

# Imidazole Functionalized Polyaniline: Synthesis, Characterization, and Cu (II) Coordination Studies

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**ABSTRACT:** Polyaniline functionalized with imidazole as strategically designed receptor group in its backbone was synthesized for copper binding. The synthesized polymer has been characterized using FTIR, NMR, and UV-Vis spectroscopic techniques. The addition of copper (II) to the polymer distinctly changes the properties such as crystallinity, molecular weight, aggregation, and electronic properties. XRD, DLS, SEM, and four-point probe techniques have been

used for study of these changes. It is observed that the secondary ion generated as a result of copper coordination results in the doping of the polyaniline backbone, which enhances the conductivity by one order of magnitude. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 526–534, 2012

**Key words:** functionalization of polymers; conducting polymers; metal-polymer complexes

## INTRODUCTION

Functionalized conducting polymers have been studied for various applications like sensors,<sup>1–3</sup> liquid crystalline materials,<sup>4,5</sup> charge storage batteries,<sup>6</sup> and light-emitting polymers,<sup>7</sup> etc. The introduction of substituent groups into conjugated polymer backbone can bring about changes in the structural and electronic properties.<sup>8</sup> At the same time, a specific prosthetic group can be introduced into a conducting polymer backbone for enhancement of the physical–chemical properties after interaction with analyte.<sup>9</sup> Among these conjugated polymers, polyaniline (PANI) has found wide application due to its relatively higher stability, ease of processability, variable intrinsic redox states, and controllable electrical conductivity.<sup>10</sup> The interaction of PANI with metal ion has evoked interest, because its electronic and physical properties are modified. There are several reports showing the interaction of metal ion with PANI backbone,<sup>11–16</sup> through imine and amine nitrogen atoms.<sup>17</sup> However, the metal uptake capacity is comparatively less, and this can be improved by incor-

porating metal ion receptors onto the conducting polymer backbone.

Imidazole with *N*-donor atoms has gained importance as the most common copper binding sites in proteins.<sup>18</sup> Furthermore, unlike the imidazole in its native form the inactivity of the *N*-methyl imidazole toward oxidizing agents like ammonium persulphate facilitates prefunctionalization of imidazole to polyaniline.<sup>19</sup> There are also reports of postfunctionalized imidazole containing polyacetylene and polycarbazole as a fluorescence probe for metal ion sensors.<sup>20,21</sup> However, there is a paucity of literature on prefunctionalized imidazole containing electroactive polymers.

In this study, the synthesis of imidazole functionalized polyaniline (IMPANI) in the emeraldine base form by the chemical polymerization of the prefunctionalized aniline monomer was initially performed. This was followed by copper coordination to produce Cu-IMPANI. NMR and FTIR spectroscopic were used to confirm the structure of IMPANI and Cu-IMPANI. Dynamic light scattering, X-ray diffraction, and conductivity measurements were performed to ascertain the resulting changes in molecular weight, crystallinity, and electrical conductivity consequent to copper coordination. Possible mechanisms of interaction of copper with the synthesized polymer (IMPANI) are discussed.

## EXPERIMENTAL

### Materials

All the chemicals obtained except aniline and tetrahydrofuran are analytical grade reagents and are

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used without further purification; 2-aminophenol was obtained from sigma-Aldrich. Acetic anhydride was obtained from Fisher Scientific. Epichlorohydrin was obtained from Sisco Research Laboratories Pvt. Limited. Imidazole was obtained from Spectrochem Pvt. Limited. Sodium carbonate was obtained from Merck Limited. Aniline, tetrahydrofuran, ammonium persulphate (APS), cuprous chloride, ammonium hydroxide, and potassium carbonate were purchased from s. d. Fine-Chem Limited. Aniline was purified by double distillation under reduced pressure and stored at low temperature. Tetrahydrofuran (THF) was distilled twice over pressed sodium and preserved under inert conditions.

### Measurements

All synthetic works were carried out under nitrogen atmosphere. NMR spectra were recorded in a Bruker 400 MHz. spectrometer. Molecular mass of compounds was evaluated by using Waters Q-TOF micro mass spectrometer. Samples were pressed into pellet using KBr for FTIR and scanned from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$  in a Perkin-Elmer FTIR spectrometer. X-ray diffraction (XRD) patterns of powdered samples were analyzed using a Pan Analytic X-ray diffraction spectrometer ranging from 6 to 70°. Dynamic light scattering (DLS) studies were performed using a Wyatt DynaPro Protein Solutions instrument. An FEI Quanta 200 electron microscope was used for the morphological studies. UV-Vis spectra were recorded in a Perkin-Elmer Lamda-35 spectrophotometer in the spectral range from 200 nm to 1100 nm. The conductivity of the films were measured by Keithley 2182A (nanovoltmeter), 6221 (AC and DC sources). Four-probe head from Cascade Microtech with tungsten carbide tips of 0.5  $\mu\text{m}$  radius and separated by 0.016 cm distance with a spring load of 40 to 70 g was used for the conductivity measurements.

### Synthesis and characterization

#### Synthesis of 2-hydroxy acetanilide (1)

The synthesis of 2-hydroxy acetanilide was according to the method described elsewhere.<sup>22</sup> In this investigation 2-aminophenol (11 g, 0.1 mol) was suspended in 30 mL of deionized water (D.I.) by magnetic stirring for 15 min. Acetic anhydride (12 mL, 0.13 mol) was added drop wise, and the mixture was heated to 70°C for 3 h under constant stirring. The mixture was then cooled, filtered, and washed with D.I. water and dried in a vacuum oven at 50°C for 24 h. The obtained solid was further purified by recrystallization from hot methanol. Yield: 10.1 g (66.5%).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400 MHz):  $\delta$  ppm 9.69 (s, 1H, OH), 9.28 (s, 1H, NH), 7.65 (d, 1H, Ar H), 6.94 (1H, t, Ar H), 6.84 (M, 3H, Ar H), 2.08 (s, 3H, CH<sub>3</sub>) (see Supp. Info., Fig. 1).

