Copper nano composites functionalized by bis-benzimidazole diamide ligand: Effect of size, co-anion dependent conductivity and band gap studies

Manisha Singlaa, Subash Chandra Mohapatrab, Sharif Ahmadb,∗

a Dept. of Chemistry, University of Delhi, New Delhi, India
b Dept. of Chemistry, Jamia Millia Islamia, New Delhi, India

HIGHLIGHTS

► Nano composites of copper, capped by bis benzimidazole diamide ligand.
► Such copper nano composites have not been used in conductivity studies before.
► Conductance studies for these thus make this work unique.
► The dc conductivity of these composites is much higher than normal.

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ABSTRACT

Copper (I) and copper (II) nano composites capped with a bis-benzimidazole diamide ligand were prepared by reverse micelle method and characterized using CHNS, FTIR, 1H NMR, TEM and DLS studies. All particles were spherical ranging between 10 and 70 nm. They displayed a quasi reversible redox wave due to the Cu (II)/Cu (I) reduction process. The E° values shift anodically as NO3− < Cl− < SCN−. Electrochemical HOMO and LUMO band gap (Eg) for the nano composites were +1.80 (NO3−), +2.80 (Cl−) and +4.10 (SCN−) eV, respectively. However, the optical band gap (Eg) for the nano composites was calculated from their absorption edges and lie between 1.77 and 4.13 eV. Fluorescence studies reveal that nano composites in themselves behave as an enhancer and quencher in respect to ligand. Quantum yield (ϕ) is varying from 0.008 to 0.02 photon. The activation energies range from 34 to 54 kJ mol−1 and are quite low in comparison to that of the free bis-benzimidazole diamide ligand (137 kJ mol−1). The lower activation energies further re-emphasize the nano size of these composites. At room temperature, the dc conductivity lies between 1 × 10−4–9.33 × 10−4 S cm−1 [NO3− > SCN− > Cl−] indicating them to be on the semiconductor insulator interface. The dielectric constant, dielectric loss and the ac conductivity were measured for all nano at room temperature and below the room temperature for the nano composite containing nitrate as co-anion. The conductivity was found to follow the correlated barrier hopping (CBH) mechanism; the exponent factor (s) varies from 0.5 to 1.

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1. Introduction

Metal nano particles have gained considerable interest due to their potential applications in diverse fields including catalysis, electronics and magnetic media recordings [1]. Copper is the most widely used material in the world due to its cost effective electrical applications. Copper Nano particles have been synthesized and characterized by many different methods. Stability and reactivity make them much reliable and encourage their use and development in new generation of nano electronic devices [2–5]. Among the various methods used for synthesis of nano materials, surfactants play an important role as stabilizers and size controllers [6–21].

Use of suitable surfactants prevents surface oxidation by protecting the outer surface of metal nano-particles other than those of silver and gold. They also control nucleation of particles and thus act as particle growth terminators. Recently, a number of articles have appeared describing the synthesis of copper nano-particles by various methods [21].

Transition metal nano materials have gained a lot of attention because of their technical applications in areas of material science, catalysis and nano electronics [22,23]. Size dependent magnetic and electrical properties are important for the utilization of these...
materials as magnetic/electrical devices [24,25]. These nano particles exhibit superior properties than those of their bulk materials. They also show a high catalytic activity as heterogeneous catalysts [26]. Ac conductivity measurements are extensively used to characterize electrical properties of various materials and help in the understanding of the nature of conduction mechanism [27]. Dielectric loss is a manifestation of the fundamental properties of a crystalline and amorphous semiconductor material [28]. The temperature dependence is analyzed in terms of phonon frequencies participating in the corresponding electron—phonon interaction [29].

In molecular material science, there is a current trend to combine physical properties such as magnetism and electrical conductivity in a synergetic way [30] and development is expected to lead to material of high technical interest.

Measurement of ac conductivity, dielectric constant and dielectric loss of semiconductors has been extensively used to understand the conduction process [31,32] and it is a powerful tool for obtaining information about the defect states in amorphous semiconductors. Various models such as the quantum mechanism tunneling (QMT) model [33,34] and correlated barrier hopping (CBH) model [35] have been proposed to explain the ac conduction mechanism. In the correlated barrier hopping (CBH) model the electronic conduction is via bipolaron or mixed polaron hopping process [36].

In this work, copper metal salts are being capped by an organic moiety forming stable nano coordination compounds or nano composites. Till now copper nano composites have not been used for size and co- anion dependent study of conductivity, and the correlation of band gap studies with conductivity, TGA and Cyclic voltammetry of copper nano composites. All surface and bulk properties of nano composites were found to be enhanced as compare with those of normal transition metal coordination compounds, thus distinguishing them into a new class of hybrid compounds.

2. Experimental

2.1. Materials

Glycine benzimidazole dihydrochloride and ligand, N,N'-bis (2-methyl benzimidazolyl)benzene-1,3-dicarboxamide were prepared following the procedure reported earlier [37]. Freshly distilled solvents were employed for all synthetic purposes. Spectroscopic grade solvents were employed for spectral works. All other chemicals were of AR grade.

