Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers


**Electronic Supplementary Information**

# Design and Synthesis of Nucleobase-Incorporated Metal-Organic Materials

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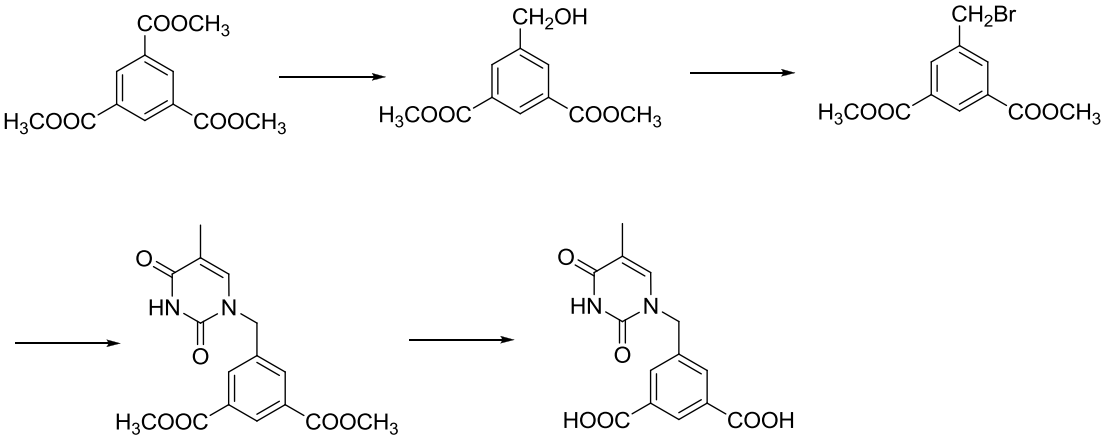
# Contents

# Section 1. Materials and Instrumentation

The $H_3$TATB (4,4*'*,4*''*-*s*-triazine-2,4,6-triyl-tribenzoic acid) was synthesized by a reported procedure. [1] All commercial chemicals were purchased from VWR and used without further purification unless otherwise mentioned. The dry THF was produced by a THF still. $^1$H nuclear magnetic resonance (NMR) data were recorded on a Mercury 300 MHz NMR spectrometer at the Center for Chemical Characterization and Analysis (CCCA), Department of Chemistry, Texas A&M University. Fourier transform infrared spectroscopy (FTIR) data were collected using a SHIMADZU IRAffinity-1 FTIR Spectrophotometer.

# Section 2. Ligand Synthesis

The ligand $H_2$MDPI (5-((5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl) methyl)isophthalic acid) was synthesized from the following route (Scheme S1).




**Scheme S1**. The synthesis of $H_2$MDPI Ligand

## 1) Dimethyl-5-(hydroxymethyl)isophthalate

Dimethyl-5-(hydroxymethyl)isophthalate was synthesized by a reported procedure with some modifications. [2] Trimethyl-1,3,5-tricarboxybenzoate (10 g, 39.65 mmol), $NaBH_4$ (1.8 g, 47.58 mmol) and 30 mL dry THF were charged in a round bottom flask equipped with a condenser under $N_2$ atmosphere. The resulting suspension was cooled in ice bath. A mixture of THF/MeOH (25 mL/7.4 mL) was added dropwise while stirring. After the addition, the ice bath was removed, and the reaction mixture was refluxed for 1 h. After cooling down to R. T., the reaction was slowly quenched with 40 mL 1 N HCl. The reaction mixture was then extracted with EtOAc (3 × 50 mL). The organic phase was combined and washed with $NaHCO_3$ (*aq*), brine, and water, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotavap, and the crude product was purified by silica gel column chromatography with EtOAc/hexanes (40%) to afford 5.30 g (23.60 mmol, yield 60%) pure product as white solid. Analytical data were in good agreement with the reported data. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.59 (t, J = 1.5 Hz, 1H), 8.23 (d, J = 1.5 Hz, 2H), 4.81 (d, J = 6.0 Hz, 2H), 3.95 (s, 6H), 1.98 (t, J = 6.0 Hz, 1H).

