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Designed synthesis of CO$_2$ promoted copper(II) coordination polymers: synthesis, structural, spectroscopic characterization and versatile functional property studies†

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Introduction

In the modern age, global warming has resulted due to the key factors of uncontrolled burning of fossil fuel and excessive deforestation. CO$_2$ is known to be one of the biggest contributing partners of green house gas (GHG) family, to be checked, keeping in mind its major contribution in global warming. Extensive research works in this respect is taking place worldwide to reduce the concentration of CO$_2$ from air. In this regard very cheap, safe and easy to perform technique for fixation of CO$_2$ using suitable transition metal complex is a promising approach for utilization of CO$_2$ as raw material for preparing useful chemical feedstock. Mankind can be benefitted hugely in the future if CO$_2$ can be utilized as a raw material for production of robust functional material. A viable approach in carbon dioxide inclusion chemistry is the reduction of CO$_2$ in presence of suitable coordination complexes. Electrochemical reduction of electroactive materials on metal electrodes generally requires higher negative electrode potentials. The one electron reduction of CO$_2$ to [CO$_2$]$^-$ generally occurs at very high potential of -2.21 eV vs SCE. For conversion and ligation of CO$_2$ into metal centre it is always important to reduce its potential as much as possible and in doing so the main engineering is lying in the selection of properly chosen catalyst which can facilitate its reduction. Use of transition metal complexes as electrocatalyst towards the reduction reaction generally occurs at lower negative potential. Direct CO$_2$ incorporated useful chemical feedstock via transition metal complex mediation has hitherto been very less explored. Our concern is to understand the CO$_2$ inclusion chemistry in presence of low cost copper complexes and suitable solvent medium as catalyst.

In this present work our aim is to investigate CO$_2$ mediated reaction chemistry of several low cost copper complex precursors having redox active organic co-ligands as electron reservoir towards catalytic reaction. Reductive coupling of CO$_2$ molecules leads to oxalato bridged robust copper coordination polymers. Notably these coordination polymers have potential electrical conducting property.

Results and discussion

Synthesis and Characterization

The reaction of anhydrous CuCl$_2$ with bpy (1:1) in benzonitrile medium with CO$_2$ purging at room temperature yields upon the complex [Cu(bpy)(C$_2$O$_4$)$_2$]$_n$ (1). Reductive coupling of CO$_2$ to form oxalate dianion (C$_2$O$_4^{2-}$) may occur either via outersphere pathway using mercury or lead electrodes for electrocatalysis or via innersphere pathways using transition metal complex or anion radicals of aromatic hydrocarbons.

![Molecular view of the complex 1.](image)

Fig. 1 Molecular view of the complex 1. Hydrogen atoms are omitted for clarity. 1D chain propagation is directed by yellow arrow. Selected bond distances (Å) and angles (°) are given in Table S1, ORTEP is shown in Fig. S1 (ESI†).

In this case in presence of benzonitrile as catalyst, bpy acts as electron reservoir for the conversion of CO$_2$ to C$_2$O$_4^{2-}$. Gas...
flowing in presence of bpy first initiate 1e- reduction of [CO$_2$] to form [CO$_2^-$] which on further dimerisation form [C$_2$O$_4^{2-}$] due to the close proximity of [CO$_2^-$] species in starting Cu-bpy complex solution mixture, resulting formation of a 1D polynuclear chain [Cu(bpy)(C$_2$O$_4$)$_2$]$_n$ (1) (Fig. 1). We also perform the same reaction in presence of PPh$_3$ as a good σ donor to make the reaction more facile towards CO$_2$ incorporation. Unfortunately in presence of PPh$_3$ the yield of the reaction is even less (ca. 25%) rather than it is enhanced. Here, PPh$_3$ is directly participating in the reaction solution by forming [Cu(bpy)(PPh$_3$)$_2$]ClO$_4$ (1') which is confirmed by ESI-MS, ORTEP and FT-IR studies (see, Fig. S2, S3 and S11, Table S5, ESI†).

After picturing the Cu-bpy solution chemistry over CO$_2$ we are interested with another N, N donor synthesized ligand L$_1^1$ (N-phenyl(pyridin-2-ylamino)methyl)pyridin-2-amine). The molecular view of the ligand is shown in Fig. 2.