<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 400 MHz):  $\delta$  ppm 168.96, 147.84, 126.39, 124.60, 122.32, 118.93, 115.92, 23.55 (see Supp. Info., Fig. 2).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3085,2981,2882,1658,1598,1527, 1449,1387,1282,1244,1032,764 (see Supp. Info., Fig. 3).

$m/z = 152.07$  ( $M + H$ ) (see Supp. Info., Fig. 4).

#### Synthesis of 2-(2-oxiranylpropoxy) acetanilide (2)

Six grams of 2-hydroxy acetanilide (0.039 mol) and K<sub>2</sub>CO<sub>3</sub> (33 g, 0.317 mol) in 80 mL dry THF was stirred for 15 min to make a uniform suspension. Epichlorohydrin (31 mL, 0.397 mol) was added drop wise over a period of 30 min. The resultant mixture was stirred at 70°C for 24 h under nitrogen atmosphere. The mixture was cooled to room temperature and poured into 400 mL of D.I. water. The organic layer was extracted three times with 50 mL of chloroform. The combined layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated, and purified by column chromatography (silica gel 100–200 mesh, 30 : 70 ethyl acetate/petroleum ether mixture) to obtain a white solid. Yield: 5.65 g (68.8%).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400MHz):  $\delta$  ppm 9.02 (1H, s, NH), 7.88 (1H, d, Ar.H), 7.03 (2H, d, Ar H), 6.89 (1H, m, Ar H), 4.33 (1H, dd, Ali H), 3.91 (1H, dd, Ali H), 3.37 (1H, m, Ali H), 2.84 (1H, t, Ali H), 2.73 (1H, dd, Ali H), 2.08 (3H, t, CH<sub>3</sub>) (see Supp. Info., Fig. 5).

<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, 400 MHz):  $\delta$  ppm 168.35, 148.77, 127.72, 124.26, 122.42, 120.74, 112.86, 69.83, 49.78, 43.78, 23.83 (see Supp. Info., Fig. 6).

FTIR (KBr,  $\text{cm}^{-1}$ ): 3297, 3060, 3011, 2935, 2879, 1661, 1600, 1537 (see Supp. Info., Fig. 7).

$m/z = 230.07$  ( $M + \text{Na}$ ) (see Supp. Info., Fig. 8).

#### Synthesis of 2-(1-imidazolyl-2-hydroxy propoxy) acetanilide (3)

Compound 2 (4 g, 0.0193 mol) and imidazole (1.31 g, 0.0193 mol) were mixed in 4 mL of dry THF. The mixture was heated to 70°C till complete dissolution occurred and was left stirring for another 12 h under nitrogen atmosphere. The resultant crude mixture was later purified by column chromatography (silica gel 100–200 mesh, 15 : 85 methanol/ethyl acetate) to obtain a white solid. Yield: 4.9 g, (92.4%).

<sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400MHz):  $\delta$  ppm 9.00 (1H,s, NH), 7.93 (1H, d, Ar H), 7.62 (1H, s, IM H), 7.16 (1H, s, IM H), 6.98 (2H, br, Ar H), 6.91 (1H, br, Ar H), 6.92 (1H, s, IM H), 5.66 (1H, s, OH), 4.19 (1H, dd, Ali H), 4.10 (2H, br, Ali H), 3.89 (1H, dd, Ali H),

3.79 (1H, dd, Ali H), 2.10 (3H,s, CH<sub>3</sub>) (see Supp. Info., Fig. 9).

<sup>13</sup>C-NMR (DMSO-d<sub>6</sub>):  $\delta$  ppm 168.34, 148.49, 137.87, 128.02, 127.62, 124.24, 121.95, 120.64, 120.11, 112.27, 70.23, 68.28, 48.86, 23.93 (see Supp. Info., Fig. 10).

FTIR (KBr, cm<sup>-1</sup>): 3395, 3191, 2938, 1673, 1601, 1532, 1448, 1373, 1325, 1287, 1253, 1114, 1082, 1036, 922, 820, 749 (see Supp. Info., Fig. 11).

$m/z = 298.11$  ( $M + Na$ ) (see Supp. Info., Fig. 12).

#### Synthesis of 2-(1-imidazolium-2-hydroxypropoxy) aniline hydrochloride (4)

About 2.47 g (8.9 mmol) of compound **3** was dissolved in 10 mL of ethanol under nitrogen atmosphere. To this 20 mL of 1 : 1 ethanol/concentrated hydrochloric acid was added drop wise. The resultant solution was refluxed for 24 h under inert atmosphere. The mixture was then cooled to room temperature and the volume reduced by [1/4]th under reduced pressure. The precipitate formed was centrifuged, washed with acetone, and recrystallized from D.I. water to obtain a white crystalline solid, which was then dried at 60°C under vacuum. Yield 2.27 g (87.9%).

<sup>1</sup>H-NMR (D<sub>2</sub>O):  $\delta$  ppm 8.82 (1H, s, IM H), 7.58 (1H, s, IM H), 7.51 (1H, s, IM H), 7.48 (1H, dd, Ar H), 7.43 (1H, dd, Ar-H), 7.21 (1H, dd, Ar H), 7.14 (1H, dt, Ar H), 4.58 (1H, d, Ali H), 4.49 (2H, s, Ali H), 4.25 (2H, dq, Ali H) (see Supp. Info., Fig. 13).

<sup>13</sup>C-NMR (D<sub>2</sub>O):  $\delta$  ppm 151.09, 135.28, 130.74, 124.15, 122.52, 121.84, 119.83, 118.67, 113.14, 69.31, 68.00, 51.52 (see Supp. Info., Fig. 14).

FTIR (KBr, cm<sup>-1</sup>): 3316, 3126, 3053, 3000, 2945, 2828, 2623, 2580, 1626, 1572, 1536, 1497, 1457, 1323, 1295, 1268, 1195, 1148, 1105, 1075, 1026, 840, 769 (see Supp. Info., Fig. 15).

