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Solvent Directed Synthesis of Molecular Cage and Metal Organic Framework of Copper(II) Paddlewheel Cluster

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Abstract: A solvothermal reaction of a clip-type dicarboxylic acid H_2**DCA** [3,3′-((5-nitroisophthaloyl)bis(azanediyl))-dibenzoic acid] and $Cu(NO_3)_2$ in equimolar ratio in dimethylformamide (DMF) yielded **MOF(CuCG1)** which was formed by interlinking [4 + 2] self-assembled polyhedral cages via coordination between amide moiety present in the linker and the axial position of copper paddlewheel $Cu_2(CO_2)_4$. Upon a change in the solvent from DMF to DMA [dimethylacetamide] the interlinking among the polyhedra was successfully terminated to get single crystals of a discrete coordination cage with DMA bound to axial position of Cu(II) (**CuCG2**). Similar termination of the interlinking was also achieved by a fast crystallization process to get discrete architecture **CuCG1**.

Keywords: copper(II) · self-assembly · cage compounds · crystal structure · MOF

1. Introduction

Metal-ligand coordination has emerged as an exciting tool to design and synthesize molecular architectures of various shapes and sizes constructed by from organic ligands and metal ions with desired directionality.[1] Self-assembly of such organic/inorganic building blocks may produce either metal-organic frameworks (polymeric)[2] or discrete molecular polyhedron (single entity).[3] Chemists mainly interest on these materials due to the prospect of hosting guest molecules using supramolecular interaction and carry out diverse applications e.g. sensing,[4] gas storage,[5] separation,[6] catalysis,[7] proton conductivity,[8] drug delivery[9] and trapping transient metastable state[10] etc. Although, from a design perspective some of the MOFs can be considered as an assembly of discrete molecular polyhedron, very few examples are reported in the literature.[11] Stepwise assembly of MOFs by interlinking discrete polyhedra imposes difficulty as the intermediate interlinked polyhedra are not always soluble.[12] Zhou et al. have used molecular polyhedra designed from a dicarboxylic acid and a copper(II) paddlewheel cluster[13] and interlinked them with pyridyl bridging ligands to access metal-organic framework.[11a] However, introduction of such bridging ligands may complicate the self-assembly process by interacting with the molecular polyhedra to disrupt their original shape.

Herein, we report the design and synthesis of a unique discrete molecular architecture **CuCG1** from the self-assembly of an amide-functionalized clip-type donor 3,3′-((5-nitroisophthaloyl)bis(azanediyl))-dibenzoic acid (H_2**DCA**) and a Cu(II) paddlewheel $Cu_2(CO_2)_4$ cluster (Scheme 1) in DMF. Interestingly, the pseudo donor unit (amide group) present into H_2**DCA** interlinks these polyhedra to produce a 3D metal-organic framework **MOF(CuCG1)**. However, when the same reaction was carried out in DMA (DMA = *N,N-dimethylacetamide*), formation of similar discrete polyhedron **CuCG2** was observed. Surprisingly, this produced only a discrete architecture and no interlinking among the polyhedra was observed.

2. Result and Discussion

The ligand H_2**DCA** was synthesized following the modified reported procedure,[14] and characterized by ^{1}H NMR and ^{13}C NMR (Figures 1 and SI). All the peaks in the ^{1}H NMR spectra were successfully assigned with the help of ^{1}H–^{1}H COSY spectrum. The ligand was incorporated with functionality like nitro and amide which would interact with the solvent molecules through hydrogen-bonding, to improve the solubility of the desired molecular architecture. The ligand H_2**DCA** attains different conformations which would produce various donor angles, however DFT calculation suggests the presence of two possible conformers **1** and **2** respectively having an almost 0° donor angle (Scheme 1). Moreover, the conformer **1** is energetically more favoured having a planar configuration which would be preferred during the self-assembly process; whereas, the paddlewheel $Cu_2(CO_2)_4$ cluster having a 90° bite angle can interact with this 0° conformer to produce a [2 + 4] self-assembled molecular polyhedron.

Therefore, a self-assembly reaction between $Cu(NO_3)_2 \cdot 3H_2O$ and H_2**DCA** in an equimolar ratio was carried out in DMF under solvothermal condition for 48 h at 110 °C. The resulting blueish solution indicates the formation of a discrete molecular architecture **CuCG1** which is soluble in

