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Letter

Thermal effects on urea–copper binding within a supramolecular assembly

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Copper(II) ions can be embedded in the channels of urea to give complexes with thermal sensing properties.

Sensing is important in all spheres of life. Photo[1] and thermal sensing[2] are two aspects that are being pursued with great interest. Heat sensing by living beings is a natural phenomenon and the capability to withstand heat by living beings differs. Thus, the understanding of such phenomenon at the molecular level would provide insight into the mechanism. Amino acids and analogous compounds containing amide bonds are indispensable basic components in biology[3] and possibly take part in sensing processes. Urea is a compound that contains an amide bond and is also known to form channels through H bonds. These channels may be compared to the secondary structure of proteins in biological systems.[4] In this regard supramolecular aggregates have shown promising ability in sensing.[5] It is also well known that small inorganic and organic molecules can be embedded in such channels.[6] The pore sizes of urea channels[6] have a diameter of 5.25 Å, that can accommodate small inorganic molecules. Analogous channels in thiourea can embed ferrocene and have a reversible phase transition at low temperature.[7] In a recent study the layered structure of urea was used to make π stacks which show interesting irradiation induced conductivity.[8] Assembled aggregates of transition metals also show high temperature superconducting properties.[9] Recently, we have found that it is possible to combine proton conductivity with radical conductivity and structural changes to obtain thermoelectric switching properties.[10] We demonstrate here a thermoelectric switch using the biologically important molecule urea in which copper(II) ions are embedded under biocompatible conditions.

Slow evaporation of solvent from water–acetonitrile solutions of urea and copper(II) salts such as copper(II) acetate, copper(II) chloride, or *cis*-bis-glycinato copper(II) monohydrate results in the inclusion of copper(II) ions in the channels of urea.[4] This incorporation procedure gives a uniform distribution of metal ions in the channel as the conditions used are homogeneous. The channel-like structure of urea is generated through hydrogen bonds and can have some structural flexibility. In these channels, copper(II) ions can have a change in geometry around the metal centre and can posses a metal–N dative bond. This is shown by the ESR spectrum at room temperature of the urea channel containing copper(II) acetate, which has a broad signal at 3020 G exhibiting hyperfine coupling with nitrogen around the copper(II) centre in a distorted octahedral environment (Fig. 1, curve *a*). In addition to this signal, a new signal at 3100 G was observed upon heating, showing the structural changes occurring around the copper(II) centre (Fig. 1, curve *b*). This clearly indicates a coordination change during heating of the sample. Efforts are underway to completely elucidate the geometrical changes occurring during the heating. Similarly, the *cis*-bis-glycinato copper(II) containing urea has an absorption at 3010 G at room temperature showing hyperfine coupling with the surrounding nitrogen. These copper containing channels have the ability to sense heat. The resistance of pellets prepared from each urea–copper sample increases initially and then drops exponentially beyond a particular temperature. A sample prepared from urea without incorporated copper(II) ions does not show this behaviour. Representative plots of resistance normalised to the resistance at 122 °C *vs.* temperature of urea containing *cis*-bis-glycinato copper(II) for two independent heating cycles of the same sample are shown in Fig. 2 (for experimental details refer to footnote of Table 1). The concentration of copper(II) ions in the channels has an important role in the shape, temperature to which the hike in resistance occurs and also on the maximum hike in the resistance. The results are tabulated in Table 1. The anion also plays an important role in the maximum temperature to which the resistance increases. For example, urea channels containing copper(II) acetate show maximum resistance at 70 °C whereas a copper(II) chloride containing channel has its maximum resistance at 57 °C.

The plots of the change in normalised resistance *vs.* temperature of samples prepared from urea and copper(II) acetate monohydrate or copper(II) chloride dihydrate can be fit by a simulated normal Gaussian curve, shown by dotted lines in Fig. 3. Such plots indicate that the concentration of charge carrier during the conduction process passes through a minimum and is controlled by two thermally convertible states in the system through structural changes around the metal ion. In all cases the resistance measurements were

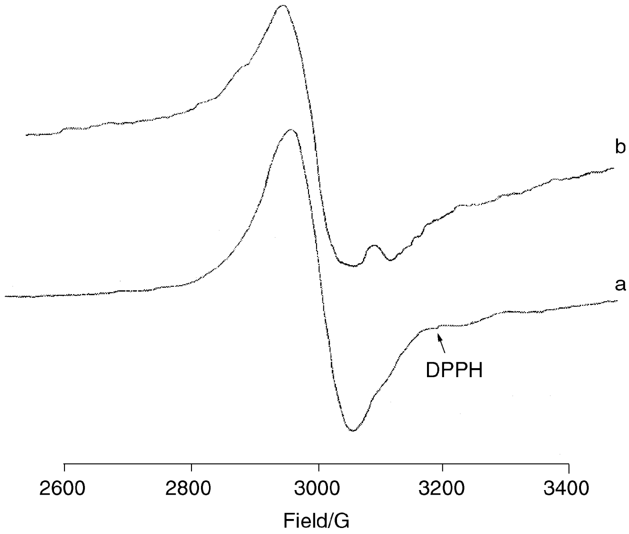

Fig. 1 ESR spectra of urea channel containing copper(II) acetate (*a*) at 30 °C, (*b*) at 100 °C. Instrument setting 3200 G central field, 1500 G sweep width, 9.70 GHz microwave frequency.

