Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI)

A 2D azine-linked covalent organic framework for gas storage applications

Zhongping Li,[a] Xiao Feng,[b] Yongcun Zou,[d] Yuwei Zhang,[a] Hong Xia,[c] Xiaoming Liu*[a] and Ying Mu[a]

[a] *State Key Laboratory for Supramolecular Structure and Materials, School of Chemistry, Jilin University, 2699 Qianjin Avenue, Changchun, 130012, P.R.China.*
[b] *Department of Chemistry, School of Chemistry, Beijing Institute of Technology, Beijing, 100081, P. R. China.*
[c] *State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Technology, Jilin University, Changchun, 130012, P.R.China*
[d] *State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Technology, Jilin University, Changchun, 130012, P.R.China*

Email: xm_liu@jlu.edu.cn

Section 1. Materials and Methods

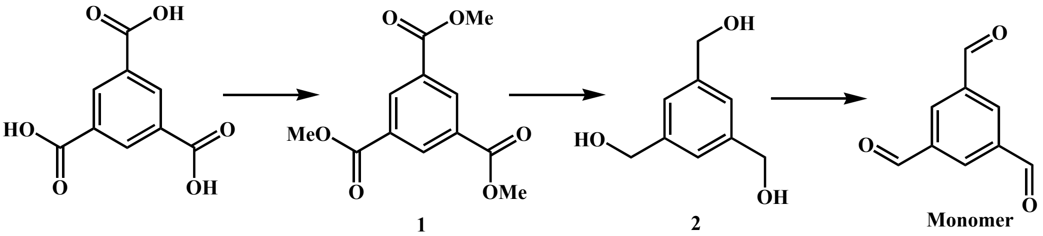
The 1,3,5-Benzenetricarboxylic acid, $LiAlH_4$, $KHSO_4$, *o*-iodoxybenzoic acid, Hydrazine hydrate and Benzaldehyde were obtained from Aldrich. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aldrich.

^1H spectra were recorded on a Varian Mercury-300 NMR spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Solid-state ^{13}C CP/MAS NMR measurements were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. All ^{13}C CP MAS chemical shifts are referenced to the resonances of adamantane ($C_{10}H_{16}$) standard (δ CH_2 = 38.5). The infrared spectra were recorded from 400 to 4000 cm^{-1} on an Avatar FT-IR 360 spectrometer by using KBr pellets. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. The presence of elemental palladium was determined with energy dispersive spectroscopy (EDS) coupled with scanning electron microscopy (SEM) (JEOLJSM-7500F, Japan). The sample was prepared by drop-casting a supersonicated methanol suspension of HP_E-CMP onto a copper grid. Powder X-ray diffraction data were recorded on a PANalytical BV Empyrean diffractometer diffractometer by depositing powder on glass substrate, from $2\theta = 4.0°$ to $60°$ with $0.02°$ increment at 25 °C. UV/Vis spectra have been carried out on a Perkin Elmer Lambda 950 spectrophotometer within the wavelength range 200–700 nm. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min^{-1} from 25 to 800 °C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size distribution.

Molecular modeling and Pawley refinement were carried out using Reflex, a software package for crystal determination from XRPD pattern, implemented in MS modeling ver 4.4 (Accelrys Inc.)[S1]. Unit cell dimension was first manually determined from the observed XRPD peak positions using the coordinates. We performed Pawley refinement to optimize the lattice parameters iteratively until the RWP value converges. The pseudo-Voigt profile function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The final RWP and RP values were 3.32% and 2.62%, respectively.

Section 2. Syntheses and characterization

Scheme S1: Synthetic route for monomer



Synthesis of trimethyl benzene-1,3,5-tricarboxylate (1).

The 1,3,5-Benzenetricarboxylic acid (5.54 g, 0.026 mol) was dissolved in 20 mL of methanol. The concentrated sulfuric acid (2 mL) was added dropwise and the mixture was heated at 80 ^oC for 6 h. After cooling to room temperature, a salt solution of $NaHCO_3$ (20 mL) was added into the mixture and then solids were filtered. The crude products were washed with water three times and give target products as a white solid (6.5 g, 98%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 3.98 (s, 9H, OCH_3), 8.86 (s, 3H, Ar–H) ppm.