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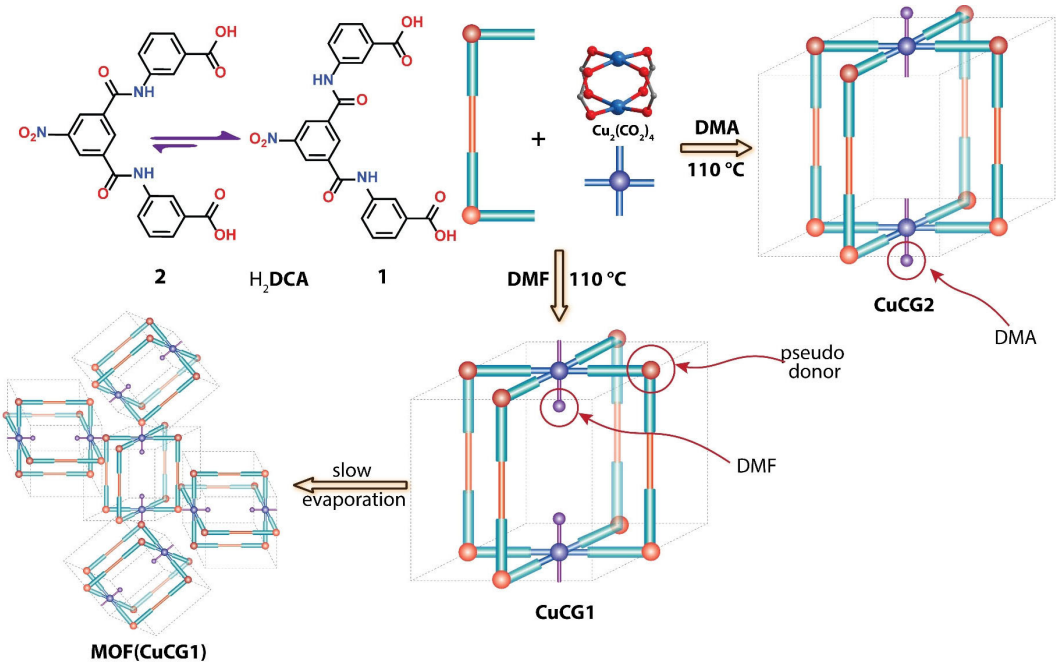

Scheme 1. Schematic representation of the synthesis of **CuCG1** and **CuCG2** and the formation of **MOF(CuCG1)** from **CuCG1** by interlinking through pseudo donor incorporated in the ligand unit.

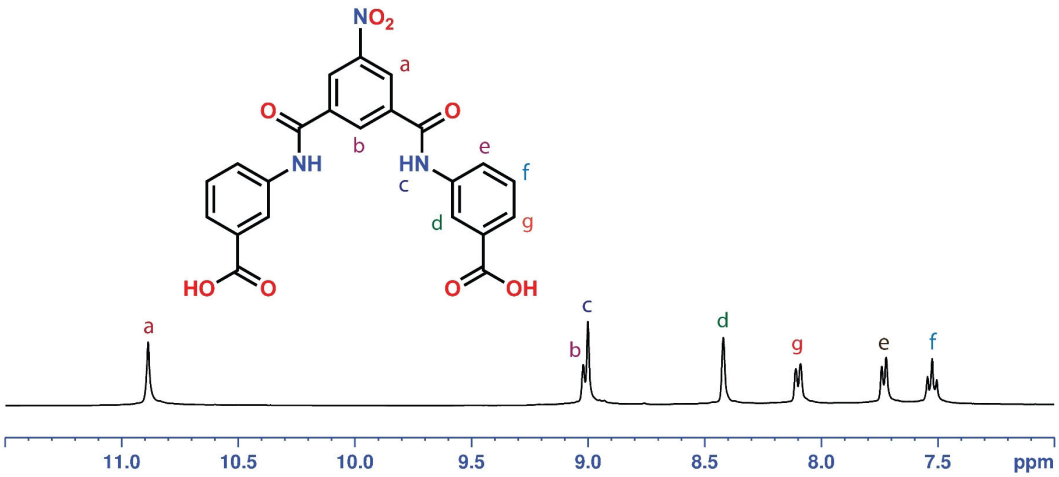

Figure 1. ^{1}H NMR spectrum of the dicarboxylate linker H_2**DCA** recorded in DMSO-d_6.

DMF. Subsequently, slow evaporation of the DMF solution over a period of 30 days produced block shaped blue crystals suitable for single crystal XRD analysis. The SC-XRD analysis revealed the formation of molecular polyhedron composed of paddlewheel $Cu_2(CO_2)_4$ and the ligand H_2**DCA** as a [2+4] self-assembly. Surprisingly, formation of a 3D network **MOF(CuCG1)** was observed by linking the neighbouring polyhedra through the amide oxygen. Such coordination of amide group is unprecedented and noteworthy. **MOF (CuCG1)** was crystallized in a *P*-1 space group (Figure 2). Both the asymmetric unit and the unit cell contain a whole unit of the discrete polyhedron. Here, only two of the amide groups participate in coordination with two different polyhedra at the opposite end. The exterior axial position of each paddlewheel units is connected to a labile amide group from a different polyhedron; whereas, the interior axial position is occupied by a DMF molecule. Thus, the cavity of the polyhedron contains two coordinated DMF molecules. Moreover, the self-assembly between paddlewheel $Cu_2(CO_2)_4$ and H_2**DCA** produced the desired discrete molecular architecture, and over the course of crystallization it slowly interlinked into a 3D metal-organic framework by the coordination of a pseudo