2.2. Physical measurements

Transmission Electron Microscopy (TEM) were obtained from USIC, Delhi University, Delhi, India (JEOL 2000 EX electron microscope operating at 200 kV) and TEM micrograph of SCN− containing Cu (I) nano composite were obtained from All India Institute of Medical Sciences (AIIMS) (Philips Morgagni 268 electron microscope, Megaview III Focus, 1100×, 80 kV).

The light scattering experiments were performed on a Photocor FC. All the measurements were done at a scattering angle of 90° at temperature of 20 °C.

IR spectra of these nano composite particles were obtained in the solid state as KBr pellets on a Perkin Elmer FTIR-2000 spectrometer. The thermogravimetric analysis was performed on a Diamond TG-DTA, Perkin Elmer; USA, system on well ground samples with a heating rate of 10 °C min−1 from room temperature to 600 °C. Elementary analysis were obtained from USIC, University of Delhi.

Cyclic voltammograms of all the composites were performed on Micro auto lab type III (M3AVT 70762) and recorded in DMSO/DMF solution with 0.1 M TBAP as a supporting electrolyte. A three-electrode configuration composed of Pt−disk working electrode, a Pt wire counter electrode, and an Ag/AgNO3 reference electrode was used for measurements. The reversible one-electron Fc+/Fc couple has an E1/2 of 0.145 V versus an Ag/AgNO3 electrode.

1H NMR was taken on a 300 MHz Bruker instrument in d6-DMSO. Fluorescence studies were carried out on FL3-11, Fluorolog-3 spectrophotometer at IIT, New Delhi.

The dielectric measurements were carried out in a frequency range 100 Hz–1 MHz at room temperature using an Agilent-LCR meter in the metal−insulator−metal (MIM) capacitor configuration. The electrical measurements were done on the powdered sample in the form of a pellet. The composite was finally ground and the resulting powder was compressed into a pellet of 13 mm diameter and 1 mm thickness under a pressure of 5 tonnes cm−2.

The pellet was then silver electrode on both sides with a layer of silver paint. The dc conductivity of the nano composite pellet so obtained was studied using Keithley 236 source measure unit. The dielectric measurements were carried out in a frequency range 100 Hz–1 MHz and over a temperature range 150 K–300 K using an Agilent-LCR meter in the metal−insulator−metal (MIM) capacitor configuration. The temperature dependent dielectric studies were carried out using a specifically designed three terminal sample cell. The LCR meter directly provided the values of capacitance (C) and dielectric loss (tan δ). Other parameters like dielectric constant (ε’) and the ac conductivity (σ ac) were completed using:

\[
ε’ = \frac{Ct}{ε_0A}
\]

\[
σ ac = 2πfε_0ε’\tan δ
\]

where f is the frequency (Hz) of the applied electric field.

2.3. Synthesis

2.3.1. Preparation of the ligand

N,N'-bis (2-methyl benzimidazolyl)-benzene-1,3-dicarboxamide (L)

The bis benzimidazolide diamide ligand, N,N'-bis (2-methyl benzimidazolyl)-benzene-1,3-dicarboxamide C2H2O2:1.25H2O (L), was synthesized by using procedures reported earlier [37]. It was characterized by 1H NMR and IR spectral studies. This multidentate ligand has been utilized to functionalize the copper metal ions to generate the new nano composites.
CHN Data: 64.3 (65.1) 5.2 (4.9) 19.0 (19.0).

UV (MeOH): $\lambda_{\text{max}}$ (e): 282 (4.32); 276 (4.34).

NMR spectra: ($d_6$-DMSO) $\delta$(ppm): 9.27 (Amide NH); 8.54 (s, 1H) 8.13–8.11 (d, 2H) 7.63–7.58 (t, 1H); Benzene H linker adjacent to C=O; 7.45–7.54 (m, 4H) 7.14 (q, 4H); Benzene (H), of benzimidazole group; 4.7 (d, 4H): CH$_2$ linked to benzimidazolyl group.

IR spectra: $\nu$(OH): 3390; $\nu$(NH (amide)): 3290; $\nu$(NH (benzimidazole)): 3159; $\nu$(C=O (amide-I)): 1643; $\nu$($\text{C}=\text{N}$ (amide-II)): 1530; $\nu$($\text{N}+\text{C}=\text{C}$ (benzimidazole)): 1481; $\nu$(C=C (benzene)): 739.

