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Encapsulation of Ag-nanoparticle in an Amine-Functionalized Porphyrin MOF and its Use as a Heterogeneous Catalyst for CO₂ Fixation under Atmospheric Pressure

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Abstract: А new porphyrin based compound, $[Zn_3(C_{40}H_{24}N_8)(C_{20}H_8N_2O_4)_2(DEF)_2](DEF)_3$ (1) has been synthesized employing 5,10,15,20-tetrakis(4-pyridyl)porphyrin (H₂TPyP), 1,2diamino-3,6-bis(4-carboxyphenyl)benzene and Zn²⁺ salt at 100°C under solvothermal condition. The structure, determined by single crystal X-ray diffraction studies, is three dimensional with three-fold interpenetration. The usefulness of free -NH₂ groups in the ligand was exploited for anchoring Ag-nanoparticles via a simple solutionbased route. The Ag-loaded sample, Ag@1, was characterized by PXRD, EDS, HRTEM, SEM, XPS and ICP-MS analysis which clearly indicate Ag-nanoparticles with size of 3.83 nm were uniformly distributed within the MOF. The Ag@1 sample was evaluated for possible catalytic activity for the carboxylation of terminal alkyne employing CO₂ under atmospheric pressure, which gave excellent results. The Ag@1 catalyst was found to be robust, active and recyclable. The present studies suggest that the porphyrin MOFs not only exhibit interesting structures but also show good heterogeneous catalytic activity towards fixation of CO₂.

Introduction

The use of metal nanoparticles to catalyse organic reactions has attracted considerable attention over the years.^[1] The possible applomeration of metal nanoparticles during the catalytic reactions was avoided by employing suitable substrates such as inorganic oxides, organic polymers etc.^[2] The last few years witnessed the use of metal nanoparticles anchored in metal-organic framework (MOF) compounds to improve catalytic and related properties, which appears to be superior to the individual (unsupported) nanomaterials.^[3] The metal loaded (generally based on noble metals), MOF based heterogeneous catalytic systems appear to exhibit advantages over traditional catalysts; (a) shorter duration and (b) good recyclability. Many metal@MOF systems have been explored and found to exhibit good catalytic behavior towards olefin hydrogenation,^[4] aerobic oxidation of alcohol,^[5] C-C coupling^[6] etc. Among these, the Agloaded MOFs have been known to exhibit good catalytic activity.^[7]

 CO_2 is an important greenhouse gas and there have been considerable attempts to convert it into useful products.^[8] It is important to develop viable CO_2 capture and sequestration

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methodologies to reduce overall greenhouse emission. CO2 is an attractive C₁ building block for organic synthesis.^[9] However, carbon dioxide is a symmetrical linear molecule and difficult to activate and involve in bond formation.^[10] There has been intense research activities during the last decade towards fixation of CO₂:carboxylation of organometallic reagents,^[11] epoxides,^[12] carboxylative cyclization of propargylic amines and alcohols^[13] etc. Of these, the direct C-H carboxylation of terminal alkynes employing CO₂ as the carbon source is important as the alkynyl carboxylic acid and its derivatives have important industrial applications.^[14] The carboxylation reactions, in general, were carried out under homogeneous catalytic conditions. This would prevent the recovery of the catalyst. In our efforts towards fixation of CO₂ into useful products we have recently employed a MOF compound synthesized from tetra-(4-pyridyl)porphyrin (H₂TPyP) and 4,4'-Oxybis(benzoic acid) (H₂OBA), which catalyzes and converts CO₂ into cyclic carbonates.^[15] In continuation of the theme, we have now attempted CO₂ fixation employing a Ag-nanoparticle loaded porphyrin based MOF, [Zn₃(C₄₀H₂₄N₈)(C₂₀H₈N₂O₄)₂(DEF)₂](DEF)₃, **1**. It may be noted that the reports of metal loaded MOF materials for catalytic conversion of CO₂ are not many.^[16] The porphyrin support $[Zn_3(C_{40}H_{24}N_8)(C_{20}H_8N_2O_4)_2(DEF)_2](DEF)_3$, **1** was prepared by solvothermal method employing Zn(NO₃)₂.6H₂O, tetra-(4pyridyl)porphyrin (H_2TPyP) and 1,2-diamino-3,6-bis(4carboxyphenyl)benzene as a linker. The free amine groups, present in the linker, are attractive for anchoring Agnanoparticles. The metal loaded MOF material (Ag@1) was employed for the carboxylation of terminal alkyne employing gaseous CO₂ under 1 atm pressure. In this manuscript synthesis. structure and heterogeneous catalytic activity of this compound is presented.

