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Assembling Porphyrins into Extended Network Structures Employing Aromatic Dicarboxylates: Synthesis, Metal-exchange and Heterogeneous Catalytic Studies

Gargi Dutta,[a] Ajay Kumar Jana[a] and Srinivasan Natarajan*[a]

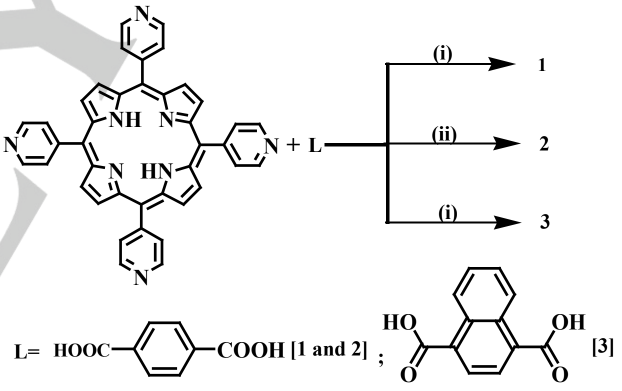
Abstract: Three new metal-organic porphyrinic framework compounds of zinc and 5,10,15,20-tetrakis(4-pyridyl)porphyrin(TPyP) have been synthesized under solvothermal conditions. The compounds $[Zn_5(C_{40}H_{24}N_8)(C_8H_4O_4)_2(NO_3)_6(DMA)_2](DMA)_3(H_2O)_8$, **1;** $[Zn_3(C_{40}H_{24}N_8)(C_8H_4O_4)_2(DMF)](DMF)_5(H_2O)_{12}$, **2**; and $[Zn_3(C_{40}H_{24}N_8)(C_{12}H_6O_4)_2(DMA)_2](H_2O)_7$, **3** have two- (**1**) and three-dimensionally (**2** and **3**) extended structures. All the three structures contain porphyrinic unit connected through the carboxylate linkers. The different binding modes of nitrate in the structure of **1** has been observed for the first time in a porphyrin based MOF. The nitrates in the structure are metal binding and not hydrogen bonded. The openness of the structure allowed to explore the metal exchange through a room temperature metathetic route. Compound **2** undergoes 100% exchange for copper, whereas compound **3** exchanges 70% for copper. The copper exchanged compounds **Cu∈2** and **Cu∈3** were observed to be good heterogeneous catalysts for many important organic reactions. The reactions, chemo and regioselective enamination of β-ketoesters, preparation of propargylamine derivatives as well as regioselective cycloaddtion of alkyne and azide (click reaction) have been carried out with good yields and selectivity. All the compounds have been characterized by PXRD, IR, UV-vis, AAS and EDAX (for Cu-exchange).

Introduction

Porphine is a biologically important fully conjugated macrocyclic compound. Substituted porphines are known as porphyrins and metallo porphyrins. The iron containing ones are important for oxygen transport in vertebrates and have been investigated in detail over the years. Many other metalloporphyrins have been studied for a wide range of applications.[1] Metal-organic frameworks (MOFs) or inorganic coordination polymers (CPs) have attracted considerable attention during the last two decades.[2] Porphyrins and metalloporphyrins are easy to synthesize with multiple functionalities and exceedingly useful building blocks for the construction of framework solids through interporphyrin van der waals interactions, hydrogen bonding and metal-organic coordination bonding.[3] Robson, Suslick, Strouse, Goldberg and their co-workers have reported porphyrin and metalloporphyrin based framework solids since early 1990s.[4]The porphyrinic MOFs exhibit interesting properties that find applications in photonic devices, conductive polymers, chemical sensors and selective catalysis.[5]

During the past few years, there has been considerable interest in the post-synthetic modifications of MOFs.[6] Majority of the studies concentrated towards functionalizing the organic linkers and there have been attempts at transmetallation employing the Irving-Williams approach.[7] The transmetallation studies, on the other hand, has been limited in porphyrinic MOFs.[8] We have now prepared new porphyrinic MOFs $Zn_5(C_{40}H_{24}N_8)(C_8H_4O_4)_2(NO_3)_6(DMA)_2](DMA)_3(H_2O)_8$,(**1**); $[Zn_3(C_{40}H_{24}N_8)(C_8H_4O_4)_2(DMF)](DMF)_5(H_2O)_{12}$,(**2**);$[Zn_3(C_{40}H_{24}N_8)(C_{12}H_6O_4)_2(DMA)_2](H_2O)_7$, (**3**) employing porphyrin TPyP (scheme 1). As a model study we have attempted to exchange Cu^{2+} in place of Zn^{2+} ions in **2** and **3** and prepared the corresponding **Cu∈2** and **Cu∈3** compounds.

In this paper we present the synthesis, structure, transmetallation studies and heterogeneous catalytic studies of these new porphyrinic MOFs.



Reaction condition : (i) $Zn(NO_3)_2.4H_2O$/ DMA/ 100°C/ 3 days ;
(ii)$Zn(NO_3)_2.4H_2O$/ DMF/ 100°C/ 3 days

Scheme 1. Synthesis of **1**, **2** and **3** using solvothermal technique

Results and Discussion

Structure of $[Zn_5(C_{40}H_{24}N_8)(C_8H_4O_4)_2(NO_3)_6(DMA)_2](DMA)_3(H_2O)_8$, 1: Compound **1** crystallizes in orthorhombic *I222* space group. The asymmetric unit of the framework contains 29 non-hydrogen atoms of (Figure S1 in the supporting information) which two zinc atoms are distinct. Both the zinc atoms are octahedrally coordinated. Zn(1) occupies a special position (2a) with a site multiplicity of 0.25. Zn(1) is octahedrally coordinated with four pyrrole nitrogen atoms [N(1), N(2), N(1)(#1), N(2)(#2)] in the equatorial position and by two oxygen atoms from the solvent

