Supporting Information

Unusual Preservation of Polyhedral Molecular Building Units in A Metal-Organic Framework with Evident Desymmetrization in Ligand Design

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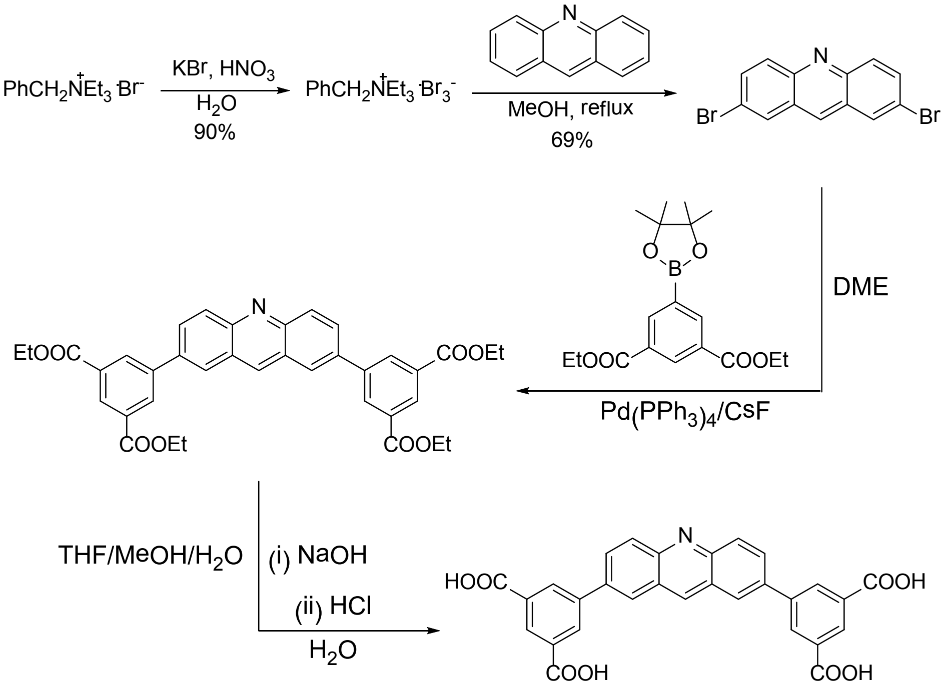
1. Materials and Methods

All general reagents and solvents (AR grade) were commercially available and used as received. $Cu(NO_3)_2\cdot2.5H_2O$, benzyltriethylammonium bromide, acridine, 3-(methoxycarbonylphenyl)boronic acid, and 4-(methoxycarbonyl)phenylboronic acid were purchased from VWR. ^1H NMR data were collected on a Mercury 400 spectrometer. Elemental microanalyses (EA) were performed by Atlantic Microlab, Inc. FT-IR data were recorded on an IRAffinity-1 instrument. TGA data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 2 °C min^{-1} under N_2 atmosphere. The powder X-ray diffraction patterns (PXRD) were recorded on a BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178) at room temperature. Simulation of the PXRD spectrum was carried out by the single-crystal data and diffraction-crystal module of the *Mercury* program available free of charge *via* internet at http://www.iucr.org. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System. The sample for gas adsorption measurement was activated by a supercritical carbon dioxide (SCD) approach.[1] As-synthesized sample (about 120 mg) was soaked in ethanol for 12 h, and the extract was discarded. Fresh ethanol was subsequently added, and the sample was allowed to stay in ethanol for an additional 12 h. This procedure was again repeated three times. After the ethanol exchange process was completed the sample were placed inside the SCD dryer and the ethanol was exchanged with liquid CO_2 over 8 hours. During this time the liquid CO_2 was vented under positive pressure for 5 minutes each hour. After 10 hours of venting and soaking the CO_2 chamber was sealed and the temperature was raised to 40 ºC. The chamber was held above the critical point for 1 hour and then was slowly vented over 7 hours at this temperature. The dried sample was directly transferred to a sample tube for N_2 adsorption immediately. Finally, 91 mg sample was used in the gas adsorption measurement.

2. Syntheses and General Characterizations

2.1. 5,5'-(Acridine-2,7-diyl)diisophthalic acid (H_4ADDI)



(a) Benzyltriethylammonium tribromide[2]

A modified literature procedure was adopted. To a solution of benzyltriethylammonium bromide (47.0 g, 0.17 mol) and potassium bromide (60.0 g, 0.50 mol) in water (200 mL) in a 1 L round-bottomed flask was added nitric acid (70%, 50 mL, 0.80 mol) dropwise over 20 min, and the mixture was stirred at room temperature for 2 h to give a large amount of orange solid with little visible liquid. The mixture was filtered, washed with water (300 mL) and ether (75 mL x 2), redissolved in dichloromethane (140 mL), washed with brine (30 mL), dried (Na_2SO_4), decanted, and cooled at 0 ^oC overnight to give orange block-like crystals. The crystals were filtered and washed with ethyl acetate (20 mL). The filtrate was evaporated to dryness and redissolved in dichloromethane (10 mL). Ethyl acetate (~1 mL) was added dropwise until the solution became slightly milky, and the mixture was cooled at -20 ^oC for 5 h to give more orange block and needle-like crystals, which was again filtered and washed with ethyl acetate (20 mL). All the crystals were then combined and dried under high vacuum to afford pure benzyltriethylammonium tribromide (65.9 g, 90%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.52 (m, 5H), 4.50 (s, 2H), 3.35 (q, 6H), 1.53 (t, 9H).

(b) 2,7-Dibromoacridine[3]

A modified literature procedure was adopted. A solution of benzyltriethylammonium tribromide (60.0 g, 0.14 mol) and acridine (10.8 g, 60.1 mmol) in methanol (500 mL) was heated at reflux for 16 h, cooled to ambient temperature, filtered, washed with pyridine (10 mL) and dichloromethane (100 mL), and dried under high vacuum to afford 2,7-dibromoacridine (14.0 g, 69%) as a yellow solid. ^1H NMR (DMSO-d^6, 300 MHz): δ 9.06 (s, 1H), 8.50 (d, 2H), 8.10 (d, 2H), 7.87 (dd, 2H).