![Fig. 2 Molecular view of the ligand L$_1^1$ [H atoms are omitted for clarity]. Selected bond distances (Å) and angles (°) are given in supporting Table S2, ORTEP is shown in Fig. S4 (ESI†).](image)

An interesting result is obtained when we start with same starting material, anhydrous cupric chloride in presence of ligand L$_1^1$ in benzonitrile medium at room temperature in O$_2$ free CO$_2$ atmosphere, where CO$_2$ purging was continued for ~ 0.5 h. C-N bond activation followed by C-N bond cleavage reaction takes place in the ligand backbone and CO$_2$ promoted another complex [Cu(2-AMP)$_2$(C$_2$O$_4$)$_2$] (2) is formed (Fig. 3). Once again CO$_2$ to C$_2$O$_4^{2-}$ formation occurs where the truncated amino pyridine coligand working as an electron reservoir in presence of benzonitrile solvent as a catalyst in this whole transformation and produces [Cu(2-AMP)$_2$(C$_2$O$_4$)$_2$] (2).

![Fig. 3 Molecular view of the complex 2. Hydrogen atoms are omitted for clarity. 1D chain propagation is directed by yellow arrow. Selected bond distances (Å) and angles (°) are given in supporting Table S3, ORTEP is shown in Fig. S5 (ESI†). Apart from bpy and a cleaved ligand of L$_1^1$ containing Cu-coordination polymer, another CO$_2$ incorporated polymeric copper complex was also synthesized starting from a mononuclear copper complex [Cu(L$_1^1$)Cl] (3) (Fig. 4). The tripod ligand L$_2^2$ [2-(t-(2-pyridin-2-yl)ethyl)(pyridin-2-yI)methylamino)methyl]phenol was synthesized by literature method. For betterment of yield we always added 2-chloromethyl pyridine hydrochloride in excess. CO$_2$ mediated reaction of mononuclear tripod complex 3 in benzonitrile at room temperature will result an oxalato bridged Cu-dinuclear complex 4 containing cleaved L$_2^2$ ligand, L$_2^2'$ = 2-(pyridin-2-yl)-N-(pyridin-2-yl)methyl)ethanamine. Herein CO$_2$ to C$_2$O$_4^{2-}$ are formed in presence of several heterocyclic aromatic rings of L$_2^2$. These aromatic rings are working as electron reservoir similar to co-ligands of 1 and 2 in similar solvent medium for in situ oxalate generation. The di-nuclear oxalato bridged copper complex resulted in dissociation of one of its side arm in ligated L$_2^2$ due to JT distortion of copper(II) d$^5$ system. We were not fortunate enough to grow single crystal of dinuclear complex 4.

![Fig. 4 Molecular view of the complex 3. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) are given in supporting Table S4, ORTEP is shown in Fig. S6a (ESI†).](image)

However from solid as well as solution state material characterisation tools like FT-IR, Magnetic study, elemental analysis, FAB and ESI–MS study we are confirmed regarding its formation. [see, Fig. 5 and 9 (infra), Fig. S7-S8, Table S6 ESI†]. Moreover, TEM and sorption studies have shown it’s mesoporous nature with interesting sorption properties within it. 1 and 2 both are distorted octahedral in nature (Table S5, ESI†).

A mononuclear tripod complex of Cu(II) (3) having square pyramidal geometry is formed around central Cu$^{II}$ atom where a Cl atom and three nitrogen atoms from L$_1^1$ (two nitrogen atoms from two pyrido side arms and one central nitrogen) form the base of the pyramid with the O atom occupying the apical position. This type of geometry can be assigned based on the $\tau$ factors defined by Reedijk et al.$^{11}$ $\tau$ = 0 for a perfect square pyramidal geometry and $\tau$ = 1 for trigonal bipyramidal structure (here $\tau$ = 0.068, less distorted square pyramidal geometry).