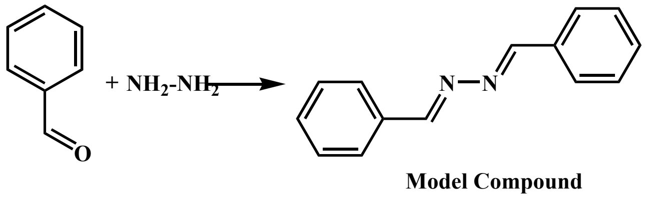
Synthesis of 1,3,5-tris-(hydroxymethyl)benzene (2).[S2]

The $LiAlH_4$ (1.0 g, 0.026 mol) was dissolved in THF (30 mL). The trimethyl benzene-1,3,5-tricarboxylate (3 g, 0.012 mol) was added and then the mixture was stirred at 70 ^oC for 12 h. After cooling to room temperature, the $KHSO_4$ and Celite were added into the mixture. The solution was filtered and washed with methanol (3 × 20 mL). The solvent was evaporated and the residue was purified by column chromatography on silica gel. The product was isolated as a white powder (1.4 g, 70%). ^{1}H-NMR (DMSO-d_6, 300 MHz): δ (ppm) 4.47 (s, 6H, CH_2), 7.12 (s, 3H, Ar–H).

Synthesis of 1,3,5-triformylbenzene (Monomer).[S3]

1,3,5-tris-(hydroxymethyl)benzene (1.4 g, 8.3 mmol) was dissolved in 80 mL of tert-butanol at room temperature with vigorous stirring over 10 minutes. To this solution was added 80 mL of tert-butanol solution of *o*-iodoxybenzoic acid (14 g, 49.9 mmol) and mixture was heated at 110 ^oC overnight. After cooling to room temperature, the saturated aqueous $Na_2S_2O_3$ (30 mL) was added to the system followed by 30 mL of saturated aqueous $NaHCO_3$. The resulting solution was extracted with ethyl acetate (3 × 30 mL), and the combined organic extracts were washed with water (20 mL) and saturated aqueous NaCl (30 mL). After drying over MgSO4, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel and afforded 1.05 g (78%) of the desired product. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 8.64 (s, 3H), 10.21 (s, 3H, C*H* = O). IR (KBr, ν; cm^{-1}): 426, 651, 673, 890, 968, 1021, 1144, 1379, 1457, 1598, 1696, 2873 and 3064. UV-Vis (λ; nm): 229, 304, and 353.

Scheme S2: Synthetic route for model compound.



Synthesis of model compound.

Benzaldehyde (5.1 mL, 0.05 mol) was dissolved in 100 mL of ethanol at room temperature with vigorous stirring over several minutes. Hydrazinehydrate (1.49 mL, 0.025 mol) was slowly added and heated for another 15 minutes, cooled at room temperature, filtered and washed with MeOH, dried under vacuum to afford model compound as bright yellow powder in 91 % yield (4.7 g). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.45-7.47 (m, 6H, Ar–H), 7.84-7.87 (m, 4H, Ar–H), 8.67 (S, 2H, C*H* = N). IR (KBr, ν; cm^{-1}): 447, 500, 674, 689, 752, 858, 958, 1021, 1070, 1170, 1210, 1289, 1313, 1445, 1491, 1571, 1628, 1671, 2944 and 3048. UV-Vis (λ; nm): 304, 339, and 390.

Synthesis of ACOF-1.