Results and Discussion

Structure of $[Zn_3(C_{40}H_{24}N_8)(C_{20}H_8N_2O_4)_2(DEF)_2](DEF)_3$ (1)

Compound 1 crystallizes in triclinic P-1 space group. The asymmetric unit of 1 contains 58 non-hydrogen atoms (Figure S1 in the Supporting Information) that includes two crystallographically distinct Zn²⁺ ions: Zn(1) occupies a special position (1a) with a site multiplicity of 0.50 and bonded with four pyrrole nitrogen atoms [N(1), N(2), N(1)(#1) and N(2)(#2)] and two oxygen atoms [O(1) and O(1)(#1)] from two DEF molecules and has octahedral coordination whereas Zn(2) has a tetrahedral geometry formed by two oxygen atoms [O(2) and O(5)] from the acid linker and two nitrogen atoms [N(3) and N(4)] from the H₂TpyP ligand. The Zn-N bond distances are in the range of 2.044(3)-2.049(3) Å [average 2.045Å] and the Zn-O bond distances are in the range of 1.931(2)-2.422 Å [average 2.178Å] (Table S1 in the Supporting Information). Zn(1) occupies the plane of the porphyrin ring and Zn(2) links the porphyrin units through the pyridyl nitrogens forming a one dimensional unit (Figure 1a). The 1D chains are connected by



Figure 1. (a) Zn-porphyrinic units connected by ZnO_2N_2 tetrahedra forming the 1D chains; (b) The 1D chains are connected by the dicarboxylate forming the

2D layer; (c) The connectivity between the 2D layers through another carboxylate forming the 3D structure; (d) The topological view of the 3-fold interpenetrated structure.

the dicarboxylate linker forming a 2D layer (Figure 1b). The 2D layers are further crosslinked by another dicarboxylate linker forming the 3D structure (Figure 1c). It may be noted that the amine groups present in the carboxylate linker is free. The 3D structure would have resulted in large cavities, which were avoided by interpenetration of identical units. The structure, infact, has a 3-fold interpenetrated porous framework (Figure 1d). Inspite of the interpenetration a solvent accessible void of 2042Å³ per unit cell is available in this structure, which is

approximately 59.5% of the unit cell volume.

Optical Studies

The UV-Vis absorption spectra and photoluminescence studies at room temperature were carried out on the powdered sample of the porphyrin H₂TPyP and **1** [Figure S3 in Supporting Information]. The studies indicate typical features of the porphyrin ligand exhibiting sharp Soret and Q bands arising from the π - π^* transitions. The as-synthesized compound **1** also exhibits intense Soret band at 412 nm [a_{1u}→e_g (allowed)] and a number of Q-bands [a_{2u}→e_g (forbidden)] in the range 450-600 nm. A red shift of the absorption bands observed in **1** with respect to the ligand H₂TPyP along with the reduction in the number of Q-bands can be attributed to the successful insertion of the Zn²⁺ ion within the porphyrin core.

The photoluminescence spectrum for compound **1** was also investigated employing a excitation wavelength of 412 nm (Figure S3(b) in Supporting Information). The observed broad emission bands in the range 533-663 nm could be due to the intraligand transitions from porphyrin ligand (H₂TPyP). An emission band observed around ~533 nm may correspond to e_g

 \rightarrow a_{1u} transition. The emission bands observed at 630 nm and 663 nm could be attributed to e_g \rightarrow a_{2u} transition.

IR Studies

IR spectra of 1,2-diamino-3,6-bis(4carboxyphenyl)benzene and **1** were recorded at room temperature and exhibited characteristic bands (Figure S4, Table S2). Band centered around 3388, 3396 cm⁻¹ respectively for ligand and **1** in the IR spectra corresponds to the –N-H stretch of the free amine

group. The bands at 2998 and 2977 cm⁻¹ respectively for ligand and compound **1** can be assigned to the aromatic C-H stretch. Presence of sharp bands ~ 1684, 1668 cm⁻¹ was attributed to free and metal coordinated –COO group in ligand and compound **1** respectively.