A schematic representation of all the CO$_2$ promoted reactions starting from simple anhydrous CuCl$_2$ with different co-ligands are depicted in scheme 1:

**FT-IR Study**

IR spectra of all the polynuclear Cu(II) coordination complexes shows the presence of all characteristics bands for coordinated ligands with $\nu_{C=O}$ appearing in the ranges 1590-1640 and...
CuCl$_2$(anhydrous) \[ \begin{align*}
[\text{Cu(bpy)}(\text{C}_2\text{O}_4)]_n & \quad \text{(1)} \\
[\text{Cu(2-AMP)}_2(\text{C}_2\text{O}_4)]_n & \quad \text{(2)} \\
[\text{Cu(L}^2\text{)(Cl)}] & \quad \text{(3)} \\
\text{CO}_2 & \quad \text{Benzonitrile medium} \\
\text{L}^1 \quad \text{CO}_2 & \quad \text{Benzonitrile medium} \\
\text{L}^2 & \quad \text{(4)} \\
\end{align*} \]

Scheme 1 CO$_2$ promoted polynuclear complex fabrication.

1400-1600 cm$^{-1}$ respectively. The characteristic stretching frequencies of C$_2$O$_4^2-$are coming in the expected region of 1630-1665 cm$^{-1}$ for complexes 1, 2 and 4. Here we are showing IR for 1 and 4 in Fig. 5. The stretching of C$_2$O$_4$ group in case of complex 4 is coming at ~1633 cm$^{-1}$, which bolster our prediction about fixation of CO$_2$ in form of C$_2$O$_4^2-$in complex 4 (vide Fig. S7-S8 ESI†, Fig. 9). A detailed description of IR studies are described in supporting information (see, Fig. S9-S11 and frequency details ($\nu$, cm$^{-1}$) in text ESI†).

**Powder XRD study**

Powder XRD study of (a) 1, (b) 2 and (c) 4. Small angle X-ray Powder diffraction studies do not show any powder diffraction characteristics of mesoporous material for complex 1 and 2. For complex 4 high intensity diffraction peak was observed (Fig. 6), which reflects ordered meso and very small micro structure in this material. Some sort of crystallinity observed with a slight shift of peak to the low angle(20) implies the presence of porosity in 4. Quadrupolar interaction of CO$_2$ with the unsaturated Cu centre may be the driving force for the formation of such porous complex.

**Nanostructure and porosity studies**

In Fig. 7a HR TEM image of the representative complex 4 is shown. As seen from these images that the complex is composed of very tiny nanoparticles of dimension ca. 12-15 nm. Low electron density white spots or pores at the interparticle spaces of dimensions ca. 4-5 nm are seen throughout the specimen. SAED pattern shown in Fig. 7b suggest that there are diffraction spots corresponding to the crystalline planes. Adsorption/desorption isotherm of the complex 4 is shown in Fig. 7c. This isotherm can be classified as type IV corresponding to those of mesoporous materials. From the N$_2$ sorption isotherms the BET surface area for 4 is found to be 240 m$^2$g$^{-1}$ and a total pore volume of 0.318 cm$^3$ g$^{-1}$. Pronounced desorption hysteresis suggests the existence of large mesopores in this material. This hysteresis is an intermediate between typical H1 and H2-type hysteresis loop, which originates in the P/P$_0$ range from 0.50 to 0.85. This result suggests that large uniform mesopores with a cage like pore...
structure could exist. Pore size distribution of 4 employing non
local density functional theory (NLDFT) is shown in Fig. 7d. An
observed peak maximum from this isotherm was at 4.34 nm.
Interparticle porosity could be the origin of this mesopores.
Pore width at around 1.47 nm is responsible for its microporous
feature which can also be discernible at very low relative pressure
in the nitrogen adsorption/desorption isotherm (P/P0 < 0.01) (Fig.
7c).

Magnetic study

The metal complexes 1, 2 and 4 are the end product of CO2
inclusion reaction. Though Cu(II) polynuclear chains are not very
prospective candidate from magnetoo chemical point of view, but
as these coordination polymers have been produced as a result of
CO2 inclusion chemistry, it is always interesting to observe the
effect of bridging C2O4 at each paramagnetic Cu(II) centre of 1, 2
and 4. Magnetic properties of 1 and 2 as shown are Tm vs T plot
in Fig. 8 (the magnetic data are reported for one Cu ion). At room
temperature the Tm value is ~0.4 cm2 mol-1 K, for both
complexes, which is close to the expected magnetic moment for
one uncoupled Cu(II) ion. This value remains practically constant
upon cooling until ~60 K and further increases continuously to
reach 0.78 cm2 mol-1 K, for 1 and 0.62 cm2 mol-1 K, for 2 at 2 K.
This behaviour is characteristic of a ferromagnetic interaction
between the Cu(II) ions in the one dimensional system. The experimental Tm data were analysed with the numerical
expression proposed by Baker and Rushbrooke[16] for a
ferromagnetic uniform chain:

\[
\chi M^2 = (N g^2 \beta^2 / 4 k)(1.0 + 5.7979916 x^6 + 16.902653 x^5 + 29.376885 x^4 + 86.6538644 x^3 + 14.036918 x^2 + 0.757825 x + 29.832959 x)
\]

where x = J/ kT. Least-squares fit of the experimental data lead to the following values J = 0.77 cm-1, g = 2.09 and R = 9.10x10-5
for 1 and J = 0.44 cm-1, g = 2.07 and R = 1.62x10-5 for 2.

Fig. 8 Plot of the thermal variation of \( \chi M T \) vs T for
(1) (A) and (2) (O). The solid lines are the best fit to the
experimental data.

The ferromagnetic coupling found in 1 and 2 are weak in nature
and correspond to a case of accidental orthogonality between the
interacting magnetic orbitals through the out-of-plane exchange
pathway. The Cu(II) ions show an elongated coordination
octahedral, with a parallel disposition of the Jahn-Teller axes
along the chain. The unpaired electron on each Cu(II) ion is
located in a d_{2s2} type metal centered magnetic orbital [the x and
y axes being roughly defined by the Cu-N bonds] which is
positioned in the equatorial plane and the two magnetic orbitals
are parallel to each other and perpendicular to the C2O4 plane of
the octahedra (scheme 2). According to the Khan’s model[17],
the magnetic coupling constant J has two contributions, a
ferromagnetic contribution \( J_F \) and an antiferromagnetic
contribution \( J_A \), that depends on the overlap between the
magnetic orbitals. For complexes 1 and 2, due to the parallel
disposition of the magnetic orbitals, the antiferromagnetic
contribution could be negligible and a weak ferromagnetic
behavior is observed. Several C2O4-bridged Cu(II) complexes
having the out-of-plane exchange pathway have been reported in
the literature; Table 1 collects the magneto-structural data of
these complexes. Analogous complexes to 1 and 2 have also been
reported in the literature[18,19], however, due to the different
synthetic route these complexes show small structural
differences, that influence to the magnetic coupling. Complexes 1
and 2 show weaker ferromagnetic coupling than the analogous
compounds reported in the literature. \( \chi M T \) vs T plot for complex 4
is shown in Fig. 9 (the magnetic data are reported for one Cu
ion). At room temperature the \( \chi M T \) value is ~0.4 cm2 mol-1 K,
close to the expected value for one uncoupled Cu(II) ion. This
value remains practically constant upon cooling until ~30 K and
further decreases continuously to reach 0.26 cm2 mol-1 K at 2 K.
This behaviour is characteristic of an antiferromagnetic
interaction between the Cu(II) ions, and suggests the presence of
a bridging ligand between the Cu(II) ions. The experimental
data fit well with the equation of Bonner and Fisher[20] for a
one-dimensional system with antiferromagnetic coupling:

\[
\chi M T = (N g^2 \beta^2 / k)((0.25 + 0.074975 x + 0.075235 x^2) / (1.0 + 0.9931 x + 20.97 x^2 + 120 x^3))
\]

where x = J/kT. Least-squares fit of the experimental data lead to the following values J = -1.04 cm-1, g =
2.11 and R = 3.04x10-5.
The weak antiferromagnetic interaction suggests a parallel
disposition of the two Cu-centered magnetic orbital’s which are
perpendicular to the C2O4 bridging ligand. Unfortunately, it was
not possible to obtain enough quantity of pure compound of 3
to measure the magnetic data. However, the crystal structure of
this compound shows a mononuclear complex with distances between
two neighboring Cu(II) ions of 4.5 Å and the distance of one
Cu(II) ion and the Cl ligand of the other entity is 3.7 Å. These
data suggest that the magnetic interaction between the
mononuclear complexes could be expected to be negligible.

Scheme 2 A schematic representation of the interaction between
the magnetic orbitals in the C2O4-bridged Cu(II) fragments of 1
and 2.