The filtrate was evaporated to dryness, redissolved in a mixture of water (200 mL) and dichloromethane (100 mL), filtered, and partitioned. The organic phase was discarded, and the aqueous phase mixed with potassium bromide (60.0 g, 0.50 mol) and treated with nitric acid (70%, 50 mL, 0.80 mol) as described for benzyltriethylammonium tribromide above to give the recycled benzyltriethylammonium tribromide (30.9 g, 51% recovery) as a mixture of red block and needle-like crystals.

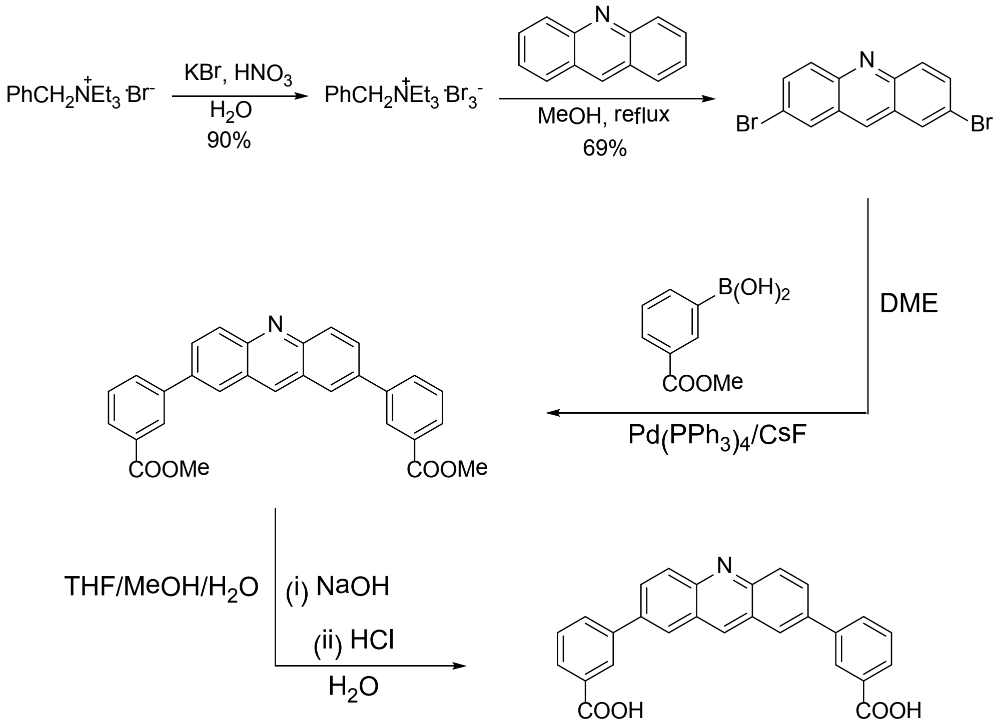
(c) Tetraethyl 5,5'-(acridine-2,7-diyl)diisophthalate

To a 500 mL Schlenk flask, 2,7-dibromoacridine (4.00 g, 8.90 mmol), diethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalate (8.68 g, 24.90 mmol, synthesized according a reported procedure,[4] CsF (6.00 g), and $Pd(PPh_3)_4$ (0.50 g) were added. The flask was connected to Schlenk line, and evacuated and refilled with nitrogen gas (repeat three times). 300 mL of 1,2-dimethoxyethane (DME) was degassed (two hours) and added to the flask through a canula. The flask was equipped with a water condenser and the reaction mixture refluxed under nitrogen atmosphere for 3 days. The solvent was removed on rotary evaporator. The solid was dissolved in CH_2Cl_2 and washed with water three times. After removed the CH_2Cl_2 solvent, the crude product was washed with acetone to give pure product of tetraethyl 5,5'-(acridine-2,7-diyl)diisophthalate with a yield of 68% (4.74 g) based on 2,7-dibromoacridine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (t, 12H), 4.39 (q, 8H), 8.15 (d, 2H), 8.32 (s, 2H), 8.39 (d, 2H), 8.66 (m, 4H), 8.73 (s, 2H), 8.95 (s, 1H).

(d) 5,5'-(Acridine-2,7-diyl)diisophthalic acid (H_4ADDI) (FW = 507.5)

4.74 g of tetraethyl 5,5'-(acridine-2,7-diyl)diisophthalate was dissolved in 120 mL of mixed solvent of THF and MeOH (v/v = 1:1), to which 30 mL of 3N NaOH aqueous solution was added. The mixture was stirred at 50 ^oC overnight. After removed the organic phase, the aqueous phase was acidified with diluted hydrochloric acid to give grey-yellow solid of 5,5'-(acridine-2,7-diyl)diisophthalic acid (H_4ADDI), which was filtered, washed with water, and dried under vacuum. Yield: 3.46 g, 89%. ^{1}H NMR (300 MHz, DMSO-d^6): δ 8.27 (s, 4H), 8.45~8.59 (m, 8H), 9.29 (s, 1H). Anal. Calcd. (%) for $C_{29}H_{17}NO_8$ (FW = 507.5): C, 68.64; H, 3.38. Found: C, 68.01; H, 3.62. FT-IR (neat, cm^{-1}): 2921(w), 2311(w), 1670(s), 1593(s), 1521(s), 1456(w), 1406(m), 1320(w), 1253(m), 1167(s), 1110(w), 1022(w), 831(w), 766(m), 688(w).