A 10 mL pyrex tube was charged with 1,3,5-triformylbenzene (60 mg, 0. 37 mmol), hydrazine hydrate (38 μL, 0.56 mmol), dioxane(2 mL) and AcOH (0.2 mL, 6 M), the mixture was sonicated for 2 minutes, degassed through three freeze–pump–thaw cycles, sealed under vacuum. The reaction was heated at 120 ºC for 72 h yielding a pale-yellow solid at the bottom of the tube which was isolated by centrifugation and washed with anhydrous dioxane, anhydrous tetrahydrofuran and anhydrous acetone, and dried under vacuum at 100 °C for 10 h to afford pale yellow powder in 86% isolated yield. For other solvent conditions, such as mesitylene, ethanol and mesitylene/dioxane (1/1 by vol.) followed the same experimental procedure to obtain the ACOFs. Elemental analysis for the calculated C (69.22%), H (3.87%), N (26.91%) and observed C (64.62%), H (5.40%), N (23.67%).

Section 3. Supporting Table

Table S1. Synthesis of the ACOFs under variable solvothermal conditions

Conditions	Temperature (°C)	Reaction Time (h)	BET Surface Area (m^2 g^{-1})	Yield (%)
Dioxane (2 ml)/ AcOH (3M, 0.2 mL)	120	72	1176	86
Dioxane (1 mL)/ Mesitylene (1 mL)/ AcOH (6M, 0.2 mL)	120	72	1128	82
Mesitylene (2 mL)/ AcOH (6M, 0.2 mL)	120	72	1062	79
Ethanol (2 mL)/ AcOH (6M, 0.2 mL)	120	72	1002	81

Section 4. PXRD Profile of ACOF-1

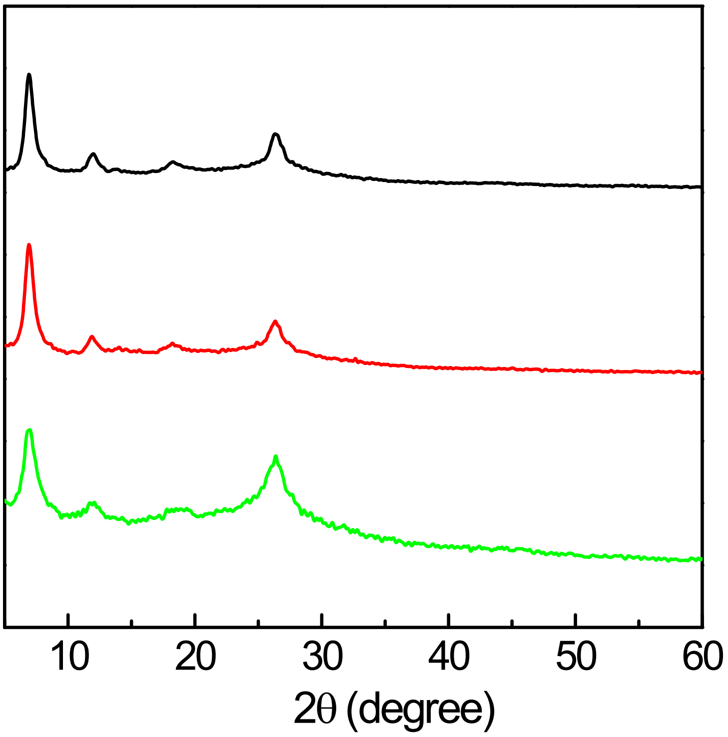


Figure S1. PXRD profiles of the ACOF-1 synthesized under different conditions (black: mesitylene/6 M AcOH (10/1 by vol.); red: mesitylene/dioxane/6 M AcOH (5/5/1 by vol.); green: ethanol /6 M AcOH (10/1 by vol.).