Thermogravimetric Studies

á b

The TGA study of **1** (Figure S5(a) in Supporting information) indicates a continuous two step weight loss of 32.7% in the temperature range 30-215°C; which could be attributed to the loss of 5DEF molecules (calcd 31.9%). A flat region in the temperature range 215-350°C suggests that the framework may

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be stable upto 350°C. A continuous weight loss beyond 350°C suggests collapse of the framework. The final calcined product was found to be ZnO by PXRD studies (JCPDS: 36-1451; Figure S5(b) in Supporting information). To examine the framework stability during solvent removal, the as-synthesized compound 1 was kept in a vacuum oven at 200°C for 1 day. The evacuated and heated sample exhibits the same PXRD pattern as that of the as-synthesized sample, which indicates that the framework is retained (Figure S5(c) in supporting information). A TGA analysis of the evacuated and heated sample exhibits a small initial weight loss, possibly due to the surface adsorbed water molecules. The vacuum treated sample appears to be stable upto a temperature of 335°C after which it exhibits a sharp weight loss of 67%, suggesting the collapse of the framework. The calcined sample again was found to be ZnO by PXRD. The vacuum treated sample was soaked in DEF, which readily readsorbs the DEF molecules. The resolvated sample was again analyzed by TGA, which exhibited comparable weight loss behavior as that of the as-synthesized compound (Figure S5 (a) in Supporting Information).

Ag@1 Characterizations

It has been known that the free amine group of the ligand could be employed for anchoring metal nanoparticles^[17]; and it occurred to us that we could use the amine groups for the encapsulation of Aq nanoparticle. Thus, the Aq@1 material was synthesized employing AgNO₃ as the precursor and NaBH₄ as the reducing agent. The PXRD pattern of the silver loaded compound 1 (Ag@1) indicates that the framework remains intact after Ag nanoparticle loading (Figure S2 in Supporting Information). The characteristic peak of Ag(111) (20~38) and Ag(200) (20~45) confirms successful deposition of Agnanoparticle. The Ag@1 compound was characterized by EDS, TEM, IR and ICPMS analysis. TEM study of the Ag-loaded compound indicates that the particles are evenly distributed with particle sizes in the range of 3.83 ± 0.05 nm (Figure S6(a) in supporting information). The presence of silver nanoparticles was confirmed from the energy-dispersive X-ray spectrum (EDS) (Figure S6(b) in supporting information) and high resolution transmission electron microscopy (HRTEM) (Figure2b). The observed atomic lattice fringes with spacing of 0.236 nm corresponds to the (111) plane of Ag (Figure 2b). The oxidation state of the Ag nanoparticle was determined employing X-ray photo electron spectroscopy (XPS) (Figure S7 in supporting information). From the XPS analysis, the Ag core level binding energies for Ag $3d_{5/2}$ and Ag $3d_{3/2}$ were found to be 368.08eVand 373.66eV, respectively, which are generally observed for silver in the native state [Ag(0)].^[16] Inductively coupled plasma (ICP) analysis indicated that the amount of Ag loaded in Ag@1 was 7.85% (Table S3 in Supporting Information). The IR spectral studies of Ag loaded compound (Ag@1) indicated a shift of 45cm⁻¹ compared to the as-synthesized **1** in the –N-H stretching region (3351 cm⁻¹) (Figure S4(c) in Supporting Information). It is likely that the shift in the N-H stretching frequency is due to the electrostatic interactions between the NH₂ group and the silver nanoparticle. Similar observations have been made before. [17b] It is likely that the higher loading of Ag nanoparticles is due to the presence of a number of available amino groups from the ligand.

It may be noted that only 1.47% of silver nanoparticles could be loaded on a porphyrin MOF reported by us $^{[18]}$ with no $-\rm NH_2$ group under the same condition (Table S3 in Supporting Information).

Adsorption of CO₂

The presence of free $-NH_2$ groups in the structure prompted us to investigate the possible CO_2 adsorption in sample. Prior to the adsorption measurement the as-synthesized **1** was kept in MeOH for 5 days at room temperature for solvent exchange, by refreshing the solvent every day.



Figure 2: (a) Figure shows the Ag-loaded MOF compound (Ag@1); (b) HRTEM image of a Ag nanoparticle in Ag@1. The interplanar spacing of 0.226 nm corresponds to the (111) plane of Ag^0

The resulting methanol exchanged sample was heated at 100°C for 12 hrs under vacuum to get the activated **1**. The CO₂ adsorption was carried out at 298K and 195K and upto a relative pressure P/P₀= 1 (Figure 3). The maximum CO₂ uptake capacity at 298K and 195K was found to be 13.55 and 51.10 cm³g⁻¹ respectively(Figure 3), which compares well with the reported porphyrin based MOF.^[19] The **Ag@1** was examined under identical condition which showed an uptake of 5.309 cm³g⁻¹(298K) and 37.9 cm³g⁻¹(195K) of CO₂ (Figure 3).