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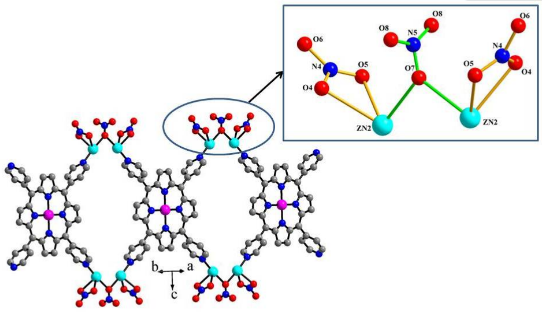
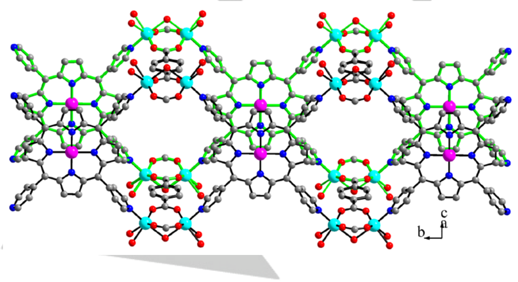
molecules [O(1), O(1)(#2)] in the axial position. Zn(2) is coordinated by two oxygens from the terephthalate [O(2), O(3)]; one pyridyl nitrogen from the porphyrin [N(3)] and three oxygens from nitrate species [O(4), O(5) and O(7)]. The Zn-N bond distances are in the range of 2.026(6)Å-2.094(5)Å [average : 2.039Å] and Zn-O bond distance are in the range of 1.961(6)Å-2.449(13)Å [average : 2.249 Å] (Table S1 in the supporting information). The structure of **1** can be considered from simpler building units. Thus the metalloporphyrin units are connected to each other via a zinc nitrate bridge forming a one-dimensional arrangement as shown in Figure 1a. There have been reports of nitrate bridging as well as terminal nitrate units in MOF structures,[9] but a single nitrate unit bridging two metal centers appears to be a new structural feature in the present compound (Figure 1a).[10] As can be seen that there are two distinct nitrate species in the structure, while one satisfies the coordination requirement of Zn(2), the other bridges two metalloporphyrin units leading to a one dimensional chain arrangement (Figure 1a). The 1D chains are connected by the terephthalate units forming an extended two-dimensional structure (Figure 1b). The 2D layers are stacked one over the other in an ABAB….fashion (Figure 1c).

(a)



(b)



(c)

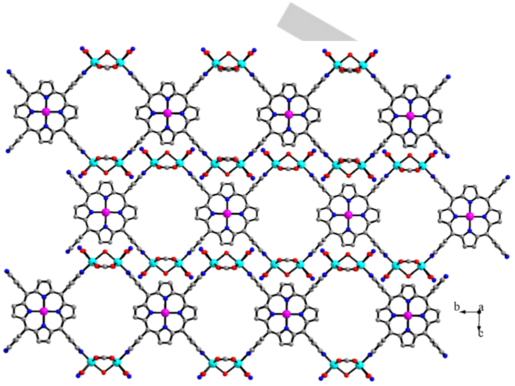
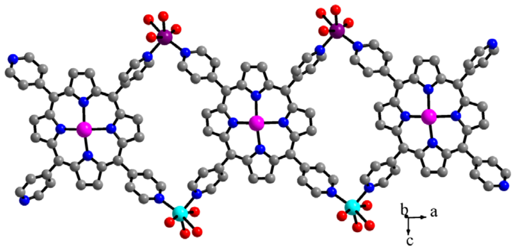


Figure 1. (a) Figure shows the connectivity between the Zn-porphyrinic units through the nitrate units forming a one-dimensional arrangement (note the unusual nitrate binding, highlighted by green bonds), (b) The connectivity between the 1D porphyrinic networks through the 1,4-benzenedicarboxylate forming the 2D structure, (c) The arrangement of layers. Note the formation of ABAB…type stacking. The solvent molecules are not shown for clarity.

Structure of [$Zn_3(C_{40}H_{24}N_8)(C_8H_4O_4)_2(DMF)](DMF)_5(H_2O)_{12}$, 2: Compound **2** crystallizes in triclinic *P*-1 space group. The asymmetric unit of the framework of **2** contains one TPyP ligand, two 1,4-benzenedicarboxylic acid and three crystallographically distinct Zn^{2+} ions (Figure S2 in the supporting information). Zn(1) exhibits a distorted square pyramidal geometry with four pyrrole nitrogen atoms [N(1), N(2), N(3) and N(4)] and one oxygen atom from the solvent molecule [O(1)]; and Zn(2) and Zn(3) are in a distorted octahedral geometry with four carboxylate oxygen [O(2), O(3), O(4) and O(5)] for Zn(2); [O(6), O(7), O(8) and O(9)] for Zn(3) from the terephthalate units and two nitrogen atoms [N(7), N(8) for Zn(2); N(5) and N(6) for Zn(3)] from the pyridyl groups of the TPyP ligand. The Zn(1) was found to be deviated by 0.324 Å from the plane of the porphyrin unit and moved towards the axially coordinated solvent molecule. The Zn-O bond distances are in the range of 1.9411(19) Å-2.095(2) Å [average: 1.966Å for Zn(2) and 1.957Å for Zn(3)]. The Zn-N bond distances are in the range of 2.036(2)-2.077(2) Å [average: 2.070Å for Zn(1); 2.052 Å for Zn(2) and 2.048Å for Zn(3)] (Table S2 in the supporting information). Similar to the structure of **1**, compound **2** can be understood by considering simpler building units. Thus the metalloporphyrin units are linked through the Zn(2) and Zn(3) units forming a one-dimensional chain as shown in Figure 2a. Of the two terephthalate units, one of them links two 1D chains forming a two-dimensional layer (Figure 2b). The two dimensional layers are further cross-linked by the other terephthalate unit forming a three-dimensional structure (Figure 2c). The 3D structure possesses a large one-dimensional channel of 27ÅX23Å (shortest atom-atom contact distance not including the van der waals radii). The disordered solvent molecules occupy these channels. A PLATON calculation indicates a solvent accessible volume of ~60% in this structure.

