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Article

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MOF derived CuO-NPs for the green synthesis of a-aminonitriles via Strecker reaction in solid state.

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A MOF to CuO Nanospheres of Uniform Morphology for Synthesis of α-Aminonitriles under Solvent-Free Conditions along with Crystal Structure of the MOF

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ABSTRACT:

Herein, we have reported the synthesis, crystal structure, thermogravimetric property and photoluminescence activity of a new Cu-based metal organic framework (MOF): { $[Cu_2(2,5-pdc)_2(ald-4)(H_2O)_2]$ ·3H₂O,MeOH}n (where 2,5-pdc = 2,5-pyridine-dicarboxylate, ald-4 = aldrithiol-4) along with catalytic activity of CuO nanopaticles (Cu-NPs) derived from the MOF for green synthesis of organic molecules having biological relevance. The regular arrangement of metal centers and presence of oxygen and carbon in metal-organic frameworks (MOF) enable us to utilize them as template/precursor for synthesis of monodispersed metal-oxide and metal-carbide nanoparticles having high surface area with well defined and uniform morphology. The MOF derived oxide nanoparticles generally exhibit improved catalytic activities and product selectivity and significantly reduce the chemical waste production. The structural analysis has revealed that in the complex under investigation, the 2,5-pdc bridges the Cu(II) centers to form both left handed and right handed infinite 1D helical chains and the complex is a 3D achiral

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framework composed of neighboring 2D sheets of opposite chirality. The thermogravimetric study suggests that the framework is stable up to 500 °C. Single phase, highly crystalline, nearly monodispersed and spherical CuO-NPs having average paticle size ~27.9 nm has been synthesized by heating the framework at 650 °C for 4 hrs. The CuO-NPs are characterized by using powder x-ray diffraction, high resolution transmission electron microscopic, selected area electron diffraction, energy dispersive x-ray spectroscopic and dynamic light scattering techniques. Further, the crystal structure of the CuO-NPs has also been illustrated by Rietveld refinement of powder pattern. Finally, the as-synthesized CuO-NPs were employed in the one-pot three component Strecker synthesis of α -aminonitriles *via* the condensation of benzaldehyde, aniline and trimethylsilyl cyanide under solvent-free condition. This work will be helpful in utilizing the MOF derived oxide nanoparticle for development of sustainable chemical processes.

KEYWORDS

1) 2D coordination polymer, 2) Helicity and Chirality, 3) MOF-derived CuO-nanoparticles, 4) Strecker synthesis and 5) Solvent free catalytic reaction

INTRODUCTION

Over past two decades, metal organic frameworks (MOFs) have attracted substantial attention due to their aesthetically pleasing architecture, topological diversity, high porosity with large surface area and remarkable functional properties.¹⁻⁴ MOFs are considered as excellent candidates for application in gas and solvent adsorption, storage and separation, catalysis, sensing/recognition, magnetic devices, proton conduction, drug delivery, fuel storage, water splitting, electrode material of lithium ion batteries, supercapacitor, solar cell, fuel cell and so on.⁵⁻¹⁰ Beyond these conventional applications, owing to their structural robustness and regular arrangement of atoms within the framework, MOFs are used as self-sacrificing precursor/template for synthesis of easily customizable nano/micro-structured materials (porous carbon, metals, metal oxides and carbides) with the morphological inheritance of the MOFs' architecture.¹¹⁻⁴³

Porosity and secondary building units (SBUs) formed by metal and coordinated atoms are two intriguing features of MOFs. Up till now, a little attention has been paid to the use of SBUs of the MOFs. Recently, the SBUs of the MOFs are utilized for synthesizing nanostructured materials with diverse type of morphology, wherein, the MOF behaves as self-sacrificing precursor in which metal centers are used as an intrinsic metal source and organic linkers act as resource of carbon, oxygen, nitrogen etc.¹¹⁻¹³ The porous carbon nanoparticles (NPs),¹⁴⁻¹⁶ multi-walled carbon nanotubes,¹⁷ mesoporous carbon,¹⁸ nitrogen-doped porous carbon,¹⁹ metal/metal oxide nanoparticles¹¹⁻¹³ (nanoparticles of transition metal oxide, main group metal oxide, lanthanide oxide etc.), core-shell nanoparticles of Au@ZnO,²⁰ Fe₃O₄@Fe₅C₂,²¹ Co@Co₃O₄@C,^{22,23} and Fe₂O₃/N-doped carbon hollow sphere,²⁴ double-shelled nanocages of Co₃O₄/NiCo₂O₄,²⁵ nanocomposites of Pt/ZnO,²⁶ LiFePO₄/carbon networks,²⁷ Fe₃O₄/C,²⁸ Fe₂O₃/TiO₂,²⁹ and