$m/z = 234$  ( $M+$ ) (see Supp. Info., Fig. 16).

#### Polymerization of poly (2-(1-imidazolium-2-hydroxypropoxy) aniline hydrochloride (5) and aniline hydrochloride

About 2.71 g of the monomer (4) was dissolved in 30 mL of D.I. water and kept at 0°C under magnetic stirring. To this, a solution of APS (2.02 g, 8.86 mol) in 30 mL of D.I. water at 0°C was added drop wise. The solution was stirred for another 6 h under 0°C. The resultant green colored solution was then neutralized with 1M NH<sub>4</sub>OH to precipitate out the polymer. It was then centrifuged, washed with D.I. water, methanol, and finally with plenty of D.I. water till the pH of the filtrate became 7. The powder obtained was then dried at 55°C under vacuum for 24 h. Yield 0.9258 g (34.1%).

The PANI-EB was synthesized from aniline hydrochloride and chemically polymerized using ammonium persulphate as reported.<sup>23</sup>

#### Coordination of copper with polymers

Two hundred milligrams of the polymer IMPANI was mixed with 200 mL of 0.1M CuCl<sub>2</sub> solution and stirred for 12 h. The suspension was centrifuged and the residue washed with plenty of D.I. water to remove the unreacted free CuCl<sub>2</sub>. It was then dried in a vacuum oven for 24 h at 50°C to obtain copper coordinated complex of imidazole functionalized polyaniline (Cu-IMPANI).

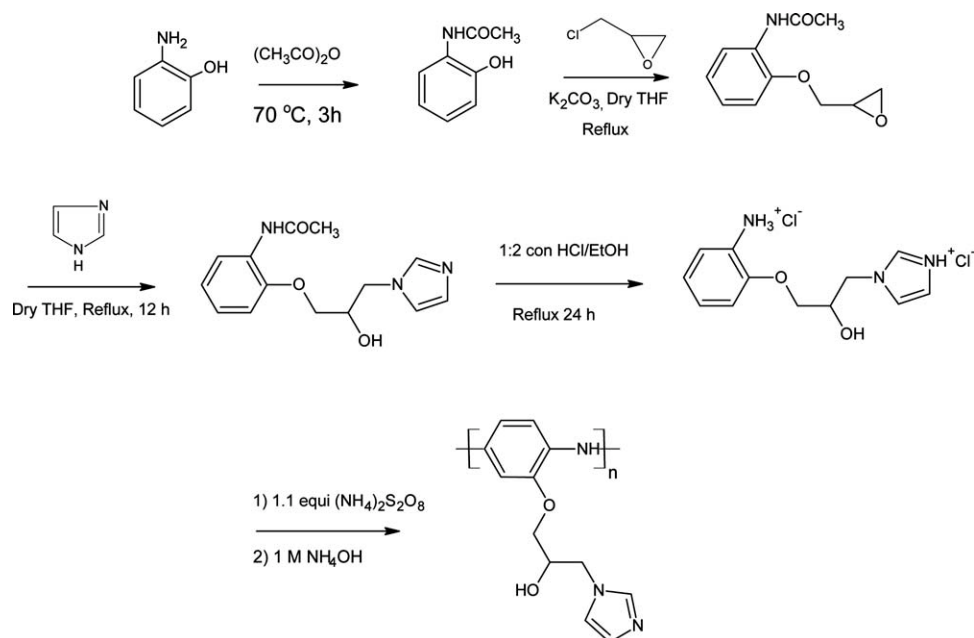
The synthesized PANI-EB was reacted with CuCl<sub>2</sub> in the same way as that of IMPANI to form the Cu-PANI powder.

#### Fabrication of thin films of PANI, Cu-PANI, IMPANI and Cu-IMPANI

Hundred milligrams of each of IMPANI, Cu-IMPANI, PANI-EB, and Cu-IMPANI was dispersed in 1 mL of *N,N'*-dimethylpropyleneurea (DMPU) by magnetic stirring for 24 h. The resultant dispersion was drop casted onto a glass substrate and then allowed to dry in a high vacuum oven at 55°C for 24 h.

## RESULTS AND DISCUSSION

Imidazole functionalized polyaniline was synthesized by a sequence of reactions as shown in Scheme 1. In the first step, ortho amino group of *o*-hydroxy aniline was protected by reacting with acetic anhydride to form *o*-hydroxy acetanilide. (1) In the second step, the epoxy group was introduced by reacting with epichlorohydrin in dry THF in the presence of a weak base, K<sub>2</sub>CO<sub>3</sub> at 70°C to produce compound. (2) The weak base, K<sub>2</sub>CO<sub>3</sub> was chosen over a strong base like NaOH, because the former will deprotonate ortho hydroxyl group selectively and will produce the desired compound. Conversion of the basic amino group in the first step prevents possible polymerization of *o*-hydroxy aniline with epichlorohydrin to form a long chain polymer in the next step. In the third step, compound (3) was prepared by following the procedure reported by Torregrosa<sup>24</sup> with a slight modification. In this step the ring opening reaction of compound (2) with basic imidazole group was carried out by refluxing in neutral media keeping the amount of solvent minimum. The volume of solvent was kept minimum to obtain a higher yield of compound. (3) In the next step, deprotection of the amino group was carried out by refluxing the compound (3) in 1 : 2 ratio of concentrated hydrochloric acid and absolute ethanol



