# Supplementary Information

## A flexible thioether-based MOF as the crystalline sponge for structural characterization of liquid organic molecules

Xin-Yu Yang,[b] Shuai Yuan,[b] Jun-Sheng Qin,[b] Christina Lollar,[b] Ali Alsalme*[a] and Hong-Cai Zhou*[a,b]

a.    Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia. E-mail: aalsalme@ksu.edu.sa.

b.    Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States. E-mail: zhou@chem.tamu.edu.

# S1. Materials and instrumentation

1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, 4-mercaptopyridine were purchased from Tokyo Chemical Industry Co., LTD. Cuprous iodide (CuI), N,N-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), acetonitrile (CH$_3$CN), *N*-Methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), benzaldehyde (PhCHO) were purchased from Alfa Aesar. All commercial chemicals were used without further purification unless otherwise mentioned. $^1$H Nuclear magnetic resonance (NMR) data of L were collected on a Mercury 300 spectrometer (CDCl$_3$). Powder X-ray diffraction (PXRD) was carried out with a BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ($\lambda$ = 1.54178 Å) at 40 kV and 40 mA.

# S2. Synthesis of PCN-41·2DMA

*S2.1 The synthesis of L*
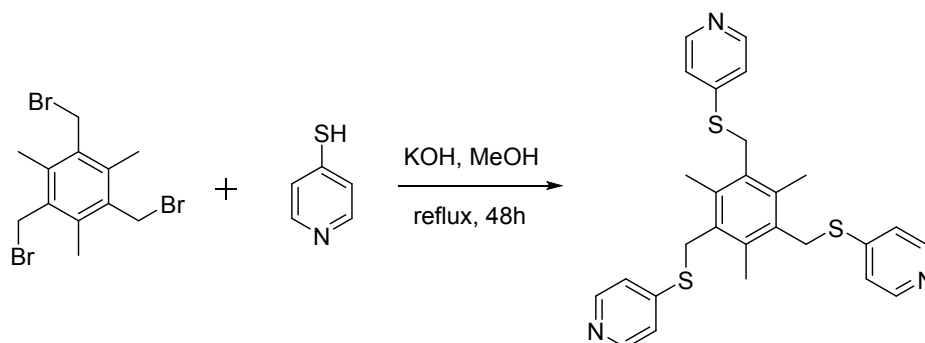


1,3,5-tris-(bromomethyl)-2,4,6-trimethylbenzene (1.2 g, 3 mmol) was added to an ice-cooled solution of 4-mercaptopyridine (1 g, 9 mmol) and KOH (1.68 g, 30 mmol) in methanol whilst stirring. The mixture was heated at reflux for 48 h at 80 ºC. The solution was poured into ice-cold water, the crude product (L) was filtered, dried and the white solid was obtained.

*S2.2 The synthesis of PCN-41·2DMA*

L (20 mg), CuI (10 mg), hydroiodic acid (3 drops), DMA (2.25 mL) and H$_2$O (0.75 mL) were charged in a 4 mL Pyrex vial. The mixture was heated in 75 ºC oven for 48 h. After cooling to room temperature, yellow, needle like crystals were harvested.

## S3. The sponge-like study of PCN-41·2DMA

After the immersion of as-synthesized PCN-41·2DMA (10 mg) in DMF (4 mL) at room temperature overnight, PCN-41·DMF was obtained. With the replacement of DMF by $CH_3CN$, NMP, DMSO or PhCHO, PCN-41·2CH$_3$CN, PCN-41·2NMP, PCN-41·2DMSO or PCN-41·PhCHO were produced, respectively, as confirmed by single-crystal X-ray diffraction analysis (Table S1).

## S4. Single crystal X-ray crystallography

All crystals were taken from the mother liquid without further treatment, transferred to oil and mounted into a loop for single crystal X-ray data collection. Diffraction was measured on a Bruker Smart Apex diffractometer equipped with a Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å, graphite monochromated) or Cu-$K_\alpha$ ($\lambda$ = 1.54184 Å, graphite monochromated) sealed-tube X-ray source. The data frames were recorded using the program APEX2 and processed using the program SAINT routine within APEX2.[1] The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS. The structures were solved by direct method using SHELXS and refined by full-matrix least-squares on $F^2$ using SHELXL software.[2] The crystallographic data were presented in Table S1. CCDC numbers: 1541830-1541835.