Fig. 9 Plot of the thermal variation of \( \chi M T \) vs T for 4.
The solid line is the best fit to the experimental data.
Table 1 Selected magneto-structural data for C$_2$O$_4$-bridged complexes having the out-of-plane exchange pathway

<table>
<thead>
<tr>
<th>Complexes</th>
<th>d(Cu-O$_{ax}$)</th>
<th>h$_{Cu}$</th>
<th>$\beta^\circ$</th>
<th>$\phi^\circ$</th>
<th>d(Cu-$\cdots$Cu)</th>
<th>$J$</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>[[Cu(bpy)(C$_2$O$_4$)]2H$_2$O]$_n$</td>
<td>2.31</td>
<td>0.034</td>
<td>108.3</td>
<td>86.8</td>
<td>5.56</td>
<td>2.4</td>
<td>18</td>
</tr>
<tr>
<td>[[Cu(bpy)(C$_2$O$_4$)]H$_2$O]$_n$</td>
<td>2.31</td>
<td>0.035</td>
<td>108.6</td>
<td>83.8</td>
<td>5.55</td>
<td>0.77</td>
<td>This work</td>
</tr>
<tr>
<td>[Cu(2-ampy)(C$_2$O$_4$)]$_n$</td>
<td>2.38</td>
<td>0.02</td>
<td>107.8</td>
<td>75.6</td>
<td>5.63</td>
<td>2.0</td>
<td>19</td>
</tr>
<tr>
<td>[Cu(2-amp)(C$_2$O$_4$)]$_n$</td>
<td>2.39-2.37</td>
<td>0.01</td>
<td>108.8</td>
<td>83.2</td>
<td>5.65</td>
<td>0.44</td>
<td>This work</td>
</tr>
<tr>
<td>[Cu(3-ampy)(C$_2$O$_4$)]$_n$</td>
<td>2.17</td>
<td>0.0</td>
<td>111.0</td>
<td>85.2</td>
<td>5.46</td>
<td>-1.3</td>
<td>19</td>
</tr>
<tr>
<td>[Cu(4-ampy)(C$_2$O$_4$)]$_n$</td>
<td>2.35</td>
<td>0.0</td>
<td>109.7</td>
<td>88.7</td>
<td>5.66</td>
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<tr>
<td>[Cu(isq)(C$_2$O$_4$)]$_n$</td>
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<td>0.06</td>
<td>109.5</td>
<td>88.5</td>
<td>5.48</td>
<td>0.63</td>
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<tr>
<td>[Cu(py)]$_2$(C$_2$O$_4$)]$_n$</td>
<td>2.27</td>
<td>0.0</td>
<td>108.0</td>
<td>80.0</td>
<td>5.46</td>
<td>1.4</td>
<td>20</td>
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<tr>
<td>[[NMe$_2$][Cu(C$_2$O$_4$)]$_2$H$_2$O]$_n$</td>
<td>2.38</td>
<td>0.04</td>
<td>106.9</td>
<td>79.1</td>
<td>5.59</td>
<td>1.14</td>
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</tr>
<tr>
<td>[Cu$_2$(bpca)]$_2$(C$_2$O$_4$)]$_n$</td>
<td>2.26</td>
<td>0.16</td>
<td>107.5</td>
<td>92</td>
<td>5.44</td>
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<td>[Cu$_2$(bpca)]$_2$(H$_2$O)]$_2$(C$_2$O$_4$)]$_2$H$_2$O</td>
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<tr>
<td>[Cu$_2$(bpcam)]$_2$(H$_2$O)]$_2$(C$_2$O$_4$)]$_2$H$_2$O</td>
<td>2.44</td>
<td>0.0</td>
<td>106.6</td>
<td>101.8</td>
<td>5.68</td>
<td>0.75</td>
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</tr>
</tbody>
</table>

5 Abbreviations of the ligands: bpy: 2,2-bipyridine; py: pyridine; 2-ampy: 2-aminopyridine; 3-ampy: 3-aminopyridine; 4-ampy: 4-aminopyridine; isq: isoquinoline; bpca: bis(2-pyridyldicarbonylamidate; bpcam: bis(2-pyrimidylcarbonylamidate. 6 Value of the axial Copper to oxalate-oxygen. 7 The height of the Cu atom from the equatorial plane. 8 Bond angle at the axial oxalate-oxygen (Cu–O–C). 9 Dihedral angle between the equatorial and C$_2$O$_4$ planes.