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ZnFe₂O₄/Carbon nanotubes,³⁰ meso-porous α-Fe₂O₃,³¹ α-Fe₂O₃ spindles,³² carbon coated ZnO quantum dots³³ etc. are among some of the remarkable MOF derived nanostructure. These nanostructures have huge application potential¹¹⁻¹³ in combating environment and energy related problems by virtue of their wide spread applications in solar cell,¹¹ hydrogen adsorption¹⁵, gassensing,^{12,13} catalysis^{11-13,23,34,35} radionuclide separations³⁶, extraction of heavy metals from nuclear waste,³⁷ supercapacitors,³⁸ and electrode material for lithium ion batteries³⁹⁻⁴³. MOF derived metal oxide nanoparticles (MDMO-NPs) exhibit excellent electrocatalytic,^{11-13,34} photocatalytic^{12,13,35} and common catalytic²³ activity with high selectivity and very good reusability in water splitting, removal of hazardous heavy metals/waste water treatment and green synthesis of fine chemicals, respectively. MDMO-NPs display uniform morphology, Lewis acidic-basic, red-ox properties and high reactivity of the surface which are the prime requirement for having good catalytic response in general.

To the best our knowledge, up till now no attempt has been made to synthesize metal oxide nanoparticles (MO-NPs) from the MOF composed of 1D helical chain. However, MO-NPs with narrow size distribution and uniform morphology can be easily produced through thermal decomposition of 3D homochiral or achiral frameworks in open air or oxygen atmosphere utilizing the metal oxygen bonds and uniform spatial distribution of atoms in such frameworks. Several 3D chiral and achiral frameworks have been designed to testify the manner in which chiral message is exchanged between adjacent chiral SBUs and then to the whole frameworks and the conditions that lead to the formation of either the 3D chiral or achiral frameworks.⁴⁴⁻⁵² If the entire "chirality transfer" process from lower to higher dimension occurs in homochiral fashion, the resultant 3D framework will be chiral. Earlier investigation on structural properties of $[M(HIDC)(H_2O)(prz)_{0.5}]_n$ (M= Fe, Mn, Cd),⁴⁴ $[Co(HIDC)(H_2O)(pyz)_{0.5}]_n$,⁴⁴ [Mn(HIDC)

 $(H_2O)]_n$,⁴⁴ [Cu₂(pda)₂(phen)₂(H₂O)₂].6H₂O,⁴⁵ {[Zn₂(L-trp)₂(bpe)₂(H₂O)₂]·2H₂O·2NO₃}_n,⁴⁶ {[Co (L-trp)(bpe)(H₂O)]·H₂O·NO₃}_n,⁴⁶ {[Co(L-trp)-(bpa)(H₂O)]·H₂O·NO₃}_n,⁴⁶ (H₃O)₂[Cd₈((S)-TMTA)₆(bipy)₃(H₂O)₄]⁴⁷ and (H₃O)₂[Cd₈((R)-TMTA)₆(bipy)₃(H₂O)₄],⁴⁷ where H₃IDC = imidazole-4,5-dicarboxylic acid, prz = piperazine, pyz = pyrazine, H₂pda = 1,3phenylenediacetic acid, phen = 1,10-phenanthroline, LHtrp = L-tryptophan, bpe = 1,2-bis(4pyridyl)ethylene and bpa = 1,2-bis(4-pyridyl)ethane, (R/S)-H₃TMTA = (R/S)trimesoyltrialanine frameworks composed of 1D chiral SBUs having two linkers has helped in understanding the mechanism of chiral crystal formation through spontaneous resolution, however, the detail of it is yet to be fully understood.

Further, we have reported the crystal structure, supramolecular structure and physical properties of chiral 3D [$\{Co(2,5-pdc)(H_2O)_2\}H2O]_n$ (2,5-pdc = 2,5-pyridine dicarboxylate) framework.⁴⁸ It may be noted that non-centrosymmetric 2,5-pdc is fairly rigid ligand and it exhibits twenty three coordination modes.^{53,54} On the other hand, flexible aldrithiol (ald-4) can be used as a very efficient linker for synthesizing organometallic complexes together with carboxylate ligands.^{55,56} Thus, from the standpoint of rational design of new solid state structure, synthesizing a Cu containing 3D MOF built up with 1D helical SBUs having both 2,5-pdc and ald-4 linkers appears to be very much promising. Further, if this attempt becomes successful then it will be interesting to explore the possibility of synthesizing CuO nanoparticles through thermal decomposition of the obtained framework.