Section 5. FT-IR Spectral Profile

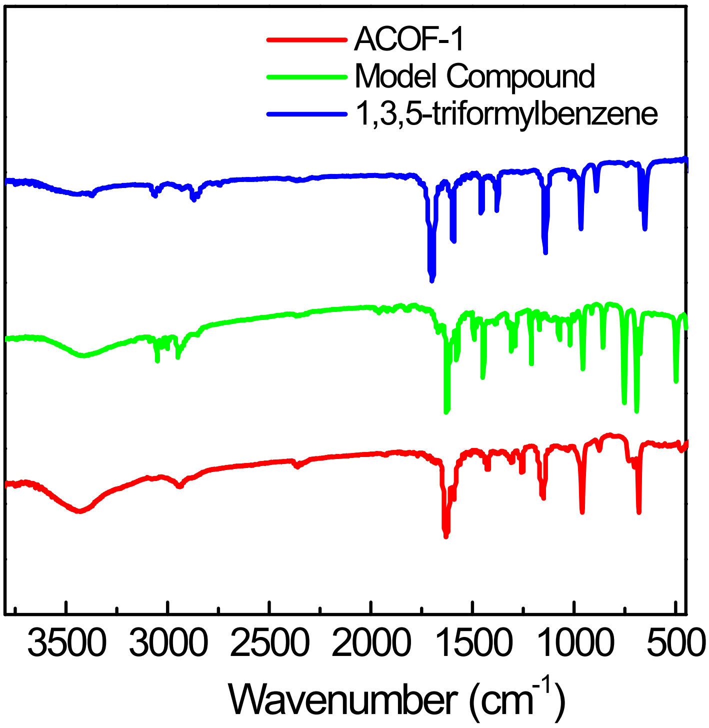
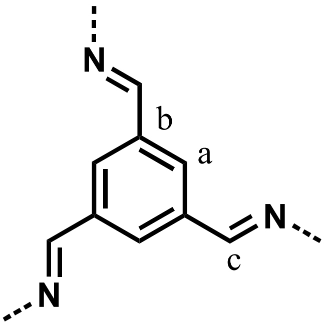


Figure S2. The IR spectra of ACOF-1 (red line), its monomers (blue line) and model compound (green line).

Section 6. Solid State ^{13}C CP/MAS NMR Spectrum



ACOF-1

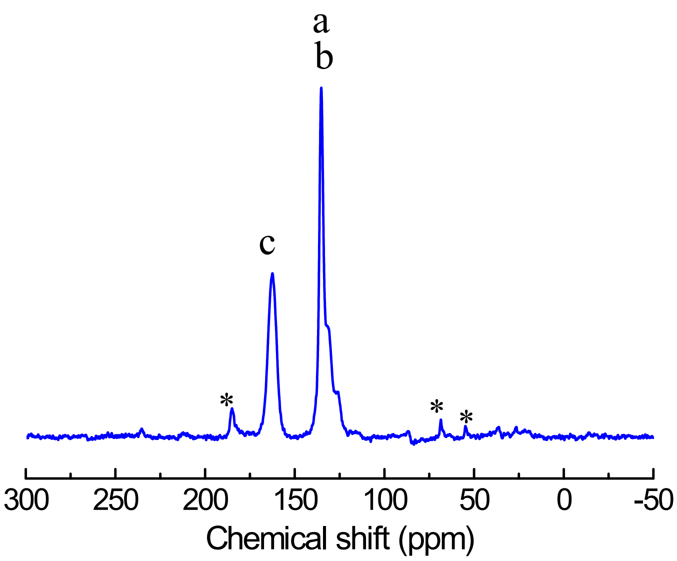


Figure S3. ^{13}C CP/MAS NMR spectroscopy of ACOF-1. Signals with * symbols are side peaks.