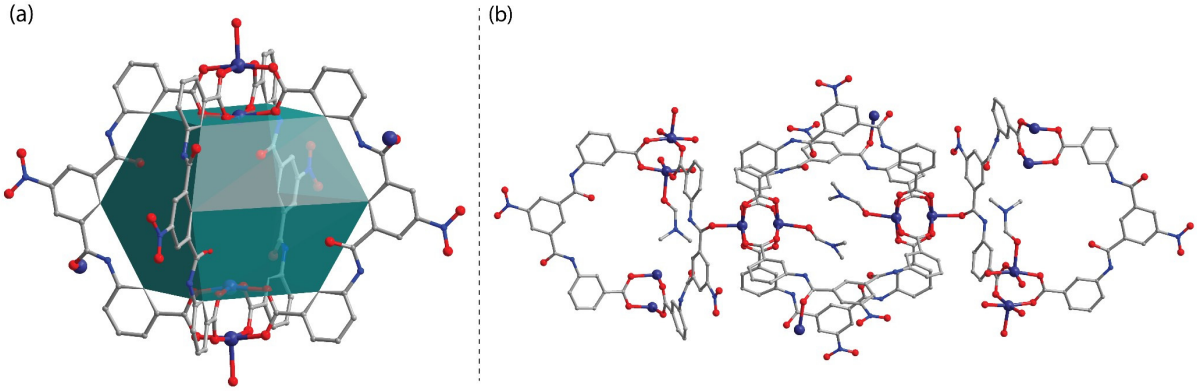

Figure 2. (a) Crystal structure of **MOF(CuCG1)**. (CCDC No-1876260) (b) solid-state packing of the **MOF(CuCG1)** showing the interlinking of discrete polyhedra through the pseudo donor. (colour code: grey: carbon; red: oxygen; blue: nitrogen and deep-blue: copper; hydrogen atoms are omitted for clarity).

donor group. So, it was not possible to obtain the discrete architecture as single crystal.

Careful examination of the crystal structure of **MOF (CuCG1)** indicated that the interlinking among the polyhedra is possible because of a comparable strength in the coordination of DMF and the amide moiety of the ligand unit. Therefore, a solvent molecule having a higher donor capacity than that of DMF, for example DMA (dimethylacetamide) could be introduced instead of DMF. It was expected that the DMA molecule would be able to compete with the pseudo donor sites of the ligand unit and thus can disrupt the interlinking process to give a discrete molecular architecture. The similar self-assembly reaction was carried out in DMA, which led to the formation of blue solution indicating the formation of a discrete molecular polyhedron. To check the behaviour of this solvent, the blue solution was kept for slow evaporation and formation of blue single crystals suitable for SC-XRD were obtained after 20 days. The XRD analysis indeed revealed the formation of discrete molecular architecture **CuCG2. CuCG2** has a similar structure to **CuCG1** except the coordination of labile axial position of the paddlewheel $Cu_2(CO_2)_4$. It was crystallized in P-1 space group. Significant π-π stacking was observed among the phenyl rings containing the nitro group as well as the phenyl rings containing the carboxylate group leading to successful crystal packing (Figure 3). The exterior axial position of the paddle-