Scheme1. Carboxylation of terminal alkynes with CO2

alkyne to the corresponding carboxylic acid.^[16]

Silver nanoparticles immobilized on MOFs such as MIL-101 has

been shown to effectively catalyze the carboxylation of terminal

Catalytic Studies

heterogeneous catalyst for the chemical fixation of CO_2 , especially, towards the activation of terminal alkyne. For this reaction we employed milder reaction conditions compared to the known ones.

In a typical reaction terminal alkyne (1 mmol), Cs_2CO_3 (1.2 mmol), **Ag@1** (5 mol %), nBul (1.2 mmol) and 4 ml DMF were introduced in a Schlenk flask. The reactants in the Schlenk flask were put through a freeze-pump-thaw sequence to remove all the dissolved gases. The resulting reaction mixture was heated under CO_2 atmosphere (99.99% balloon) at 60°C for 6h. The reaction mixture was cooled to room temperature and the catalyst was recovered by filtration followed by extraction of the products employing n-hexane. The hexane from the extracted



The alkynyl carboxylic acid and its derivatives have been known as key synthons in many biologically active molecules: spiroindoles (antimalarial behavior)^[14c,20]; spirobenzofuranones (antifungal behavior) ^[14a]; coumarin and its derivatives (cholesterol lowering activity)^[14d]; to name a few. In many of these compounds, propiolic acid derivatives are the main component, which can be prepared through a number of approaches: (i) oxidation of propargylic alcohol or aldehyde derivatives ^[21]; and (ii) insertion of CO₂ into the alkynyl species, obtained by the deprotonation of alkynes employing alkali metal hydride or organometallic reagents.^[22] In addition, metal catalyzed insertion of CO₂ onto the alkynyl group has also been established.^[23] There is a need to look for newer catalysts that can be employed for this organic transformation in a heterogeneous manner. Thus, we explored the **Ag@1** as a solution was removed by evaporation and the crude product was purified by column chromatography (silica gel, CHCl₃/EtOAC) to get the desired alkyl-2-alkylnoates.The yield of the products was found to be good, in the range of 72-91% (Table1). The **Ag@1** catalyst was examined for possible re-use in the same reaction and we have observed that the catalyst remains active for atleast three cycles (Figure 4).



Figure 5: Hot filtration experiment for carboxylation of terminal alkyne

Figure 4: Recyclability studies for carboxylation reaction of terminal alkynes employing Ag@1

We have also examined the structural integrity of the catalyst by PXRD (Figure S8 in Supporting Information) as well as SEM, TEM and HRTEM studies (Figure S9 and S10 in Supporting Information) to probe the framework structural damage as well as changes in the morphology of Ag-nanopartcles. Our studies did not reveal any major noticeable change in the framework structure (PXRD) and also no agglomeration of Ag-nanoparticles was noticed.

We have also made studies employing samples with different Ag-loadings (3% and 15%). The TEM image of 3% Ag-loaded compound indicates that the Ag-nanoparticles have particle sizes in the range 3.07±0.14. In addition, the Ag nanoparticles are also evenly distributed across the compound. The higher loading (15%), on the other hand, results in agglomeration of the Ag-nanoparticles (Supporting Information Figure S11). We have carried out the catalytic reaction with 3% Ag-loaded compound under the same experimental conditions taking phenyl acetylene as a substrate. We observed a conversion of 66% with 3% Ag-loaded sample. This is lower than the conversion obtained with the 7.85% Ag-loading. It is likely that the 7.85% Ag-loading could be the optimal one.

