Rapid Communication

Thermoelectric switch from anilinic compounds

A Puzari, J G Handique, A Purakayastha, & J B Baruah*
Department of Chemistry, Indian Institute of Technology,
Guwahati 781 001, India
and
A Srinivasan
Department of Physics, Indian Institute of Technology,
Guwahati 781001, India

Received 24 March 1999: revised 25 April 1999

Copper(II) ion can be embedded in the aggregates formed by anilinic compounds, such as 2,4-dimethoxyaniline, 2-aminophenol, 4-aminophenol, protonated polyaniline, through a reaction of catalytic amounts of copper complexes such as cis-bis(glycinato)copper(II) monohydrate and copper(II) acetate in the presence of hydrogen peroxide. These aggregates have the property of an irreversible thermoelectric switch.

Design of organic materials is an area being pursued with great interest. Among these materials, polyanilines have been identified as potential advanced materials. They are used in rechargeable battery and possess novel electrical properties. Further, polyanilines need to have uniform chains in order to have controlled electrical properties. Polyanilines also require dopant or acid treatment to exhibit novel electrical properties. The high solubility of these oligomers makes them potential candidate for further modifications. Anilinic compounds can form hydrogen bonded aggregates, and polyanilinic compounds can posses secondary structure due to hydrogen bonding. Polyanilines are usually formed during oxidative reactions of aniline under catalytic condition. The present study demonstrates the formation of copper(II) containing aggregates of a few substituted anilines through oxidative catalytic method that can exhibit properties of an irreversible thermoelectric switch.

We have observed that copper(II) ion can be embedded in aggregates of anilinic compounds such as 2-aminophenol, 4-aminophenol, 2,4-dimethoxyaniline, protonated polyaniline, diphenylammonium sulphate, etc., through the reaction of a catalytic amount of copper complex (such as cis-bis(glycinato)monohydrate, copper(II) acetate monohydrate) and hydrogen peroxide. The aggregates thus formed are found to have low molecular weights ranging from 1200 to 3500. The aggregates are prepared from a homogeneous reaction and thus they contain copper(II) ions evenly distributed in the aggregates. They possess novel electrical properties. The change in resistance vs temperature of films prepared from samples obtained from two separate reactions of 2,4-dimethoxyaniline and 2-aminophenol with cis-bis(glycinato)copper(II) monohydrate with hydrogen peroxide are shown in Fig. 1. We have also prepared protonated polyaniline by the standard procedure. These protonated polyanilines when doped with copper(II) through our oxidative method show similar electrical properties.

As a representative case the reaction of 2,4-dimethoxyaniline is carried out by hydrogen peroxide with the aid of cis-bis(glycinato) copper(II) monohydrate as the catalyst (10 mol%). The GPC of the aggregate is shown in Fig. 2 which has four components of (Mn, Mw) values (2592, 2843); (1473, 1486); (1006, 1081); (611, 639) respectively. The 'H NMR of the material has two sets of signals at 6.8-6.5 and 3.9-4.1 ppm along with a minor signal at 8.5 similar to that of the starting compound suggesting it to be an aggregate. The 'H NMR of the sample thus recorded in DMSO-<sup>d</sup><sub>6</sub> has a water signal that becomes much sharper compared to the corresponding signal of the water present in the solvent. We do not have the three-dimensional structure of the material at the moment but from the existing literature and the spectral data it is felt that they are aggregates having hydrogen bonded units with copper(II) ions embedded inside the spaces created through interaction of such aggregates.