## 2) Dimethyl-5-(bromomethyl)benzene-1,3-dioate

Dimethyl-5-(bromomethyl)benzene-1,3-dioate was synthesized by a reported procedure with some modifications. [3] To a solution of dimethyl-5-(hydroxymethyl)isophthalate (4.0 g, 17.84 mmol) and carbon tetrabromide

(6.1 g, 18.39 mmol) in 50 mL $CH_2Cl_2$, cooled to 0˚C, was added dropwise a solution of triphenylphosphine (5.0 g, 19.06 mmol) in 30 mL $CH_2Cl_2$. The reaction was stirred at 0˚C for 1.5 h, diluted with another 50 mL of $CH_2Cl_2$, washed with water and brine, dried over $MgSO_4$. After filtration, the solvent was removed by rotavap, and the crude product was purified by silica gel column chromatography with $CH_2Cl_2$ to afford 4.5 g (15.67 mmol, yield 88%) pure product as white solid. Analytical data were in good agreement with the reported data. $^1$H NMR (300MHz, $CDCl_3$): $\delta$ = 8.63 (t, J = 1.5 Hz, 1H), 8.27 (d, J = 1.5 Hz, 2H), 4.56 (s, 2H), 3.98 (s, 6H).

**3) Dimethyl 5-((5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)methyl) isophthalate**

To a mixture of thymine (0.65 g, 5.15 mmol) and $K_2CO_3$ (0.73 g, 5.29 mmol) in 20 mL DMF, dimethyl-5-(bromomethyl)benzene-l,3-dioate (0.50 g, 1.74 mmol) was added slowly at room temperature in 5 min. The resulting mixture was heated up to 60˚C overnight. After cooling down, 100 mL of water was added, and then extracted with EtOAc (6 × 25 ml). The organic phase was dried over $MgSO_4$. After filtration, the solvent was removed by rotavap, and the crude product was purified by silica gel column chromatography with EtOAc/$CH_2Cl_2$ (10 – 40%) to afford 0.48 g (1.44 mmol, yield 83 %) pure product as white solid. $^1$H NMR (300MHz, DMSO-$d_6$): $\delta$ = 11.36 (s, 1H), 8.39 (t, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 1.5 Hz, 2H), 7.73 (d, *J* = 1.2 Hz, 1H), 4.95 (s, 2H), 3.87 (s, 6H), 1.73 (d, *J* = 1.2 Hz, 3H).

### 4) 5-((5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)methyl)isophthalic acid, $H_2$MDPI

To a mixture of the diester (0.72 g, 2.17 mmol) in MeOH/$H_2O$ (100 mL/40 mL), LiOH (0.60 g, 14.3 mmol) was slowly added. The resulting mixture was stirred at room temperature overnight. After removal of the majority of MeOH *in vacuo*, and the rest part of reaction mixture was acidified with 1 N HCl till pH = 2. Precipitate was collected and washed with water twice, dried to afford pure product (0.45 g, 1.48 mmol, yield 68 %) as white solid. $^1$H NMR (300MHz, DMSO-$d_6$): $\delta$ = 13.37 (s, 2H), 11.39 (s, 1H), 8.39 (t, $J$ = 1.5 Hz, 1H), 8.10 (d, $J$ = 1.5 Hz, 2H), 7.74 (d, $J$ = 1.2 Hz, 1H), 4.96 (s, 2H), 1.76 (d, $J$ = 1.2 Hz, 3H).

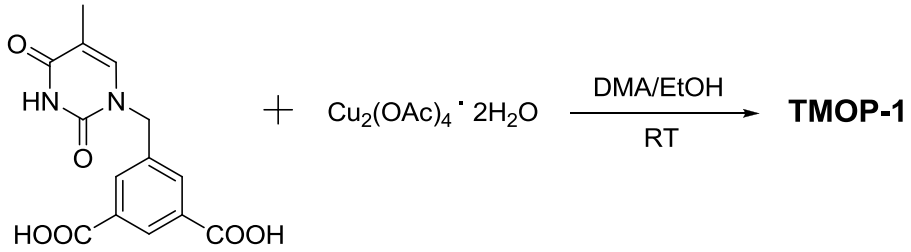
## Section 3. Syntheses of PCN-530 and TMOP-1

### 1) PCN-530, $Zn_3[Zn_2(\mu_2\text{-}H_2O)]_3(Ad)_6(TATB)_4(DMF)$

Adenine (16.9 mg, 0.125 mmol), $H_3$TATB (74 mg, 0.17 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (83 mg, 0.375 mmol) were ultrasonically dissolved in 10 mL of DMF in a 20 mL Pyrex vial and many white precipitates formed instantaneously. A minimal amount of concentrated $HBF_4$ (48% w/w in water) were added dropwise to dissolve all the precipitate and make it a clear solution before deionized water (1 mL) was added. The mixture was then heated in a 120 ℃ oven for 48 h. Large, colorless,

blocky single crystals of PCN-530 were yielded and harvested (26 mg, 39% based on adenine).