2.2. 3,3'-(Acridine-2,7-diyl)dibenzoic acid (H_2ADDB)



(a) Dimethyl 3,3'-(acridine-2,7-diyl)dibenzoate

To a 250 mL Schlenk flask, 2,7-dibromoacridine (2.00 g, 4.45 mmol), 3-(methoxycarbonylphenyl)boronic acid (2.40 g, 13.35 mmol), CsF (4.00 g), and $Pd(PPh_3)_4$ (0.40 g) were added. The flask was connected to Schlenk line, and evacuated and refilled with nitrogen gas (repeat three times). 150 mL of 1,2-dimethoxyethane (DME) was degassed (two hours) and added to the flask through a canula. The flask was equipped with a water condenser and the reaction mixture refluxed under nitrogen atmosphere for 4 days. The solvent was removed on rotary evaporator. The solid was dissolved in CH_2Cl_2 and washed with water three times. After removed the CH_2Cl_2, the crude product was washed with acetone to give pure product of dimethyl 3,3'-(acridine-2,7-diyl)dibenzoate with a yield of 68% (1.35 g) based on 2,7-dibromoacridine. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.99 (s, 6H), 7.61 (t, 2H), 7.98 (d, 2H), 8.09 (m, 4H), 8.25 (s, 2H), 8.37 (d, 2H), 8.48 (s, 2H), 8.89 (s, 1H).

(b) 3,3'-(Acridine-2,7-diyl)dibenzoic acid (H_2ADDB) (Fw = 419.4)

1.35 g of dimethyl 3,3'-(acridine-2,7-diyl)dibenzoate was dissolved in 50 mL of mixed solvent of THF and MeOH (v/v = 1:1), to which 15 mL of 3N NaOH aqueous solution was added. The mixture was stirred at 50 ^{o}C overnight. After removed the organic phase, the aqueous phase was acidified with diluted hydrochloric acid to give green-yellow precipitate of 3,3'-(acridine-2,7-diyl)dibenzoic acid (H_2ADDB), which was filtered, washed with water, and dried under vacuum. Yield: 1.17 g, 92%. ^{1}H NMR (300 MHz, DMSO-d^6): δ 7.69 (t, 2H), 8.00 (d, 2H), 8.14 (d, 2H), 8.38 (m, 6H), 8.65 (s, 2H), 9.55 (s, 1H). Anal. Calcd.

(%) for $C_{27}H_{17}NO_4$ (FW = 419.4): C, 77.32; H, 4.09. Found: C, 76.95; H, 4.43. FT-IR (neat, cm^{-1}): 2923(w), 2386(w), 2310(m), 1674(s), 1580(s), 1511(s), 1401(m), 1314(w), 1256(s), 1168(s), 1108(w), 1043(w), 830(w), 766(m), 694(w), 629(w).

3. X-ray Crystallography (Single-Crystal X-ray Diffraction)

Single-crystal X-ray diffraction data were collected on a Bruker-AXS APEX-II CCD X-ray diffractometer equipped with a low temperature device and a fine-focus sealed-tube X-ray source (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scans with a 0.5° step). Suitable single crystals were directly picked up from the mother liquor, attached to a glass loop and transferred to a designed cold stream of liquid nitrogen (110 K) for data collections. Raw data collection and reduction were done using APEX2 software.[5] Absorption corrections were applied using the SADABS routine.[6] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package.[7] There are large solvent accessible pore volumes in the crystals of **1** and **2** which are occupied by highly disordered solvent molecules. No satisfactory disorder model could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove these electron densities of these disordered species.[8] Thus, all of electron densities from free solvent molecules have been "squeezed" out, while for the coordinated solvent molecules, only oxygen atoms were left and refined in **1**. The details of structural refinement can be found in Tables S1 and S2.

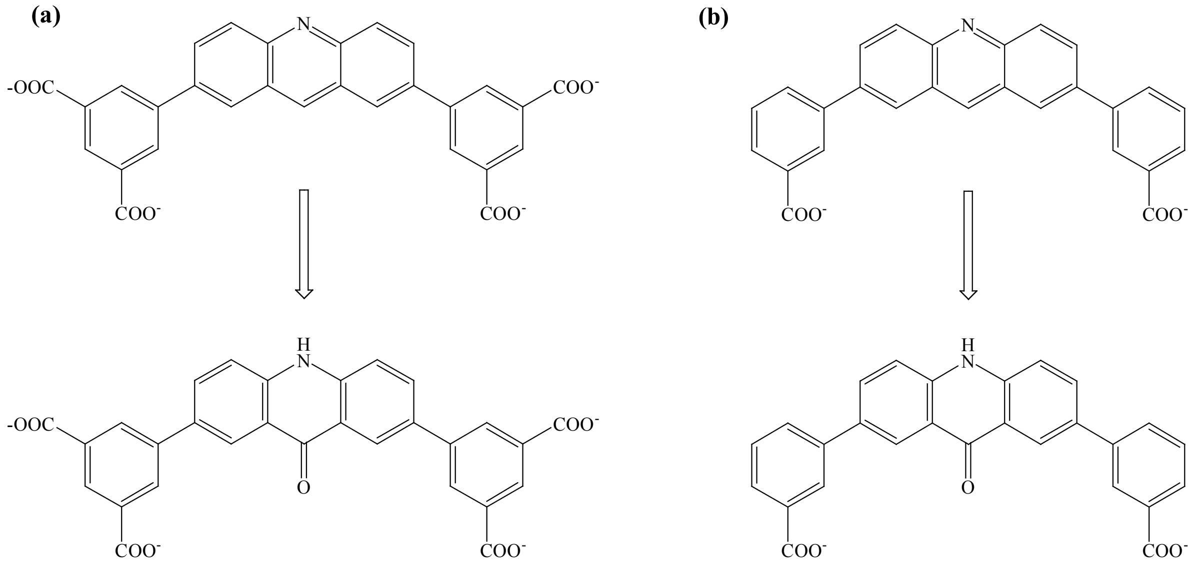
Table S1 Crystal data and structural refinement of **1**.

