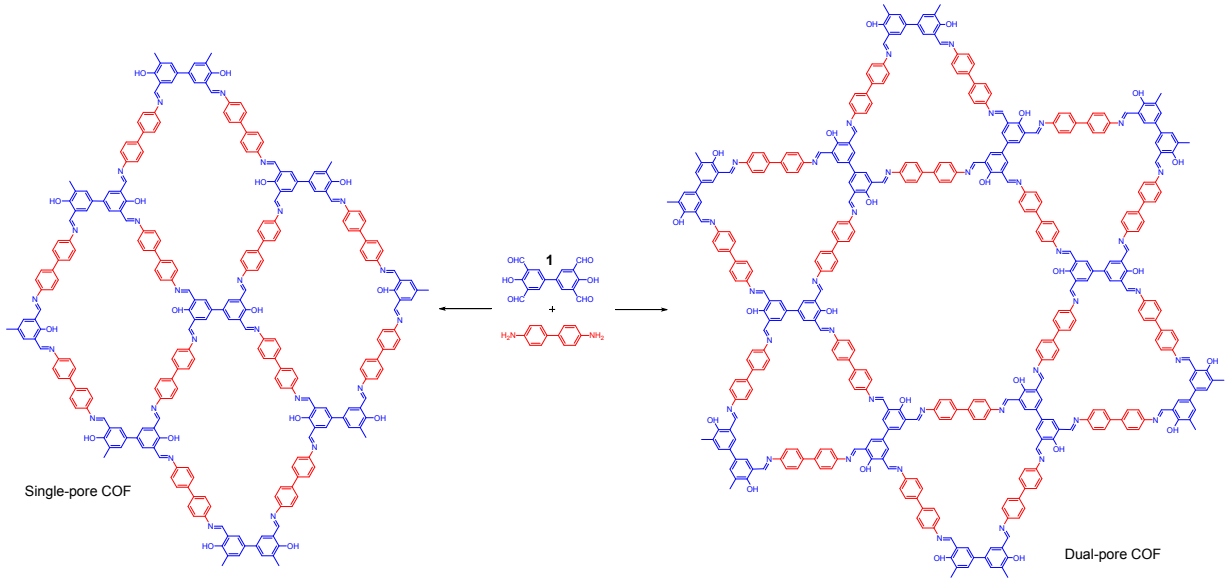


Figure S45. PXRD patterns for four COFs before and after the gas sorption experiments.

Section S-8. Structures, Simulations, and Fractional Atomic Coordinates of COF-NJU-1.



Scheme S1. The possible frameworks constructed from **1** and benzidine.

Structural simulation and powder X-ray diffraction analysis. The simulations of the possible structures were carried out in Accelrys Material Studio 7.0 software package. Before the simulations, the structures were firstly optimized in Gaussian 09 package by semiempirical calculations at PM3 level. The stimulated PXRD patterns were determined by the Reflex module. P1 space group was chosen for the primitive models in the initial simulations. The Pawley refinement of the experimental PXRD was conducted by the Reflux module in the Material Studio 7.0.

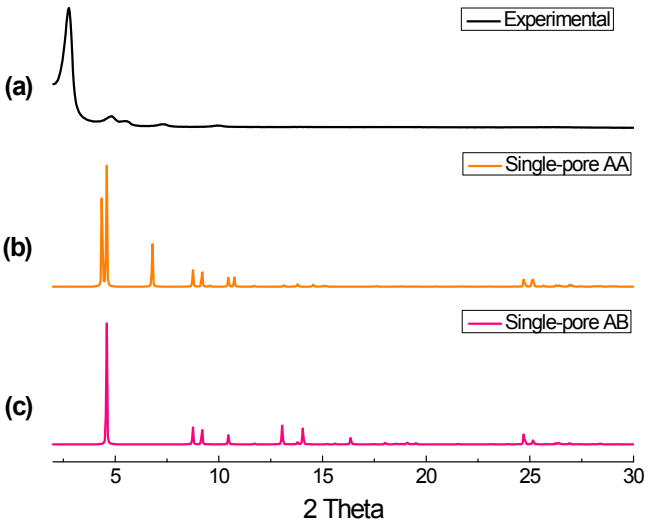


Figure S46. Comparison of the experimental PXRD of **COF-NJU-1** with the simulated patterns of the single-pore isomer with AA and AB stacking.

Table S-3. Fractional atomic coordinates for the unit cell of **COF-NJU-1** with AA stacking.

*P*6			
$a = b = 39.10$ Å, $c = 3.38$ Å, $\alpha = \beta = 90°$ and $\gamma = 120°$			
C1	1.21252	0.76536	0.98914
C2	1.25171	0.80246	0.97941
C3	1.28649	0.80165	0.8895
C4	1.32316	0.83643	0.88722
C5	1.32589	0.87286	0.96325
C6	1.29138	0.87397	1.05383
C7	1.25482	0.83919	1.06366
N8	1.36421	0.90774	0.97278
C9	1.37106	0.94337	0.90671
C10	1.17774	0.76594	0.89522
C11	1.14102	0.7314	0.90927
C12	1.13793	0.69532	1.01142
C13	1.17255	0.69431	1.10242
C14	1.20933	0.72899	1.09363
N15	1.09922	0.66086	1.01175
C16	1.08971	0.62489	1.10261
C17	1.04833	0.59214	1.0656
C18	1.01622	0.5989	1.02805
C19	0.97782	0.56657	0.95947
C20	0.97226	0.52823	0.93715
C21	1.00346	0.52075	1.00443
C22	1.04136	0.55333	1.07196
O23	1.02318	0.63746	1.07786
H24	1.28493	0.77241	0.81759
H25	1.35117	0.83525	0.82298
H26	1.29312	0.90339	1.11986
H27	1.227	0.8403	1.14058
H28	1.34606	0.94838	0.80713
H29	1.17936	0.79484	0.80643
H30	1.11305	0.73239	0.83692
H31	1.1707	0.66514	1.18375
H32	1.23721	0.72806	1.17164
H33	1.11329	0.61816	1.21237
H34	0.94189	0.50222	0.863
H35	1.06728	0.54847	1.13367
H36	0.99644	0.6364	1.20343

References

1. C. Gorbitz, *Acta Crystallogr. Sect. B*, 1999, **55**, 1090-1098.

2. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
3. A. Spek, *J. Appl. Cryst.,* 2003, **36**, 7-13.
4. A. Eiji, C. Mitsuyoshi, Y. Atsushi, S. Yoshiteru and S. Ken-ichi, *Chem. Lett.*, 2000, **29**, 678-679.
5. J. H. Chong, M. Sauer, B. O. Patrick and M. J. MacLachlan, *Org. Lett.*, 2003, **5**, 3823-3826.