2.3.2. Preparation of the nano composites using CTAB as surfactant 2.3.2.1. Synthesis of copper (II) nano composite containing nitrate as co-anion [LCu(NO$_3$)$_2$]. It was prepared using the reverse micelle route, for which two micro-emulsion systems (I and II) were prepared. Micro emulsion I, comprised of cetyl trimethyl ammonium bromide (CTAB) as the surfactant, n-butanol as the co-surfactant, iso-octane as the hydrocarbon phase, conductivity water and 0.417 mmol of the diamide ligand (GBBA). Similarly, a micro emulsion II, was prepared which consisted of the same constituents as micro emulsion I excepting that instead of the diamide ligand GBBA, it had 0.417 m mol of a Cu(NO$_3$)$_2$·3H$_2$O. The weight fractions of the various constituents utilized in these micro emulsions are: 16.66% of CTAB, 17.70% of n-butanol, 57.4% of iso-octane and 8.1% of the aqueous phase. The two micro emulsions were mixed together very slowly and stirred over night using a magnetic stirrer. This method has been reported earlier [21]. Green precipitate so obtained was separated from the apolar solvent and surfactant by centrifuging and was thoroughly washed with HPLC grade chloroform. The compound so obtained was then air dried and used without any further purification.

Yield: 155 mg, (53%).

IR (cm$^{-1}$): 3380 ($\nu$(H$_2$O)), 3235 ($\nu$(NH amide)), 3140 ($\nu$(NH benzimidazole)), 1630, 1616 ($\nu$(C=O amide-I)), 1552 ($\nu$($\text{C}=\text{N}$ amide-II)), 1452 ($\nu$($\text{N}+\text{C}=\text{C}$ benzimidazole)), 747 ($\nu$(C=C benzene)), 1384 ($\nu$(O=C=O sym stretch))

UV–vis: $\lambda_{\text{max}}$ (nm, log $\epsilon$) in methanol: 276 (4.14), 282 (4.12), 700 (1.65).

Elemental analysis (%) calc. for Cu(C$_{24}$H$_{20}$N$_6$O$_2$)(NO$_3$)$_2$·H$_2$O: C 45.75, H 3.49, N 17.79; found: C 45.50, H 3.39, N 17.20.

2.3.2.2. Synthesis of copper(II)–L nano composite containing chloride as co-anion [LCuCl$_2$]. This preparation was similar to that reported for nitrate, only instead of copper (II) nitrate, copper (II) chloride

**Fig. 1.** a: TEM picture of NO$_3^-$ containing Cu (II) nano composites. b: TEM picture Cl$^-$ containing Cu (II) nano composites. c: TEM picture of SCN$^-$ containing Cu (I) nano composite.
was taken. Green precipitate so obtained was separated from the apolar solvent and the surfactant by centrifuging and thoroughly washed with HPLC grade chloroform. The compound so obtained was air dried and used without any further purification.

Yield: 160 mg, (63%).

IR (cm\(^{-1}\)): 3390 (\(\nu_{\text{H}_2\text{O}}\)), 3240 (\(\nu_{\text{NH \ amide}}\)), 3160 (\(\nu_{\text{NH benzimidazole}}\)), 1635, 1621 (\(\nu_{\text{C-O amide-I}}\)), 1557 (\(\nu_{\text{C-N amide-II}}\)), 1450 (\(\nu_{\text{C=C benzimidazole}}\)), 737 (\(\nu_{\text{C=C benzene}}\)).

UV\textvis: \(\lambda_{\text{max}}(\text{nm, log e})\) in methanol: 276 (4.12), 282 (4.08), 690 (1.69).

Elemental analysis (%) calc. for Cu\((\text{C}_2\text{H}_2\text{O}_2\text{N}_6\text{O}_2)\text{Cl}_2\text{H}_2\text{O}\): C 50.04, H 3.82, N 14.59; found: C 50.12, H 3.74, N 14.52.

2.3.2.3. Synthesis of copper (I)–I nano composite containing thiocyanate as co-anion [LCuI(SCN)]. For the preparation of this nano composite, CuCl\(_2\)·2H\(_2\)O was first converted to Cu(SCN)\(_2\). A solution of KSCN in MeOH was added dropwise to the solution of CuCl\(_2\)·2H\(_2\)O (0.48 mmol) in 5 ml MeOH, till there was no further precipitation. A green precipitate was obtained after \(\frac{1}{2}\) h of slow stirring of solution-mixture in a septum sealed three neck flask. A solution of quinol (0.48 mmol) in methanol (10 ml) was then transferred under nitrogen, via a double end needle, to the solution. Immediate color change from peacock green to pale yellow was observed. Stirring for 10 min resulted in a white solid that was filtered off, washed with methanol and air-dried. This compound was prepared with similar method by using two micro emulsions each containing 0.48 mmol ligand and respective Cu\(_4\)(SCN)\(_2\)·2H\(_2\)O salt with mixing together. The compound so obtained was air dried and used without any further purification.

Yield: 170 mg, (61%).

IR (cm\(^{-1}\)): 3400 (\(\nu_{\text{H}_2\text{O}}\)), 3264 (\(\nu_{\text{NH amide}}\)), 3152 (\(\nu_{\text{NH benzimidazole}}\)), 1668, 1640 (\(\nu_{\text{C=O amide-I}}\)), 1510 (\(\nu_{\text{C=N amide-II}}\)), 1455 (\(\nu_{\text{C=C benzimidazole}}\)), 742 (\(\nu_{\text{C=C benzene}}\)). 2106 cm\(^{-1}\) (\(\nu_{\text{S=C=N stretch}}\)), 846 cm\(^{-1}\) (\(\nu_{\text{C=N stretch}}\)).