Given this background, preliminary aims of the present work are: (i) to synthesize a Cubased MOF composed of 1D chiral SBUs having both 2,5-pdc and ald-4 spacers (ii) to study the "chirality transfer" mechanism in the framework from the structural viewpoint (iii) to characterize the residue obtained after decomposition of the MOF for exploring the further

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possibility of synthesizing CuO-NPs from this MOF. Here, we have synthesized a Cu-based MOF, {[Cu₂(2,5-pdc)₂(ald-4)(H₂O)₂].3H₂O, MeOH}_n, by solvent diffusion process and characterized it by single crystal x-ray diffraction (SC-XRD) technique. The thermogravimetric (TGA) analysis revealed that the framework decomposes at 550 °C. The powder x-ray diffraction (PXRD), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), energy dispersive x-ray spectroscopy (EDS) and dynamic light scattering (DLS) technique were employed to characterize the decomposed material obtained by sintering the MOF at 650 °C. It has been found that the decomposed material is CuO-NPs of uniform size (~27.9 nm) and spherical shape. Thus, the present MOF under investigation can be used as self-sacrificing precursor for synthesizing CuO-NPs. It is noteworthy that catalytic activity of MDMO-NPs toward green synthesis of organic compounds with biological relevance is yet to be explored. The main objective of the present work is to study the catalytic performance of the MOF derived CuO-NPs in the one-pot three component synthesis of α -aminonitriles (Scheme 1) under solvent-free condition.



Scheme 1. MOF derived CuO-NPs for the green synthesis of α -aminonitriles via Strecker

reaction under solvent free condition

EXPERIMENTAL SECTION

Materials and Methods. Out of the reagents used Copper (II) acetate monohydrate (99.99 %); pyridine-2,5-dicarboxylic acid (98 %) and aldrithiol-4 (98 %) were purchased from Sigma-Aldrich. All other chemicals used were AR grade. All chemicals were used as received without any further purification. Elemental analysis (C, H, N) was carried out using a Perkin-Elmer 240C elemental analyzer. The thermogravimetric analysis was carried out using a Mettler Toledo TG-DTA 85 thermal analyzer under constant flow of N₂ (30 ml/min). The sample was heated at a rate of 10 °C/min in an inert alumina crucible. The FTIR spectrum of the complex between 400 and 4000 cm⁻¹ was recorded by a Nicolet Impact 410 spectrometer using the KBr pellet method. Photoluminescence spectrum of the complex was collected by a Shimadzu RF-5301PC spectrophotometer. The transmission electron micrographs and the selected area diffraction (SAED) pattern were recorded by Jeol 2100 high resolution transmission electron microscope (HRTEM). The dynamic light scattering (DLS) experiment was performed by using SZ 100 nano Partica instrument. The FESEM micrographs were recorded by FEI INSPECT F50 field emission scanning electron microscope (FESEM). Elemental analysis for CuO-NPs was performed by BRUKER energy dispersive x-ray spectrometer (EDS) attached with the FEI FESEM equipment.

Sample Preparation.

Synthesis of $\{[Cu_2(2,5-pdc)_2(ald-4)(H_2O)_2] \cdot 3H_2O, MeOH\}_n$. The complex under investigation was synthesized via layering technique. Metal solution was prepared by dissolving 1 mmol Cu(OAc)_2 in 50 ml water and 50 ml (30 ml MeOH and 20 ml H_2O) ligand solution containing 1 mmol disodium salt of ligand 2,5-pyridine dicarboxylic acid and 0.5 mmol

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aldrithiol-4 was prepared separately. The metal and the ligand solution (v/v) were kept isolated in a layering tube by pouring a buffer solution of methanol and water in between them. After seven days deep blue needle shaped crystals suitable for single crystal x-ray diffraction study were obtained and collected. The product was characterized by single crystal x-ray diffraction (SCXRD) technique, C, H, N analysis and FTIR measurement. Yield ~70%. Anal. cald. for $C_{25}H_{28}Cu_2N_4O_{14}S_2$ revealed C: 37.52% (37.54% theo), H 3.54% (3.504% theo) and N: 7.1% (7.008% theo). IR (KBr pellet, cm⁻¹): 3238(s), 1667(s), 1565(s), 1473(w), 1396(s), 1372(s), 1280(w), 1130(w).

Synthesis of CuO and other metal oxide nanoparticles. The CuO-NPs were derived by heating the as synthesized {[Cu₂(2,5-pdc)₂(ald-4)(H₂O)₂]•3H₂O,MeOH}_n at 650 °C for 4 hrs in a muffle furnace in presence of air. Herein, the MOF acts as a self-sacrificing precursor for synthesizing CuO-NPs. It is pertinent to mention that we have tried to reduce the particle size by decreasing the sintering temperature but upon decreasing the sintering temperature the morphological uniformity gets lost while particle size reduces by 2-3 nm which is insignificant. The CuO NPs were characterized by FTIR, PXRD, HRTEM, SAED, EDS and DLS techniques. The IR bands (KBr pellet method) were obtained at 601(s), 508(s), 487(s) cm⁻¹ due to the vibrations of Cu(II)-O bonds. The details of synthesis procedure adopted for preparation of NiO, ZnO, Co₃O₄, SiO₂ and Fe₃O₄ NPs have been depicted in the supplementary information file. The PXRD patterns and the FESEM micrographs of these NPs are presented in Figures S1 to S10.

Methodology of Catalysis Test.