Section 7. TGA Profile

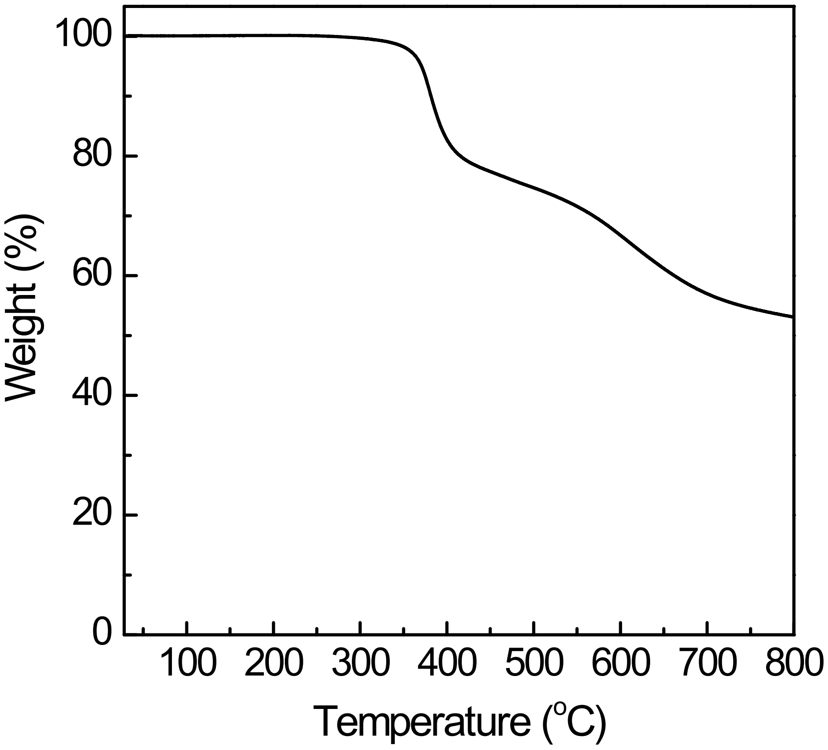


Figure S4. TGA curve of ACOF-1 under nitrogen.

Section 8. BET Surface Areas, PXRD and IR Spectra of ACOF-1@300

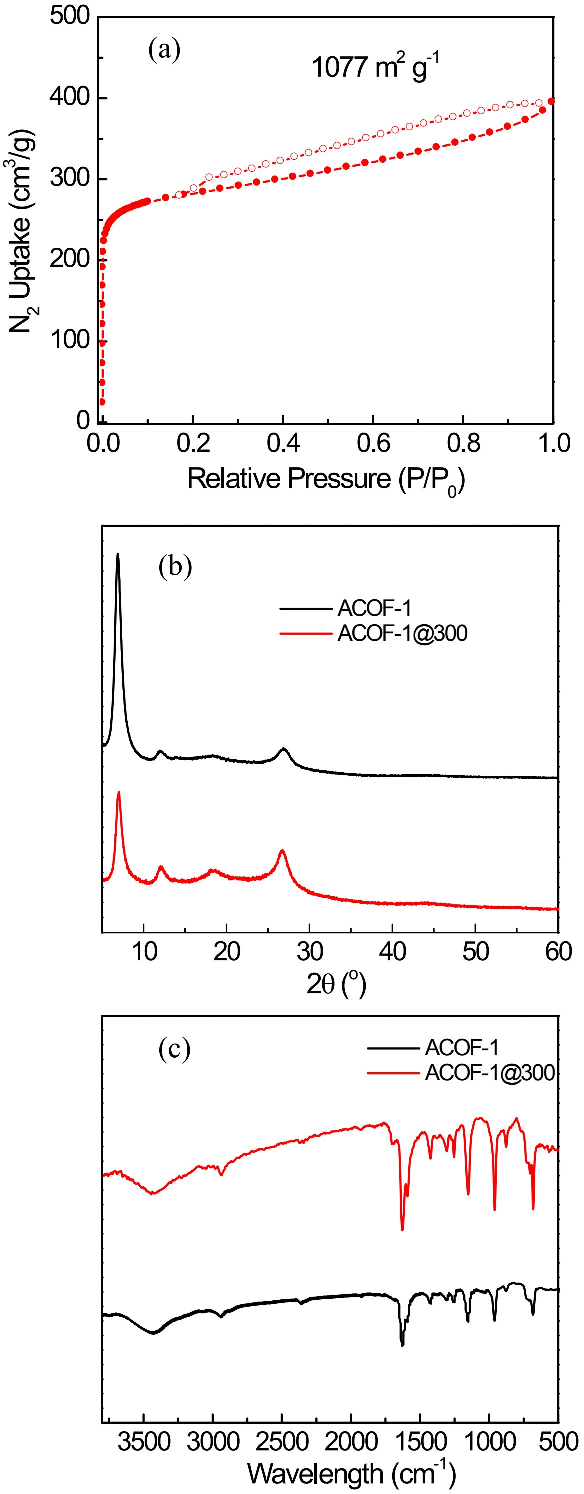


Figure S5. The polymer ACOF-1 was heated for 5 h at 300 °C under nitrogen. After heat treatment the framework was recorded as ACOF-1@300. (a) Surface area of ACOF-1@300 (b) PXRD curves ACOF-1 and ACOF-1@300 (c) IR spectra ACOF-1 and ACOF-1@300.