Table 1 Thermoelectric properties of some copper(II) salts incorporated into urea channels[a]

Cu(II) salt (amount/mmol)	$R_{max}/R_{122\,°C}$	T_{max}/°C for R_{max}
Copper(II) acetate monohydrate (0.025)	8	106
Copper(II) acetate monohydrate (0.075)	96 000	70
Copper(II) acetate monohydrate (0.15)	3 60 000	54
cis-Bis-glycinato copper(II) monohydrate (0.025)	136 000	94
Copper(II) chloride dihydrate (0.032)	66 500	57

[a] All samples were prepared by dissolving the specified amount of copper(II) salt in a water (2 cm^3) and acetonitrile (5 cm^3) mixture containing urea (1.67 mmol), followed by evaporation of the solvent in a water bath. The solid samples thus prepared were made into pellets and the change of resistance *vs.* temperature was measured by a set-up composed of a Hewlett–Packard 34401 multimeter, Kiethley 6512 programmable electrometer and Agronics 93-C DC power supply with a two-point probe.

carried out to 122 °C, keeping in mind that this is below the melting point of the samples. The samples once heated to 122 °C retain their sensing property, however, the magnitude of the highest resistance decreases in the repeated measurement of resistance *vs.* temperature (see Fig. 2, curve *b*).

The infrared spectra at room temperature of the fresh sample and the sample after heating do not show significant differences. The DSC of the samples were recorded for two cycles in the range of 30–122 °C at a heating rate of 5 °C per minute. A continuous exothermic process was observed with an endothermic process at the temperature where the resistance maximum was obtained. The DSC of the samples recorded the second time have a similar profile with lower slope and also with an endothermic process at the temperature where the maximum resistance occurs.

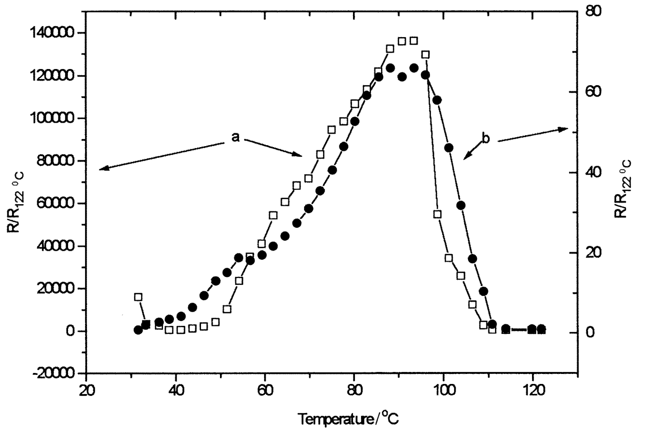

Fig. 2 Plot of normalised resistance *vs.* temperature of a urea channel having *cis*-bis-glycinato copper(II) (urea = 1.665 mmol, *cis*-bis-glycinato copper(II) monohydrate = 0.025 mmol). (*a*) First heating cycle: 30–122 °C, (*b*) second heating cycle: 30–122 °C.

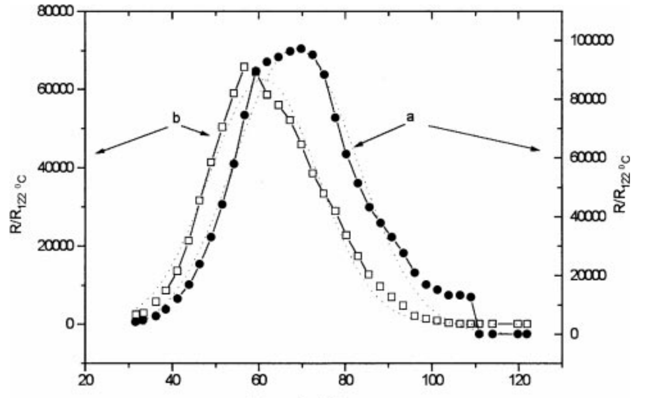

Fig. 3 Plot of normalised resistance *vs.* temperature of copper(II) acetate containing urea channels. (*a*) [urea] = 1.67 mmol, [copper(II) acetate monohydrate] = 0.075 mmol. (*b*) [urea] = 1.67 mmol, [copper(II) chloride dihydrate] = 0.032 mmol. Dashed lines are the Gaussian fit to the points.

The results obtained show that the sensing property arises from a combination of proton conductivity with a change of co-ordination around the copper(II) centre with temperature. The conducting properties in highly hydrogen-bonded systems are well documented.[11]

To conclude, the present study demonstrates a thermal sensing phenomenon by supramolecular ligand binding and the use of resistance measurements as a tool for such studies. The property exhibited by the materials described above may find use in microelectronics and in electronic memory devices as well as in thermoelectric switching.

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