UV\textvis: \(\lambda_{\text{max}}(\text{nm, log e})\) in methanol: 272 (4.35), 282 (4.30), 300 (3.80).

Elemental analysis (%) calc. for Cu\((\text{C}_2\text{H}_2\text{O}_2\text{N}_6\text{O}_2)\text{SCN}\text{H}_2\text{O}\): C 53.23, H 3.90, N 17.39; found: C 53.41, H 4.02, N 17.47.

3. Results and discussions

The copper nano composites are green and white in color corresponding to the Cu(II) and Cu(I) states respectively.

3.1. Transmission Electron Microscopy (TEM) and dynamic light scattering (DLS)

TEM images show a spherical distribution of the nano composites (Fig. 1a, b, c). The average sizes of the composites were found to be 10 nm for LCu(NO\(_3\))\(_2\) (for the copper nano composites with NO\(_3^-\) as the co-anion) and 50–55 nm for LCu(SCN)\(_2\) (for the copper nano composites with SCN\(^-\) as the co-anion) respectively.

Fig. 2. a: Size distribution plot for the copper (II) nano composites [LCu(NO\(_3\))\(_2\)]. b: Size distribution plot for the copper (II) nano composites [LCu(SCN)]. c: Size distribution plot for the copper (II) nano composite [LCuCl\(_2\)].
However, LCuCl₂ (nano composites with Cl⁻ as the co-anion) shows poly dispersity varying in the range 60–90 nm. The dynamic light scattering experiments (Fig. 2a, b, c) gave the same range of size in liquid state and agreed with TEM results in solid state. The above trend corroborates with dynamic light scattering experiments however, the hydration sphere was found to be smaller for the particles of nitrate bound nano composite than the other nano composites.

3.2. UV–visible spectroscopy

The electronic spectra were recorded in MeOH. The electronic spectrum of the ligand (L) had two strong bands in the UV region 276–282 nm which were assigned to the π−π* transition characteristic of the benzimidazole group. Two peaks were observed in the range 276–282 nm for the nano composites with extinction coefficients (log e) ranging from 4.09 to 4.17. These peaks correspond to the π−π* transition in the –C=–N−C=– system of the benzimidazole group (these bands are slightly blue shifted with lowered extinction coefficient as compared to the ligand) [37]. A broad, much less intense d–d band was observed in the region between 650 and 750 nm indicating the presence of Cu (II) ion, which is coordinated with the ligand (L), while a shoulder at 300 nm was observed for the Cu (I) nano composite due to LMCT. In general, these bands are due to the overlapping transition and dyz, zx → dx² − y² and dxy → dx² − y². The low energy of the d–d transition suggests severely distorted tetragonal copper (II) nano composite solids in the solution state. As a matter of fact, copper chloride gives d transitions suggests severely distorted tetragonal copper (II) nano-particles exists in the solution state. The above trend corroborates with dynamic light scattering experiments (Fig. 2a, b, c) gave the same range of size in liquid state and agreed with TEM results in solid state. The above trend corroborates with dynamic light scattering experiments however, the hydration sphere was found to be smaller for the particles of nitrate bound nano composite than the other nano composites.

3.3. 1H NMR spectra

To ascertain the oxidation states of copper in the Nano composites synthesized, 1H NMR of the pale-white colored nano composite (with SCN⁻ as the co-anion) was taken. This nano composite gives well defined 1H signals which have been compared with the free ligand, (L).

The 1H NMR spectrum of the free ligand (L) [37] shows signals for aliphatic and aromatic protons with theoretically predicted splittings. A signal was observed between 9.27 ppm corresponding to N—H amide proton; while multiplets in the range 7.1–7.8 ppm arise due to the benzimidazole ring protons characteristic of an AA’BB’ pattern. The linker benzene ring protons were found at 7.5, 8.1 and 8.5 ppm for the ligand. The –CH₂— group adjacent to the benzimidazole ring gives rise to a doublet between 4.2 and 4.9 ppm due to coupling with the adjacent amide NH protons.

In the 1H NMR spectrum of the nano composite synthesized using SCN⁻ as the co-anion, shifted signals were observed with the loss of splittings (Fig. 3(a)). Some of the 1H signals were found to be downfield shifted as compared to the free ligand (L). These include the NH proton at 9.41 ppm instead of 9.27 ppm, the benzimidazole ring protons which appear at 7.28 ppm instead of 7.17 ppm and the methylene protons that appear at 4.8 ppm instead of 4.7 ppm. Protons of the linker benzene show only a very slight shifting. Loss of splitting, downfield shifting and slight broadening is indicative of slight paramagnetic surroundings which confirms that copper in the nano-particles exists in the +1 oxidation state [38]. The green colored nano-particles did not give rise to 1H NMR spectra under identical conditions, confirming that the oxidation state of these nano particles is +2.