**Table S1.** Crystal data and structure refinements

|  | PCN-41·2DMA | PCN-41·DMF | PCN-41·2CH$_3$CN |
|---|---|---|---|
| Empirical formula | $C_{35}H_{45}Cu_2I_2N_5O_2S_3$ <br> [Cu$_2$I$_2$][C$_{27}$H$_{27}$N$_3$S$_3$][(C$_4$H$_9$NO)$_2$] | $C_{30}H_{34}Cu_2I_2N_4OS_3$ <br> [Cu$_2$I$_2$][C$_{27}$H$_{27}$N$_3$S$_3$][(C$_3$H$_7$NO)] | $C_{31}H_{33}Cu_2I_2N_5S_3$ <br> [Cu$_2$I$_2$][C$_{27}$H$_{27}$N$_3$S$_3$][(CH$_3$CN)$_2$] |
| $M_w$ | 1044.82 | 943.67 | 952.68 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P$-1 | $P$-1 | $P$-1 |
| $a$ (Å) | 9.252(4) | 9.174(6) | 8.962(3) |
| $b$ (Å) | 14.347(7) | 14.442(10) | 14.515(4) |
| $c$ (Å) | 17.158(8) | 17.023(11) | 16.577(5) |
| $\alpha$ (º) | 113.914(6) | 113.404(8) | 112.653(3) |

| | | | |
|---|---|---|---|
| $\beta$ (º) | 91.450(6) | 90.013(8) | 91.205(4) |
| $\gamma$ (º) | 99.705(5) | 99.203(8) | 98.338(3) |
| $V$ (Å³) | 2041.1(16) | 2038(2) | 1962.1(10) |
| $Z$ | 2 | 2 | 2 |
| $D_c$ (Mg·m⁻³) | 1.700 | 1.538 | 1.612 |
| Abs. coeff. (mm⁻¹) | 2.745 | 2.737 | 2.843 |
| $R_{int}$ | 0.0306 | 0.0608 | 0.0357 |
| $F(000)$ | 1036 | 924 | 932 |
| reflns collected | 12881 | 21299 | 22983 |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| Independent reflns | 8829 | 8016 | 9152 |
| GOF on $F^2$ | 1.078 | 1.053 | 1.025 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0625 | 0.0643 | 0.0474 |
| $wR_2$ [$I > 2\sigma(I)$][a] | 0.1806 | 0.1914 | 0.1371 |
| $R_1$ (all data)[b] | 0.1014 | 0.0977 | 0.0657 |
| $wR_2$ (all data)[b] | 0.2102 | 0.2156 | 0.1490 |

| | PCN-41·2NMP | PCN-41·2DMSO | PCN-41·PhCHO |
|---|---|---|---|
| Empirical formula | $C_{37}H_{43}Cu_2I_2N_5O_2S_3$ [Cu₂I₂][C₂₇H₂₇N₃S₃][(C₅H₈NO)₂] | $C_{31}H_{39}Cu_2I_2N_3O_2S_5$ [Cu₂I₂][C₂₇H₂₇N₃S₃][(C₂H₆SO)₂] | $C_{34}H_{33}Cu_2I_2N_3OS_3$ [Cu₂I₂][C₂₇H₂₇N₃S₃][(C₇H₆O)] |
| $M_w$ | 1066.82 | 1026.83 | 970.64 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P$-1 | $P$-1 | $P$-1 |
| $a$ (Å) | 9.102(3) | 9.353(6) | 9.4203(6) |
| $b$ (Å) | 14.511(4) | 14.189(9) | 14.3226(9) |
| $c$ (Å) | 17.160(5) | 17.257(10) | 17.3309(12) |
| $\alpha$ (º) | 66.114(3) | 113.336(7) | 65.977(3) |
| $\beta$ (º) | 88.537(4) | 94.402(7) | 77.856(3) |
| $\gamma$ (º) | 80.515(4) | 100.137(7) | 79.467(3) |
| $V$ (Å³) | 2042.1(10) | 2043(2) | 2075.6(2) |
| $Z$ | 2 | 2 | 2 |
| $D_c$ (Mg·m⁻³) | 1.735 | 1.669 | 1.553 |
| Abs. coeff. (mm⁻¹) | 2.745 | 2.838 | 14.564 |
| $R_{int}$ | 0.0274 | 0.0638 | 0.0453 |

| | | | |
|---|---|---|---|
| $F(000)$ | 1056 | 1012 | 944 |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ | Cu-$K_\alpha$ |
| reflns collected | 11836 | 19791 | 32396 |
| Independent reflns | 7210 | 8323 | 6941 |
| GOF on $F^2$ | 1.026 | 1.062 | 1.059 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0411 | 0.0655 | 0.0688 |
| $wR_2$ [$I > 2\sigma(I)$][a] | 0.0964 | 0.1788 | 0.2128 |
| $R_1$ (all data)[b] | 0.0568 | 0.1182 | 0.0892 |
| $wR_2$ (all data)[b] | 0.1050 | 0.2093 | 0.2592 |