	After SQUEEZE	Before SQUEEZE
Empirical formula	$C_{159}H_{255}Cu_6N_3O_{63}S_{36}$	$C_{159}H_{255}Cu_6N_3O_{63}$ S_{36}
Formula weight	4752.43	4752.43
Temperature (K)	110(2)	110(2)
Crystal system	Tetragonal	Tetragonal
Space group	*P*4/*mnc*	*P*4/*mnc*
Unit cell dimensions		
a (Å)	30.988(6)	30.988(6)
b (Å)	30.988(6)	30.988(6)
c (Å)	45.964(8)	45.964(8)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	44137(14)	44137(14)
Z	8	8
Calculated density (mg/m^3)	0.613	0.613
Absorption coefficient (mm^{-1})	0.602	0.602
F(000)	8160	8160
Crystal size (mm^3)	0.40 × 0.36 × 0.32 mm	0.40 × 0.36 × 0.32 mm
Reflections collected	395795	395795
Independent reflections	19857 [*R*(int) = 0.1616]	19857 [*R*(int) = 0.2025]
Completeness to theta = 25.50°	99.6%	99.6%
Data/restraints/parameters	19857/0/589	19857/0/589
Goodness-of-fit on F^2	1.038	1.977
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0533$, $wR_2 = 0.1499$	$R_1 = 0.1718$, $wR_2 = 0.4686$
R indices (all data)	$R_1 = 0.1032$, $wR_2 = 0.1670$	$R_1 = 0.2454$, $wR_2 = 0.5256$
Largest diff. peak and hole (e.Å^{-3})	1.270 and –0.290	5.389 and -0.942

Table S2 Crystal data and structural refinement of **2**.

	After SQUEEZE	Before SQUEEZE
Empirical formula	$C_{156}H_{168}Cu_4N_{16}O_{32}$	$C_{156}H_{168}Cu_4N_{16}O_{32}$
Formula weight	3033.32	3033.32
Temperature (K)	110(2)	110(2)
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions		
a (Å)	16.1715(16)	16.1715(16)
b (Å)	16.3070(16)	16.3070(16)
c (Å)	17.9780(18)	17.9780(18)
α (°)	79.1310(10)	79.1310(10)
β (°)	71.7320(10)	71.7320(10)
γ (°)	86.3630(10)	86.3630(10)
Volume (Å^3)	4421.2(8)	4421.2(8)
Z	1	1
Calculated density (mg/m^3)	0.877	0.877
Absorption coefficient (mm^{-1})	0.523	0.523
F(000)	1204	1204
Crystal size (mm^3)	0.40 × 0.40 × 0.28 mm	0.40 × 0.40 × 0.28 mm
Reflections collected	44616	44616
Independent reflections	16420 [*R*(int) = 0.0224]	16420 [*R*(int) = 0.0225]
Completeness to theta = 25.50°	99.7%	99.7%
Data/restraints/parameters	16420/2/722	16420/2/722
Goodness-of-fit on F^2	1.173	2.464
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0584$, $wR_2 = 0.1992$	$R_1 = 0.1777$, $wR_2 = 0.5190$
R indices (all data)	$R_1 = 0.0740$, $wR_2 = 0.2095$	$R_1 = 0.2061$, $wR_2 = 0.5425$
Largest diff. peak and hole (e.Å^{-3})	1.006 and -0.454	4.220 and -0.790

4. Ligands Transformation from the In-Situ Reactions



Scheme S1. The ligands transformation in **1** (a) and **2** (b)

5. Topological Representation of 1 and NOTT-115.

TOPOS was used to identify the net.[9]

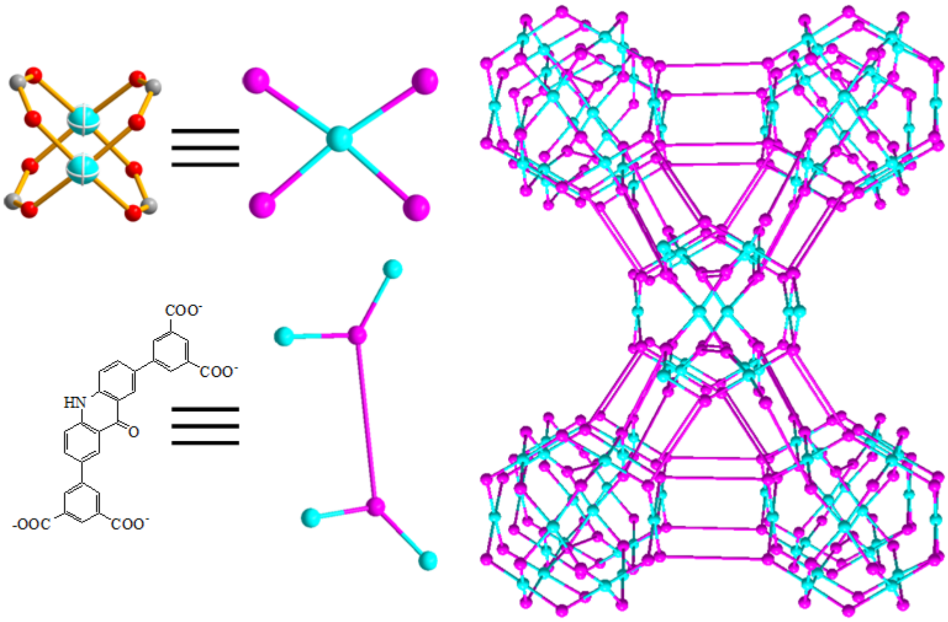


Fig. S1 Topological representation of **1**.

