Electronic Supplementary Material (ESI) for Dalton Transactions.

Polycatenation tuned microporosity of two metal–tris(4'-carboxybiphenyl)amine frameworks with multilayer structures

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Experimental section

1. Materials and instrumentation

All reagents were purchased commercially and used without further purification. The purity of all gases is 99.999%. All syntheses were carried out in a 20 ml vial under autogenous pressure. Elemental analysis (EA; C, H, and N) was carried out on a Vario Micro E III analyzer. All Powder X-ray diffraction analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 0.05°. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System. Fluorescence spectra were measured with a HORIBA Jobin-Yvon FluoroMax-4 spectrometer.

2. Synthesis

Synthesis of FIR-37: K_3TPA (72 mg, 0.1 mmol), DMP (20 mg, 0.2 mmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (60 mg, 0.2 mmol) were dissolved in DEF/MeOH (3:1, v/v) mixed solvents, which were placed in a small vial. The mixture was heated at 120 °C for 3 days and then cooled to room temperature. Yellow block-shaped single crystals were formed and collected by filtration and washed with DMF several times. (Yield: 32% based on K_3TPA). Elemental analysis for $C_{219}H_{316}N_{24}O_{42}K_2Zn_3$, Calcd (%): C, 62.16; H, 7.52; N, 7.94. Found: C, 62.73; H, 7.47; N, 7.89.

Synthesis of FIR-38: K_3TPA (72 mg, 0.1 mmol), DBO (22 mg, 0.2 mmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (60 mg, 0.2 mmol) were dissolved in DEF/EtOH (3:1, v/v) mixed solvents, which were placed in a small vial. The mixture was heated at 120 °C for 3 days and then cooled to room temperature. Yellow block-shaped single crystals were formed and collected by filtration and washed with DMF several times. (Yield: 48% based on K_3TPA). Elemental analysis for $C_{267}H_{354}N_{25}O_{47}K_2Zn_4$, Calcd (%): C, 66.06; H, 7.12; N, 6.99. Found: C, 65.98; H, 7.25; N, 6.87.

3. Crystallographic data collection and refinement

Crystallographic data of **FIR-37** and **FIR-38** were collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic Cu/Mo-Kα radiation at 100K/293 K. Absorption correction was applied using SADABS. Structure was solved by direct method and refined by full-matrix least-squares on F^2 using SHELXTL-2014 program. In these structures, some cations and free solvent molecules were highly disordered and could not be

located. The diffused electron densities resulting from these residual cations and solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated. A summary of crystal data and refinement results are provided in Table S1.

Table 1 A summary of crystal data and refinement results for Compounds **FIR-37** and **38**.

Compounds	**FIR-37**	**FIR-38**
Empirical formula	$C_{127}H_{86}N_7O_{18}K_2Zn_3$	$C_{168}H_{120}N_8O_{24}K_2Zn_4$
Formula weight	2272.40	2974.39
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*-1
a (Å)	21.6847(10)	21.1565(7)
b (Å)	36.8675(17)	21.6297(6)
c (Å)	27.338(2)	34.3390(8)
α (°)	90	86.156(2)
β (°)	98.212(6)	85.309(2)
γ (°)	90	61.408(3)
V (Å^3)	21632(2)	13744.3(8)
Z	4	2
D_{calcd} (g cm^{-3})	0.698	0.719
μ (Mo K*a*) (mm^{-1})	0.405	0.987
F (000)	4675	3068
Temperature (K)	293	100
Theta min, max (deg)	2.505, 19.998	1.117, 20.00
Crystal size	0.30 × 0.25 × 0.20	0.40 × 0.25 × 0.15
Tot., uniq. Data	22383/9945	66424/29657
Observed data [($I > 2\sigma(I)$]	4093	16461
R_{int}	0.0773	0.0464
Data/restraints/parameters	9945/1514/711	17055/1014/1855
R_1, wR_2 [$I > 2\sigma(I)$]	0.0983, 0.2504	0.0766, 0.2095
R_1, wR_2 (all data)	0.1750, 0.2862	0.1147, 0.2286
Goodness-of-fit on F^2	0.898	0.977
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å^{-3})	-0.274, 0.658	-0.335, 0.734