The present studies clearly suggest that the catalyst is reusable as well as stable under the conditions of carboxylation studies. It may be noted that the efficiency of Ag@1 was comparable with other Ag-nanoparticle supported catalysts (Table S4 in supporting information). We have also carried out hot filtration experiment to confirm the heterogeneous nature of the reaction (Figure 5). A reaction mixture of phenyl acetylene (1 mmol), Cs₂CO₃ (1.2 mmol), Ag@1 (5 mol %), nBul (1.2 mmol) and 4 ml DMF was heated at 60°C under CO₂ atmosphere. After 1h Ag@1 was taken out from the reaction mixture by centrifugation and the reaction was allowed to continue at 60°C. No further increase of the yield of the product was observed during the course of the reaction in the absence of Ag@1. In order to confirm the encapsulated Ag-nanoparticles were responsible for catalytic activity few controlled experiments were also carried out. In the absence of any catalyst there was no conversion (Table 1, entry 6). When 1 was used as the catalyst we obtained a 14% conversion (Table 1, entry 7) and employing AgBF₄ as a catalyst a 21% conversion was obtained (Table 1, entry 8). Hence we believe that loaded Ag(0) nanoparticles embedded on the MOF may be responsible for the observed heterogeneous catalytic activity.



Conclusions

In summary, the synthesis, structure and catalytic studies of a new three-fold interpenetrated 3D framework compound $[Zn_3(C_{40}H_{24}N_8)(C_{20}H_8N_2O_4)_2(DEF)_2](DEF)_3$, 1, employing H_2TPyP , 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene and Zn(NO₃)₂.6H₂O under solvothermal conditions has been



were deposited on the MOF employing simple solution route to get **Ag@1**. The **Ag@1**

Scheme 2: Synthesis of 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene

sample was examined as a heterogeneous catalyst towards converting CO₂ via a carboxylation reaction of terminal alkyne through C-H bond activation under mild conditions (1 atm, 60°C). The studies indicate that **Ag@1** exhibits good catalytic activity, excellent stability as well as good recyclability for this reaction. Our continuing investigations reveal that the porphyrin based MOFs could be good heterogeneous catalysts for other reactions as well, which are being pursued currently.

Experimental Section

Materials: The metal salts and other chemicals were procured from commercial suppliers [SD fine (India), Alfa Aesar (USA), Sigma Aldrich (USA), TCI (India) etc.] and used without further purifications. The Solvents were purified by standard procedures prior to use.

The ligand employed in the present synthesis was prepared from dimethyl 4,4'-(benzothiadiazole-4,7-diyl)dibenzoate^[24]. The procedure is as follows:

Synthesis of 1,2-diamino-3,6-bis(4-methoxycarbonylphenyl) benzene

4,4'-(benzothiadiazole-4,7-diyl)dibenzoate (1.00 gm, 2.5 mmol) was dissolved in 200 ml of 1,4-dioxane/AcOH (1:1) mixture. Zndust (2.60 gm, 40 mmol) was added to it slowly. The resulting mixture was refluxed at 110°C for 12 hrs and filtered hot. The resultant filtrate was concentrated on a rotary evaporator. The obtained residue was washed with distilled water to get the pure product. Yield: 0.677 gm, (72%).

Synthesis of 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene The synthesized 1,2-diamino-3,6-bis(4-methoxycarbonylphenyl) benzene (0.500gm, 1.3 mmol) was dissolved in a mixture of MeOH (10 ml), THF (10 ml) and water (5 ml). KOH (2.91gm, 52 mmol,) was added to the above solution and the mixture was refluxed at 80°C for 12 h. The resulting mixture was cooled to room temperature and conc. HCl was added slowly to obtain a pH of 2. The resultant precipitate was filtered, washed with water and dried under vacuum. Yield: 0.430 gm, (95%).

Synthesis of $[Zn_3(C_{40}H_{24}N_8)(C_{20}H_8N_2O_4)_2(DEF)_2](DEF)_3(1)$ Compound 1 was prepared by employing a solvothermal method (Scheme 3). A mixture of H₂TPyP (0.02 mmol, 0.012gm), 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene

(0.04mmol,0.015gm) and Zn(NO₃)₂.6H₂O (0.1 mmol, 0.029 gm) was placed in a 7 mL Teflon lined stainless steel autoclave and heated at 100°C for 3 days.This resulted in purple colored crystals, which were filtered, washed with dry methanol and vacuum dried at room temperature. Yield≈0.019 gm, 62% based on H₂TPyP. Elemental analysis calcd (%) C 68.57, H 5.21, N 12.95; found: C 68.51, H 5.19, N 12.97.