(a)



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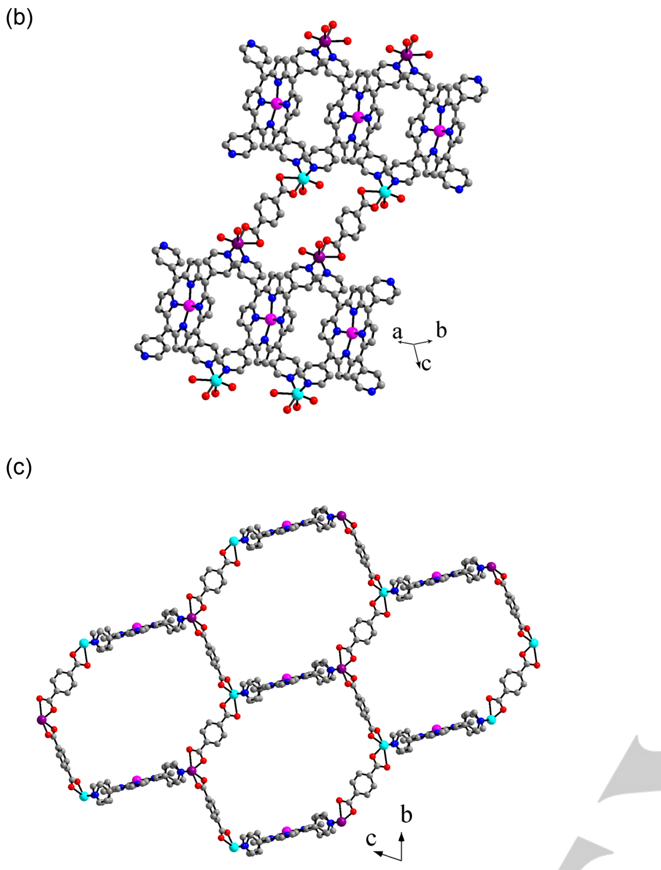

Figure 2. (a) Figure shows the connectivity between the Zn-porphyrinic units through the metal-centers forming a one-dimensional unit, (b) The connectivity between the 1D units and the 1,4-benzenedicarboxylate forming two-dimensional arrangement, (c) The three-dimensional structure of **2** resulting from the connectivity between the 2D arrangement and the carboxylates. The solvent molecules are not shown for clarity.

Structure of $[Zn_3(C_{40}H_{24}N_8)(C_{12}H_6O_4)_2(DMA)_2](H_2O)_7$, 3: Compound **3** crystallizes in monoclinic *C2/c* space group. The asymmetric unit of the framework consists of 43 non-hydrogen atoms. Two crystallographically independent Zn^{2+} ions are present in the asymmetric unit (Figure S3 in the supporting information). Zn(1) occupies a special position (4d) with a site multiplicity of 0.5 and is octahedrally coordinated with four nitrogen [N(1), N(2), N(1)(#1), N(2)(#1)] and two oxygens [O(5), O(5)(#1)] from the solvent molecule. The coordination geometry around Zn(2) is also octahedral with two nitrogens from the pyridyl group of the porphyrin [N(3), N(4)] and four oxygens [O(1), O(2), O(3), O(4)] from 1,4-napthalenedicarboxylic acid. The average Zn-O and Zn-N distances are 2.567 Å and 2.033 Å for Zn1; 1.955 Å and 2.068 Å for Zn(2) (Table S3 in the supporting information). The porphyrin ring is essentially flat and Zn(1) lies in plane with the porphyrin macrocycle. Structural arrangement of **3** is similar as that of **2**. In this case, the Zn(2) links the metalloporphyrin units to form a 1D chain (Figure 3a). Out of the two 1,4-napthalenedicarboxylates one bridges the two 1D chains which results in the 2D layer (Figure 3b). These 2D layers are further connected through the other 1,4-napthalenedicarboxylate forming the three dimensional structure (Figure 3c). The 3D structure possess a large one dimensional cavity of 25.83X23.72 $Å^2$ where the disordered guest solvent molecules reside. The solvent accessible void volume is 51% (calculated from PLATON).