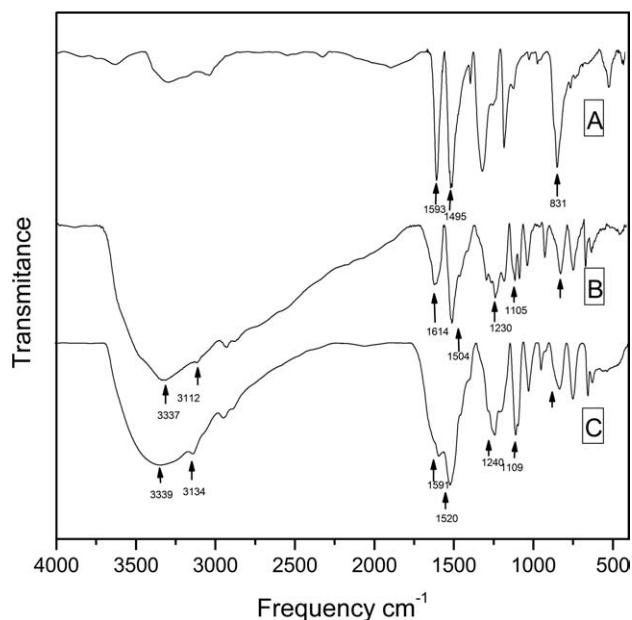
**Scheme 1** Synthesis of imidazole functionalized polyaniline.

under nitrogen atmosphere for 24 h. This yielded a white solid precipitate after reduction of the volume by [1/4]th, which was later purified by recrystallization from distilled water to obtain compound. (4) This resultant monomer (4) obtained in its hydrochloride form, was used for the oxidative polymerization at room temperature to obtain the final imidazole functionalized polyaniline (IMPANI). It was observed that the IMPANI formed by polymerization of monomer (4) remained in the solution, which needs to be precipitated out. This may be due to the presence of protonated imidazole group present in the side chain which makes the polymer highly water soluble. The resultant IMPANI was precipitated out by neutralizing with 1M ammonium hydroxide. The precipitate formed was then washed with copious amount of D.I. water till the filtrate become neutral. The obtained yield was about 34.1%. The observed low yield is due to the bulky imidazole group present in the monomer 4 which imparts steric hindrance during polymerization.

The synthesized IMPANI and Cu-IMPANI were tested for their solubility in dimethylsulphoxide (DMSO). It is found that after the copper coordination, the solubility of Cu-IMPANI has been reduced dramatically in comparison with the native IMPANI in DMSO. Taking advantage of the less soluble nature in DMSO, the filtrate obtained after the removal of undissolved fraction of Cu-IMPANI was used for further studies. To study the effect of copper coordination on the PANI backbone present in the IMPANI, the synthesized PANI-EB was used as a reference material.

FTIR and NMR techniques were used to elucidate the structure of IMPANI and Cu-IMPANI. Figure 1

shows the FTIR spectra of PANI, IMPANI, and Cu-IMPANI. It is observed that, there are similar peaks present in both PANI-EB [Fig. 1(A)] as well as in IMPANI [Fig. 1(B)] corresponding to the characteristic peaks of PANI backbone. These characteristic peaks observed at  $1614\text{ cm}^{-1}$ ,  $1504\text{ cm}^{-1}$ , and at  $817\text{ cm}^{-1}$  are due to quinonoid, benzenoid and C-H out of plane bending of 1, 4-ring vibration, respectively.<sup>10</sup> This indicates that IMPANI is formed by the oxidative polymerization of the aniline group present in the monomer (4) via head to tail polymerization mechanism.<sup>25</sup> The relative intensity ratio of the two peaks due to benzenoid and quinonoid shows that the benzenoid ring predominates over quinonoid ring.<sup>10</sup> Further, the presence of the functionalized imidazole in the polymer backbone is confirmed by the presence of characteristic imidazole peaks. These characteristic peaks observed at  $3112\text{ cm}^{-1}$ ,  $1230\text{ cm}^{-1}$ , and at  $1105\text{ cm}^{-1}$  are attributed to imidazole C=C-H/N=C-H stretching, imidazole ring vibration, and in plane C-H bending, respectively.<sup>26</sup> It can be seen from Figure 1(C) that, after copper coordination the imidazole characteristic vibrational frequencies are found to be shifted to higher wave numbers,  $3134\text{ cm}^{-1}$ ,  $1240\text{ cm}^{-1}$ , and  $1109\text{ cm}^{-1}$ , respectively. This increase in vibrational frequency is due to the increased ring rigidity arising from the copper imidazole coordination bond.<sup>26</sup> An analysis of the FTIR spectra of IMPANI and Cu-IMPANI shows the reduction in the relative intensity ratio of NH/OH vibration observed at  $3337\text{ cm}^{-1}$  compared with that of benzenoid and quinonoid vibrational frequencies, indicating the lack of available NH/OH group after copper coordination.



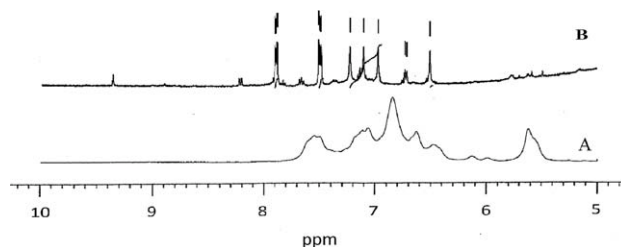
**Figure 1** FTIR spectra of, A) PANI, B) IMPANI, and C) Cu-IMPANI.

This is due to the fact that the coordination of copper ion reduces the amount of free hydroxyl group present in the IMPANI. Additionally, the characteristic peaks due to quinonoid and benzenoid ring, observed at  $1614\text{ cm}^{-1}$  and  $1504\text{ cm}^{-1}$  are found to be shifted to  $1591\text{ cm}^{-1}$  and  $1520\text{ cm}^{-1}$ , respectively. These shifts in the vibrational frequencies of quinonoid and benzenoid ring are explained in terms of metal coordination to imine and amine nitrogen present in the PANI backbone.<sup>16</sup> These shifts in the characteristic peaks of both imidazole and PANI backbone demonstrate that copper coordination occurs not only to imidazole containing side chain but also to the PANI backbone.