Section 9. SEM Images

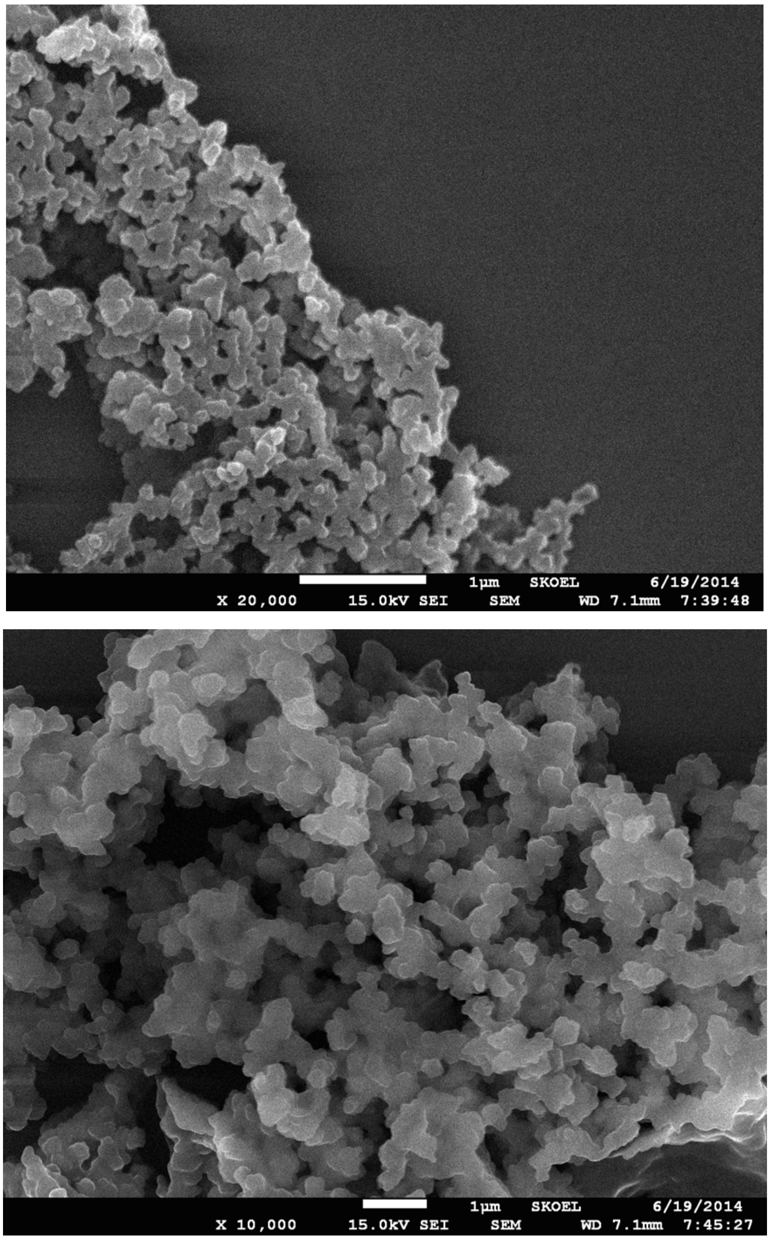


Figure S6. SEM images of ACOF-1.