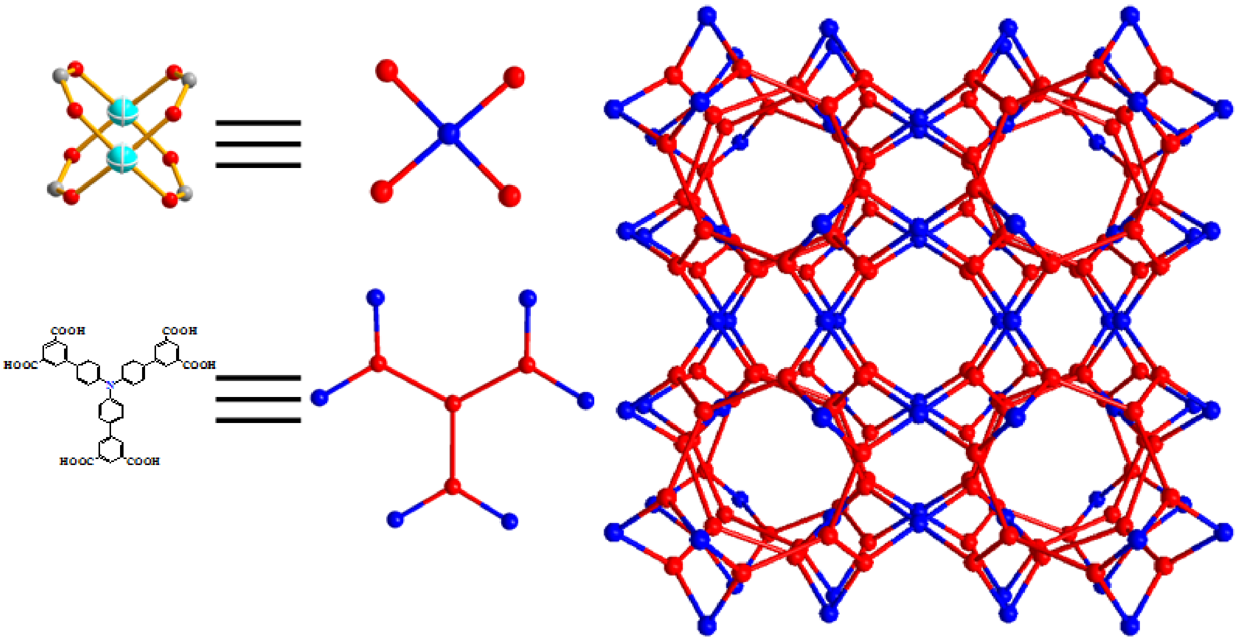


Fig. S2 Topological representation of NOTT-115.

6. Powder X-ray Diffraction (PXRD)

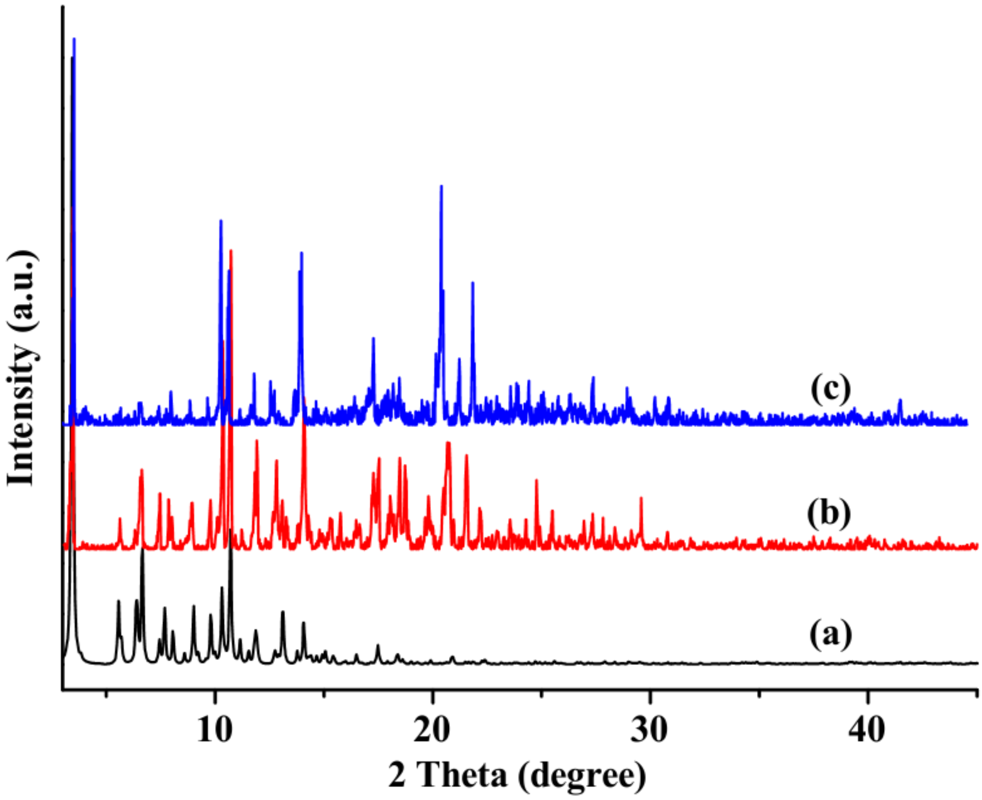


Fig. S3 The PXRD patterns of **1**: (a) simulated; (b) experimental on the as-synthesized sample; (c) experimental on the sample after activation.