**2) TMOP-1, $Cu_{24}(MDPI)_{24}(DMA)_4(H_2O)_{20}$**




An *N, N'*-dimethylacetamide (DMA) solution (1 mL) of $H_2$MDPI (15 mg, ~0.05 mmol) was mixed with a DMA solution (10 mL) of $Cu_2(OAc)_4 \cdot 2H_2O$ (10 mg, ~0.025 mmol) in a glass vial (4 mL) and stirred for 5 min at room temperature. After stirring, 1.5 mL EtOH was layered upon this solution and then allowed the vial stand at room temperature. After 5 days homogeneous green-blue block crystals of $Cu_{24}(MDPI)_{24}(DMA)_4(H_2O)_{20} \cdot x$S (TMOP-1, where S represents non-assignable solvent molecules) were collected and washed with a little EtOH (yield, ~15 mg). The crystals of TMOP-1 slowly lose transparency when solvent molecules evacuated in air for a longer time. This compound is insoluble in DMA, DMSO, MeOH, THF, acetone, and $H_2O$.

# Section 4. Single-Crystal X-ray Crystallography of PCN-530 and TMOP-1

The crystals of both PCN-530 and TMOP-1 were taken from the mother solution directly, transferred into oil, and mounted onto a loop for single crystal X-ray data collection. Diffractions were measured on a Bruker Smart Apex diffractometer equipped with a Mo-Kα sealed-tube X-ray source (λ = 0.71073 Å, graphite monochromator) and a cooling device (110 K). The data frames were recorded using APEX2 and processed using *SAINT* within APEX2. The data were corrected for absorption and beam corrections based on the semi-empirical technique as implemented in *SADABS*. The structures were solved by direct methods using *SHELXS* and refined by full-matrix least-squares on $F^2$ using *SHELXL* in OLEX2.*

PCN-530 was integrated and refined in the triclinic crystal system. *XPREP* showed an R(sym) of 0.000 as standard for the Bravais lattice, Triclinic P. There was no more probable reasonable symmetry shown. XPREP listed 2 possible space groups, $P\bar{1}$ and P1, for centrosymmetric CFOM 2.14 and noncentrosymmetric CFOM 8.48 respectively. Mean |E*E-1| of 0.986 also indicated a centrosymmetric space group and thus $P\bar{1}$ was chosen. We obtained an R value of 0.0493 and $wR_2$ of 0.1221 after using the SQUEEZE routine in PLATON for the solution in $P\bar{1}$.

For PCN-530, no disorder modeling or restraints (except for hydrogen) were necessary. Thermal parameters were reasonable for the framework.

The thymine MOP was integrated and refined in the triclinic crystal system. *XPREP* showed an R(sym) of 0.000 as standard for the Bravais lattice, Triclinic P. The next most probable symmetry was Monoclinic C or I, both of which had an R(sym) of 0.621 and were dismissed. XPREP listed 2 possible space groups, $P\bar{1}$ and P1, for centrosymmetric CFOM 3.21 and noncentrosymmetric CFOM 7.88 respectively. Mean |E*E-1| of 0.950 also indicated a centrosymmetric space group and thus $P\bar{1}$ was chosen. We obtained an $R_1$ of 0.0997 for and a $wR_2$ of 0.2557 after using the SQUEEZE routine in PLATON for the solution in $P\bar{1}$.

For the TMOP-1 refinement, AFIX and DFIX restraints were used on several of the disordered thymine moieties, and PART and SPLIT commands combined with partial occupancy were used to model disorder on these moieties. Several other thymine moieties required no restraints or disorder modeling, and appeared to be in more confined and hydrogen-bonded parts of the structure and thus have a more consistent position.

For both solutions, all non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were located in calculated positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atoms. The solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the *SQUEEZE* routine of *PLATON*;[**] structures were then refined again using the data generated. The contents of the

solvent region are not represented in the unit cell contents in the crystal data. The CIF files can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 962335 for PCN-530 and 962336 for TMOP)

*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. G.M. Sheldrick, University of Göttingen, Germany.