Section 10. UV-Vis Spectral Profiles

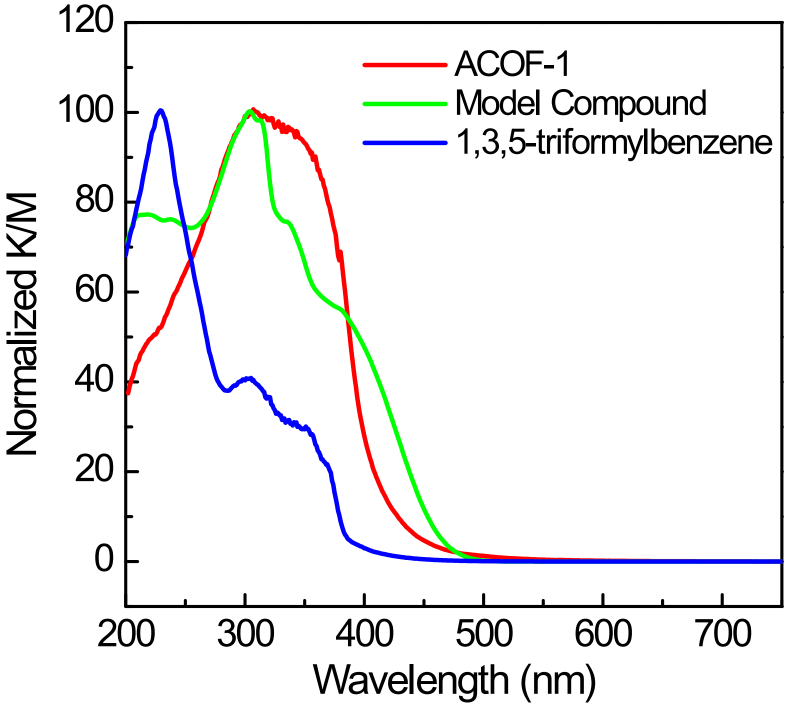


Figure S7. The absorption spectra of ACOF-1 (red line), its monomer (blue line) and model compound (green line).

Section 11. Gas Adsorption Isotherms

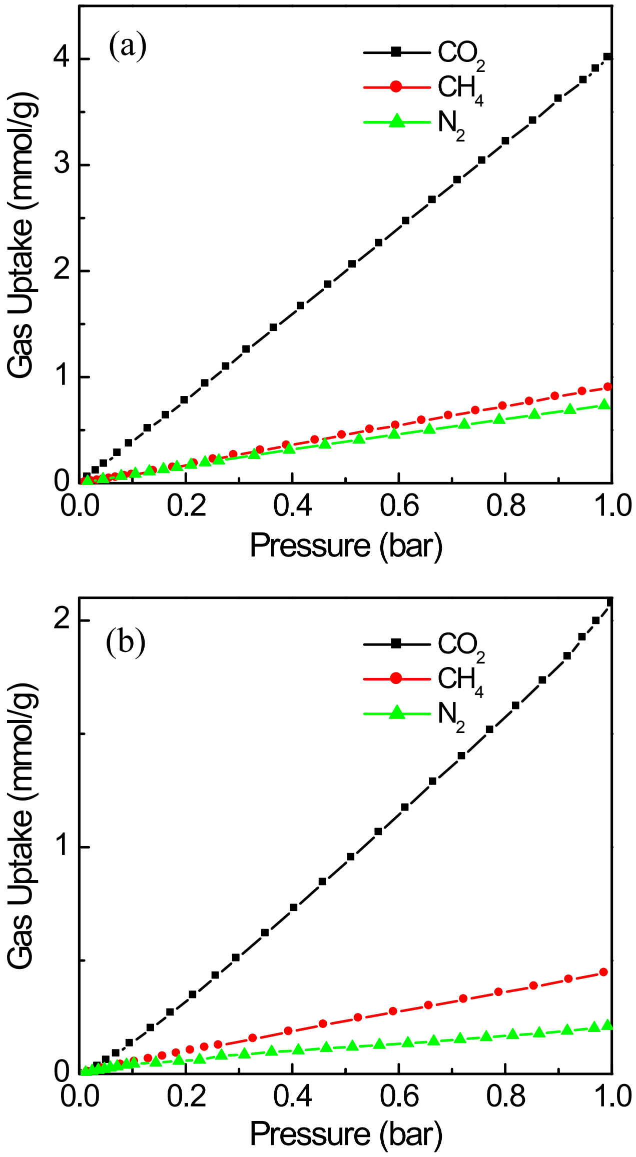


Figure S8. Gas adsorption isotherms (CO_2, square; CH_4, circle; N_2, triangle) of ACOF-1 at 273 K (a) and 298 K (b).