$R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$

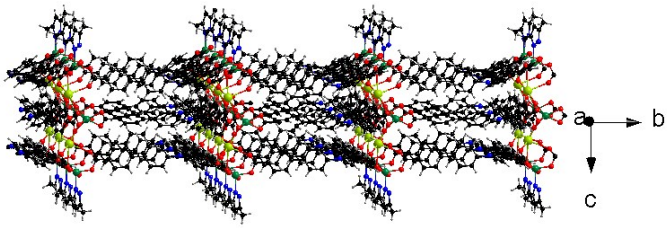

Figure S1 The single 2D layer in **FIR-37** along a axis.

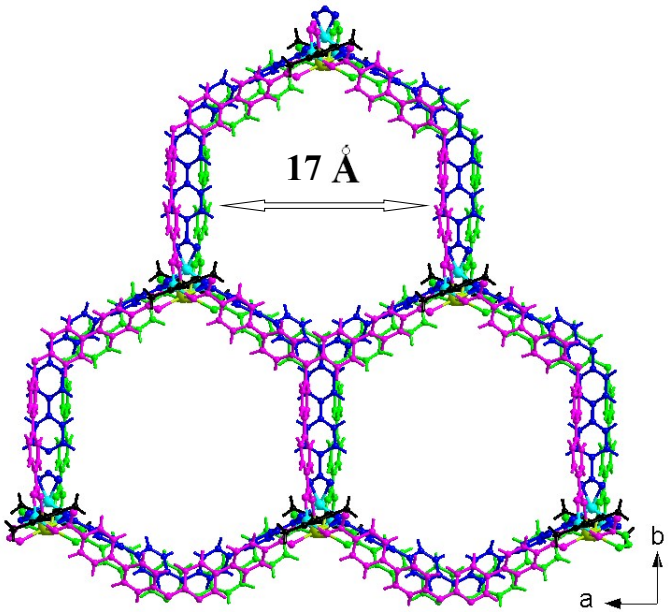

Figure S2 The single 2D layer in **FIR-37** along c axis.

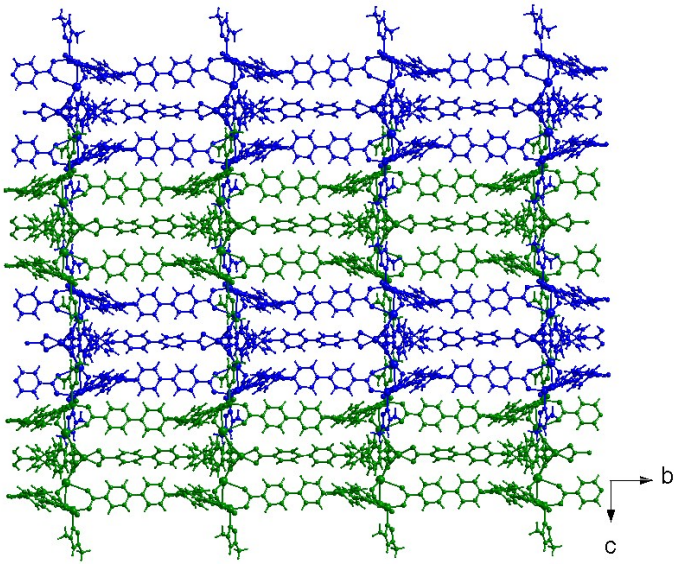

Figure S3 Packed layers of **FIR-37** in an AB fashion.

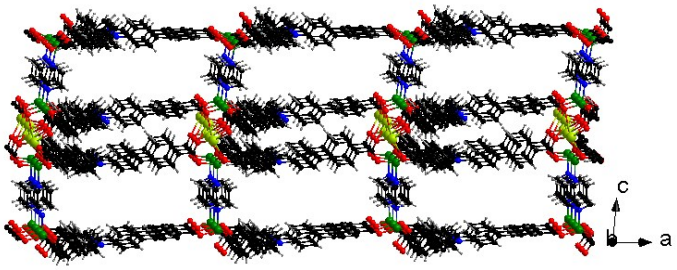

Figure S4 The single 2D layer in **FIR-38** along b axis.