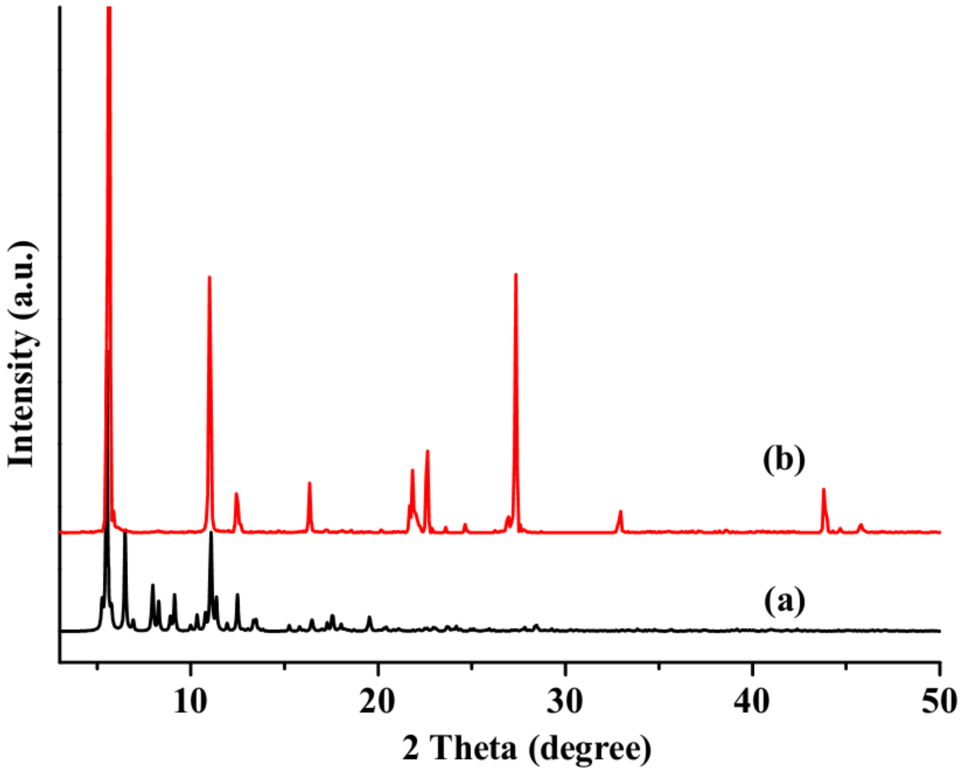


Fig. S4 The PXRD patterns of **2**: (a) simulated; (b) experimental on the as-synthesized sample.

7. Thermogravimetric Analysis (TGA)

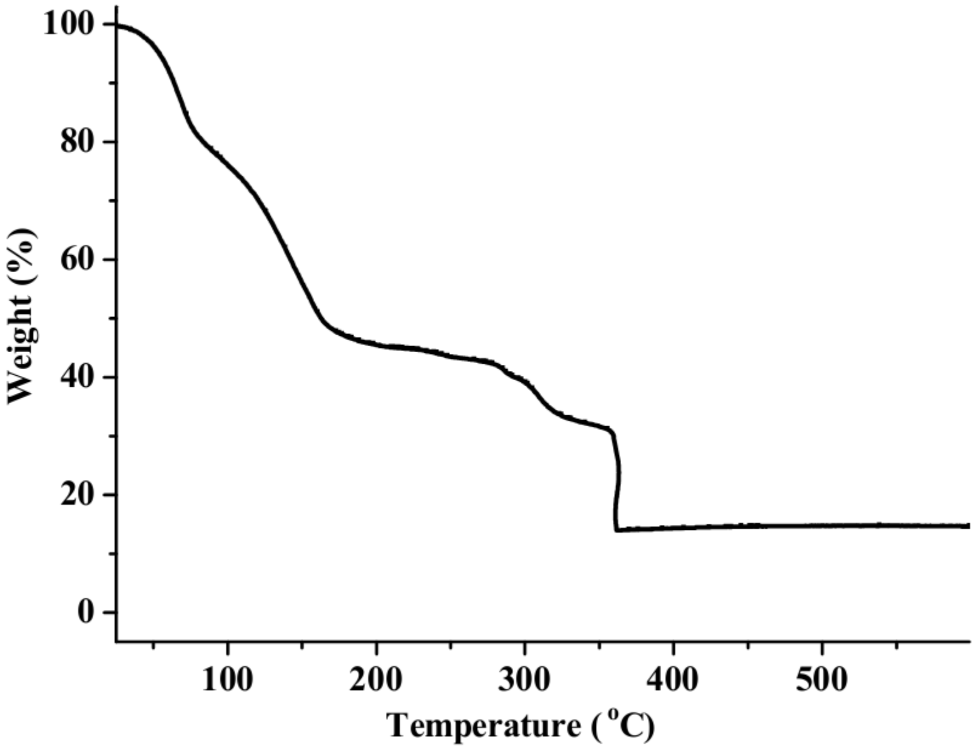


Fig. S5 The TGA curve of as-synthesized **1**·*n*S.

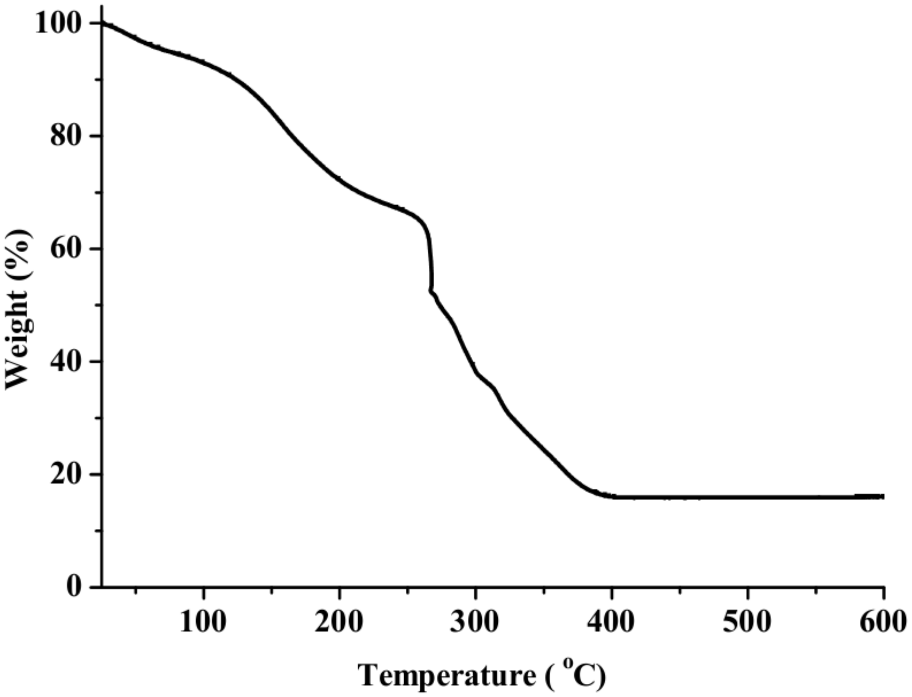


Fig. S6 The TGA curve of **2**·*n*S.