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

**Table S1.** Crystal data and structure refinements for PCN-530 / TMOP-1.

| Compound PCN-530 | | Compound TMOP-1 | |
|---|---|---|---|
| Formula | $C_{129}H_{79}N_{43}O_{28}Zn_9$ | Formula | $C_{184}H_{156}N_{28}O_{84}Cu_{12}$ |
| *CCDC #* | 962335 | *CCDC #* | 962336 |
| *Fw* | 3267.68 | *Fw* | 4865.85 |
| Shape | Block | Shape | Block |
| Crystal system | Triclinic | Crystal system | Triclinic |
| Space group | $P\bar{1}$ | Space group | $P\bar{1}$ |
| *a* (Å) | 19.801(7) | *a* (Å) | 27.990(3) |
| *b* (Å) | 20.162(7) | *b* (Å) | 28.102(3) |
| *c* (Å) | 27.225(9) | *c* (Å) | 28.303(5) |
| *α* (°) | 97.544(5) | *α* (°) | 109.319(2) |
| *β* (°) | 100.609(5) | *β* (°) | 106.426(2) |
| *γ* (°) | 111.627(5) | *γ* (°) | 107.182(1) |
| *V* (Å$^3$) | 9692(6)Å$^3$ | *V* (Å$^3$) | 18196(4) |
| *Z* | 2 | *Z* | 2 |
| $d_{calcd.}$ (g/cm$^3$) | 1.120 | $d_{calcd.}$ (g/cm$^3$) | 0.888 |
| $\mu$(mm$^{-1}$) | 1.156 | $\mu$(mm$^{-1}$) | 0.744 |
| *F*(000) | 3296 | *F*(000) | 4952 |
| $\theta_{max}$ [deg] | 22.62 | $\theta_{max}$ [deg] | 26.00 |
| Completeness | 0.991 | Completeness | 0.995 |
| Collected reflections | 56718 | Collected reflections | 190892 |
| Unique reflections | 25509 | Unique reflections | 71236 |
| Parameters | 1882 | Parameters | 2158 |
| Restraints | 0 | Restraints | 171 |
| $R_{int}$ | 0.0615 | $R_{int}$ | 0.0761 |
| *R*1 [I > 2σ(I)] | 0.0492 | *R*1 [I > 2σ(I)] | 0.1014 |
| *wR*2 [I > 2σ(I)] | 0.1221 | *wR*2 [I > 2σ(I)] | 0.2622 |
| *R*1 (all data) | 0.0836 | *R*1 (all data) | 0.1691 |
| *wR*2 (all data) | 0.1321 | *wR*2 (all data) | 0.2841 |
| GOF on $F^2$ | 1.003 | GOF on $F^2$ | 1.006 |
| $\Delta\rho_{max}$/ $\Delta\rho_{min}$ [e·Å$^{-3}$] | 1.44/-0.44 | $\Delta\rho_{max}$/ $\Delta\rho_{min}$ [e·Å$^{-3}$] | 2.22/-1.62 |