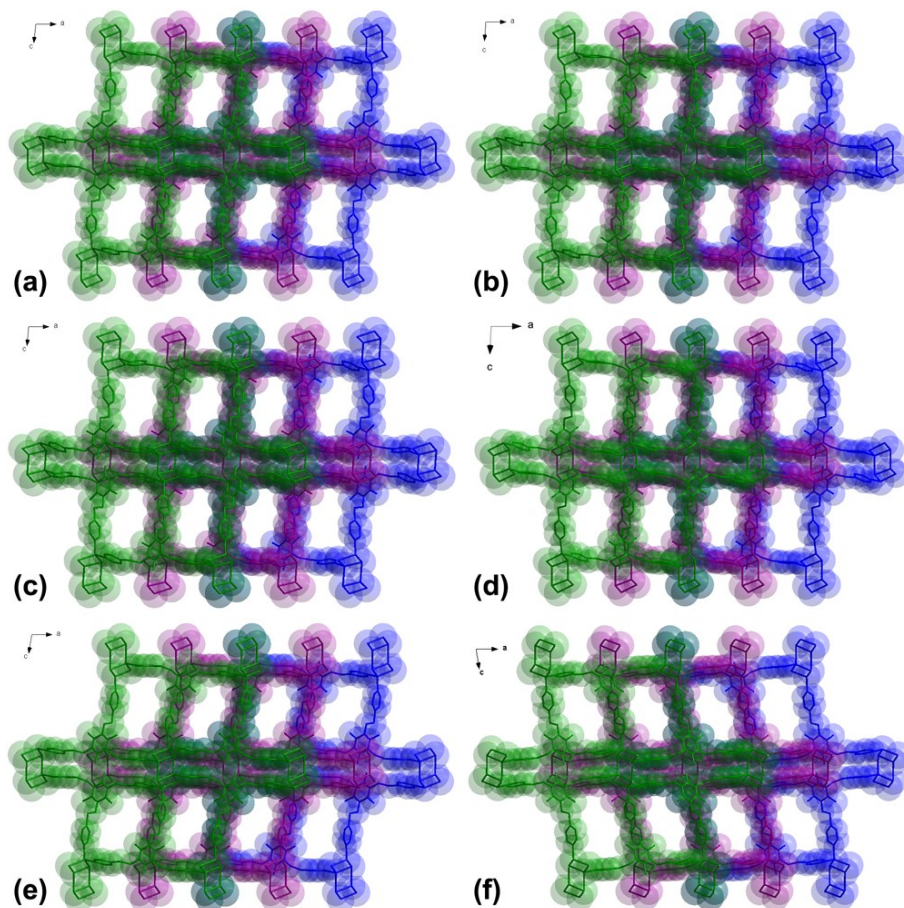[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o{}^2)^2|^{1/2}$.
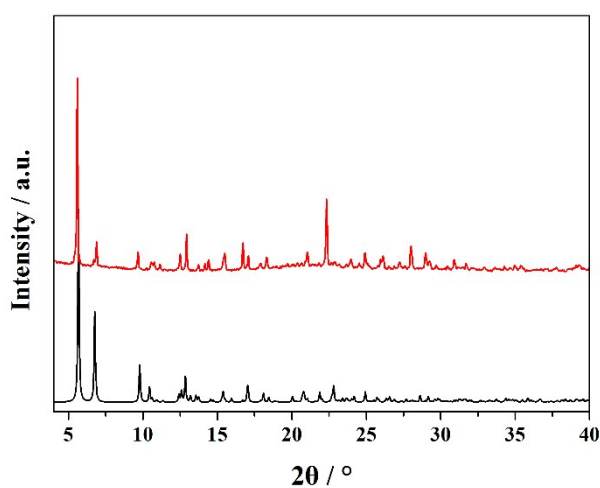
# S5. Supporting Figures
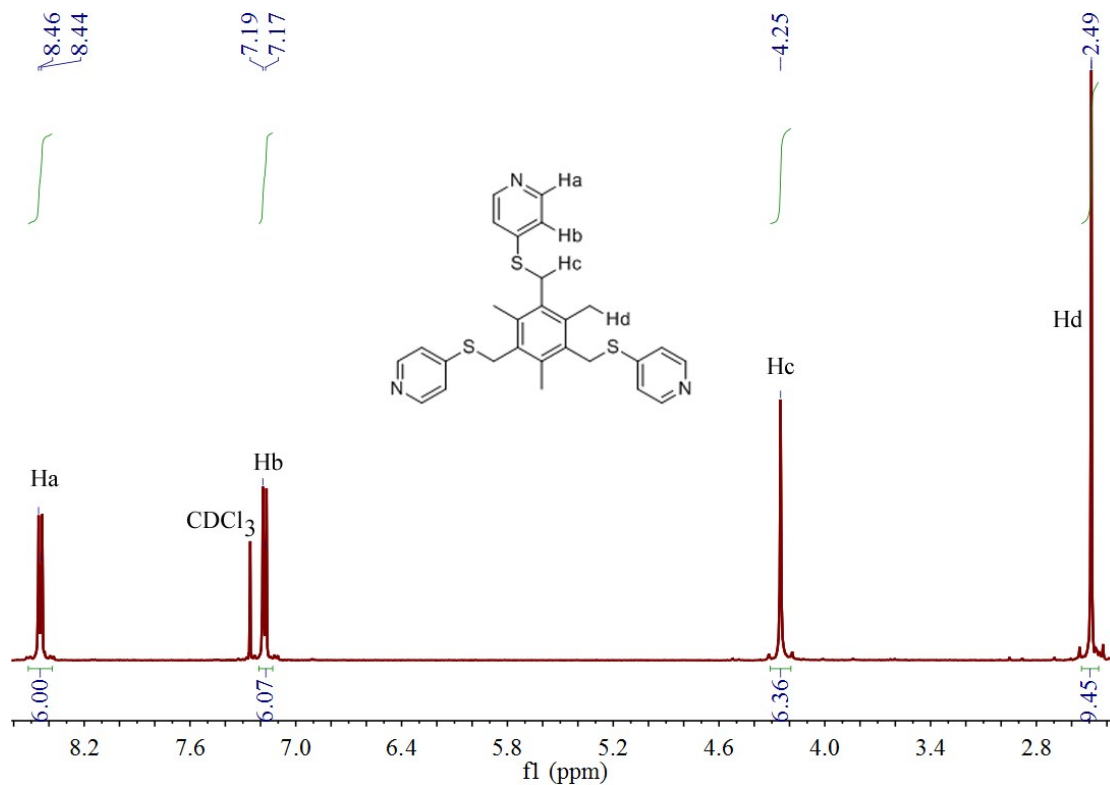