Scheme 3: Synthesis of 1 by solvothermal method

Synthesis of Ag@1

The as synthesized crystals of **1** (0.1 gm, 0.063 mmol) were dispersed in 10 ml acetonitrile and transferred to a 25 ml RB flask. AgNO₃ (0.010 gm; 0.058 mmol) dissolved in 1 ml of acetonitrile was added to it and the reactants were stirred for. The RB flask was kept in ice bath and methanolic solution (1 ml) of NaBH₄ was slowly added. The resulting mixture was stirred for another 4 hrs at room temperature. The product was separated through centrifugation and washed with acetonitrile (3x10 mL) to obtain the desired **Ag@1**.

Initial Characterizations

The ligand 1,2-diamino-3,6-bis(4-carboxyphenyl)benzene, and the products from the catalytic studies were characterized by NMR spectroscopic studies (Figure S14-S19 in supporting information) using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm employing tetramethylsilane as the internal reference. The IR spectrum of the prepared compounds was recorded as KBr pellets in the mid IR region (4000-400 cm⁻¹) using FTIR spectrometer (PerkinElmer, model no: L125000P)

(Figure S4 in Supporting Information). UV-Vis spectra (Perkin Elmer, Lambda-35) and solid state photoluminescence (Perkin-Elmer model-LS55 instrument) of the compound 1 were recorded at room temperature. (Figure S3 in supporting Information). The PXRD patterns were recorded in the 20 range 5-50°C (Philips X'pert) (Cu_{Ka} radiation). The simulated PXRD pattern from the single crystal structure was generated employing Mercury software (1.4.1) (Figure S2 in supporting information). Thermogravimetric analysis (TGA) (Metler-Toledo) was carried out in N₂ atmosphere (flow rate = 20 mL/min) in the temperature range 30-1000°C (heating rate = 10°C/min) (Figure S5 in Supporting Information). The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images (Figure2) and energy-dispersive X-ray spectroscopy (EDS) were obtained employing a JEM 2100F, JEOL transmission electron microscope with an accelerating voltage of 200 kV(Figure S6 in supporting information).

Single-crystal structure determination:

A suitable single crystal of 1 was carefully selected and mounted onto a thin fibre loop using paratone oil. Single crystal data was collected at 110K on an Oxford Xcalibur (Mova) diffractometer equipped with an EOS CCD detector. X-ray generator operated at 0.8 mA and 50 kV (Mo K α , λ = 0.71073 Å) during data collection. Crysalis Red [25] was used for cell refinement and data collection. The structure was solved by Direct Methods and refined using WINGX suit of program (version 1.63.04a)^[26]. The hydrogen atoms of the ligands were located from the difference fourier map and were fixed in geometrically idealized positions and refined using a riding model. Hydrogen positions of the disordered solvent molecules could not be located and the solvent molecules were accounted using the SQUEEZE option present in the WinGX PLATON program. 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. CCDC 1842924 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table 2: Crystal Data and Structure Refinement Parameters for the prepared compound

	1
Empirical Formula	$C_{80}H_{40}N_{16}O_{10}Zn_3$
FormulaWeight	1581.45
Crystal System	Triclinic
Space Group	P-1
a(Å)	14.2899(13)
b(Å)	16.1798(15)
c(Å)	16.5216(16)
a (deg)	69.713(4)

β (deg)	88.135(4)
γ (deg)	73.712(4)
Volume (Å ³)	3430.3(6)
Ζ	1
Temperature (K)	110(2)
ρ _c (gcm ⁻³)	0.766
µ(mm⁻¹)	0.559
heta range (deg)	2.35-23.69
Wavelength (Å)	0.71073
<i>R1</i> , <i>wR2</i> [I>2σ(I)]	0.0628, 0.1776
R1, wR2 (all data)	0.0836, 0.1864

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR_2 = {\Sigma |w(F_o^2 - F_c^2)] / \Sigma [w(F_o^2)^2]}^{1/2}. w = 1/[\rho^2(F_o)^2 + (aP)^2 + bP]. P = [max (F_o O) + 2(F_o)^2] / 3, where a= 0.1027 and b= 0.0000 for$ **1**.

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Keywords: Porphyrin • MOF • Nanoparticle • CO₂ • Carboxylation • Catalysis

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FULL PAPER

Synthesis and single crystal structure of an amine-functionalized three-fold interpenetrated 3D porphyrin MOF is described. The free amine groups present in the MOF have been utilized for encapsulating Ag nanoparticles. The Ag@MOF exhibits heterogeneous catalytic activity for the conversion of terminal alkyne to propiolic acid derivatives employing CO₂ under atmospheric pressure.



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