# Section 5. High-Resolution Figures of PCN-530 and TMOP-1

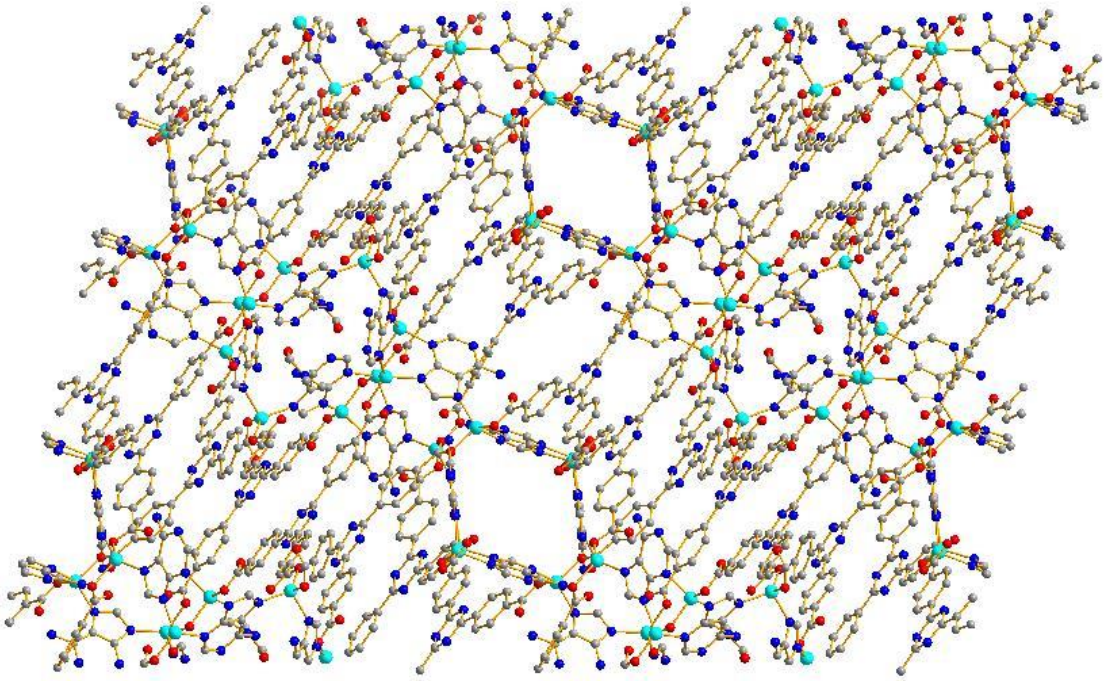


**Figure S1** The crystal structure of PCN-530 along *a* axis. Windows with the size of 7.4 × 11.9 Å are presents in this direction. The grey, red, blue and cyan spheres represent C, O, N and Zn, respectively. H atoms were omitted for clarity.