Materials. Aryl aldehydes, aryl amines, trimethylsilyl cyanide (TMSCN) and all other chemicals used in catalytic experiments were purchased from Merck chemical company and used

without further purification. All the products were characterized by measuring their melting points along with ¹H/¹³C NMR studies. The ¹H and ¹³C NMR studies were carried out by using a 300 MHz Bruker NMR spectrometer.

Catalytic Strecker reaction, Catalyst Separation and Product Isolation. A mixture of the aryl aldehyde (1 mmol), aryl amine (1 mmol), TMSCN (1.2 mmol) and CuO-NPs (10 mmol) was stirred at room temperature under solvent-free condition for appropriate time until the reactants got solidified (also indicated by thin layer chromatography (TLC)). All the as-synthesized α aminonitrile derivatives were solid. It may be noted that α -aminonitrile derivatives dissolve in ethanol while CuO does not. Therefore, after the completion of the reaction, 10 ml of ethanol was added to the reaction mixture to dissolve the solid product and this mixture was then ultracentrifuged. Finally, the solid part at the bottom of the ultracentrifuge tube and the liquid in the upper part of it were carefully separated by decanting. Afterwards, the product was isolated from the liquid part while the catalyst (CuO-NPs) was recovered from the solid residue. For getting the product the liquid part collected by decanting the centrifuged mixture was filtered again and vigorously sonicated to check the presence of any solid residue in it but no trace of any dispersed/suspended solid particles were found in the filtrate. Thereafter, this filtrate was kept in undisturbed condition up till (for few hours) the solvent (ethanol) got completely evaporated and pure crystals of the desired products were obtained. Thus, column chromatography is not required for the purification of the compounds produced in the catalytic reaction. On the other hand, to recover the catalyst the solid part settled at the bottom of the centrifuge tube during separation of the solid residue (in the first step of product and catalyst separation through ultracentrifugation) and the dissolved product was collected and then washed several times with

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ethanol and water, respectively. After that it was dried in vacuum oven keeping the temperature at 110 °C to recover the CuO-NPs for reusability test.

Primarily, the products obtained in catalytic reaction were identified by checking their melting points. Further, the compounds were analyzed by ¹H/¹³C NMR studies. The melting points and NMR data of all the compounds were in accordance with the corresponding results reported previously.

SCXRD Data Collection and Refinement. The SCXRD data of the complex was recorded by mounting a suitable single crystal of the complex on a Bruker SMART diffractometer equipped with a graphite monochromator, Mo-K α (λ = 0.71073 Å) radiation and CCD camera. The structure was solved by the Patterson method and followed by successive Fourier and difference Fourier synthesis. Full matrix least-squares refinements were performed on F² using SHELXL-97 with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were refined anisotropically and their locations were determined from the difference Fourier map. All calculations were carried out using SHELXS 97,⁵⁷ SHELXL 97,⁵⁸ PLATON 99,⁵⁹ ORTEP-32⁶⁰ and WinGX⁶¹ system Ver-1.64.

PXRD Data Collection and Refinement: The PXRD data of CuO-NPs were collected at ambient temperature (20 °C) by a Bruker D8 Advance diffractometer operating in the reflection geometry using Cu-K α radiation having wavelength 1.5418 Å. The generator voltage and current were set at 40 kV and 40 mA, respectively. The PXRD data were collected within 20 range of 20°–90° (step size 0.02°) at scan speed 6 s/step. The PXRD pattern of the sample was indexed by DICVOL06⁶² and TREOR90⁶³ of Fullprof.2 k⁶⁴ package. The Rietveld refinement of PXRD pattern was carried out using the GSAS⁶⁵ program with EXPGUI⁶⁶ interface. The peak shapes

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were assessed by pseudo-Voigt functions. The background was fitted by the shifted Chebyshev function of first kind with 20 points regularly distributed over the entire 20 range. Initially, the values of atomic coordinate and site occupancy were provided in accordance with JCPDS no. 80-0076 for CuO. In the beginning, the lattice parameters, profile parameters and background were refined. After few cycles of refinement, the atomic coordinates and isotropic thermal parameters were refined. At the final stage, preferred orientation correction was applied using the generalized spherical harmonic model. The Rietveld refinement yielded good fit with $R_p = 0.030$, $R_{wp} = 0.038$ and $\chi^2 = 1.04$. Further, the crystalline size and micro-strain of CuO-NPs have been obtained by analyzing PXRD pattern of the sample using MAUD 2.70⁶⁷ software package.