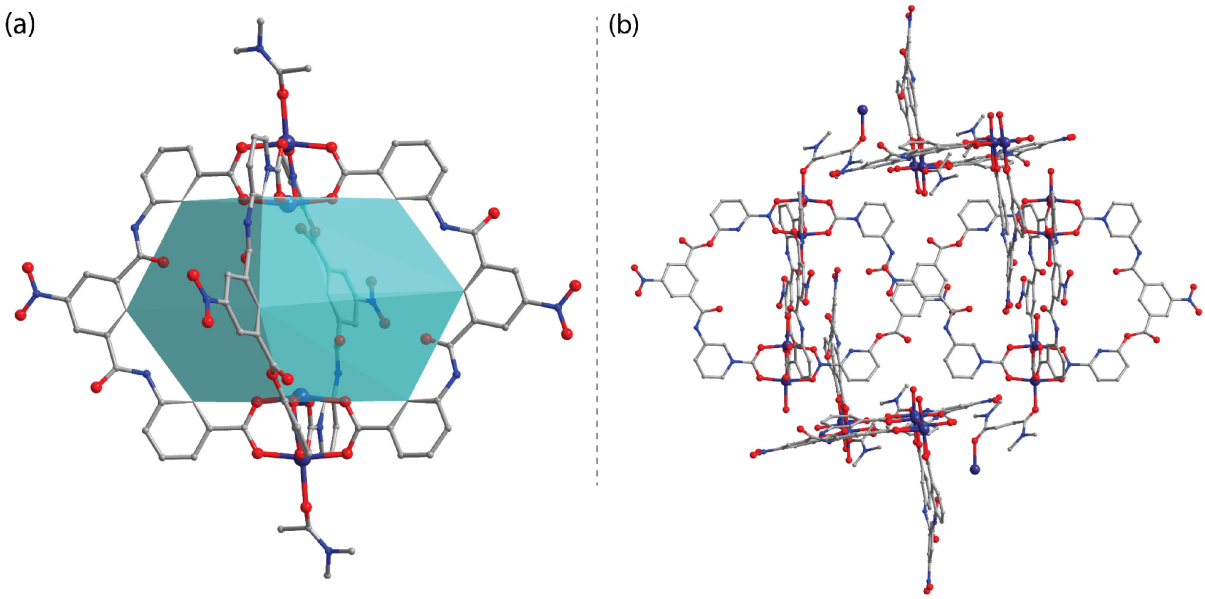

Figure 3. (a) Crystal structure of **CuCG2**. (CCDC No-1876261) (b) solid-state packing of the **CuCG2** showing the no interlinking of discrete polyhedra through the pseudo donor. (colour code: grey: carbon; red: oxygen; blue: nitrogen and deep-blue: copper; hydrogen atoms are omitted for clarity).

wheel was coordinated by the DMA molecule as predicted from the binding capacity of DMA and amide group. This capping of the exterior axial position by the DMA molecules disrupts the interlinking process, thus formation of discrete polyhedron as single crystals was observed. Interestingly, the interior axial positions of the paddlewheel were occupied by water molecules. This could be due to the more steric demand of the bulky DMA molecule.

Although, the formation and crystallization of **MOF (CuCG1)** is the result of interlinking between the amide moiety and the copper paddlewheel, the process has an extremely slow kinetics. Therefore, it can be hypothesized that a fast isolation of **CuCG1** as solid form would not allow the discrete polyhedra to interlink with each other. This idea can be verified through a fast crystallization process by vapour diffusion technique using a highly volatile solvent such as diethyl ether. A solvent diffusion of diethyl ether into the blue DMF solution of **CuCG1** produced blocked shaped blue coloured crystals. Single crystal XRD analysis of the crystals unequivocally confirmed the formation of discrete polyhedra **CuCG1. CuCG1** was crystallized in a *P*-1 space group. The unit cell contains two polyhedra. As predicted, absence of any interlinking among the polyhedra was observed. Interestingly, formation of two different polyhedra were observed, where the labile axial positions of the copper paddlewheel are occupied by different solvent molecules. Polyhedra similar to the **MOF (CuCG1)**, where DMF molecules were coordinated from the interior axial position of the paddlewheel and a water molecule coordinates from the exterior axial position of the paddlewheel. Whereas, the other polyhedron had an opposite coordination mode of the solvent molecules (Figure 4). These two polyhedra were connected by H-bonding interaction between the nitro groups of the ligand and the axially coordinated water molecule.

The labile axial positions of the copper paddlewheel enable the self-assembly of polyhedron or MOF in different solvents. Therefore, it can be assumed that interconversion between polyhedron to MOF can be achieved by introducing appropriate solvent molecules. To verify this, a conversion from discrete polyhedra [**CuCG2**] to metal-organic-framework [**MOF(CuCG1)**] was attempted by synthesizing **CuCG2** in crystalline form and dissolving it in DMF by heating at 60 °C. However, the resulting DMF solution of **CuCG2** crystallized in a very short period of time to give block shaped blue