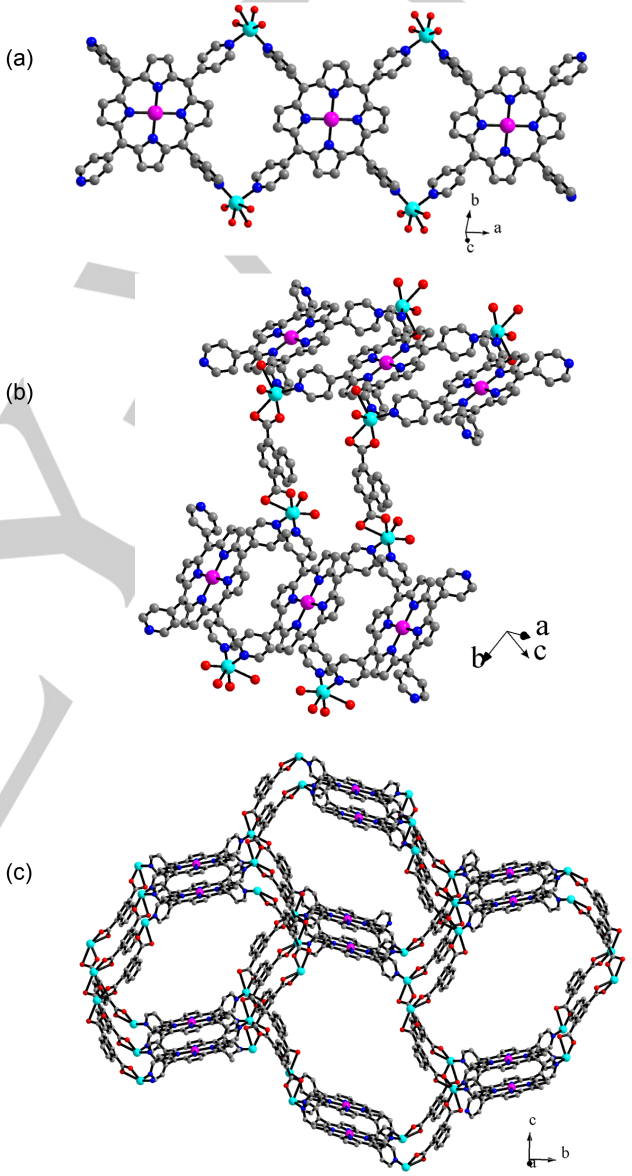

Figure 3. (a) The connectivity between the Zn-porphyrinic units through the metal centers forming a one-dimensional network, (b) The connectivity between the 1D units and the 1,4-napthalenedicarboxylate forming two-dimensional arrangement, (c) The 3D structure of **3** resulting from the connectivity between the 2D arrangement and the dicarboxylates. The solvent molecules are not shown for clarity.

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Table 1. Crystal Data and Structure Refinement Parameter

	1	**2**	**3**
Empirical Formula	$C_{56}H_{32}N_{14}O_{28}Zn_5$	$C_{56}H_{32}N_8O_9Zn_3$	$C_{64}H_{36}N_8O_{10}Zn_3$
FormulaWeight	1675.91	1157.07	1273.18
Crystal System	Orthorhombic	Triclinic	Monoclinic
Space Group	*I* 2 2 2	*P*-1	*C* 2/*c*
a (Å)	10.3770(7)	14.1504(15)	14.123(3)
b (Å)	17.2302(11)	19.257(2)	36.166(9)
c (Å)	28.198(2)	19.430(2)	18.341(4)
α (deg)	90	69.873(6)	90
β (deg)	90	82.011(6)	99.380(6)
γ (deg)	90	75.484(7)	90
Volume ($Å^3$)	5041.7(6)	4804.4(10)	9242(4)
Z	2	2	8
Temperature (K)	120(2)	120(2)	120(2)
ρ_c (gcm^{-3})	1.104	0.800	0.915
μ(mm^{-1})	1.236	0.778	0.815
θ range (deg)	2.92-25.00	1.118-27.650	2.93-25
Wavelength (Å)	0.71073	0.71073	0.71073
R1, *wR2* [I>2σ(I)]	0.0692, 0.1991	0.0521, 0.1120	0.0866, 0.2026
R1, *wR2* (all data)	0.0833,0.2088	0.1040, 0.1231	0.1859, 0.2429

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma|w(F_o^2 - F_c^2)|/\Sigma\, [w(F_o^2)^2]\}^{1/2}$. $w = 1/[\rho^2(F_o)^2 + (aP)^2 + bP]$. $P = [\max\,(F_o{\cdot}O) + 2(F_c)^2]/3$, where a = 0.1151 and b = 14.5934 for **1**, a = 0.0435and b =0.0000 for **2**, a = 0.1346 and b = 0.0000 for **3**.

Photophysical Studies:

All the compounds have the porphyrinic ring system and were expected to exhibit interesting absorbance and emission behavior.[11] To investigate the optical behavior of the compounds, we have evaluated the pristine ligand, tetra-(4-pyridyl)porphyrin as well. The UV-vis spectrum of the ligand tetra-(4-pyridyl)porphyrin exhibits an intense Soret band at 349 nm [$a_{1u}{\rightarrow}e_g$ (allowed)] along with a series of Q bands at 425, 464, 555, 587 and 644 nm [$a_{2u}{\rightarrow}e_g$ (forbidden)]. The UV-vis spectra of the compounds exhibit a red-shift compared to the ligand H_2TPyP. Similar observations have made in many MOF compounds.[12] Thus the soret band was observed to be shifted to 394, 395 and 388 nm for the compounds **1**, **2** and **3** respectively. The insertion of zinc within the ring resulted in the disappearance of a number of Q-bands. The free base, H_2TPyP has a rectangular geometry with a D_{2h} symmetry and after the metalation the four nitrogens of the pyrrole become equivalent which results a change in geometry (D_{4h} symmetry) and reduces the number of Q-bands. Thus the Q-bands appear in the range 452 - 598 nm in **1**; 446 - 594 nm in **2** and 451nm- 600 nm in **3** (Figure S4 in the supporting information).

Solid state photoluminescence studies were carried out on the powdered samples of the compounds **1**-**3**, as well as the ligand H_2TPyP at room temperature using an excitation wavelength of 390 nm (Figure S5 in the supporting information). The emission bands observed in the range of 445-670 nm range are due to the intraligand emission from porphyrin ligand. An emission bands observed at ~446 nm for the ligand as well as for the synthesized compounds could be due to the $e_g \rightarrow a_{1u}$ transition. The fluorescence emission is characterized by the enhancement of emission bands in the region around ~620-660 nm while the band at 734 nm is quenched for the compounds. This spectral change in the emission bands could be due to insertion of zinc into the porphyrin core. The bands observed at 668nm, 662nm and 663 nm for **1**, **2** and **3** could be due to the $e_g \rightarrow a_{2u}$ transition

Thermal Stability Studies:

The thermal stability of the compounds was investigated employing thermogravimetric analysis (TGA). The TGA study of **1** (Figure S6 in the supporting information) exhibits weight loss of 35.1% in the range of 30-295ºC which would correspond to the loss of 5 DMA and 8 H_2O molecules (calc.34.6%). A weight loss of 48.7% in the range of 290-500ºC could be due to loss of the porphyrin and three nitrate molecules (calc. 48.1%).