8. ^{1}H NMR spectra of H_4OADDI and H_2OADDB

In order to further confirm the formation of H_4OADDI and H_2OADDB ligands during the synthesis of **1** and **2**, the collected ligands from the degradation of **1** and **2** were characterized by ^{1}H NMR.

Typically, 30 mg of as-synthesized sample of **1** or **2** was soaked in methanol for 24 h, and the extract was discarded. Fresh methanol was subsequently added, and the sample was allowed to stay in methanol for an additional 24 h. This procedure was again repeated three times. After decanting the methanol extract, dichloromethane was used instead of methanol for three similar soaking recycles. The solvent exchanged sample was dried under a dynamic vacuum at room temperature for 5 hour. This dried sample was stirred in 2 mL of 2N NaOH aqueous solution at room temperature. After six hours, the resulting black solids were separated by centrifugation to obtain a colorless solution. To the solution 1N HCl aqueous solution was added until pH = 2 and red precipitate formed. The water was removed from the system under vacuum to give a black red solid, to which DMSO-d^6 was added for the measurement of the ^{1}H NMR. As shown in Fig. S7 and S8, ^{1}H NMR results indicated that the formation of H_4OADDI and H_2OADDB, although with a little bit impurity in each case.

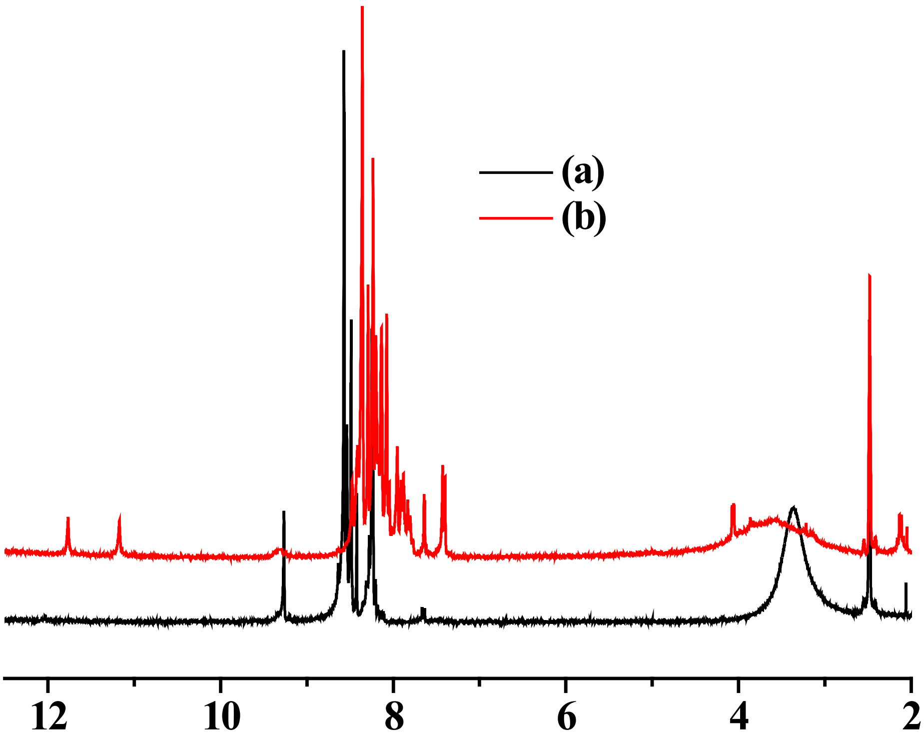


Fig. S7 The ^{1}HNMR spectrum of (a) H_4ADDI and (b) H_4OADDI.

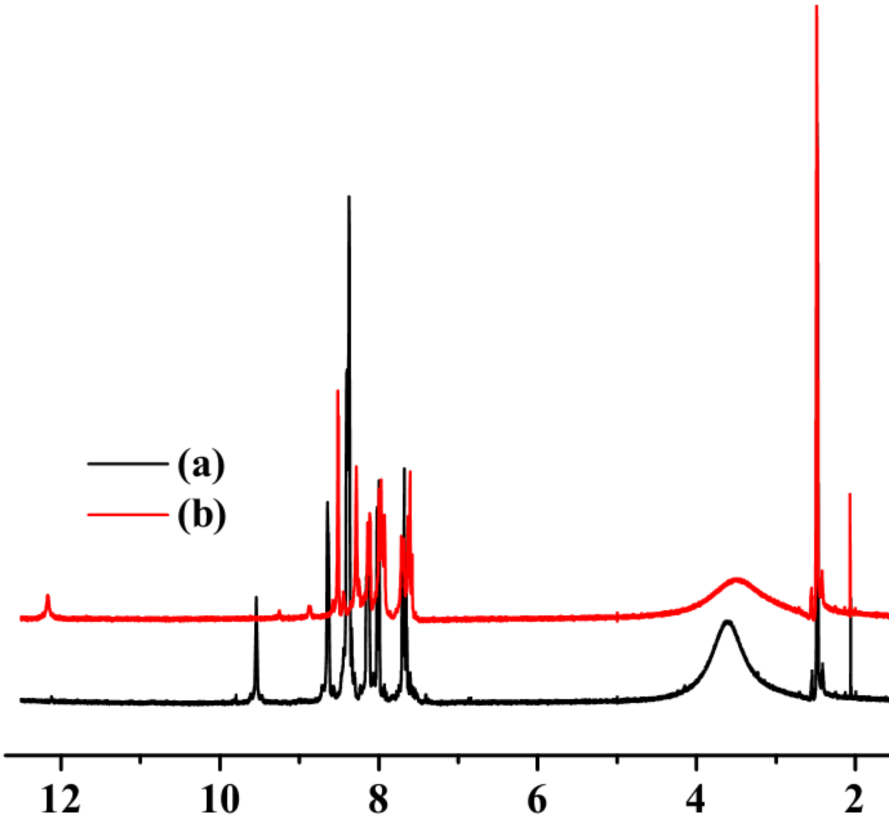


Fig. S8 The ^{1}HNMR spectra: (a) H_2ADDB; (b) H_2OADDB.