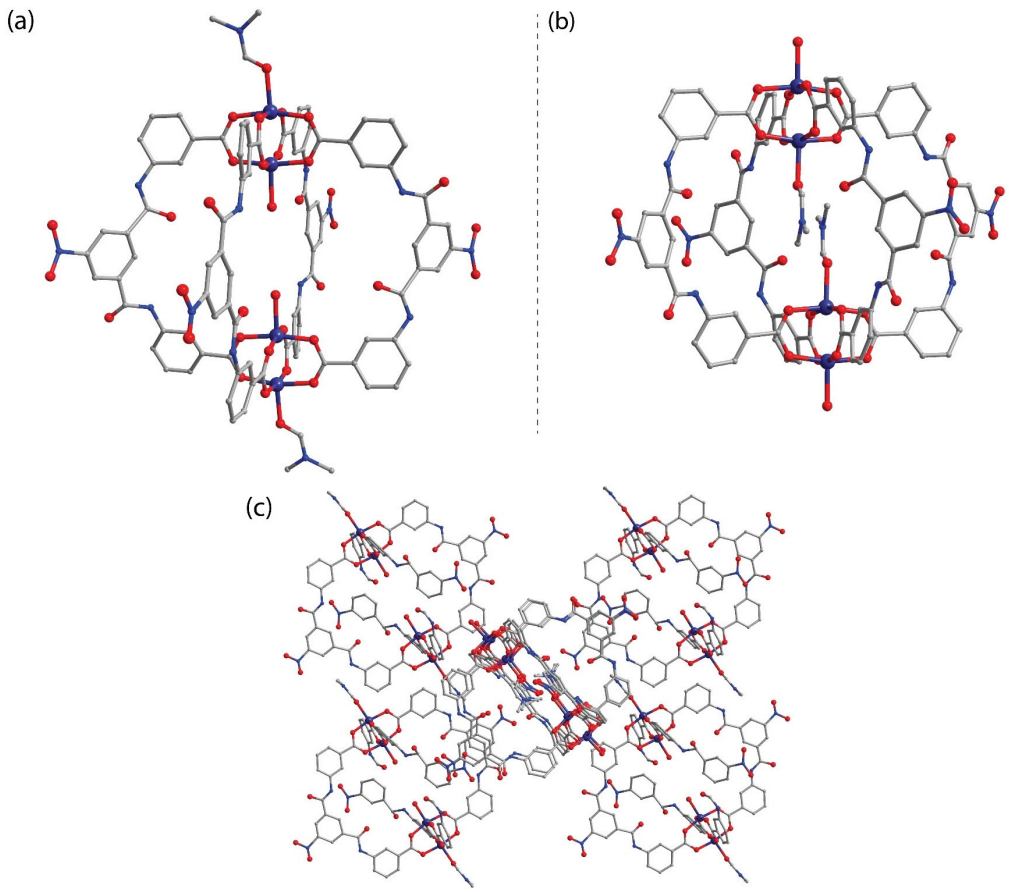

Figure 4. Crystal structure of **CuCG1** (CCDC No-1876259), (a) where DMF molecule is outside of the cavity and (b) where DMF molecule is inside of the cavity. (c) solid-state packing of the **CuCG1** showing the presence of two different discrete polyhedra. (colour code: grey: carbon; red: oxygen; blue: nitrogen and deep-blue: copper; hydrogen atoms are omitted for clarity).

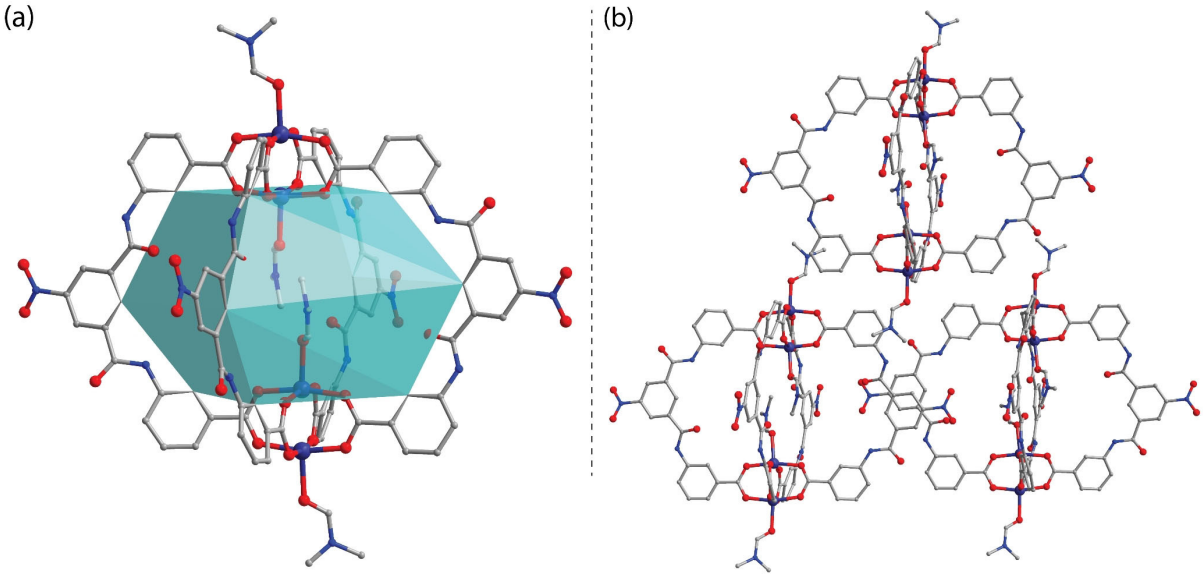

Figure 5. Crystal structure of (a) **CuCG1a** (CCDC No-1882868) and (b) solid-state packing of the **CuCG1a** (colour code: grey: carbon; red: oxygen; blue: nitrogen and deep-blue: copper; hydrogen atoms are omitted for clarity).

crystals. Interestingly, single crystal XRD analysis showed the formation of an unexpected discrete polyhedron (**CuCG1a**) instead of a metal organic framework. The polyhedron **CuCG1a** contains coordinated DMF molecule to both the axial position of the copper paddlewheel (Figure 5).