RESULTS AND DISCUSSION

Crystal Structure and Supramolecular of the MOF. Analysis of SCXRD data of the complex under investigation has revealed that it crystallizes in achiral P_{21}/n space group. Data collection conditions, refinement and structural parameters of the complex are provided in Table 1 and the values of selected coordination bond lengths and bond angles are listed in Table S1. The ORTEP diagram showing the asymmetric unit is presented in Figure 1. Each asymmetric unit contains two independent Cu(II) ions, two 2,5-pdc linkers, one aldrithiol-4 moiety and two coordinated water molecules together with guest water molecules and methanol. Each Cu atom shows five coordinated square pyramidal geometry. The N1 and O3 atoms of the 2,5-pdc ligand, N2 atom of the aldrithiol-4 ligand and O2 carboxylic oxygen atom of another 2,5-pdc ligand form the basal plane and the coordinated water molecule O1W is at the axial position for the Cu1 atom. Similarly, for Cu2, N4 and O5 atoms of one 2,5-pdc ligand form the basal plane and O2W water molecule is at the axial position. Here, the τ values of Cu1 and Cu2 are 0.09 and 0.02,

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respectively. This indicates a slight distortion in the square-pyramidal environment of Cu1 and Cu2 centers. The Cu-O bond distances vary in the range of 1.930 - 1.973 Å and Cu-N bond distances lie between 2.002 - 2.035 Å. The Cu1-O1W and Cu2-O2W bond distances are 2.241 Å and 2.225 Å, respectively.

The complex is a 2D coordination polymer. All carboxylate ligands of the complex bind two metal centers in μ_2 -bridging pattern. In both cases, the 2,5-pdc ligands bind one Cu(II) centre by using one nitrogen and one carboxylic oxygen atom as a chelating ligand and also connects a different Cu(II) center by its another donor carboxylic oxygen atom and in turn two different infinite 1D helical coordination chains, one pertaining to Cu1 and other pertaining to Cu2, are formed along crystallographic b-axis. The bidentate aldrithiol-4 links the adjacent Cu-2,5-pdc helical chains to form 2D coordination sheet, shown in Figure S11. The Cu•••Cu distances separated by aldrithiol-4 and 2,5-pdc are 10.581 Å and 7.49 Å, respectively. The π ••• π interactions among the pyridyl groups further stabilize the 2D coordination sheets (Figure S12). The π ••• π interaction parameters are presented in Table S2. These 2D coordination sheets are further connected by guest mediated supramolecular hydrogen bonding interactions (mainly O2W-H2W2···O6 and O1W-H2W1···O4) to form 3D supramolecular structure (Figure S13). The dimensions of hydrogen bonds are given in Table S3.

Helicity and Chirality. According to the space group consideration, this complex is achiral but composed of two neighboring 2D sheets of opposite chirality. The 2,5-pdc bridges the Cu(II) centers to form both 1D left handed and right handed infinite helical chains of $[Cu(pdc)]_{\infty}$ along b-axis with the pitch of 8.4867Å (Figure 2A and 3A). The dihedral angle between two dicarboxylato groups of 2,5-pdc ligands for Cu1 is 13.0°(9) and for Cu2 is 25.4°(8). The 2,5-pdc ligands help in formation of 1D helical chains. The aldrithiol-4 molecules join two adjacent chains in zigzag way to form 2D homochiral coordination sheets. Interestingly, only the left handed helical chains are connected by aldrithiol-4 ligands to form homochiral 2D coordination sheets (A) of left handed helicity, shown in Figure 2B. Similarly, another set of homochiral sheets (B) containing only right handed helical chains are formed. Thus, linear covalent interactions transfer similar stereochemical information between two neighboring chiral units. It is interesting to note that A and B sheets are related by inversion symmetry, Figure S14. The sheets are connected by linear hydrogen bonding interactions to form achiral 3D supramolecular structure. Therefore the linear supramolecular interactions develop inversion symmetry to transfer opposite chirality between adjacent homochiral sheets, and thus overall stereochemical property of the MOF becomes achiral in nature. In the 3D supramolecular framework sheets A and B are adjacent to each other and they are arranged in alternative manner.

Thermogravimetric Investigation. Thermogravimetric (TGA) analysis was carried out to study the thermal stability of the complex. The result shows that the complex is very stable in air at ambient temperature. The sample was heated up in flowing N₂ with a heating rate of 10 °C/min within the temperature range of 25 to 500 °C. The complex shows weight loss in three steps. The weight loss occurring between 50 and 135 °C corresponds to loss of solvent water, methanol and coordinated water molecules, loss of weight in the temperature range of 260 - 370 °C takes place due to loss of ligand (aldrithiol-4) and weight loss observed between 390 and 470 °C can be attributed to the release of 2,5-pdc (Figure S15).

Photoluminescence Study. The emission spectra of the complex were studied in solid state at room temperature. The complex shows emission maxima at ~ 377 nm with a shoulder at 291 nm (Figure S16) due to π - π * transition between the aromatic π -rings.