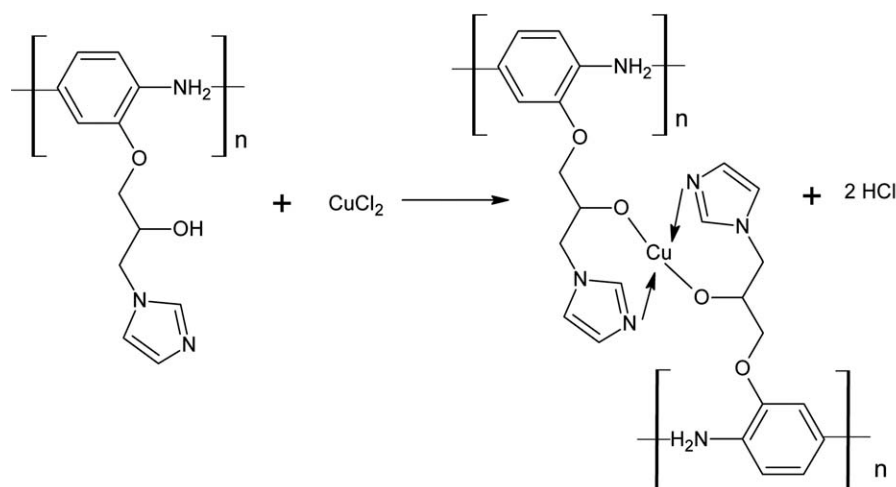
Unlike the parent PANI base, the presence of polar imidazole and hydroxyl groups present in the IMPANI side chain makes the polymer highly soluble in DMSO. This facilitates the study of the polymer structure by nuclear magnetic resonance spectroscopy technique. The NMR spectra of IMPANI and Cu-IMPANI in DMSO- $d_6$  are recorded and shown in Figure 2. The NMR spectrum of IMPANI shows broad peaks probably due to the polymer conformation, which results in the anisotropy in proton environment. The six aromatic protons present in imidazole and benzene ring are observed in the region 6.4 to 7.7 ppm. This indicates that *N*-substituted imidazole is unreactive toward ammonium persulphate and still carries aromaticity as observed from the FTIR data. The hydroxyl group present in the side chain is observed at 5.6 ppm as a broad peak. Also the five aliphatic protons present in the side chain are found to be in the range of 3.6 to 4.3 ppm, hampering separation (see Supp. Info., Fig.

17). After complexation with the copper ion, each peak due to the aromatic protons of imidazole and benzene ring are found to be separated and became split into various peaks. The peaks due to imidazole protons are observed at 7.9, 7.5, 6.7, and 6.5 ppm as shown in Figure 2(B). The splitting of the imidazole peaks is probably due to the unsymmetrical coordination sphere formed by the polymer constrained in its matrix. This unsymmetrical coordination leaves the imidazole in a nonidentical environment which reflects in the NMR of Cu-IMPANI. However, unlike that of IMPANI the peaks due to the three phenylic protons are visible in the NMR spectrum of Cu-IMPANI and are observed at 7.2, 7.1, and 6.9 ppm. The peak at 5.6 ppm, due to the hydroxyl group present in IMPANI is almost completely vanished in Cu-IMPANI as shown in the Figure 2(B), which indicates the participation of OH for copper coordination (see Supp. Info., Fig. 18 for complete spectra). From the observed results of FTIR and NMR it is evident that the imidazole and OH groups participate in copper coordination to form a copper coordinated complex. A schematic representation of copper coordination of IMPANI and liberation of secondary hydrochloric acid is shown in Figure 3.

The incorporation of the copper ion into the IMPANI polymer can change the electronic properties and can be best studied using UV-Vis absorption spectroscopy. It is reported that the change in the electronic properties mainly arises due to the copper ion coordination with the PANI backbone, which is reflected in the UV-Vis absorption spectra.<sup>11</sup> To study the change in electronic property, DMSO solutions of both IMPANI and Cu-IMPANI were prepared with identical optical density and used for absorption studies. The use of a high polar solvent like NMP was not preferred because of its basic nature,<sup>27</sup> which can deprotonate the doped Cu-IMPANI backbone formed as a result of the secondary hydrochloric acid generated as shown in Figure 3. It was shown that the copper ion coordination to IMPANI dramatically reduces the solubility in DMSO. This could be due to the crosslinking effects of the IMPANI chains as well as the effective loss of available functional groups for interaction with the

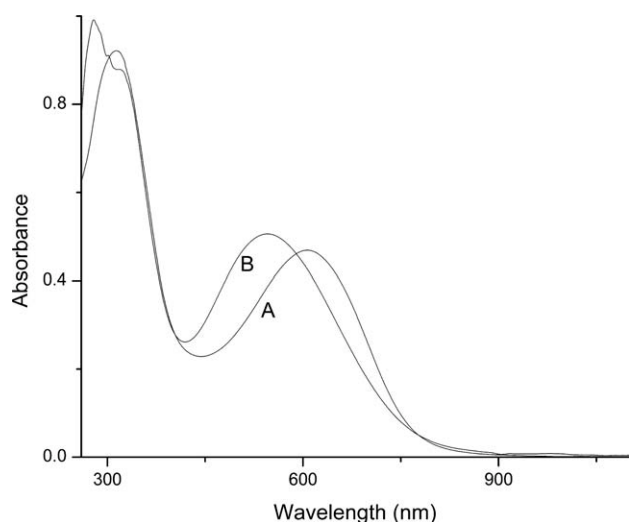


**Figure 2** NMR spectra of A) IMPANI and B) Cu-IMPANI.



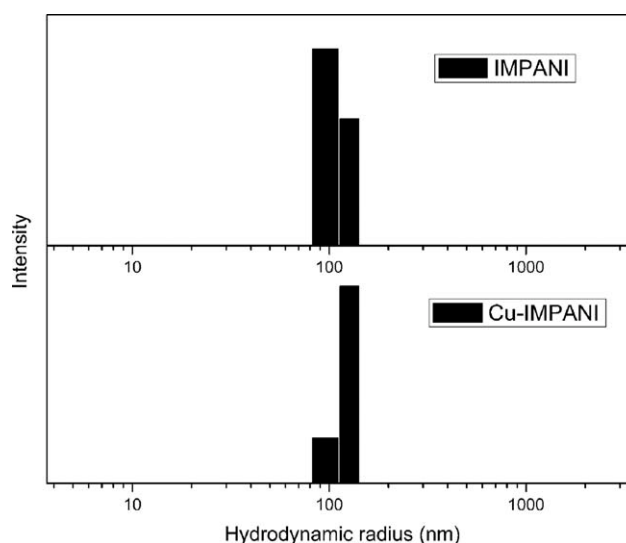
**Figure 3** Schematic of possible reaction pathway of coordination of Cu with IMPANI and generation of secondary HCl.