3. Conclusions

In summary, a functionalized dicarboxylate ligand H_2**DCA** was designed and synthesized to obtain discrete molecular architecture with Cu(II) paddlewheel. Formation of a molecular ball **CuCG1** soluble in DMF was observed. Crystallization by slow evaporation produced an unprecedented interlinking of the cages by the coordination of oxygen atoms of the amide group to the labile axial position of the paddlewheel $Cu_2(CO_2)_4$ was realized. This interlinking through the axial position was successfully inhibited by the introduction of a stronger donating solvent like, DMA, which coordinates through the axial site to prevent the interlinking to give crystals of discrete architecture **CuCG2**.

Experimental Section

Materials and Methods: Reagents used in these experiments were obtained from commercial sources and used without any purification. NMR studies were performed using a Bruker-make 400 MHz spectrometer and the chemical shifts (δ) in the spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as an internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the solvents $(CD_3)_2SO$ (2.50 ppm) and $CDCl_3$ (7.26 ppm).

Synthesis of the Ligand H_2DCA: The synthesis of the ligand includes two-step reaction. The first step includes the treatment of $SOCl_2$ (5 mL) with 5 mmol (1.05 g) of 5-nitroisophthalic acid under reflux condition followed by vacuum evaporation of the excess thionyl chloride to give 5-nitroisophthaloyl dichloride in quantitative yield. In the second step the isolated 5-nitroisophthaloyl dichloride was treated with 10 mmol (1.37 g) 3-aminobenzoic acid in 10 mL DMF under reflux condition for 24 h. The reaction mixture was then cooled to room temperature and 100 mL of ice water was added to get white precipitate. The resulting precipitate was then filtered and washed thoroughly with water followed by vacuum drying to get white powder of H_2**DCA** in pure form. Isolated yield: 1.80 g (80.03 %). ^{1}H-NMR (DMSO-d_6) δ (ppm): 10.89 (s, 2H), 9.02 (s, 1H), 9.00 (s, 2H), 8.42 (s, 2H), 8.11 (d, 2H), 7.74 (d, 2H) and 7.54 (t, 2H).

Synthesis of MOF(CuCG1): To a 10 mL cleaned glass vial containing 2 mL DMF solution of 0.05 mmol (12.80 mg) of $Cu(NO_3)_2 \cdot 3H_2O$, 0.05 mmol (22.8 mg) of H_2**DCA** was added by stirring the mixture for 10 min to get a bluish solution. The vial containing the solution was then placed in an oven and gradually heated to 110 °C and continued heating for 48 h followed by cooling to 25 °C for 10 h which yielded a deep blue solution. Finally, the solution was kept for slow evaporation for 30 days to get block shaped blue crystals of **MOF(CuCG1)**.

Synthesis of CuCG2: To a 10 mL glass vial containing 2 mL DMA solution of 0.05 mmol (12.8 mg) of $Cu(NO_3)_2 \cdot 3H_2O$, 0.05 mmol (22.80 mg) of H_2**DCA** was added followed by stirring the mixture for 10 mins to get a bluish colored solution. The vial containing the solution was then placed in an oven and gradually heated to 110 °C and continued heating for 48 h followed by cooling to 25 °C for

Table 1. Crystallographic Data and Refinement Parameters of MOF(CuCG1), CuCG2, CuCG1 and CuCG1a.

	MOF(CuCG1)	CuCG2	CuCG1	CuCG1a
empirical formula	$C_{94}H_{66}N_{14}Cu_4O_{35}$	$C_{93.43}H_{67.42}N_{14.81}Cu_4O_{36.81}$	$C_{94}H_{70}N_{14}Cu_4O_{36}$	$C_{100}H_{80}N_{16}Cu_4O_{36}$
Fw	2205.81	2240.64	2225.84	2335.96
T (K)	110(2)	110(2)	110(2)	110(2)
crystal system	triclinic	triclinic	triclinic	triclinic
space group	*P-1*	*P-1*	*P-1*	*P-1*
a/Å	19.336(5)	18.5078(9)	16.749(15)	16.489(4)
b/Å	19.550(5)	20.9248(10)	18.725(17)	16.956(4)
c/Å	20.050(5)	21.8144(11)	26.76(3)	18.026(4)
α/deg	84.419(5)	83.053(1)	88.75(2)	116.130(7)
β/deg	83.653(5)	74.769(2)	88.86(2)	94.114(7)
γ/deg	68.580(5)	74.205(1)	77.06(2)	112.431(7)
V/Å^3	6999(3)	7832.5(7)	8177(14)	4003.9(16)
Z	2	2	2	1
ρ_{calcd} (g cm^{-3})	1.047	0.950	0.940	0.969
μ (Mo Kα) (mm^{-1})	0.664	0.596	0.570	0.585
λ/Å	0.71073	0.71073	0.71073	0.71073
F (000)	2248.0	2284.2	2272.0	1196.0
collected reflns	183814	187249	94033	67549
unique reflns	18011	21708	9540	14089
GOF (F^2)	0.946	1.132	1.029	1.075
R_1[a]	0.0635	0.0962	0.1157	0.0903
wR_2[b]	0.1809	0.3102	0.3205	0.2783