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Characterization of MOF Derived CuO-NPs. Herein, we have synthesized CuO-NPs of ~27.9 nm size by sintering the MOF at 650 °C for 4 hrs in a furnace in presence of air. Upon heating the blue compound turns to deep black powder which has been characterized by PXRD, HRTEM, SAED, DLS and EDS techniques (Figure 4, 5 and 6). Indexing of the PXRD pattern of the black powder suggests that it is single phase CuO belonging to monoclinic *C*2/c space group. The Rietveld refinement of the PXRD data has been carried out to analyze the crystal structure of this sample. The final Rietveld plot is displayed in Figure 4. The experimental and simulated patterns match well with each with good enough values of reliability parameters and the difference between the two curves is negligible. The results indicate that CuO-NPs are crystallized in monoclinic C2/c space group. The Miller indices and the space group obtained by the Rietveld structure refinement method are in good agreement with JCPDS data base (JCPDS No. 80-0076). The final crystallographic data, refinement parameters and fractional coordinates are given in Table S4 and S5. The Cu-O bonding network is shown in Figure S17.

The HRTEM micrograph of the NPs, presented in Figure 5, highlights well-defined NPs of spherical shape. The size of individual particles was found to be between 20 and 34 nm. The particle size distribution follows the log normal distribution function (Figure 6a) with $\sigma \sim 0.16$. The average particle size obtained by fitting the distribution histogram is ~ 27.5 nm which corroborates with the crystallite size (~ 26.7 nm) obtained by analyzing the PXRD pattern using MAUD 2.70 program. In the high magnification HRTEM image, well-defined lattice fringes indicating the highly crystalline nature of the sample have been clearly observed. The lattice fringes with lattice spacing 0.0277 nm corresponding to the {110} plane of CuO-NPs were seen in magnified HRTEM image. We have also carried out DLS study to assess the nature of particle size distribution. The results indicate that particle size ranges between 15 - 39 nm and the

average size of CuO-NPs is ~29.7 nm which is also in good agreement with the results of HRTEM analysis. Structural information about CuO-NPs has also been acquired from the SAED pattern. SAED image of the sample exhibits prominent rings confirming good crystalline nature of CuO-NPs. In the EDS survey spectrum of the sample (Figure S18), the only characteristic peaks for constituent elements (Cu and O) of the CuO-NPs were obtained. Thus, the results of PXRD, HRTEM and DLS studies together with confirmed that the sample obtained by decomposition of the MOF is single phase, highly crystalline, nearly mono-dispersed and spherical CuO-NPs.

Catalytic activity of the MOF Derived CuO-NPs. Synthesis of α -aminonitriles *via* Strecker reactions have achieved enormous importance as α -aminonitriles are very important intermediates in synthesis of various peptides and pharmaceutical products (e.g. saframycin A, ecteinascidin 743 and phthalascidin).⁶⁸⁻⁷³ Here, we have examined the catalytic activity of CuO-NPs toward synthesis of α -aminonitriles *via* one pot three component condensation of aldehyde, amines and trimethylsilyl cyanide.

When a mixture of benzaldehyde (1 mmol), aniline (1 mmol) and TMSCN (1.1 mmol) was stirred with CuO-NPs (10 mol %) in ethanol at room temperature – a high yield (84%) was obtained in 15 min, (Table 3, entry 2). The yield was decreased (72%) when the same reaction was carried out in water (Table 3, entry 3) and interestingly, higher yield (94%) of desired product was obtained within 4 minutes when the reaction was carried out under solvent-free condition (Table 3, entry 4). Lower yield of the product was obtained when the same reaction was carried out in acetonitrile, DCM, toluene and DMF (45-68%, Table 3, entry 5, 6, 7 and 8). In absence of the catalyst, no desired product was obtained even after 1 hour (Table 3, entry 1). Further, we have examined the catalytic response of NiO, ZnO, Co_3O_4 , SiO₂ and Fe₃O₄

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nanoparticles (synthesized by common chemical methods) under same reaction conditions to compare the catalytic response of CuO-NPs with these NPs. It has been found that the MOF derived CuO-NPs exhibit better catalytic activity compared to that of the other oxide NPs like NiO, ZnO, Co_3O_4 , SiO₂ and Fe₃O₄ under the same reaction conditions (Table 3, entry 10, 11, 12, 13 and 14).

Further, using the optimized reaction conditions, we have explored the utility of this methodology by synthesizing various α -aminonitrile derivatives using a variety of substituted aryl aldehydes and anilines (Table 2, entry 1-10). A number of aryl aldehydes with electron donating (*e.g.* –OMe, –Me, –Cl etc.) and electron withdrawing (*e.g.* –NO₂) groups were found to participate in the Strecker synthesis and no significant electronic effect was observed. All the reactions listed in Table 2 were very fast (culminates within 4-12 min) and produced well to excellent yield of desired products (87-94 %).

The formation of the desired compounds was initially tested by determining their melting points (Table 2). Further, all the compounds were characterized by spectroscopic (¹H NMR) method to confirm whether the desired product has been obtained or not (Figure S19 and S20). Physicochemical properties of all the products of catalytic reaction are well known. It has been found that the values of melting points of those compounds are identical with the reported values of the corresponding compounds and the ¹H NMR spectra of the compounds match perfectly with those of the same compound reported in literature. In order to compare the catalytic efficiency of CuO-NPs for the synthesis of α -aminonitrile derivatives, a comparative study of catalytic performance of the present catalyst with the reported ones is presented in Table 4 and it clearly indicates that the CuO-NPs mediated synthesis is better alternative to the existing protocols.