One of the most probable structure is shown in Scheme. 1. In order to avoid complications in drawing,
Fig. 1 — Plot of resistance normalised to room temperature resistance vs temperature of film of (a) 2-aminophenol aggregate, (b) 2,4-dimethoxyaniline aggregate

original ligands are not shown in the structure and also the possible hydrogen bonding through the methoxy groups is not shown. It is found that the resistance normalised to room temperature resistance of the 2,4-dimethoxyaniline aggregate increases with temperature (35-65°C) and beyond 65°C the resistance of the aggregate drops down and shows an exponential pattern resembling the profile of a semiconductor in the range of temperature 65-180°C (Fig 1). Iodometric estimation showed that ~3% copper(II) ions are incorporated in the aggregate during the synthesis. The ESR of the sample recorded at different temperatures are shown in the Fig 3. The ESR of the solid sample at room temperature shows presence of distorted octahedral copper(II) center in the aggregate with its usual hyperfine coupling with the nitrogen environment. However, as the temperature increases a new ESR signal (\( g = 2.04 \)) appears. The signal is attributed to a change in geometry around copper(II) center. At higher temperature the original signal due to Cu(II) ion diminishes and the intensity of the new signal increases. Thus, the property may be attributed to a combination of proton conductivity and a structural change. The proton conductivity can be compared with the metallic conductivity, and the rise in resistance below a limiting temperature can be due to proton conductivity. It decreases on disruption of hydrogen bond on heating. It is already known that molecular wires can be constructed in DNA molecules with strong hydrogen bonding\(^7\). Further proof to the proton conductivity comes from the fact that diphenylamine on reaction with cis-bis (glycinato) copper(II) monohydrate in the presence of hydrogen peroxide gives a black solid. The 13-carbon NMR of this compound suggests that no C-N bonded oligomerisation occurs in this reaction. The aggregate thus formed from diphenylamine does not have a smooth change of resistance profile, and resistance of a film of diphenylamine aggregate thus prepared falls through a small barrier on heating (Fig 4). However, the same material yields a change in resistance vs temperature profile similar to a thermoelectric switch on treatment with sulphuric acid (Fig 4b). 2-Aminophenol forms aggregates containing copper(II) as the host ion through its reaction with hydrogen peroxide and catalytic amount of cis-bis (‘glycinato’) copper(II) monohydrate. In this case room temperature ESR shows signals at 3140 (\( g = 1.96 \)) and 3240G (\( g = 2.03 \)) due to the presence of copper(II) ion and a radical respectively. The intensity of these two signals changes on heating and the intensity
Fig. 3 — ESR spectra of aggregate prepared from 2,4-dimethoxyaniline (a-i) at 30°C - 170°C. (j) Diphenyl picryl hydrazyl radical as standard. Instrument setting: 3200G Central field, 1500 G sweep width, 9.70 GHz microwave frequency.

Fig. 4 — Plot of resistance normalised to room temperature resistance vs temperature of the film of copper-doped (a) diphenylamine aggregate, (b) protonated diphenylamine aggregate.
of the 3240G (g = 2.03) signal is enhanced. This aggregate has Mn, Mw values of 2921 and 2932 respectively. The shape of the change in resistance vs temperature plot is influenced by the type of copper salts and concentration of copper(II) complexes. The smooth plot can be obtained with a copper concentration in the range of 1 mol per cent with respect to the anilinic compounds used. The hike in the resistance is also governed by the copper complexes. For example, 2-aminophenol aggregate prepared from copper(II) acetate and hydrogen peroxide has a 50,000-fold hike around 110°C with respect to room temperature resistance, whereas similar material prepared from cis-bis(glycinato)copper(II) monohydrate and hydrogen peroxide has a 3-fold hike at 90°C in comparison to the room temperature resistance.

Thus, in this study we have demonstrated the possibility of combination of proton conductivity with structural changes and also with radical conductivity to obtain the properties of irreversible thermoelectric switch. The materials thus prepared are soluble in common organic solvents and have scope for use as sensors. The study has direct relevance to biological systems where the heat sensing occurs to a particular temperature.

Acknowledgement

We are thankful to Prof. K. Osakada of Tokyo Institute of Technology for the GPC. The authors thank the Council of Scientific and Industrial Research, New Delhi for financial assistance.

References