In the case of **2** the observed weight loss of 57% in the temperature range of 30ºC to 200ºC may be due to the loss of 6 DMF and 12 H_2O molecules (calc.56.5%). A flat region in the temperature range 200-400ºC indicates that the framework may be stable until 400ºC. A steady weight loss was observed above 400ºC suggesting a collapse of the framework. We explored the possibility of removing the solvent molecules from **2** under vacuum. The vacuum treated samples (Figure S6 in the supporting information) exhibits a small initial weight loss which could be due to surface adsorbed water molecules. The evacuated compound exhibits a sharp weight loss at 400ºC suggesting the collapse of the framework. A PXRD study on the evacuated sample also indicates that the compound is crystalline and retains the structural integrity on the removal of guest solvent molecules (Figure S7) in the supporting information). The evacuated sample was immersed in DMF which readily absorbs the solvent molecules. The solvent re-absorbed sample behaves similar to the as-synthesized sample under TGA studies (Figure S6 in the supporting information).

Compound **3** exhibits similar behavior as that of compound **2** in the initial TGA studies. A weight loss of ~28.5% in the temperature range of 30-250ºC corresponds to the loss of DMA and water molecules (calc.27.8%). A broader weight loss of 65% in the temperature range 350ºC-600ºC corresponds to the collapse of framework.

The final calcined product in all the three cases was found to be ZnO (JCPDS: 36-1451) (Figure S8 in the supporting information).

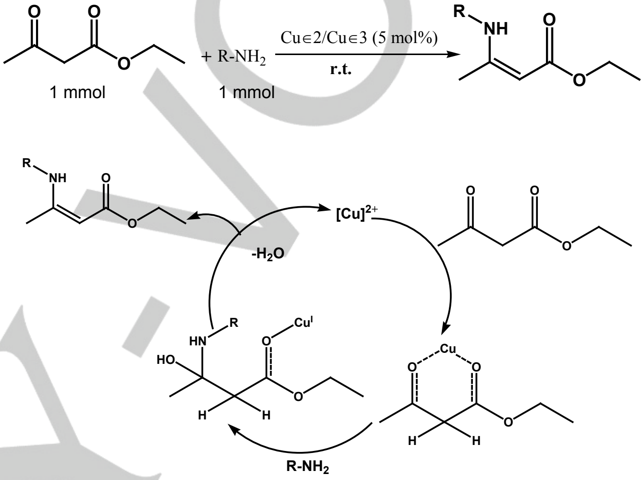
Gas Adsorption Studies:

To probe the possible openness of the structure, we carried out N_2 adsorption studies. The compound was degassed and activated at 120ºC for **1** and 200ºC for **2.** The nitrogen adsorption measurements were carried out employing Belsorp Max equipment at liq N_2 temperature. The studies indicated a type-I isotherm for both the compounds up to a relative pressure (P/P_0) of 1.0 bar (Figures S9 and S10 in the supporting information). The layer compound (**1**) exhibited a BET surface area of $93 m^2g^{-1}$ and the three-dimensional compound (**2**) exhibited a much larger surface area of $400 m^2g^{-1}$. Under the conditions of the activation, compound **3** was found to lose the original crystallinity and did not exhibit any significant adsorption (Figures S11 in the supporting information)

Metal ion metathesis: We have made attempts to prepare isomorphous frameworks of **1**, **2** and **3** with other first-row transition elements employing similar synthesis protocols. Our attempts were not successful and we employed a post-synthetic modification of the compounds **1**-**3** by performing a metal-ion exchange through the metathetic pathway. Earlier studies towards the preparation of isomorphous frameworks through this approach were successful and there were reports of the systematic metal exchange in MOF compounds.[13] It appears that a successful and facile exchange is possible whenever there is a solvent molecule binds with the metal along with a reasonable openness of the structure. The present compounds have coordinated solvent molecules as well as porosity in their structures, which made us believe that the present structures could be amenable for the metal exchange. To this end, we have made attempts with Co^{2+}, Ni^{2+} and Cu^{2+} ions as possible exchanging ions for Zn^{2+} ions. All the ion-exchange reactions were carried out at room temperature in DMF solution of the corresponding metal salts and the compounds **1**-**3** were immersed in the metal salt solution. The metal salt solutions were replenished every alternate day and the exchange reactions were carried out for a period of 12 days. We find that the copper ions exchange facilely in the case of compound **2** and **3** whereas other ions are partially exchanged which were confirmed by EDAX (Figure S12, Figure S13 in the supporting information) and AAS analysis (Figure S14, Figure S15 in the supporting information). In the case of compound **1** no metal – ion exchange was observed even after many attempts over several days. The copper ion exchange was found to be close to 100% in compound **2** whereas it was around 70% in compound **3**. The copper-exchanged products were also fully characterized similar to the starting compounds (Figure S16, Figure S17 in the supporting information).

Catalytic activity of Cu∈2 and Cu∈3:

Activation of Cu∈2 and Cu∈3: Cu∈2 and Cu∈3 was soaked in MeOH at room temperature for a period of 6 days. It was filtered and kept in vacuum oven at 60°C to get the active **Cu∈2 and Cu∈3** which was used for the catalysis.