Electrical Property study

The dc electronic properties of all the CO$_2$ inclusion polynuclear complexes [1, 2 and 4] along with the mononuclear complex 3 have been measured in the temperature range 298-373 K. Fig. 10a shows the variation in ln $\rho$(T) with 1000/T. It is evident from the Fig. 10a that all the compounds behave like semi conducting materials i.e., their resistivity decreases with the increase of temperature. The activation energy of all the investigated compound have been estimated by using the Arrhenius equation

$$\rho(T) = \rho_0 e^{E_a/RT}$$

where $\rho_0$ is the resistivity at infinite temperature, $E_a$ is the activation energy, and $k$ is the Boltzmann constant. The activation energy “$E_a$” can be calculated from the slopes of the straight line plot of ln $\rho$(T) with 1/T. For 1 the activation energy is found to be 0.56 eV and for 2 it is 0.04eV where as it is found that there are two different slopes for the 3 and 4, i.e two different activation processes are present in these complexes. The activation energy for lower temperature regions is 1.16 eV for complex 3 and 0.2 eV for complex 4. On the other hand the activation energy at higher temperature region are 3.35 eV and 1.69 eV for 3 and 4 respectively. Fig. 10b shows the variation of dielectric permittivity with frequency. The dielectric properties of the compounds have been measured in the frequency range 20 Hz-2MHz at 323 K and found that it depends on both the grain resistance and interfacial grain boundary resistance. It is also observed from the Fig. 10b that the dielectric permittivity is larger at low frequency regions and it decreases at higher frequency regions. This is because at higher frequency regions, the mobility of charge carriers is low and cannot follow the alternation of the applied alternating electric field. A large degree of dispersion occurs because of charge transfer within the interfacial diffusion layers present between the electrodes, confirmed by the sharp increase at low frequencies.

Fig. 10a and 10b. Conductivity studies of 1, 2, 3, 4 and L$^1$.

Conclusion

In the present work we have unveiled the chemistry of CO$_2$ promoted reactions of a series of low cost mononuclear copper(II) coordination complexes starting from selectively chosen heterocyclic multidentate ligands. The electrochemical reduction of CO$_2$ to one e$^-$ reduced intermediate [CO$_2$$^-$] requires very large negative potential due to its inertness. The presence of suitable metal complexes in aprotic solvent as electrocatalyst can easily drop down the high negative potential of the redox reaction. Moreover presence of redox non-innocent multidentate ligands as electron reservoir helps insitu generated copper-V coordination from CO$_2$. Carbon-di-oxide promoted reaction yields upon oxalato bridged polynuclear complexes 1 and 2 and dinuclear complex 4. The most salient feature is that during CO$_2$ mediated inclusion reaction, internal electron transfer takes place in the system involving several C-N bond breakings in the co-ligand backbones (L$^1$ and L$^2$) as well as bond making i.e. dimerization of [CO$_2$$^-$] to [C$_2$O$_4$$^-$]. Additionally, one of those insitu generated copper-coordination polynuclear complexes, is a mesoporous material and has shown interesting N$_2$ sorption properties. In a wide temperature range all the Cu polynuclear materials exhibits interesting semiconducting behavior. Constant research in this endeavor is under active progression in quest of advanced and effective transition metal polymerization catalysts for utilization of CO$_2$ like GHG.
Experimental

Materials
All solvents and chemicals used for synthesis were of analytical grade. Chemicals e.g.; benzoic acid, 2,2'-bpy, 2-amino pyridine, salicylaldehyde were purchased from Spectrochem and used without further purification. 2-chloromethyl pyridine hydrochloride, 2-(2-pyridyl)methylamine, triethyl amine are purchased from Aldrich. Analytical grade acetonitrile, methanol, dichloromethane, DMF were purchased from Fluka and used without further purification. BOC make XL grade Argon and Carbon dioxide gas were used.