solvent molecules as both the imidazole and hydroxyl group of IMPANI participate in coordination with the metal ion. Figure 4(A) shows the UV-Vis absorption spectrum of IMPANI and Figure 4(B) shows that of Cu-IMPANI in DMSO. IMPANI shows two absorption peaks observed at 315 nm and 610 nm, which are comparable with the characteristic absorption peaks of PANI-EB. These absorptions are of  $\pi \rightarrow \pi^*$  transition of benzenoid structure and exciton transition of the quinonoid structure, respectively.<sup>16</sup> Cu-IMPANI also exhibits similar absorption peaks with a blue shift in the absorption maxima. The peaks observed at 314 nm, due to  $\pi \rightarrow \pi^*$  transition is shifted to 279 nm and the quinonoid exciton transition observed at 610 nm is shifted to 544 nm after the copper coordination with the IMPANI. This change in the absorption frequencies is due to the copper ion coordination and is in agreement with the earlier report.<sup>16</sup>



**Figure 4** UV-Vis absorption spectra of A) IMPANI and B) Cu-IMPANI in DMSO.

There are two ways by which the copper ion can coordinate to the IMPANI polymer. This can be either interchain copper coordination or intrachain copper coordination, which affects the effective molecular weight as well as the polymer aggregation. DLS techniques can be best used to study the effects of copper coordination on the molecular weight and the polymer aggregation process. For this dilute solutions of both IMPANI and Cu-IMPANI in DMSO were used for DLS analysis. The resultant histograms of both IMPANI and Cu-IMPANI obtained are shown in Figure 5. It can be seen that, both IMPANI and Cu-IMPANI show characteristic unimodal distribution curves, with the values of the hydrodynamic radius centered at 108 and 121 nm, respectively. This indicates the existence of globular submicrometer aggregates of IMPANI and Cu-IMPANI in the solution state. The molecular weight



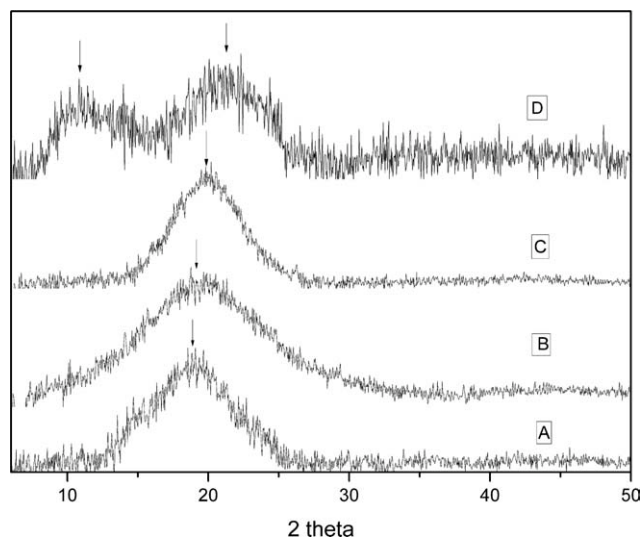
**Figure 5** DLS histograms of A) IMPANI and B) Cu-IMPANI solutions in DMSO.

**TABLE I**  
DLS Results of IMPANI and Cu-IMPANI

	Hydrodynamic radius (nm)	Molecular weight (kDa)	Polydispersity index (%)
IMPANI	108.7	195,793	14
Cu-IMPANI	122.1	256,634	9.8

and the percentage of polydispersity of both the polymers obtained from the DLS results are also shown in Table I. It can be seen that the observed molecular weight of Cu-IMPANI is higher than that of IMPANI. This increase in the molecular weight is due to the aggregation of the IMPANI chains as a result of the interchain copper coordination. Further, the decrease in the percentage of polydispersity suggests that the larger molecular weight polymer chains tend to aggregate preferentially with the low molecular weight polymer chains rather than the similar molecular weight chains. This is because of the faster mobility of the low molecular weight fraction vis-à-vis that of the larger molecular weight, which kinetically favors coordination with copper.

To study the effect of copper coordination on the crystallinity, XRD patterns of PANI-EB, Cu-PANI, IMPANI, and Cu-IMPANI were recorded. It can be seen in Figure 6 that XRD patterns of all the polymers show a broad diffraction band ranging from 19° to 22° indicating their amorphous nature. This observed broad peak is characteristic of the interchain separation of PANI in its base form,<sup>28</sup> and indicates that IMPANI also exists as amorphous in its native state. The XRD pattern of PANI-EB and Cu-PANI are almost identical, indicating less coordination of Cu ion in PANI. On the other hand, IMPANI shows a dramatic change in the internal