Scheme 2. Synthesis of different β-enaminoester using **Cu∈2** and **Cu∈3** as catalyst under solvent-free condition

(a) Chemo and regioselective enamination of β-ketoester:

Compounds **2** and **3** were found to exchange for copper and we desired to explore the possible catalytic behavior of the **Cu∈2** and **Cu∈3** samples. It has been shown that a coordinatively unsaturated copper (II) centers can act as a good Lewis acid catalytic center for many organic reactions such as Henry reaction, Diels-Alder reaction, azide-alkyne cycloaddition, ring opening of epoxides etc.[14] β-enamino esters have been considered as an important feed stock for the synthesis of a number of anti-inflammatory, antibacterial and antitumor pharmaceuticals.[15] Among the many synthetic routes available in the literature [16] the condensation of β–dicarbonyl compounds with amines is considered to be one of the best. Many catalysts such as $Zn(OAc)_2.6H_2O/MgSO_4$, $NaAuCl_4$, $ZrOCl_2.8H_2O$, $InBr_3$ etc.[17] have been employed for this reaction. Unfortunately, the separation and recovery of the catalysts after the reaction have been a problem. Recently, a Cu^{II} MOF was shown to be an effective catalyst for the enamination of β-ketoester with good selectivity.[18] We desired to test the catalytic activity of Cu-exchanged compounds, **Cu∈2** and **Cu∈3** for this reaction. The synthesis of β-enaminoesters by the condensation reaction of primary aromatic amines with β-ketoester was carried out under solvent free conditions at room temperature (Table 2). For this reaction ethyl acetoacetate (1 mmol), aromatic amine (1 mmol) and **Cu∈2/Cu∈3** (0.05 mmol) were stirred at room temperature for 1 hr. The reaction was quenched by adding distilled water.

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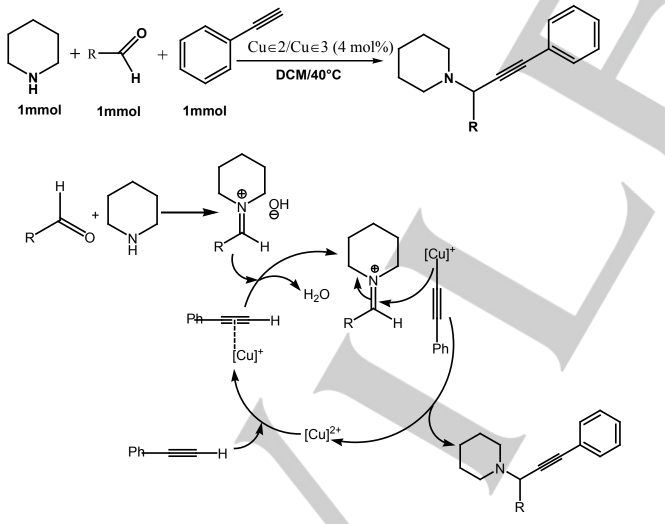
The catalyst was filtered off and the filtrate was extracted with ethyl acetate (2X10 mL) and dried over magnesium sulphate. The solvent was evaporated under reduced pressure to obtain the desired product. The results are summarized in Table 2. The reaction probably preceded by the nucleophilic attack of the amine with the ketone of the ethyl acetoacetate, giving rise to the corresponding amide. Such studies have been reported before.[15] The same reaction was also carried out without the catalyst as well as in the presence of the parent Zn-compounds (**2** and **3**) under similar condition. We did not observe the formation of the amide even after 12 hrs of the reaction (Table 2).

Table 2. Results for the β-enaminoester formation using **Cu∈2** and **Cu∈3** as catalyst under solvent-free condition

Entry	Catalyst	R	Time (h)	Yield (%)
1	**Cu∈2**	Ph	1	96
2	**Cu∈2**	4-Br-Ph	1	92
3	**Cu∈2**	4-I-Ph	1	97
4	**Cu∈2**	4-OMe-Ph	1	93
5	**Cu∈3**	Ph	1	89
6	**Cu∈3**	4-Br-Ph	1	87
7	**Cu∈3**	4-I-Ph	1	92
8	**Cu∈3**	4-OMe-Ph	1	90
9	**2**	Ph	12	No reaction
10	**3**	Ph	12	No reaction
11	**No catalyst**	Ph	12	No reaction



Scheme 3. Cu∈2 and **Cu∈3** catalyzed three component coupling reaction

In order to test the recyclability and reusability of the catalysts (**Cu∈2** and **Cu∈3),** the catalysts recovered after washing with ethyl acetate and methanol was employed for the same reaction. Our studies clearly indicate that the catalyst is active for upto four cycles (Figures S18, S19 in the supporting information).

(b) Synthesis of propargylamine derivatives by three component coupling reaction (A^3-coupling)

Propargylamines and their derivatives are known to be an important intermediate in the preparation of useful heterocycles.[16] One of the established routes for the synthesis of propargylamine is to react an aldehyde, alkyne and amine (commonly known as A^3-coupling), in the presence of a catalyst. A number of Cu^{II} complexes have been shown to be a good catalyst for this reaction.[17] We have attempted the A^3-coupling reaction using the Cu-exchanged **2** and **3** (**Cu∈2** and **Cu∈3)** employing para-formaldehyde/different aromatic aldehydes with piperidine and phenyl acetylene. In a typical reaction, the aldehyde (1 mmol), piperidine (1 mmol) and phenylacetylene (1 mmol) were stirred in the presence of 0.04 mmol of **Cu∈2/Cu∈3** at 40ºC in DCM under nitrogen for 10-12 hrs. After the reaction the catalyst was filtered and the DCM was evaporated under reduced pressure to obtain the product. The different reactions undertaken in the present study are listed Table 3. The catalytic reactions gave the desired product with good yields.

Table 3. Results of **Cu∈2** and **Cu∈3** catalyzed three component coupling reaction

Entry	Catalyst	R	Time (h)	Yield (%)
1	**Cu∈2**	H	10	97
2	**Cu∈2**	Ph	12	94
3	**Cu∈2**	4-F-Ph	10	93
4	**Cu∈3**	H	10	91
5	**Cu∈3**	Ph	12	87
6	**Cu∈3**	4-F-Ph	10	91
7	**2**	H	24	<2
8	**3**	H	24	<3
9	**No catalyst**	H	24	<4
10	**CuI**	H	10	84
11	**$Cu(OAc)_2$**	H	10	79

The same reaction was also carried out in the absence of the catalyst as well as in the presence of Zn-compounds, which resulted in the formation of negligible amounts of the propargylamine derivative (Table 3). It may be noted that the catalytic activity observed in the present study is comparable to those obtained employing other Cu-salts (Table 3). The recyclability of the catalysts was tested for this reaction and the catalysts were found to be active for at least 3 times (Figures S20 and S21 in the supporting information).