3.4. Fluorescence studies

The fluorescence spectra of the ligand N,N'-bis (2-methyl benzimidazolyl)-benzene-1,3-dicarboxamide and its Copper(II/1) nano Composites were obtained in HPLC grade dimethylformamide; the solutions were purged with pure dry N₂ gas in order to take the spectra, are shown in Fig. 3(b). The quantum yields were calculated by comparison of the spectra with that of anthracene (φ = 0.292) taking the area under the total emission φ and λ (265–500 nm). Data for the same are as follows:

![Fig. 3.](image-url)
The fluorescence spectrum of 7 μM solution in DMF for ligand (L) shows two groups of two bands each, one group (F1) arising between 310 and 400 nm, while the other arising between 400 and 500 nm (F2). The short wavelength fluorescence bands within (F1) shows red shifted with respect to simple benzimidazole and bis benzimidazole. The fluorescence quantum yield of the present ligating system is similar to that reported for bis benzimidazole but quite higher than for same of the nitrogen containing fluorophores, implying that the lone pair of the benzimidazole nitrogen could only be weakly involved in photo induced electron transfer (PET) to the aromatic fluorophore. The fluorescence spectra of the copper (II) complexes of ligand (L) show only very slight shift in the λmax of the bands in 300–500 nm region, as compared to the ligand. However, the total area under the curve between this wavelength region do change. This change is reflected in the quantum yields as reported in. The quantum yields have been calculated by utilizing the formula [38]:

\[
F_{\text{rel}} = \frac{(F_0 - F)}{F_0}
\]

where \(F_0\) = fluorescence intensity of the free ligand, \(F\) = fluorescence intensity of the complex.

The \(\Phi_{\text{rel}}\) values for the composites are −1.5 for the [Cu(L)(NO₃)₂] complex, 0.75, 0.87 for the [Cu⁺¹(L)(SCN)], [Cu(L)Cl₂] composites. The results suggest that in the ligand (L), the benzene ring acts as a quencher of fluorescence obtained due to the benzimidazole moiety. Within the Cu (II) composites series, it appears that the Cu (II) ligand system senses the effect of the bound anion, i.e. NO₃⁻, SCN⁻ and Cl⁻.

3.5. Infrared red spectroscopy

The free ligand (L) shows characteristic single IR bands at 1644 cm⁻¹, 1530 cm⁻¹ and 1441 cm⁻¹ (Fig. 4). These are assigned to amide I (mainly \(\nu_{\text{C=O}}\) amide stretch), amide II (mainly \(\nu_{\text{C-N}}\) amide stretch) and benzimidazole \(\nu_{\text{C-N \ C}}\) stretching frequencies, respectively. The benzene ring vibrations appear at 739 cm⁻¹ (due to benzimidazole ring) and at 699 cm⁻¹ (linker benzene ring). The ligand (L) has a strong and sharp IR band at 3357 cm⁻¹ confirming the presence of water and a band at 3157 cm⁻¹ which is assigned to stretching mode of \(\text{P-N-H} \text{ benzimidazole}\).

The green colored nano composites of Copper(II) show an IR spectrum wherein the amide I band is split into two sharp bands and shifted at 1630, 1616 cm⁻¹; while the amide II and

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]

where \(\epsilon\) = extinction coefficient; comp: compound, anth: anthracene

Ligand(L): \(\phi = 0.0080\),
[Cu(L)(NO₃)₂]: \(\phi = 0.020\)
[Cu⁺¹(L)(SCN)]: \(\phi = 0.0020\)
[Cu(L)Cl₂]: \(\phi = 0.0010\)

The fluorescence spectra of the Cu (II) nano composites of ligand with chloride and thiocyanate as the exogenous anions were similar to that of the free ligand except for a red shift and a change in the vibrational features. The fluorescence quantum yield was found to be lowest for the chloride bound composite (\(\phi_f = 0.0010\)) and highest for the nitrate bound (\(\phi_f = 0.02\)) with respect to the free ligand (L) (\(\phi_f = 0.0080\)) due to small size and uniformity of structural pattern of composites. This suggests that the chloride and the thiocyanate composites quench fluorescence while the nitrate composite enhances it, which may be attributed to the different geometries of the compound. A significant change is observed in the relative fluorescence intensity. The relative fluorescence intensity change is given by:

\[
F_{\text{rel}} = \frac{(F_0 - F)}{F_0}
\]

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]

where \(\epsilon\) = extinction coefficient; comp: compound, anth: anthracene

Ligand(L): \(\phi = 0.0080\),
[Cu(L)(NO₃)₂]: \(\phi = 0.020\)
[Cu⁺¹(L)(SCN)]: \(\phi = 0.0020\)
[Cu(L)Cl₂]: \(\phi = 0.0010\)

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]

\[
\phi = 0.292 \times \left(\frac{\text{Area}_{\text{comp}}}{\text{Area}_{\text{anth}}}\right) \times \left(\frac{\text{\(\nu_{\text{anth}}\)}}{\text{\(\nu_{\text{comp}}\)}}\right)
\]
benzimidazole ($r_C=\equiv N-C=\equiv C$) bands are shifted to 1552 and 1452 cm$^{-1}$ respectively for the compounds containing the co-anions nitrate and chloride respectively. The benzene ring vibration found for the free ligand at 739 cm$^{-1}$ is shifted to 747 cm$^{-1}$ for the above mentioned nano coordination compounds.