**Figure 6** X-ray diffractograms of A) PANI-EB, B) Cu-PANI, C) IMPANI and D) Cu-IMPANI.

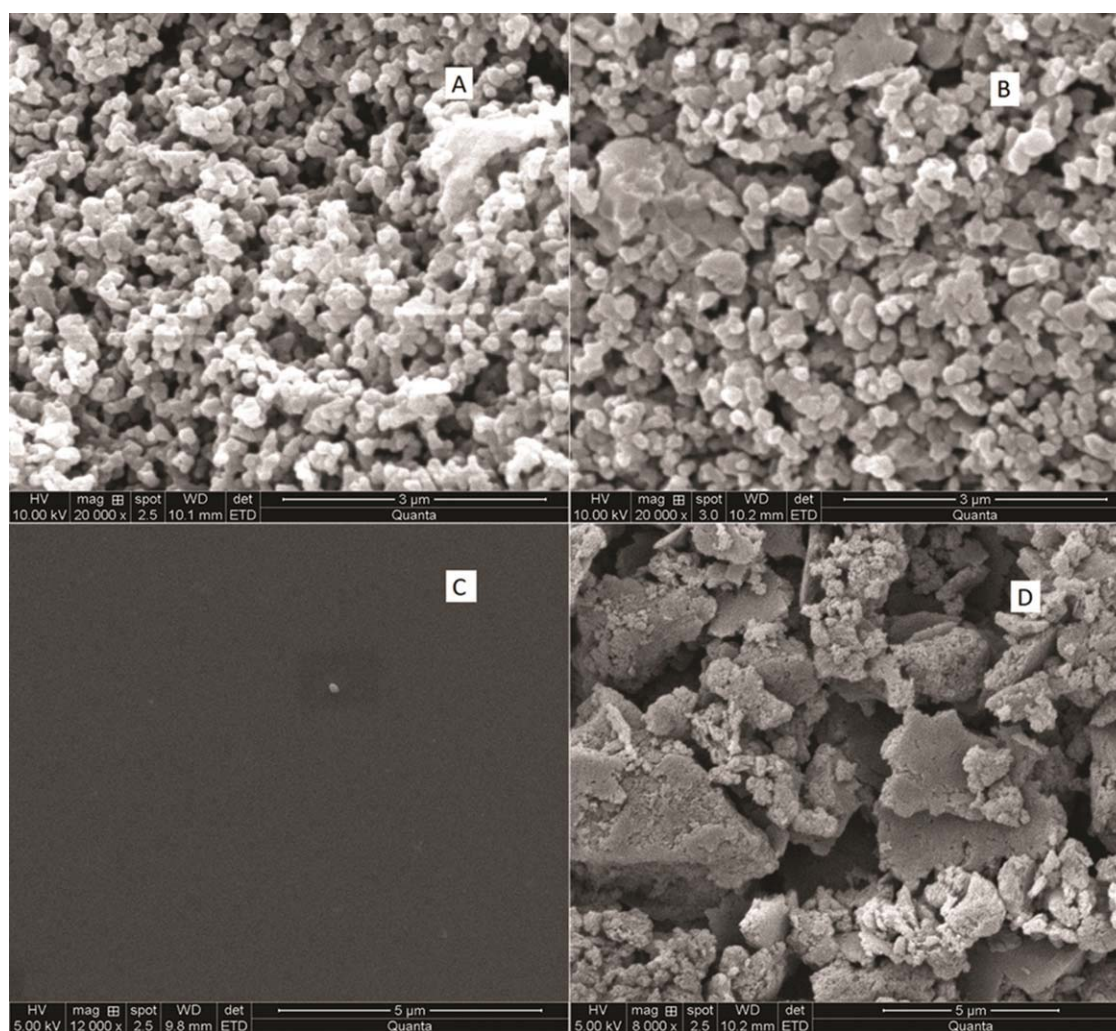
**TABLE II**  
XRD, pH, and Conductivity Data of PANI-EB, Cu-PANI, IMPANI, and Cu-IMPANI

	XRD		pH	Conductivity (Scm <sup>-1</sup> )
	2θ (degree)	d-spacing (nm)		
PANI EB	19.17	4.62	5.25	$9.40(\pm 0.48) \times 10^{-5}$
Cu-PANI	19.17	4.53	5.30	$9.85(\pm 0.44) \times 10^{-5}$
IMPANI	19.56	4.39	5.25	$4.44(\pm 0.17) \times 10^{-5}$
Cu-IMPANI	21.50, 10.90	4.44, 8.11	4.44	$1.12(\pm 0.24) \times 10^{-4}$

structure after coordination with the copper ions. Cu-IMPANI exhibits a new broad peak corresponding to the  $2\theta = 10.9^\circ$  ( $d$ -spacing = 8.11 nm) after coordination with copper ion. The new peak attests to the formation of possible copper coordinated complexes. This is due to the increased quantity of Cu ions present in the IMPANI assisted by the imidazole side chain as compared with that of PANI base. The  $2\theta$  values determined for all the peaks and the calculated  $d$ -spacing values using Bragg's law are given in Table II.

The morphology of the IMPANI and Cu-IMPANI were characterized using SEM and the micrographs are shown in Figure 7. It can be seen that the IMPANI powder has a nanosphere structure with an average diameter of  $158 \pm 17$  nm (see Supp. Info., Fig. 19 for additional pictures). The observed spherical nanoparticles can be explained on the basis of micelles formed by the self-organization of the monomer in the solution state.<sup>22</sup> It can be seen from Figure 7(B) that Cu-IMPANI has an aggregated structure with a diameter averaging from  $229 \pm 45$  nm (see Supp. Info., Fig. 20 for additional pictures). The aggregation of IMPANI chains results in the morphological changes. This observation is further supported by the reduction in the percentage of polydispersity in the case of Cu-IMPANI obtained from DLS results, attesting to the aggregation of IMPANI chains during copper coordination to form Cu-IMPANI. The morphology of IMPANI and Cu-IMPANI films were also analyzed using SEM and are shown in Figure 7(C,D), respectively. Films of IMPANI show smoother surface when fabricated from IMPANI dispersed in DMPU, whereas the Cu-IMPANI film [Fig. 7(D)], shows a morphology of flaky structure with a lot of discontinuity. This is because of the reduced ability of Cu-IMPANI chains to undergo dispersion in DMPU compared with IMPANI films, due to the resulted crosslinking within the polymer after coordination with copper.