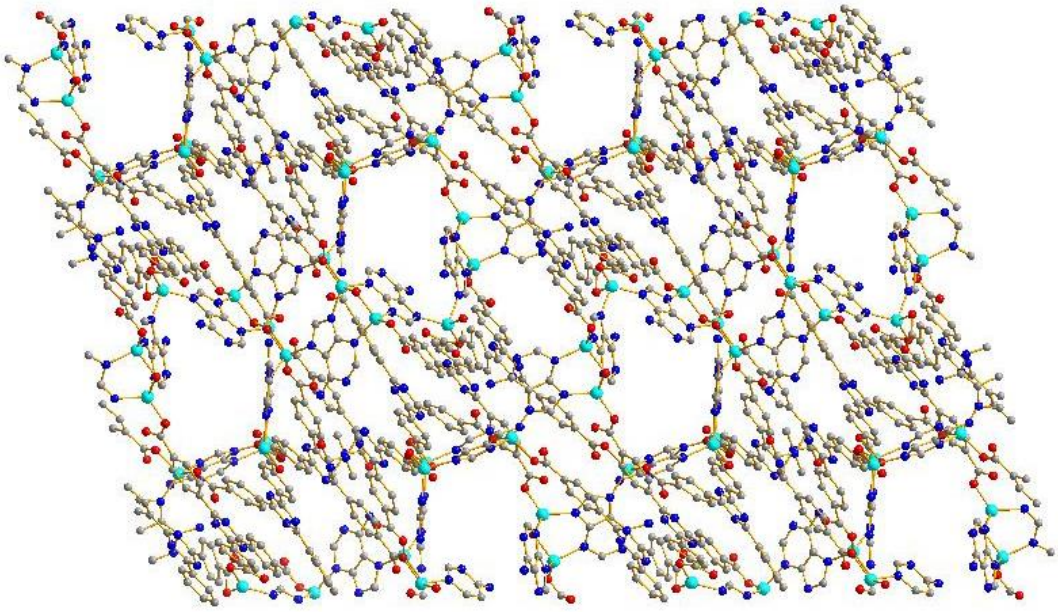


**Figure S2** The crystal structure of PCN-530 along *b* axis.

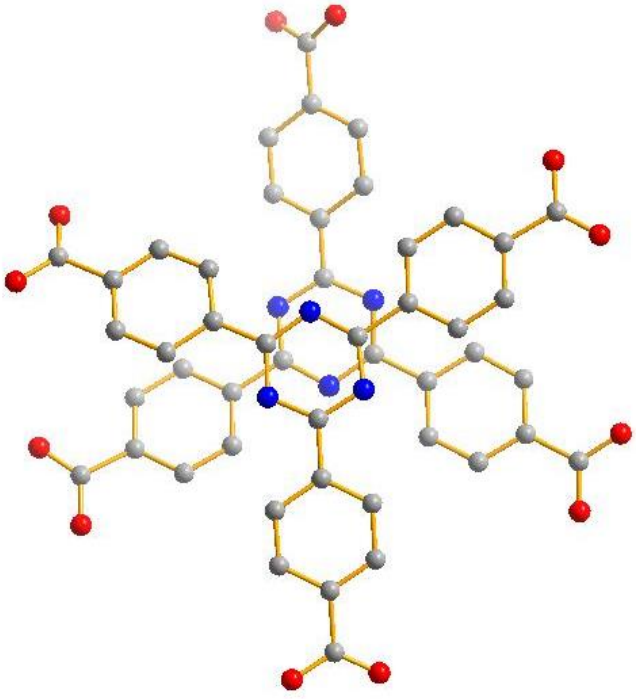


**Figure S3** The staggered conformation of the stacking of TATB ligand.

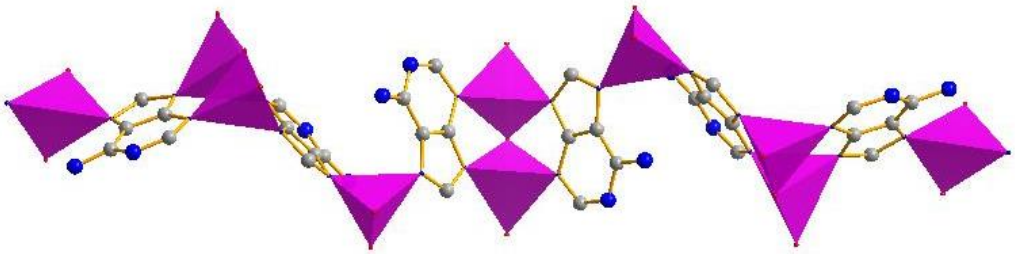


**Figure S4** The graphic representation of the one-dimensional zinc-adeninate chain. All the zinc centers were represented by pink polyhedra.

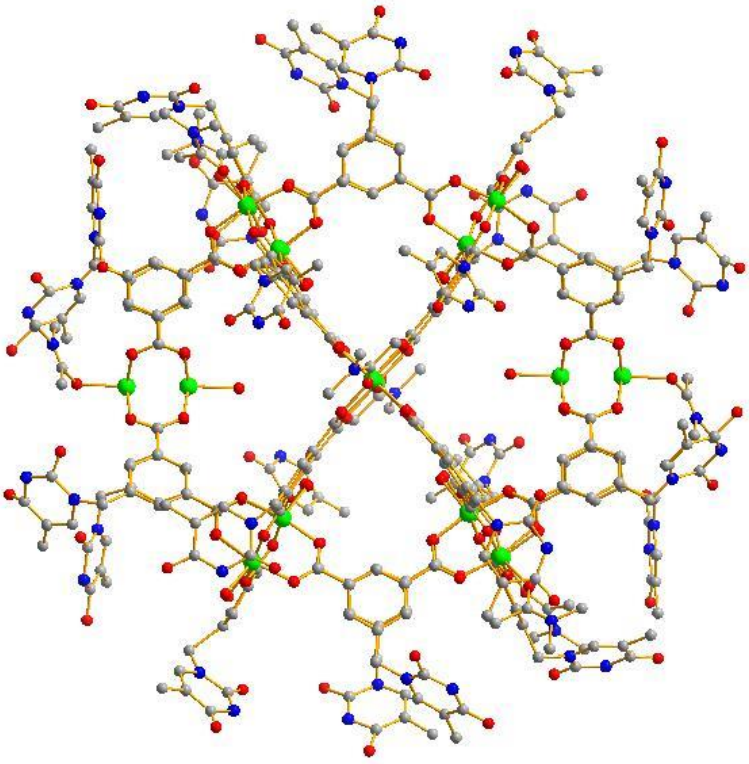


**Figure S5** The crystal structure of TMOP-1. The picture was derived when disorders were removed. The grey, red, blue and green spheres represent C, O, N and Cu, respectively. H atoms were omitted for clarity.