Section 12. N_2 sorption isotherms

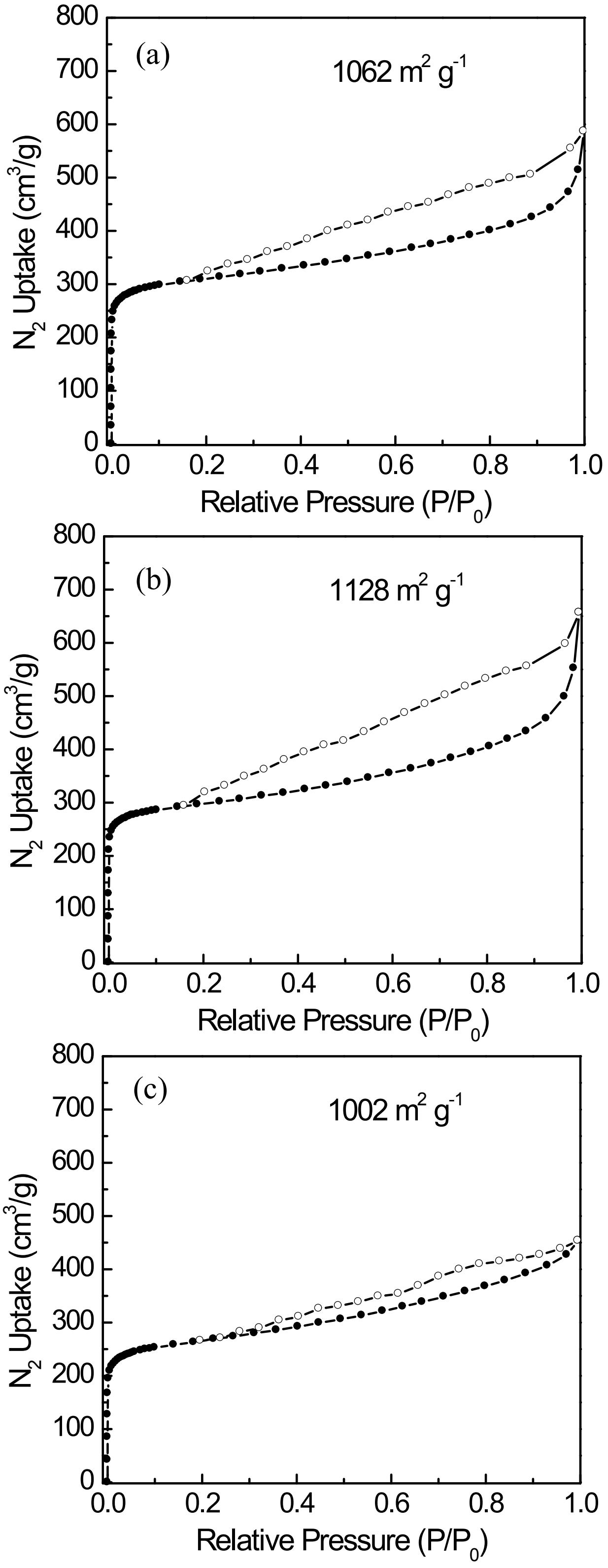


Figure S9. N_2 adsorption (●) and desorption (○) isotherm profiles of ACOF-1 prepared in Mesitylene (a), Mesitylene/Dioxane (b), and Ethanol (c) measured at 77K.

Section 13. Supporting References

S1. Accelrys, Material Studio Release Notes, Release 4.4, Accelrys Software, San Diego 2009.

S2. D. L. Reger, R. P. Watson, M. D. Smith and P. J. Pellechia, *Organometallics*, **2006,** *25,* 743–755.

S3. S. A. Van Arman, *Tetrahedron Lett.*, **2009**, *50*, 4693–4695.