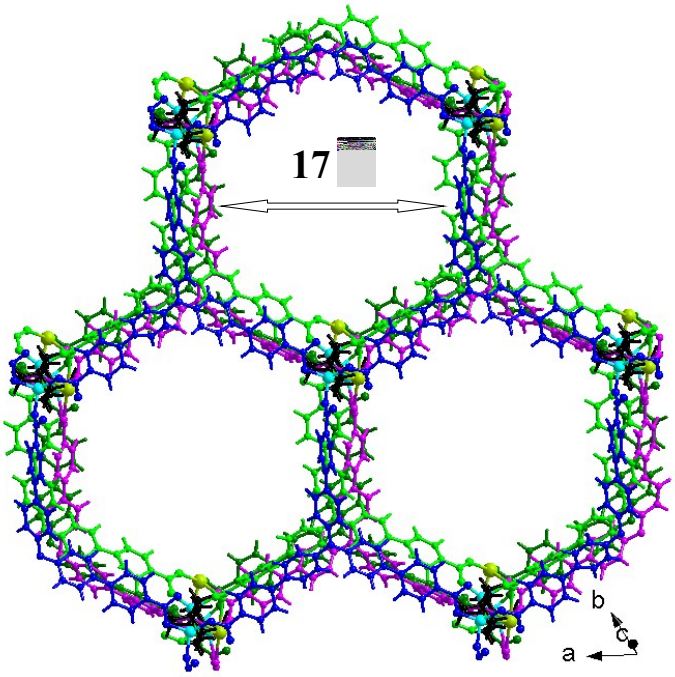

Figure S5 The single 2D layer in **FIR-38** along c axis.

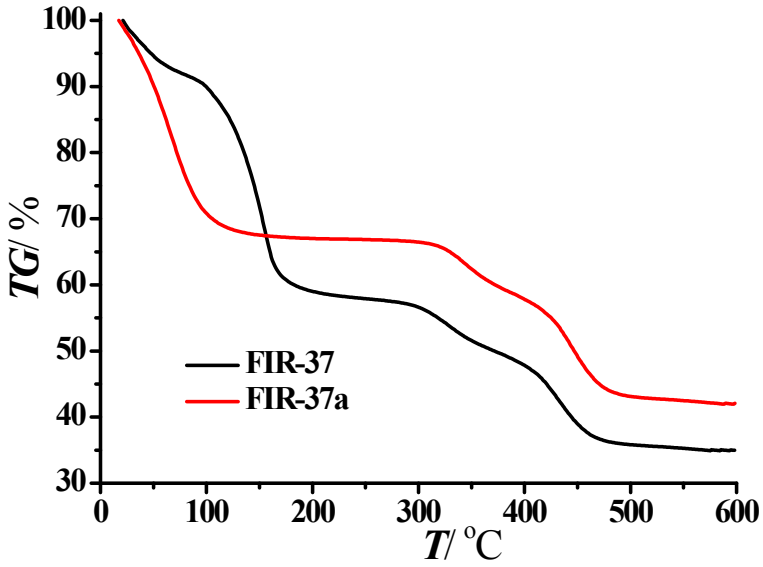

Figure S6 TGA curves of **FIR-37** and **FIR-37a**.