(c) Regioselective Alkyne-Azide Cycloaddition :

Copper based compounds have also been employed as a catalyst for the addition of organic azides and terminal alkynes and such reactions are known as Huisgen cycloaddition.[18] Though majority of the reactions reported in the literature employs Cu^{I} salts, there are reports of the use of Cu^{II} compounds as well in the literature for this reaction.[19] As part of this study, we have explored this reaction employing **Cu∈2 and Cu∈3** as the catalyst. A reaction of benzyl azide with various phenyl acetylenes have been attempted in the presence of

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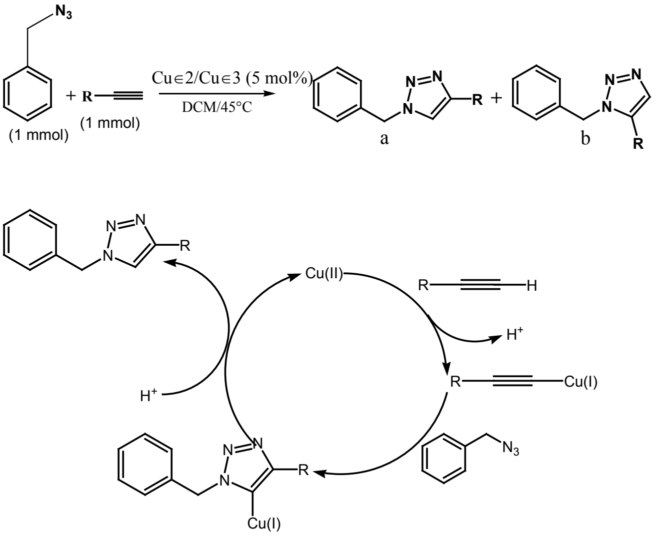
Cu∈2/Cu∈3 to obtain the 1,4-regioisomer. To this end, benzyl azide (1 mmol), substituted phenyl acetylene (1 mmol) were reacted in the presence of 0.05 mmol of **Cu∈2/Cu∈3** in DCM under nitrogen atmosphere at 45°C for 5 hrs. After the reaction, the catalyst was filtered and the solvent was evaporated under vacuum. The product was found to be 1,4-substituted triazole and the results are summarized in Table 4. The catalyst was found to be active for this reaction upto four cycles, which indicates the reusability of the catalyst. A blank reaction in the absence of the catalyst as well as in the presence of initial Zn compounds (**2** and **3**) did not yield the desired triazole product (Table 4).



Scheme 4. Cu∈2 and **Cu∈3** catalyzed Alkyne-Azide cycloaddition

Table 4. Cu∈2 and **Cu∈3** catalyzed Alkyne-Azide cycloaddition

Entry	Catalyst	R	Time (h)	Yield of **a** (%)
1	**Cu∈2**	Ph	5	97
2	**Cu∈2**	4-F-Ph	5	94
3	**Cu∈3**	Ph	5	92
4	**Cu∈3**	4-F-Ph	5	90
5	**2**	Ph	10	No reaction
6	**3**	Ph	10	No reaction
7	**No Catalyst**	Ph	10	<3
8	**Cu(NO$_3$)$_2$.3H$_2$O**	Ph	10	8

The structural integrity of the catalyst after repeated use in this reaction was checked employing PXRD, which indicates that the catalyst has the same pattern as the initial compounds (**Cu∈2, Cu∈3**) (Figures S22 and S23 in the supporting information). The same reaction when carried out employing Cu(NO$_3$)$_2$, 3H$_2$O gave the desired triazole product with a small yield (8%) after 10 hrs. This suggests that the framework copper plays an important role in this reaction.

Conclusions

The synthesis, single crystal structures, metal exchange through metathetic route have been carried out on three porphyrin based metal-organic framework compounds. The compounds have two- and three- dimensionally extended structures formed by the connectivity between the porphirinic units and metals through the carboxylates. A new nitrate binding mode has been observed for the first time in porphyrinic MOFs. The metal-exchanged (copper) compounds, **Cu∈2** and **Cu∈3** exhibits excellent catalytic behavior with good yields and selectivity. Our continuing research in this area suggests that many related compounds can be prepared by employing subtle variations in the synthetic compositions and conditions. We are actively pursuing this lead.

Experimental Section

Materials: The chemicals Zn(NO$_3$)$_2$.4H$_2$O, Cu(NO$_3$)$_2$.3H$_2$O, dimethylformamide (DMF), dimethylacetamide (DMA), methanol (MeOH), acetone were purchased from SDfine, India and 5,10,15,20-tetrakis(4-pyridyl)porphyrin(H$_2$TPyP), 1,4-benzenedicarboxylic acid, 1,4-napthalenedicarboxylic acid were obtained from Sigma-Aldrich and used as received.

Synthesis:

All the compounds were synthesized employing solvothermal method.

In a typical synthesis for **1**, tetra-(4-pyridyl)porphyrin (H$_2$TPyP) (0.04 mmol = 0.024 gm); 1,4-benzenedicarboxylic acid (0.08 mmol=0.012 gm) and Zn(NO$_3$)$_2$.4H$_2$O (0.2 mmol = 0.058 gm) were added with 2 ml DMA in a 7 ml polytertafluoroethylene (PTFE) lined autoclave (stainless steel). The reaction mixture was heated at 100°C for 3 days, which resulted in formation of purple colored rod shaped crystals. The crystals were filtered, washed (dry methanol) and vacuum-dried at room temperature (Yield ~ 58% based on Zn).