A plausible mechanism for the CuO-NPs catalyzed synthesis of α -aminonitriles has been presented in Scheme 2, where CuO-NPs promoted the in-situ formation of the imine intermediate (I) through activating the oxygen and nitrogen atom of the carbonyl and amine groups, respectively, followed by nucleophilic addition of cyanide to imine to give the desired product (Scheme 2).

Finally, the catalyst stability was investigated by checking its reusability. The reusability study was performed using the model reaction for the synthesis of **1a** (see Table 2) keeping the reaction condition unaltered. After each cycle, the CuO-NPs were recovered from the product following the procedure described in experimental section. The recovered catalyst (CuO-NPs) was successively reused for subsequent reactions. The results of reusability studies are presented in Figure 7. It was observed that even after the 10th cycle, the catalytic efficiency remained intact and a marginal (18%) loss in activity was observed.



Scheme 2. Plausible mechanism for CuO-NPs catalyzed synthesis of α -aminonitriles.

CONCLUSIONS

In summary, (i) we have successfully synthesized a Cu based MOF viz., ${[Cu₂(2,5$ pdc)₂(ald-4)(H₂O)₂]•3H₂O,MeOH}n by layering technique and characterized it by SCXRD, TGA and photoluminescence studies, (ii) the crystal structure and supramolecular structure of the MOF has been investigated in detail, (iii) highly defined spherical CuO-NPs were synthesized through combustion of the MOF, (iv) we have shown that these CuO-NPs serves as an excellent catalyst in green synthesis of α -aminonitriles – precursors of several important bio-molecules and (v) the MOF derived NPs exhibit superior catalytic activity compared to other common catalysts and MO-NPs synthesized by common chemical methods. Structural study on the complex have revealed that each discrete Cu-centers are connected by 2,5-pdc ligands to form both left handed and right handed infinite helical chains of [Cu(pdc)]_∞ along crystallographic baxis. These 1D chains are bridged by ald-4 ligands to form 2D coordination polymers and these 2D polymers are further extended by guest dependent hydrogen bonding interactions to form 3D supramolecular structure. Each 2D sheet is homochiral in nature whereas the structure contains two different types of 2D sheets of opposite chirality. Thus, the overall framework is achiral in nature. Here, the linear supramolecular hydrogen bonding interactions transfer opposite stereochemical information of adjacent coordination sheets to 3D framework. The regular arrangement of Cu within the MOF and presence of CuO bonds in the 1D helical chains of it allowed us to fabricate the single phase, highly crystalline, nearly monodisperse and spherical CuO-NPs utilizing the Cu-based MOF as self-sacrificing precursor. The PXRD, HRTEM, DLS and EDS were employed to characterize the CuO-NPs obtained by decomposition of the MOF at 650 °C. These MOF derived CuO-NPs are used for the catalytic synthesis of α -aminonitriles by Strecker reaction for the first time. By optimizing the reaction conditions, it has been established that the

MOF derived CuO-NPs exhibit excellent catalytic efficiency under solvent-free condition (in solid state) at a very fast reaction rate. Thus the MOF derived MO-NPs can be beneficially utilized in chemical industries as an excellent catalyst for synthesizing organic molecule of biological importance with enhanced productivity and reduced amount of chemical waste at low cost. In future, the alternative approach of deriving nanoparticles from MOF can be extended for fabrication of functional nanostructured ferrite from bimetallic-MOFs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:....

Synthesis procedure and characterization of NiO, ZnO, Co₃O₄, SiO₂ and Fe₃O₄ NPs, 2D-sheet, weak interactions and supramolecular architecture of the MOF, thermogravimetric and photoluminescence plots of the MOF, Cu-O bonding network and EDS spectrum of the CuO-NPs; results of NMR study, crystallographic data.

Accession Codes

CCDC no. of complex is 787145. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. This material is available free of charge via the Internet at http://pubs.acs.org.

The CCDC number 787145 is solely for the crystal structure of the compound reported in this article. This CCDC number (787145) has no relation with our earlier papers having DOI:

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10.1007/s10870-013-0449-3 and 10.1039/C0CE00505C wherein it was mentioned inadvertently. Correction in this regard for the first article has been published (please see: J Chem Crystallogr, DOI 10.1007/s10870-017-0702-2) and the correction for DOI: 10.1039/C0CE00505C will be published by the concerned journal very soon.

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Notes

The authors declare no competing financial interest.

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Table 1. Crystallographic data of the complex.