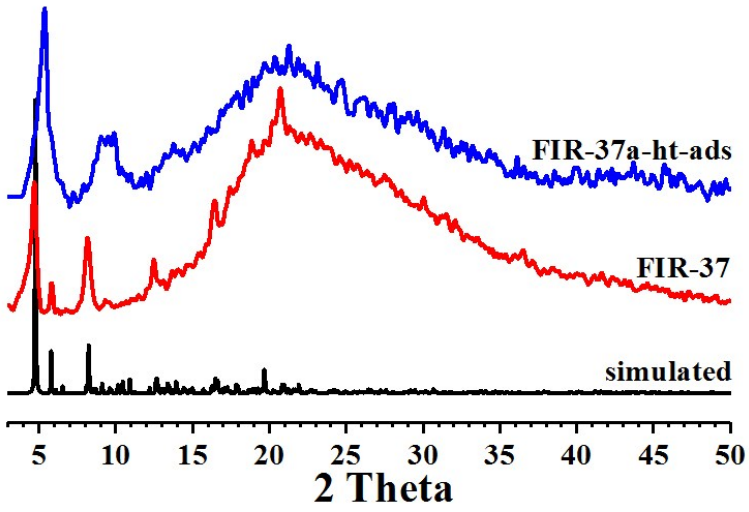

Figure S7 PXRD patterns of simulated from the single-crystal data of **FIR-37** (black); as-synthesized **FIR-37** (red); desolvated solid **FIR-37a-ht-ads** (blue).

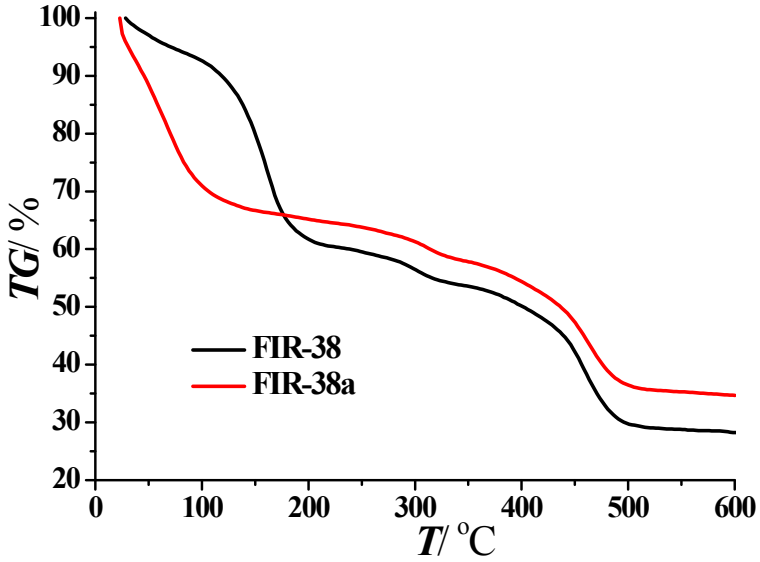

Figure S8 TGA curves of **FIR-38** and **FIR-38a**.

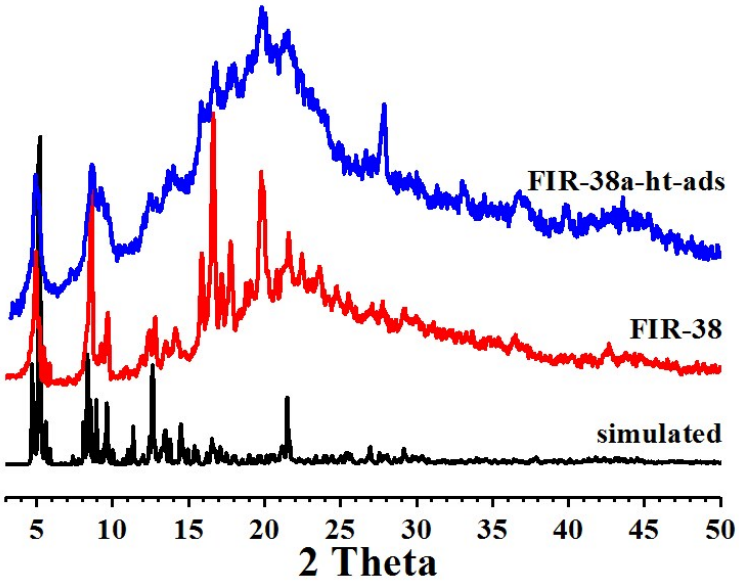

Figure S9 PXRD patterns of simulated from the single-crystal data of **FIR-38** (black); as-synthesized **FIR-38** (red); desolvated solid **FIR-38a-ht-ads** (blue).