A clue to the formation of acid hydrochloride as a secondary ion can be obtained from the measurement of the pH after the complexation with the copper ion. For this the pH of both PANI and IMPANI medium were measured before and after copper



**Figure 7** SEM micrographs of A) IMPANI powder, B) Cu-IMPANI powder, C) IMPANI film, and D) Cu-IMPANI film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

coordination reaction. It is observed that in case of Cu-PANI, the pH was found to be 5.30, which was almost the same as that of 0.1M CuCl<sub>2</sub> solution of pH 5.25. However, the pH of Cu-IMPANI was decreased to 4.44 after the interaction with the 0.1M CuCl<sub>2</sub> solution. This decrease in the pH may be attributed to the secondary acid hydrochloride generated as a result of copper coordination as depicted in the Figure 3. It is also expected that the generated acid hydrochloride further dopes the PANI backbone leading to increase in the conductivity, which was further confirmed by measuring the conductivity of the fabricated films by using a four-probe technique. On the other hand, mixing of transition metal ions with PANI is another way to dope PANI backbone by the process called pseudo protonation<sup>29</sup> and is reported to increase the conductivity. To study the effect of secondary ion effect on the electronic property, conductivity of the films were measured. It was observed that in the case of Cu-IMPANI, the increase in conductivity was higher than that of Cu-

PANI films. The mean values of conductivity of PANI and IMPANI are  $9.40(\pm 0.48) \times 10^{-5} \text{ Scm}^{-1}$  and  $4.44(\pm 0.17) \times 10^{-5} \text{ Scm}^{-1}$  respectively, and that of Cu-PANI and Cu-IMPANI are  $9.85(\pm 0.44) \times 10^{-5} \text{ Scm}^{-1}$  and  $1.12(\pm 0.24) \times 10^{-4} \text{ Scm}^{-1}$  respectively. It is noteworthy that the Cu-IMPANI shows a significant increase in the conductivity of one order of magnitude highlighting that the imidazole functionalized polyaniline has the potential to act as a conductometric sensor for copper sensing by generating the secondary hydrochloric acid, that provide higher sensitivity than PANI-EB.

## CONCLUSIONS

In summary, polyaniline functionalized with imidazole group in its side chain has been synthesized as a strategically designed metal ion receptor. The polymer has been synthesized by oxidative polymerization technique and characterized by NMR, FTIR, and UV-Vis techniques. Properties like molecular weight



and crystallinity were found to be changed after copper coordination. Due to the hydroxyl group present in the side chain, the synthesized imidazole functionalized polyaniline has a nanosphere structure and which is confirmed by SEM and DLS analysis. Coordination of the copper ion to IMPANI brought about a change in morphology, namely the formation of aggregates. In addition, the coordination of copper ion to the IMPANI chain leads to a higher magnitude of change in the conductivity compared with that of PANI-EB. This is due to the liberated acid hydrochloride as the secondary ions which further dope the IMPANI backbone.

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## References

- Zott, H.; Heusinger, H. *Macromolecules* 1975, 8, 182.
- Zon, A.; Zon, Z.; Popescu, A.; Ungureanu, M.; Moutet, J. C.; Aman, E. S. *Adv Mater* 1997, 9, 711.
- Radhakrishnan, S.; Deshpande, S. D. *Sensors* 2002, 2, 185.
- Goto, H.; Okuda, M.; Oohazama, T.; Akagi, K. *Synth Met* 1999, 102, 1293.
- Goto, H.; Akagia, K.; Itoh, K. *Synth Met* 2001, 117, 91.
- Su, Y. Z.; Dong, W.; Zhang, J. H.; Song, J. H.; Zhang, Y. H.; Gong, K. C. *Polymer* 2007, 48, 165.
- Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog Polym Sci* 2000, 25, 1089.
- Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. *J Chem Rev* 2005, 105, 1491.
- McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem Rev* 2000, 100, 2537.
- Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog Polym Sci* 1998, 23, 277.
- Gupta, K.; Jana, P. C.; Meikap, A. K. *J Phys Sci* 2008, 12, 233.
- Tang, L.; Wu, T.; Kan, J. *Synth Met* 2009, 159, 1644.
- Yang, C.; Chen, C. *Synth Met* 2005, 153, 133.
- Rivas, B. L.; Sanchez, C. O. *J Appl Polym Sci* 2001, 82, 330.
- Dimitriev, O. P. *Macromolecules* 2004, 37, 3388.
- Gupta, K.; Chakraborty, G.; Ghatak, S.; Jana, P. C.; Meikap, A. K. *J Appl Polym Sci* 2010, 115, 2911.
- Nikolaidis, M. G.; Sejdic, J. T.; Cooney, R. P.; Bowmaker, G. A. *Curr Appl Phys* 2006, 6, 457.
- Joszai, V.; Nagy, Z.; Osz, K.; Sanna, D.; Natale, G. D.; Mendola, D. L.; Pappalardo, G.; Rizzarelli, E.; Sovago, I. *J Inorg Biochem* 2006, 100, 1399.
- Wang, H. L.; O'Malley, R. M.; Fernanded, J. E. *Macromolecules* 1994, 2, 893.
- Zeng, Q.; Cai, P.; Li, Z.; Qin, J.; Tang, B. Z. *Chem Commun* 2008, 9, 1094.
- Li, Z.; Lou, X.; Yu, H.; Zhen, Li.; Qin, J. *Macromolecules* 2008, 41, 7433.
- Anilkumar, P.; Jayakannan, M. *Langmuir* 2008, 24, 9754.
- Stejskal, J.; Gilbert, R. G. *Pure Appl Chem* 2002, 74, 857.
- Torregrosa, R. *Tetrahedron* 2007, 63, 469.
- Sari, B.; Talu, M.; Yildirim, F. *Russ J Electrochem* 2002, 38, 707.
- Wu, K. H.; Chang, T. C.; Wang, Y. T.; Hong, Y. S.; Wu, T. S. *Eur Polym Mater* 2003, 39, 239.
- Lee, Y.; Park, J.; Jun, Y.; Kim, D.; Lee, J.; Kim, Y. C.; Oh, S. *Synth Met* 2008, 158, 143.
- Pouget, J. P.; Jozefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* 1991, 24, 779.
- Izumi, C. M. S.; Constantino, V. R. L.; Ferreira, A. M. C.; Temperini, M. L. A. *Synth Met* 2006, 156, 654.