9. FT-IR Spectra

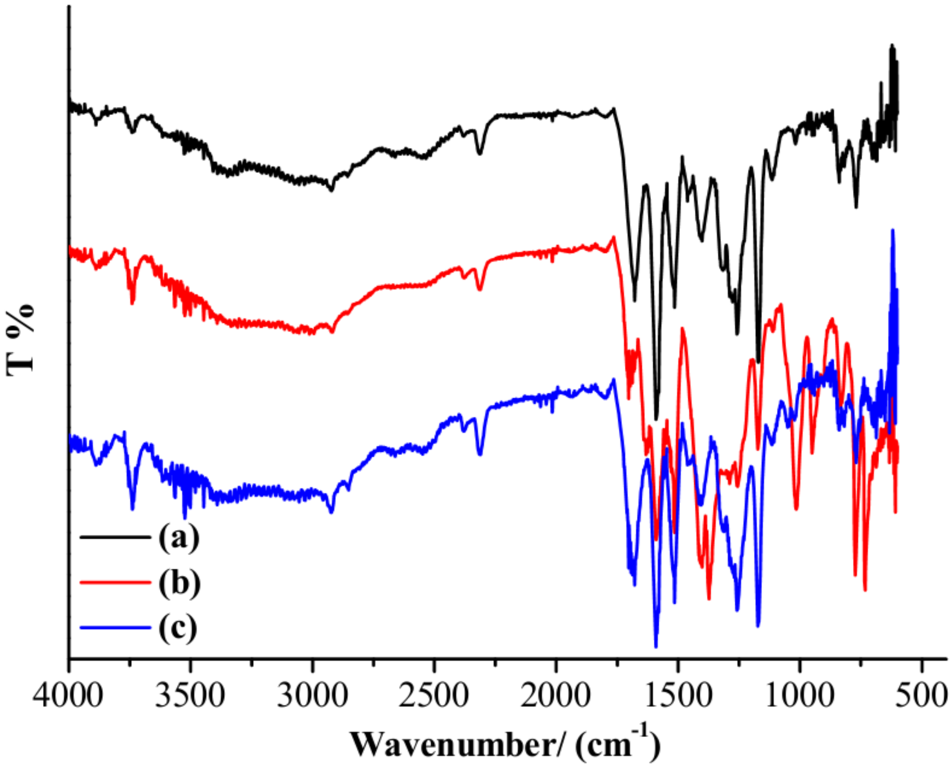


Fig. S9 The FT-IR spectrum of (a) H_4ADDI; (b) **1**·*n*S and (c) H_4OADDI.

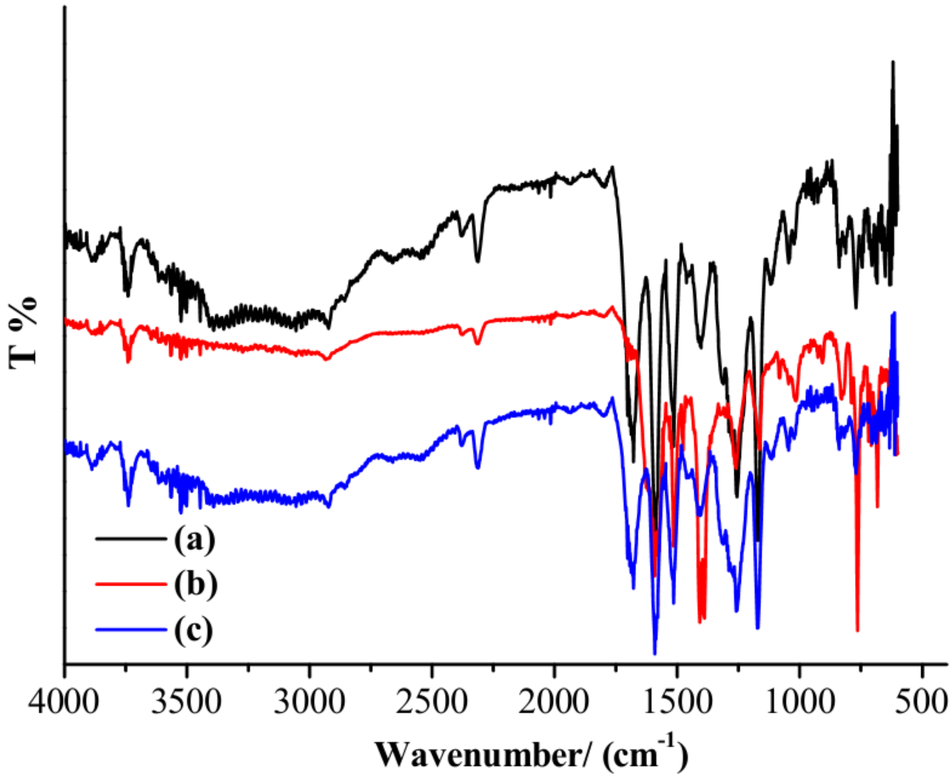


Fig. S10 The FT-IR spectrum of (a) H_2ADDB; (b) **2**·*n*S and (c) H_4OADDB.

10. References

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