Compound **2** and **3** were also prepared employing similar synthetic procedure (see Table 5)

Cu- exchange: The Copper exchange studies were carried out at room temperature by soaking 100 mg of the compound in the metal nitrate (0.1 M) solution in DMF for 12 days. The soak solution was replenished every alternate day for facilitating the ion-exchange. The cation- exchanged products were washed thoroughly with DMF. The products after washing was soaked in pure DMF for another 6 days to remove any excess metal salt occupying the pores of the compound.

Initial Characterizations and Physical Measurements: All the prepared samples were characterized by a number of techniques. Elemental analysis (C, H, N) was carried out using Thermo Finnigan EA Flash 1112 series. Powder X-ray diffraction (PXRD) patterns were recorded employing Philips X'pert in the 2θ range of 5-50° (Cu Kα radiation). The simulated powder XRD patterns were generated from the single crystal structures using Mercury software (version 1.4.1). The experimental PXRD pattern was found to be entirely consistent with the simulated PXRD patterns for the compounds **1-3** which indicates phase purity (Figures S24 in the supporting information). The IR spectrum of the ligand as well as the compounds **1-3** were recorded in the mid IR region

(4000-400 cm^{-1}) on a KBr pellet (PerkinElmer, SPECTRUM 1000) (Figure S25 in the supporting information). The room temperature IR spectra exhibited sharp characteristics bands for the different functional groups (Table S4 in the supporting information). The ligand (H_2TPyP) exhibited a band at ~3312 cm^{-1} corresponding to the N-H stretching of the free base porphyrin. No such N-H stretching frequency was observed in the synthesized compounds (**1-3**), which suggests that zinc atom has been introduced into porphyrin ring. Similar observations have been commonly seen in many metallated porphyrin systems. A broad band in the region ~3600-3100 cm^{-1}can be assigned to the presence of lattice water molecules (O-H stretch). A band at ~2900 cm^{-1} can be assigned to the aromatic C-H stretching. The bands at 1616, 1658 and 1609 cm^{-1} for the compounds **1, 2** and **3** respectively can be assigned to the coordinated –COO moiety. The band at 1393 cm^{-1} in **1** could be for the coordinated nitrate.

Table 5. Synthesis Conditions for the Compounds **1-3**

Compounds	Composition	Temp (° C)	Time (days)	Yield
1	$5Zn(NO_3)_2.4H_2O/2H_2BDC/1H_2TpyP/537DMA$	100	3	58
2	$5Zn(NO_3)_2.4H_2O/2H_2BDC/1H_2TpyP/1300 DMF$	100	3	44
3	5 $Zn(NO_3)_2.4H_2O$/ 2(1,4-Naphthalenedicarboxylic acid)/$1H_2TpyP$/1075 DMA	100	3	51

Thermo- gravimetric analysis (TGA) was carried out in the presence of nitrogen (flow rate = 20 mL/min) in the temperature range 30−800°C (heating rate = 5°C/min) (Figure S3). UV−Vis spectra of tetra-(4-Pyridyl)porphyrin and the compounds **1**-**3** were recorded at room temperature using a Perkin-Elmer Lambda 35 spectrophotometer (Figure S6 in the supporting information). Room temperature solid state photoluminescence studies were carried out using a PerkinElmer LS 55 luminescence spectrophotometer (Figure S5 in the supporting information). EDAX analysis was carried out employing Quanta 200 FESEM (Figure S12 and Figure S13 in the supporting information). Atomic absorption spectroscopy (AAS) was recorded using PerkinElmer Analyst 200 (Figures S14 and S15 in the supporting information). ^{1}H NMR spectral data (Figures S26-S34 in the supporting information) was collected using a Bruker 400 MHz spectrometer using $CDCl_3$ as solvent at room temperature. Chemical shifts are reported in ppm using tetramethylsilane as the internal reference.

Single Crystal Structure Determination:

The structure of the compounds (**1**-**3**) was determined using single crystal X-ray diffraction. A suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted carefully to a thin fiber loop using paratone oil. Single crystal data were collected at 120 K on an Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector. For collecting data the X-ray was generated by operating generator at 50kV and 0.8 mA using Mo Kα (λ = 0.71073 Å) radiation. Crysalis Red [20] was used for cell refinement and data reduction. The structure was solved by direct methods and refined using WINGX (version 1.63.04a).[21] The solvent molecules were found to be disordered in all the three compounds and were accounted by the SQUEEZE option present within the WinGX PLATON program. The hydrogen positions were located initially from the difference Fourier maps, and for the final refinement, the hydrogen positions were fixed in a geometrically ideal position and refined employing a riding model. The final refinements included the atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. The details of the structure solution and final refinement parameters are given in Table 2. The CCDC numbers for the compounds **1**, **2** and **3** are 1535743, 1535744 and 1535745 respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Porphyrin • MOF • Transmetallation • Catalysis •

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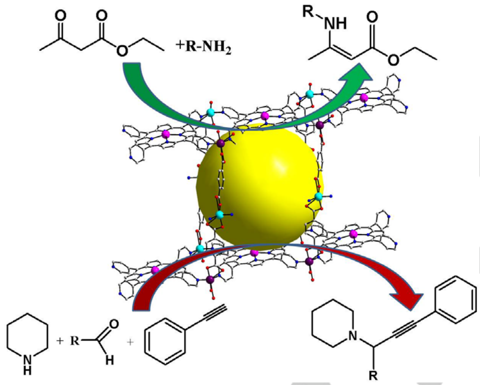
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Synthesis of three new porphyrin based MOFs are presented. The porous porphyrinic MOFs have been shown to undergo facile metal-exchange with copper. The copper-exchanged compounds exhibit excellent catalytic behavior for important organic reactions.



Gargi Dutta,[a] *Ajay Kumar Jana*[a] *and Srinivasan Natarajan**[a]

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Assembling Porphyrins into Extended Network Structures Employing Aromatic Dicarboxylates: Synthesis, Metal-exchange and Heterogeneous Catalytic Studies