Crystal data	Complex
Formula	$C_{25}H_{28}Cu_2N_4O_{14}S_2$
Formula Weight	799.71
Crystal System	Monoclinic
Space group	$P2_1/n$ (No. 14)
a [Å]	17.0525(6)
b [Å]	8.4867(3)
c [Å]	22.6931(8)
α [°]	90
β [°]	111.708(2)
γ [°]	90
V [Å ³]	3051.23(19)
Z	4
D (calc) [g/cm ³]	1.741
M (MoKα) [/mm]	1.608
F (000)	1632
Crystal Size [mm]	0.08 x 0.10 x 0.12
Temperature (K)	293
Radiation [Å]	ΜοΚα 0.71073
Theta Min-Max [°]	1.3 and 24.2
Dataset	-19: 19; -9: 9; -26: 26
Total	24920
Unique Data	4886
R (int)	0.047
Observed $[I > 2.0 \sigma(I)]$	4739
Nref, Npar	4886, 425
R	0.0586
wR ₂	0.1581
S	1.12
Max. and Av. σ/esd	0.00, 0.00
Min. and Max. $\Delta \rho [e/Å^3]$	-0.95, 1.11

 $w = 1/[\sqrt{Po^2} + (0.0827P)^2 + 4.5781P]$ where $P = (Fo^2 + 2Fc^2)/3$



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Reaction conditions: aryl aldehyde (1 mmol), aniline (1 mmol), TMSCN (1 mmol), *t*-CuO-NPs (10 mol%, 12 mg) with continuous stirring at room temperature. ^a Yield refers to that of pure isolated products. ^b melting points was determined for the pure and recrystallized products.



	O NH2	+ TMSCN <u>cata</u> Solv	lyst CN vent	
Entry	Catalyst	Solvent	Time (min)	Yield (%) ^a
1	No catalyst	EtOH	60	00
2	CuO-NPs	EtOH	15	84
3	CuO-NPs	H_2O	30	72
4	CuO-NPs	Solvent-free	04	94
5	CuO-NPs	CH ₃ CN	30	68
6	CuO-NPs	DCM	30	62
7	CuO-NPs	Toluene	30	54
8	CuO-NPs	DMF	30	45
9	Bulk CuO	Solvent-free	30	37
10	NiO-NPs	Solvent-free	30	52
11	ZnO-NPs	Solvent-free	30	67
12	Co ₃ O ₄ -NPs	Solvent-free	30	58
13	SiO ₂ -NPs	Solvent-free	30	61
14	Fe ₃ O ₄ -NPs	Solvent-free	30	72

Reaction conditions: benzaldehyde (1 mmol), aniline (1 mmol), TMSCN (1.2 mmol), catalyst (10 mol%), solvent (1 ml) with continuous stirring at room temperature.

^a isolated yield.

Table 4. Results of comparative study of catalytic response of CuO-NPs and other known catalysts for synthesis of α -aminonitrile (1a)

	H + H +						
Entry	Catalyst (amount)	Solvent	Time (min)	(1a) Yield (%)	Ref.		
1	CuO-NPs (10 mol%)	solvent-free	4	94	This work		
2	MCM-41-SO ₃ H (5 mg)	EtOH	70	97	69		
2	PVP-SO ₂ (100 mg)	DCM	360	86	70		
3	B-MCM-41 (50 mg)	EtOH	120	96	71		
5	Cellulose sulfuric acid	MeCN	45	94	72		
	(50 mg)						
6	K ₂ PdCl ₄ (10 mol%)	H ₂ O	30	91	73		
7	Chitosan (6 mg)	solvent-free	10	95	68		

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Figure Caption

Figure 1. ORTEP diagram of the complex with 30% probability (* = -1/2-x, -1/2+y, 1/2-z; ** = -1/2-x, 1/2+y, 1/2-z; *** = 3/2-x, -1/2+y, 3/2-z).

Figure 2. (A) Left handed helical chain; (B) 2D sheets contains only left handed helical chains

(Green: Cu, Red: O, Brown: S, Blue: N, Cyan: C).

Figure 3. (A) Right handed helical chain; (B) 2D sheets contains only right handed helical chains

(Green: Cu, Red: O, Brown: S, Blue: N, Cyan: C).

Figure 4. Rietveld refinement of the PXRD pattern of the as-synthesized CuO-NPs.

Figure 5. HRTEM picture of CuO nano-spheres.

Figure 6. (a) Magnified HRTEM image, (b) SAED pattern, (c) Size distribution by HRTEM, (d)

Size distribution by DLS of CuO nano-spheres.

Figure 7. Reusability of CuO-NPs for the synthesis of α -aminonitrile derivative (1a).



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Table of Content



Single phase, highly crystalline, nearly monodispersed and highly defined spherical CuO nanoparticles having average particle size ~ 27.9 nm with uniform morphology derived from a new Cu-based achiral MOF composed of 1D helical chains exhibits excellent catalytic activity for the one-pot three component Strecker synthesis of α -aminonitriles *via* the condensation of benzaldehyde, aniline and TMSCN in solid state.