For the pale white colored nano composite with the SCN$^{-}$ as the co-anion the amide I band is again split at 1668 cm$^{-1}$ and 1640 cm$^{-1}$ while the amide II appears at 1510 cm$^{-1}$. It is interesting to note that in this Cu (I) nano composite, the amide I is shifted to higher energy while the amide II is shifted to lower energy in contrast to the green colored Cu (II) nano composites. The splitting and shifting of the amide I and amide II bands has been assigned to the binding of the amide functionality to the copper ions. Similarly, benzimidazole, $r_C=\equiv N-C=\equiv C$ vibrational band is shifted from 1441 cm$^{-1}$ to 1455 cm$^{-1}$, while the benzene ring vibrations appear at 749 cm$^{-1}$ [21,38].

The presence of nitrate and the thiocyanate anions in the respective nano composites is justified by the presence of strong IR bands at 1384 cm$^{-1}$ ($\rho_O-N-D$ sym stretch) and 2106 cm$^{-1}$ ($\rho_S-N$ stretch), 846 cm$^{-1}$ ($\rho_C-N$ stretch), respectively. Thus the IR data clearly reveals that the copper ions are bound to the bis benzimidazole ligand in the Nano-composites.

3.6. Thermogravimetric analysis

The thermal analysis of the ligand shows an endothermic peak at 100 °C with a weight loss of 5.5% in comparison to that of the nano composite with NO$_3^-$. Cl$^-$ and SCN$^-$ ions as the co-anions which show 2%, 1% and 1% weight loss respectively. These mass losses can be attributed to the removal of water. Mass loss of the ligand, nitrate, chloride and thiocyanate bound nano composites, in the temperature range of 100–200 °C are 8 w%, 2 w%, 1 w% and 1 w% respectively. This can also be correlated to the decomposition of H-bonded water molecules in the lattice, which is further supported by the presence of an endothermic peak in DTA (Fig. 5).

Mass loss in temperature range from 200 to 300 °C of nitrate, chloride and thiocyanate bound nano composites were found to be 61 w%, 77 w% and 69 w% respectively in contrast to 2 w% loss for the ligand. At 300–500 °C mass loss of nano composites were 19 w% (for the composite with NO$_3^-$ as co-anion), 10 w% (for the composite with Cl$^-$ as co-anion), 25 w% (for the composite with SCN$^-$ as co-anion), while, for the free ligand 86.5 w% loss is observed (Fig. 5). These mass losses can further be attributed to the loss of the ligand moiety into two phases, first the loss of benzimidazole moiety and second the loss of carbonyl derivative of isophthalic acid. The rest of the mass loss of the nano composites reveal the formation of CuO, which is confirmed by the presence of an exothermic DTA peak, while the ligand shows complete decomposition (100 w%) up to 500 °C. For a further comparison, when thermograms were taken under identical conditions for the copper (II) coordination compounds synthesized normally i.e. not under reverse micellar conditions, the mass losses between 100 and 300 °C were 26 w% for the compound with NO$_3^-$ as co-anion, 10 w% for the compound with Cl$^-$ as co-anion and 15 w% for the copper (I) compound with SCN$^-$ as co-anion. Thus the thermograms clearly indicate that these Nano composites are quite different not only from the free ligand but also from the copper(II) and copper (I) coordination compounds synthesized under normal conditions. The activation energies and order of decomposition in the temperature region 100–500 °C were calculated for the free ligand and the Nano composites using Freeman Caroll and Coat’s methods. They were found to be 137 kJ mol$^{-1}, 0.3$ for the bis benzimidazole ligand (L), 34 kJ mol$^{-1}, 0.7$ for copper(II) nano composite with NO$_3^-$, 36 kJ mol$^{-1}, 0.5$ for copper(II) nano composite with Cl$^-$ and 54 kJ mol$^{-1}, 2.5$ for copper(I) nano composite with SCN$^-$ as the co-anion [39–41]. Lower activation energies reveal the nano size and smaller grain size of the above composites. But in case of [LCu$^+$(SCN)] nano composite activation

Fig. 5. TGA curve of the a) the ligand, (L); b) NO$_3^-$ containing Cu (II) nano composites; c) Cl$^-$ containing Cu(II) nano composites; d) SCN$^-$ containing Cu(I) nano composites.
energy has more than the other two nano composites due to +1 oxidation state of copper with SCN⁻ as co-anion avails extra stability of nano composite and thus enhanced the activation energy.