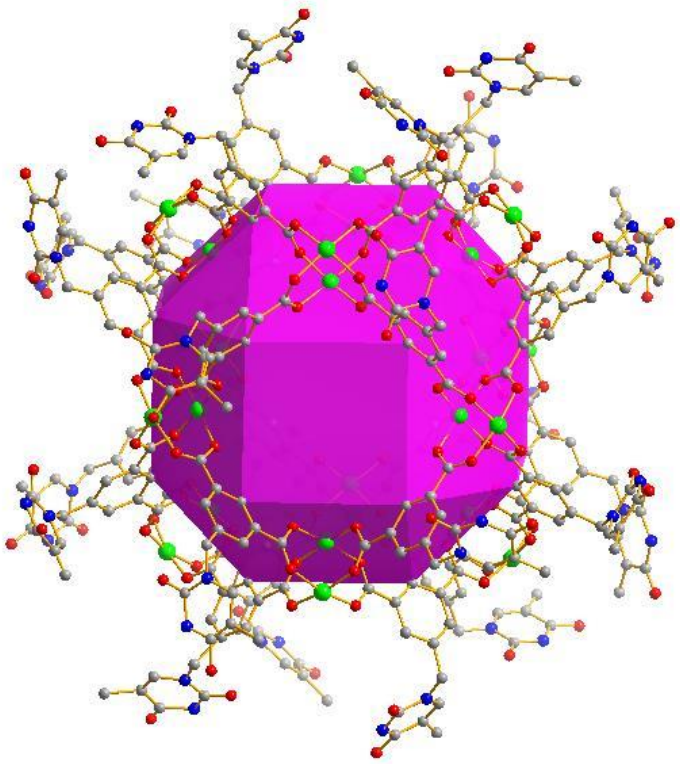


**Figure S6** The polyhedron view of TMOP-1. The polyhedron indicates the empty space inside the MOP. All the coordinating solvents were omitted for clarity.