Instrumentation
A perkin Elmer 2400C elemental analyser was used to collect the microanalytical (C, H, N) data. UV-Vis spectroscopy was done on ALS SEC 2000 and Varian (Model Cary 100 Bio) spectrophotometer. IR spectra were carried out in a Perkin Elmer FT-IR spectrometer (spectrum 65) (Using KBr pellets). Powder X-ray diffractometry (XRD) patterns of different complexes were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni-filtered Cu Kα (λ = 0.15406 nm) radiation. N2 adsorption/desorption isotherms of the complex were recorded at 77 K on a Quantachrome Autosorb-1C. Prior to measurement, the samples were degassed at 373 K for 8 h under high vacuum conditions. Transmission electron microscopy (TEM) images of the mesoporous material were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. The samples were prepared by dropping 2 μL of respective colloidal solution onto carbon-coated Copper grids. ESI-MS spectra were recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263). Advion compact mass spectrometer (serial number: 3013-0140) and FAB-MS (Jeol JMS700). Magnetic susceptibility measurements between 2-300 K were carried out in a SQUID magnetometer, MPMS Quantum Design Magnetometer, at the Unitat de Mesures Magnètiques (Universitat de Barcelona). Two different magnetic fields were used for the susceptibility measurements, 200 G (2-5 K) and 3000G (2-300 K), with superimposable graphs. Pascal’s constants were used to estimate the diamagnetic corrections for the compounds. The fit was performed by minimizing the function \[ R = \sum [(ZrT)_\text{exp} - (ZrT)_\text{calc}]^2 / \sum (ZrT)_\text{exp}^2. \]

For electrical measurements the powder was taken in a steel mould of 1 cm diameter and compacted at a pressure of 5 tons/cm². Silver paint electrodes (supplied by Acheson Colloiden B.V., Holland) were applied on two opposite faces. Direct-current (dc) conductivity was measured by an 8 1/2 digit Agilent 3458A multimeter. The temperature dependence of conductivity was measured in a furnace with a Eurotherm 8502 temperature controller. The ac measurement was done by HP4902A Impedance Analyzer.

Syntheses of complexes

[Cu(bpy)(C₂O₄)]₄ (1): An equimolar mixture of bpy (156 mg, 1 mmol) and CuCl₂ (135 mg, 1 mmol) were dissolved in 50 mL methanol and the mixture was allowed to stir for 2 hours at room temperature. Initially a light green colored precipitate was developed, which on further addition of AgClO₄ (415 mg, 2 mmol) changes to intense blue along with a precipitate of AgCl. After removal of the solvent by evaporation under reduced pressure, the dry residue was taken in 50 mL benzonitrile solvent and transferred to a 100 mL capped glass stirrer vessel of Buchi miniclavve steel. CO₂ gas purging during next ~ 0.5 h at room temperature was continued to produce light blue colored CO₂ inclusion polynuclear complex. This material on prolonging inside an argon glove box fridge (~5°C) for ~12 h produce single crystals of [Cu(bpy)(C₂O₄)]₄ (1). Yield: 255 mg, 75%. Anal. calcld. for C₁₅H₁₀N₆O₄Cu: C, 41.88%; H, 3.49%; N, 8.14%. Found: C, 42.05%; H, 3.36%; N 58.04%. Characteristic IR Peaks (KBr disk, υ, cm⁻¹): 1652(s), 1089(br), 1447(s), 773(s), 730(s), 626(s). UV/Vis peaks, λmax nm(e, M¹ cm⁻¹): 215 (20550), 245 (12950), 300(14550), 700(25).

[Cu(bpy)(PPh₃)₂ClO₄] (1): Under the same reaction condition as of complex 1, during CO₂ purging for ~ 0.5 h at room temperature, excess PPh₃ (790 mg) was added to the solution mixture. Prolong standing of the crude product over 10 h in an argon blanketeting atmosphere yielded X-Ray quality single crystals of [Cu(bpy)(PPh₃)₂ClO₄] (1) in reasonably good yield along with less proportion of complex 1. Yield: 531 mg, 63%. Anal. calcld. for C₃₀H₂₄CuN₄P₂ClO₄: C, 65.42%; H, 4.50%; N, 3.31%. Found: C, 65.37%; H, 4.43%; N, 3.41%. Characteristic IR Peaks (KBr disk, υ, cm⁻¹): 1593(s), 1480(s), 1437(s), 1092(s), 747(s), 695(s), 622(s), 514(s), 488(s). UV/Vis peaks, λmax nm(e, M¹ cm⁻¹): 240(25060), 400(3154).