3.7. Electrical measurements

The current–voltage (I–V) characteristics of the prepared nano composite samples were measured at room temperature as shown in Fig. 6a. A linear increase in the current with the applied voltage was observed for all the samples and found to follow the relation \( I \propto V^n \). The measured value of exponent ‘n’ was found to be 1.0 for all the samples indicating the ohmic nature of the electrodes. The value of the room temperature dc conductivity \( \sigma_{dc} \) was estimated for all samples at a fixed bias voltage of 25 V. The value for \( \sigma_{dc} \) for the nano composites containing nitrate, chloride and thiocyanate as the co-anions was found to be \( 9.33 \times 10^{-4} \) S cm⁻¹, \( 1 \times 10^{-4} \) S cm⁻¹ and \( 6.9 \times 10^{-4} \) S cm⁻¹ respectively, and is typical of semiconductors [42]. It is important to note that, the dc conductivity of the nitrate nano composite is approaching to one order higher than that of the chloride nano composite, both having Copper in (II) oxidation state. This shows the importance of the nature of anion used for the preparation and thus the conductivity changes from a semi conductive range to lower metallic range. The rapid increase of electrical conductance could be understood within the frame work of electric transport in semiconductors that have potential barriers at their grain boundaries. The smaller the grain boundary the higher the contact between inter particle necks and lower is the net resistivity.

The dielectric constant (\( \varepsilon \)) and the ac conductivity (\( \sigma_{ac} \)) of the prepared samples has been studied as a function of frequency over a wide range of 100 Hz–1 MHz at room temperature.

The variation of dielectric constant (\( \varepsilon \)) as a function of frequency is shown in Fig. 6b. The value of \( \varepsilon'(\omega) \) decreases gradually with increase in frequency. The observed increase in the dielectric constant at lower frequencies may be attributed to the fact that dipoles have enough time to orient themselves along the electric field. It is interesting to note from the fig. 5b that the behavior of \( \varepsilon'(\omega) \) with frequency is almost similar in nano composites having Cu(II) and NO₃⁻ and Cl⁻ as anions. However, the dielectric constant of nano composites with Cu (I) (SCN⁻ anion) exhibit large frequency dispersion.

The log–log plot of ac conductivity (\( \sigma_{ac} \)) with frequency is shown in the Fig. 6c. It is clear from the figure that conductivity increases with an increase in the frequency and can be expressed as

\[
\sigma(\omega) = A\omega^s
\]

where \( A \) is a constant, \( \omega \) is the angular frequency & \( s \) the frequency exponent.

The value of the exponent ‘s’ is determined from the slope of the log–log plot. The slope of the plot between ac conductivity and the frequency are the values of ‘s’ for all prepared samples and lie in the range of 0.5–0.6. The nano composites having Cu(II) (having Cl⁻ and NO₃⁻ as anions) have \( s \sim 0.6 \) and \( \sigma_{ac} \) follows the power law in the entire measured frequency range (100 Hz–1 MHz). The lower value of \( s \sim 0.5 \) obtained for Cu(I) nano composite (with SCN⁻ anion) may be due to the change in oxidation state of copper.

3.7.1. Electrical measurements in the temperature range 153 K–293 K

The dependence of dielectric constant (\( \varepsilon \)), dielectric loss (\( \tan \delta \)) and the ac conductivity (\( \sigma_{ac} \)) on temperature and frequency of the applied ac field is studied in the temperature range 153 K–293 K and frequency range of 100 Hz–1 MHz the results are described as follows:

i) Dielectric studies:

The variation of dielectric constant and dielectric loss as a function of frequency is shown in Figs. 7 and 9a,b respectively and that as a function of temperature is shown in Fig. 8. Both \( \varepsilon' \) and \( \tan \delta \) values decrease gradually with increase in frequency. This is

![Fig. 6. a: Plot of log I vs. log V for all nano composites. b: Plot of log dielectric constant vs. log f for all nano composites. c: Plot of log ac vs. log f for all nano composites.](image-url)
a normal dielectric behavior and can be attributed to the polarization mechanism. There are four primary mechanisms of polarization in materials i.e. dipolar or oriental, electronic, ionic or atomic and space charge or interfacial polarization. At low frequencies, all the mechanisms of polarization contribute but as frequency increases the contributions from different polarizations start decreasing. The observed increase in the dielectric constant at lower frequencies may be attributed to the interfacial/space charge polarization. This polarization may be due to blocking of charge carriers at an electrode—dielectric interface when migrated under the influence of an electric field. The dielectric constant increases with increasing temperature suggesting that the relaxation frequencies of the dispersion increases with increasing temperature and as a response, moves to higher frequencies; appearing as an apparent increase in $\varepsilon'$ at a fixed frequency. This increase with the increase in temperature also refers to the polarization related to the thermal motion of electrons, facilitating the orientation of the electrons as the temperature increases.

ii) ac conductivity:

The log ac vs. log $f$ plots at different temperatures are shown in the Fig. 10 and the plot of ac conductivity with temperature in Fig. 11. It is clear from the figure that conductivity increases with frequency and can be expressed as:

$$\sigma(\omega) = A \times (\omega)^{\gamma} \quad \text{where} \quad \omega = 2\pi f.$$