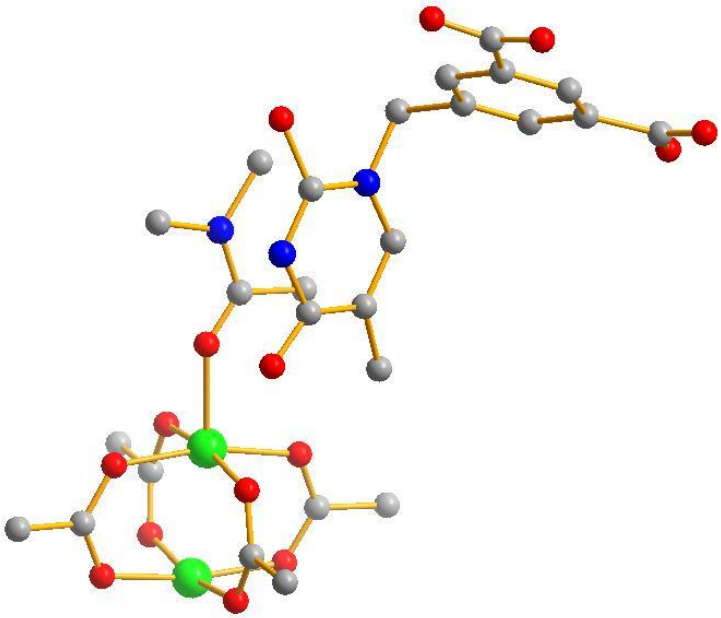


**Figure S7** The π-π stacking between a coordinating DMA and a neighboring thymine

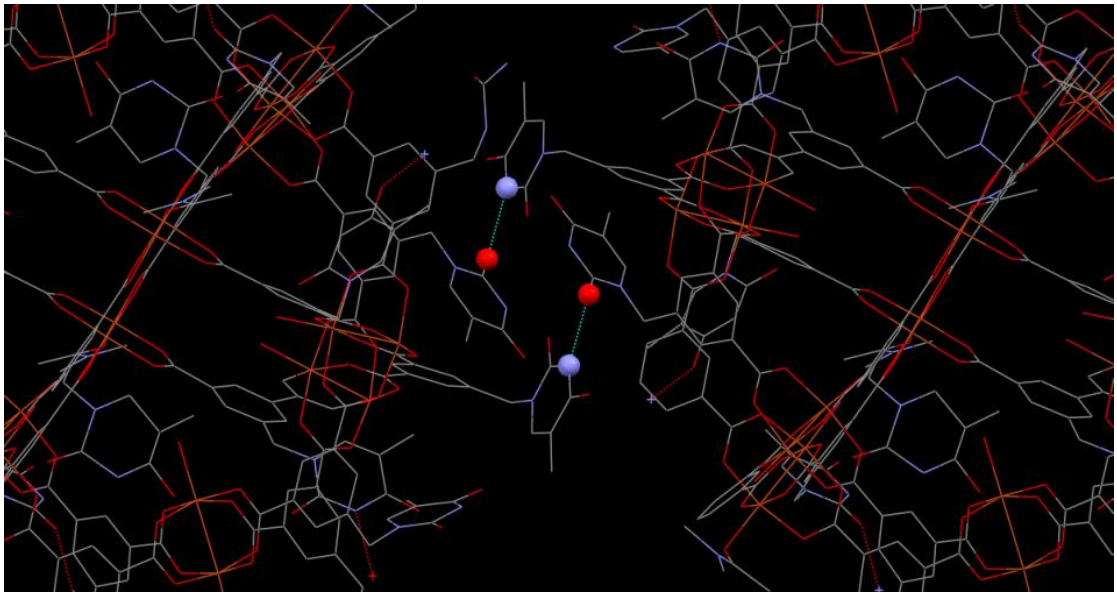


**Figure S8** The hydrogen bonding between two adjacent thymine moieties

# Section 6. The $^{1}$H NMR of Selected Compounds

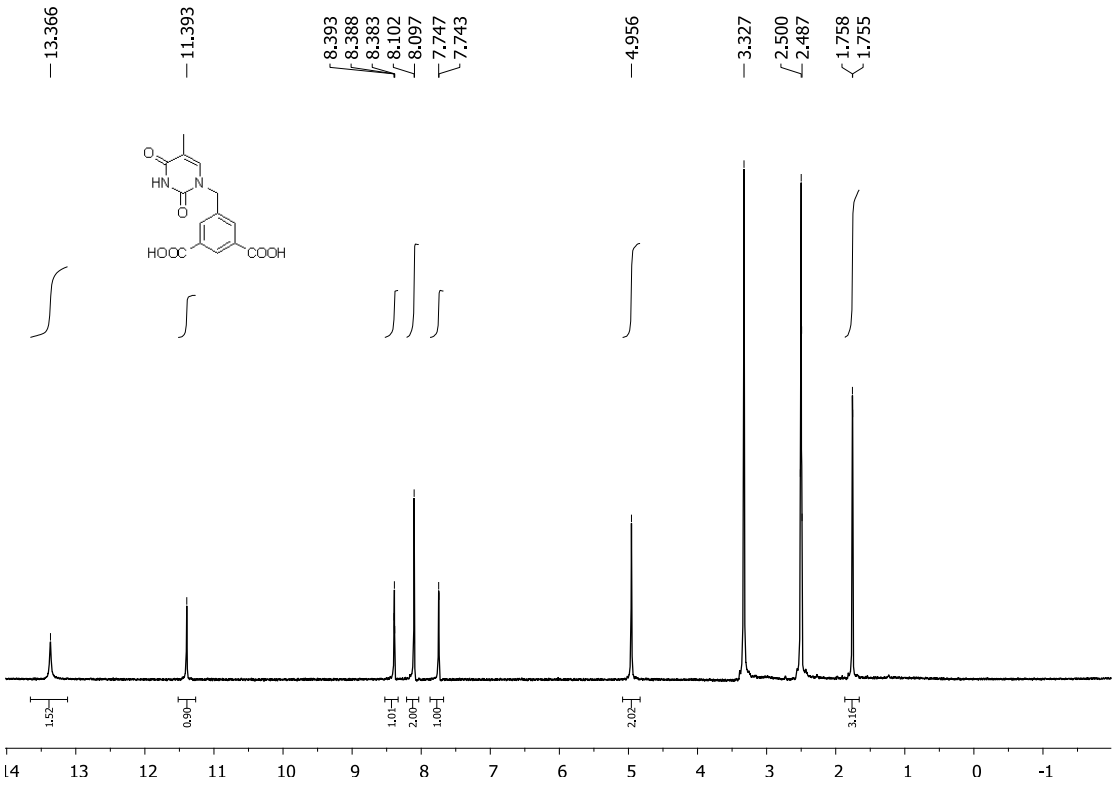



**Figure S8** The $^{1}$H NMR of $H_2$MDPI

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**References:**

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2. Rochford, J.; Galoppini, E., *Langmuir* **2008,** *24*, 5366-5374.
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