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

10 h. Finally, the solution was then kept for slow evaporation for 20 days to get block shaped blue color crystals of **CuCG2**.

Crystallization of CuCG1: To a 10 mL cleaned glass vial containing 2 mL DMF solution of 0.05 mmol (12.80 mg) of $Cu(NO_3)_2 \cdot 3H_2O$, 0.05 mmol (22.8 mg) of H_2**DCA** was added followed by heating at 110 °C for 48 h. The solution was then cooled at room temperature to get a blue colored solution. Blocked shaped blue colored crystal of **CuCG1** was obtained by diffusing diethyl ether vapor into the blue DMF solution.

Synthesis of CuCG1a from CuCG2: To a 10 mL cleaned glass vial containing 2 mL DMF, 5 mg of **CuCG2** crystals were added followed by heating at 60 °C for 5 mins. The solution was then cooled at room temperature to get a blue solution. Blocked shaped blue crystals of **CuCG1a** were obtained in overnight.

Single Crystal XRD Structures of MOF(CuCG1)and CuCG2:

Both the **MOF**(**CuCG1**) and **CuCG2** were crystallized from the slow evaporation of the DMF solution of the respective cages. Single crystal X-ray data were collected on a Bruker SMART APEX (D8 QUEST) CMOS diffractometer using the SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Kα radiation (0.71073 Å) at 110 K. The structure was solved by intrinsic phasing method with ShelXT[15] and refined by the full-matrix least-squares method based on F^2 with all observed reflections using the Olex2 program.[16] All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In addition, the structure contains a huge void of disordered solvent molecules therefore, solvent mask incorporated in the program was applied to account for embedded solvent molecules.[17] Crystallographic data and refinement parameter are given in Table 1.

Computational Studies: Full geometry optimizations and single-point energy calculations were carried out using *Gaussian 09* package. The hybrid B3LYP functional has been used in all calculations as implemented in *Gaussian 09* package,[18] mixing the exact Hartree-Fock-type exchange with Becke's expression for the exchange functional and that proposed by Lee-Yang-Parr for the correlation contribution. The LanL2DZ basis set was used for all calculations. Frequency calculations were carried on the optimized structures confirmed the absence of any imaginary frequencies.

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References

[1] a) B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043; b) M. Fujita, *Chem. Soc. Rev.* **1998**, *27*, 417–425;

c) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*; d) C.-B. Huang, L. Xu, J.-L. Zhu, Y.-X. Wang, B. Sun, X. Li, H.-B. Yang, *J. Am. Chem. Soc.* **2017**, *139*, 9459–9462; e) L. Xu, L.-J. Chen, H.-B. Yang, *Chem. Commun.* **2014**, *50*, 5156–5170.

[2] a) W. Wang, Y.-X. Wang, H.-B. Yang, *Chem. Soc. Rev.* **2016**, *45*, 2656–2693; b) M. J. Van Vleet, T. Weng, X. Li, J. R. Schmidt, *Chem. Rev.* **2018**, *118*, 3681–3721; c) Y.-Y. Ren, Z. Xu, G. Li, J. Huang, X. Fan, L. Xu, *Dalton Trans.* **2017**, *46*, 333–337.

[3] a) D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem. Int. Ed.* **2008**, *47*, 5136–5147; b) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972–983; c) B. H. Northrop, Y.-R. Zheng, K.-W. Chi, P. J. Stang, *Acc. Chem. Res.* **2009**, *42*, 1554–1563; d) L.-J. Chen, S. Chen, Y. Qin, L. Xu, G.-Q. Yin, J.-L. Zhu, F.-F. Zhu, W. Zheng, X. Li, H.-B. Yang, *J. Am. Chem. Soc.* **2018**, *140*, 5049–5052; e) W.-J. Fan, B. Sun, J. Ma, X. Li, H. Tan, L. Xu, *Chem. Eur. J.* **2015**, *21*, 12947–12959.

[4] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105–1125.

[5] a) M. S. Shah, M. Tsapatsis, J. I. Siepmann, *Chem. Rev.* **2018**, *118*, 2297–2297; b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724–781.

[6] J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869–932.