**Fig. S1** The $^1$H NMR spectrum of L.
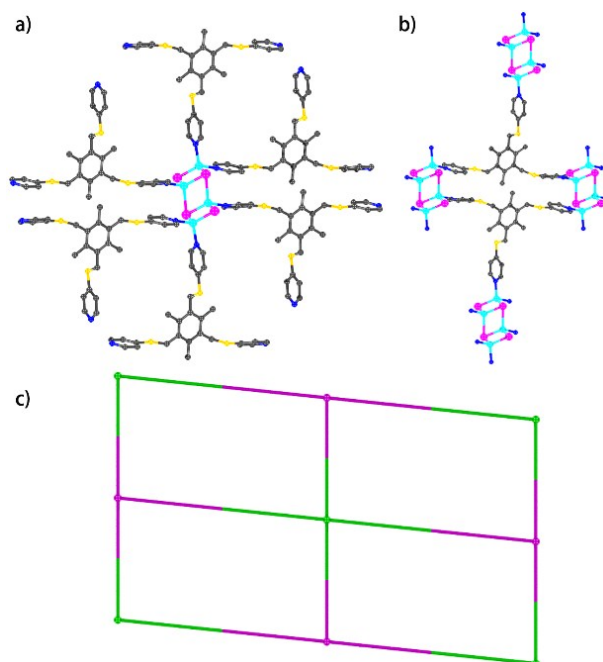


**Fig. S2** The 2D (4,4)-connected topology of PCN-41·2DMA.

**Fig. S3** The AAA sequences of adjacent layers viewed along the *b*-axis direction: (a) PCN-41·2DMA, (b) PCN-41·DMF, (c) PCN-41·2CH$_3$CN, (d) PCN-41·2NMP, (e) PCN-41·2DMSO, and (f) PCN-41·PhCHO. All the hydrogen atoms and solvent molecules were omitted for clarity.



**Fig. S4** The PXRD pattern of as-synthesized PCN-41·2DMA (*red*) and the simulated one from X-ray diffraction data (*black*).

# References

1   APEX2 v2012.2.0 and SAINT v7.68A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI; SADABS v2008/1 semi-empirical absorption and beam correction program. Sheldrick, G. M., University of Göttingen, Germany.

2   Sheldrick, G. M. *SHELXTL*, Version 6.14, Structure Determination Software Suite, Bruker AXS, Madison, WI, 2003.