[Cu(2-AMP)₂(C₂O₄)₂] (2): L¹ (276 mg, 1 mmol) and CuCl₂ (135 mg, 1 mmol) in presence of NET₃ (280 μL, 2mmol) were dissolved in 50 mL benzonitrile and allowed to stir for 1 hour at room temperature. The reaction mixture was transferred to a 100 mL capped glass stirrer vessel of Buchi miniclavve steel and concomitant CO₂ purging during ~0.5 h produces a light green colored crude product. X-Ray single crystal single crystals were obtained from a concentrated solution of benzonitrile at ~5°C. Yield: 245 mg, 72%. Anal. calcld. for C₁₅H₁₀N₆O₄Cu: C, 42.38%; H, 3.53%, N, 16.48%. Found: C, 42.28%; H, 3.48%, N, 16.42%. Characteristic IR Peaks (KBr disk, υ, cm⁻¹): 1646(s), 1632(s), 1594(s), 1566(s), 1497(s), 1452(s), 1311(s), 1263(s), 1167(s), 796(s), 763(s). UV/Vis peaks, λmax nm(e, M¹ cm⁻¹): 280(11100), 310(10210).

[Cu(L¹)(Cl)] (3): Room temperature reaction of CuCl₂ (135 mg, 1 mmol) and L¹ (320 mg, 1 mmol) in presence of NET₃ (140 μL, 1mmol) in 50 mL MeOH with constant stirring for 3 hour produces complex 3. Slow evaporation of solution mixture at room temperature yields single crystals of complex 3 suitable for X-Ray study. Yield: 488 mg, 90%. Anal. calcld. for C₂₀H₁₄N₃CuO₄Cl: 747(s), 695(s), 622(s), 514(s), 488(s). UV/Vis peaks, λmax nm(e, M¹ cm⁻¹): 215(19000), 260(18500), 600(9).

Complex (4): Complex (3 (543 mg, 1 mmol) was taken in 50 mL benzonitrile inside a glass stirrer vessel of Buchi miniclavve steel and CO₂ purging during ~0.5 h forms greenish blue crude product. The microcrystalline complex 4 were obtained by recrystallization from benzonitrile solution. Unfortunately X-Ray quality single crystals were not obtained. Yield: 554 mg, 69%. Anal. calcld. for C₃₀H₂₄N₆O₄CuCl₂: C, 51.06%; H, 4.30%; N, 12.26%. Found: C, 50.95%; H, 4.30%; N, 12.39%. Characteristic IR Peaks (KBr disk, υ, cm⁻¹): 1633(s), 1609(s), 1451(s), 1157(s), 1021(s), 763(s). UV/Vis peaks, λmax nm(e, M¹ cm⁻¹): 205(23500), 260(12600), 600(20).

X-Ray Structure Determination
Crystallographic data for the complexes 1, 1’, 2, 3 and 1’ are collected in Table S1-S5 in ESI†. All data were collected on a Bruker SMART Apex-II diffractometer equipped with graphite
monochromated Mo Kα radiation (λ = 0.71073 Å). Corrections were done for Lorentz-polarization effects. For complex 1: A total of 6459 reflections were collected, out of which 3087 were unique (Rint = 0.081), satisfying the (I > 2σ(I)) criterion, and were used in subsequent analysis. For complex 1*: A total of 29280 reflections were collected, out of which 6423 were unique (Rint = 0.056), satisfying the (I > 2σ(I)) criterion, and were used in subsequent analysis. For complex 2: A total of 6866 reflections were collected out of which 1171 were unique (Rint = 0.064), satisfying the (I > 2σ(I)) criterion, and were used in subsequent analysis. For complex 3: A total of 15481 reflections were collected out of which 4042 were unique (Rint = 0.024), satisfying the (I > 2σ(I)) criterion, and were used in subsequent analysis. There were 1171 were unique (Rint = 0.064), satisfying the (I > 2σ(I)) criterion, and were used in subsequent analysis. Th ere were 2417 were unique (Rint = 0.081), satisfying the (I > 2σ(I)) criterion, and were used in subsequent analysis.

† Electronic Supplementary Information (ESI) available: [Crystallographic details and ORTEP diagram of 1, 1', 2, 2', 3 and 3', ESI and FAB-MS data, CHN analysis, FT-IR, UV-Vis data for all the compounds are included in supporting information.] See DOI: 10.1039/b000000x/

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Notes and references


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Designed synthesis of CO₂ promoted copper(II) coordination polymers: synthesis, structural, spectroscopic characterization and versatile functional property studies†

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196×151mm (96 x 96 DPI)