[7] a) L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, *Chem. Rev.* **2017**, *117*, 8129–8176; b) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, *112*, 1196–1231; c) T. Murase, Y. Nishijima, M. Fujita, *J. Am. Chem. Soc.* **2011**, *134*, 162–164; d) P. Howlader, P. Das, E. Zangrando, P. S. Mukherjee, *J. Am. Chem. Soc.* **2016**, *138*, 1668–1676.

[8] a) P. G. M. Mileo, K. Adil, L. Davis, A. Cadiau, Y. Belmabkhout, H. Aggarwal, G. Maurin, M. Eddaoudi, S. Devautour-Vinot, *J. Am. Chem. Soc.* **2018**, *140*, 13156–13160; b) X. Liang, F. Zhang, W. Feng, X. Zou, C. Zhao, H. Na, C. Liu, F. Sun, G. Zhu, *Chem. Sci.* **2013**, *4*, 983–992; c) V. G. Ponomareva, K. A. Kovalenko, A. P. Chupakhin, D. N. Dybtsev, E. S. Shutova, V. P. Fedin, *J. Am. Chem. Soc.* **2012**, *134*, 15640–15643; d) R. Saha, A. K. Ghosh, R. N. Samajdar, P. S. Mukherjee, *Inorg. Chem.* **2018**, *57*, 6540–6548.

[9] a) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, V. Marsaud, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, R. Gref, *Nat. Mater.* **2009**, *9*, 172; b) Z. Ma, B. Moulton, *Coord. Chem. Rev.* **2011**, *255*, 1623–1641; c) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris, C. Serre, *Chem. Rev.* **2012**, *112*, 1232–1268; d) I. A. Bhat, R. Jain, M. M. Siddiqui, D. K. Saini, P. S. Mukherjee, *Inorg. Chem.* **2017**, *56*, 5352–5360.

[10] a) H. Takezawa, S. Akiba, T. Murase, M. Fujita, *J. Am. Chem. Soc.* **2015**, *137*, 7043–7046; b) H. Takezawa, T. Murase, M. Fujita, *J. Am. Chem. Soc.* **2012**, *134*, 17420–17423; c) P. Howlader, B. Mondal, P. C. Purba, E. Zangrando, P. S. Mukherjee, *J. Am. Chem. Soc.* **2018**, *140*, 7952–7960.

[11] a) J.-R. Li, D. J. Timmons, H.-C. Zhou, *J. Am. Chem. Soc.* **2009**, *131*, 6368–6369; b) J. J. Perry Iv, J. A. Perman, M. J. Zaworotko, *Chem. Soc. Rev.* **2009**, *38*, 1400–1417.

[12] A. Béziau, S. A. Baudron, D. Pogozhev, A. Fluck, M. W. Hosseini, *Chem. Commun.* **2012**, *48*, 10313–10315.

[13] M. Tafipolsky, S. Amirjalayer, R. Schmid, *J. Phys. Chem. C* **2010**, *114*, 14402–14409.

[14] X. Song, Y. Zou, X. Liu, M. Oh, M. S. Lah, *New J. Chem.* **2010**, *34*, 2396–2399.

[15] G. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.

[16] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[17] A. Spek, *Acta Crystallogr. Sect. C* **2015**, *71*, 9–18.

[18] M. Frisch, G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, *Inc., Wallingford, CT* **2009**, *200*.

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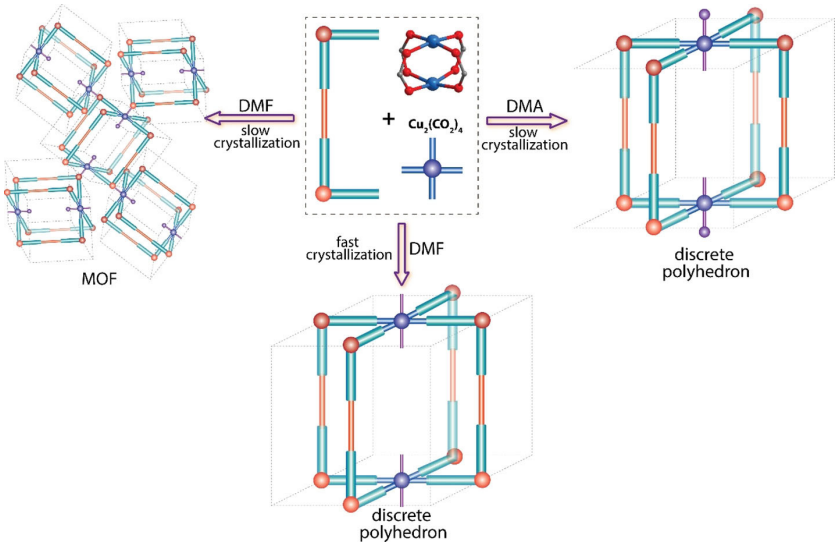

P. Howlader, P. S. Mukherjee**