The value of the exponent $\gamma$ is found by calculating the slope of the plot of log ac vs. log $f$. this exponent is used to characterize the electrical conduction mechanism in different materials. It is indicative of interaction between all the charge species participating in the polarization process. The $\gamma$ factor decreases with the increase in temperature. This decrease can be accounted for by a model given by Pike according to which the temperature variation of $\gamma$ is given by:

![Fig. 7. Plot of dielectric constant vs. frequency at different temperature.](image)

![Fig. 8. Plot of dielectric constant with temperature at different frequencies.](image)

![Fig. 9. (a): Plot of dielectric loss with frequency at different temperatures. (b): Plot of dielectric loss with temperature at different frequencies.](image)

![Fig. 10. Plot of the ac conductivity with frequency at different frequencies.](image)
(1 - s) = 6 kT/W_m

where W_m is the potential barrier.

The plot of (1 - s) as a function of temperature is shown in Fig. 12. According to this equation, the plot of (1 - s) vs. T should pass through the origin. The dependence of 's' on temperature may be explained by many-body interaction model. At high temperature, the interaction between the neighboring dipoles is negligible and the dc is to be dominant. The exponent 's' is less than unity due to the charges with extrinsic dipoles which arise from the presence of defects in the sample. The exponent decreases with temperature as the interaction between the dipoles decreases the value of W_m was calculated from the dependence of (1 - s) vs. T curve and was found to be 82.7232 × 10^{-5} eV.

At a given temperature, the magnitude of conductivity is high at higher frequencies, thereby supporting the correlated barrier hopping (CBH). This can be explained in terms of the hoping frequency between the localized states at the Fermi level. The base lies on the fact that there is a phonon assisted tunneling from a localized state to another one.

The following equation which describes the simple frequency stimulated hops is only a good numerical presentation of the more exact Austin–Mott formula:

$$\sigma_{ac} = (\pi/3)e^2 K_B T N(E_F)^2 \omega (L_{loc})^5 \ln \left( \frac{v_{ph}}{\omega} \right)^4$$

where r_ph is the phonon frequency and L_loc is the localization length.

3.7.2. Band gap energy with conductivity via size of nano composites

The cyclic voltammograms of all the complexes were recorded in DMF solution with 0.1 M TBAP as a supporting electrolyte. A three-electrode configuration composed of Pt-disk working electrode, a Pt wire counter electrode, and an Ag/AgNO_3 reference electrode was used for measurements. The reversible one electron Fc+/Fc couple has an E_{1/2} of 0.145 V versus Ag/AgNO_3 electrode. All the nano composites display a quasi reversible redox wave due to the Cu (II)/Cu (I) reduction process. Anodic shifts in E_{g1} values indicate the retention of the anion in the coordination sphere of Cu (II) (Fig. 13). The electrochemical HOMO, LUMO and energy gaps (E_{g1}) were calculated from the oxidation and reduction onset values as shown in Table 1 [43,44]. Electronic absorption band gaps energy (E_{g1}) were calculated from UV–visible absorption spectra, as shown in Table 1. The two types of band gap energy were nearly equal to each other. Band gap energy calculated by the two methods follow the order: SCN\(^-\) > Cl\(^-\) > NO_3\(^-\), whereas, at room temperature the dc conductivity value for NO_3\(^-\) > SCN\(^-\) > Cl\(^-\) and the sizes of nano composites being in the order Cl\(^-\) > SCN\(^-\) > NO_3\(^-\). The band gap energy of SCN\(^-\) bound nano composite is higher than the Cl\(^-\) bound nano composite (due to its smaller size in comparison to Cl\(^-\) bound nano composite) but it shows higher conductivity.

4. Conclusion

Correlated barrier hopping (CBH) model has been used for electron transport mainly controlled by the dominant conduction
mechanism. The exponent ‘$\gamma$’ decreases with the increase in temperature and lies between 0.5 and 0.6. Both the dielectric constant and dielectric loss decrease with increasing frequency, while they increase with increasing temperature. The rise in conductivity with the decrease in particle size was also observed as expected. At low temperature (below 300 K), ac conductivity and dielectric constant increase with increasing temperature suggesting that the relaxation frequencies of the dispersion increase with the temperature, while at higher frequencies, an apparent increase in $\gamma$ at a particular frequency is observed. The increase in $\gamma$ with the temperature also refers to the polarization related to the thermal motion of electrons, facilitating the orientation of the electrons with the increase in temperature. The dielectric loss is a manifestation for fundamental properties of crystalline semiconducting materials. The low temperature dielectric loss is a manifestation for fundamental properties of the coordination sphere of Cu(II)/(I). Electronic absorption band nearly equal to each other and be 

References

\[ E_g = E_{g1} + E_{g2} \]

\[ f = \frac{\Delta f}{f_0} \]

\[ \Delta f = f_0 \]

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