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A magnetic self-contained thermochromic system with convenient temperature range

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Dedication: **In memoriam of our co-author Kenneth R Seddon**

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New ionic liquid with sugar-based ligand has been prepared and used to coordinate cobalt (II), at low loading, in ionic liquid solution. The system obtained reveals magnetic switching and marked thermochromism in solution/polymer films over a convenient temperature range (20 – 60 °C). This system is self-contained, devoid of any volatile substances, and reproducible over multiple thermal cycles. The colour change is attributed to a change in coordination geometry from octahedral (pink) at RT to tetrahedral (blue) on warming, monitored with ⁵⁹Co NMR spectroscopy used for the first time to study the change. This material may find applications in stimuli responsive smart systems aimed at energy storage applications.

The continuous growth in energy demand by modern society has as main consequence depletion of energy sources and waste production. Although it could appear surprising, data collected by International Energy Agencies clearly demonstrate how about 40% of energy consumption in developed countries is devoted to buildings and this amount exceeds consumption by both industry and transportation sectors.¹ Consequently, the identification of systems able to reduce energy consumed in the buildings, maintaining comfort levels, represents one of the major challenges of sustainable development.

In this context, significant efforts have been made to obtain smart systems that while taking advantage from their ability to respond to external stimuli, could allow energy storage. External stimuli are frequently represented by electro-, thermo- or photoirradiation²⁻⁵ and among systems obtained, thermochromic materials, *i. e.* those able to switch their state as a consequence of a temperature change, play a significant role. Indeed, if conveniently designed, they could be applied for windows glazing, allowing the use of solar radiation energy. This should avoid the reverse heat transfer that frequently features the components of buildings, increasing their energetic efficiency. Obviously, with this aim, systems should display good optical transparency with minimum haze and acceptable device lifetime.

Preparation of thermochromic devices has been frequently performed using transition metal complexes [based on Ni(II)^{6,7} and Cu(II),^{8,9} for example]. The colour switch occurs as a consequence of complexation/decomplexation of a weakly coordinating ligand. Recently, this phenomenon has been also observed in the presence of lanthanide complexes.¹⁰ Most of chromogenic systems have been studied in conventional solvents, but their volatility sometimes compromises their recyclability. Consequently, the choice of low vapour pressure solvent systems, like ionic liquids, represents a solution.

Chromic behaviour has also been reported for many Co²⁺ complexes in solution¹¹ and in ionic liquids where the Co²⁺ salts may be dissolved¹² or indeed constitute a primary component of the molten salt mixture.¹³ In 2015 Nockemann *and co-workers* showed that such a switch was possible in a frozen solution of a cobalt-containing ionic liquid at inconvenient sub-zero temperatures.¹²

Here, we report a comprehensive optical and magnetic study on a rare example of the O_h-T_d switching in a cobalt-containing IL, prepared with sustainable materials, over the useful temperature range of 20-60 °C. The coordination change is accompanied by both a marked change in colour and a significant change in magnetic

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moment. Although, these (20–60 °C) thermochromic transitions are possible using cobalt halides dissolved in volatile alcohols which act as ligands,¹⁴ our system is devoid of any volatile ligands/media. Therefore, potential devices based on our systems will be inherently safe and self-contained. Additionally, a very low loading of cobalt is required to display switchable thermochromism/magnetism.

The design requirements of the target material, $[\text{Co}_x\text{-IL}_y]$ included (i) use of a substituted tetraalkylammonium cation with multiple coordination sites for Co^{2+} , (ii) low viscosity of the resultant system and (iii) incorporation of a sustainable sugar-based cationic ligand system.¹⁵ These were met by using a binary ionic liquid system with two types of alkyl ammonium cations, and either bistriflamide or bromide counterions, into which the magnetic ion, Co^{2+} , was introduced as its bistriflamide salt.

The first component of the mixture was the sugar-containing ligand salt $[\text{N}_{112\text{GA}8}]\text{Br}$, selected chiefly due to the large number of hydroxyl binding groups which offers both many coordination sites for Co^{2+} , and the flexibility with which the metal-ligand assembly can adopt different coordination modes under varying conditions of heat and pressure. In addition, the chosen ligand is derived from readily available renewable sugars and will degrade to environmentally innocent products.

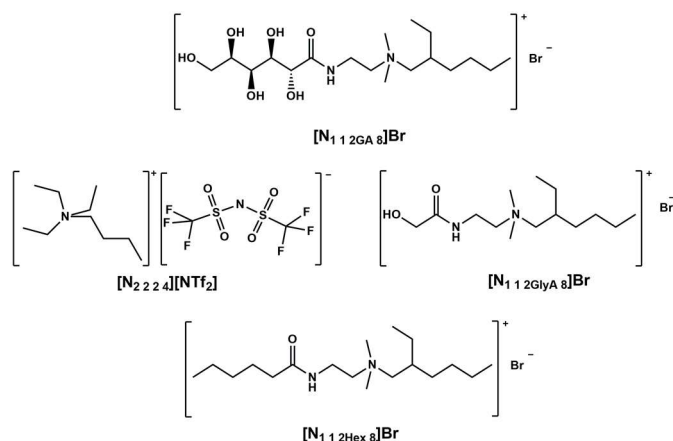


Figure 1. Structures of coordinating IL ligand $[\text{N}_{112\text{GA}8}]\text{Br}$, spectator IL $[\text{N}_{2224}][\text{NTf}_2]$, and control ILs $[\text{N}_{112\text{GlyA}8}]\text{Br}$ and $[\text{N}_{112\text{Hex}8}]\text{Br}$.

As the chosen ligand salt $[\text{N}_{112\text{GA}8}]\text{Br}$ is highly viscous, the design was complemented by the non-coordinating, low-viscosity “spectator” ionic liquid triethylbutylammonium bistriflamide, $[\text{N}_{2224}][\text{NTf}_2]$, which had a purely solvating role, Figure 1 (3:1 ligand/ Co^{2+} molar ratio was used). The good thermal stability of both the ligand and spectator ILs permits their use in a high temperature range with decomposition temperatures of ~ 200 °C for $[\text{N}_{112\text{GA}8}]\text{Br}$ and > 300 °C for $[\text{N}_{2224}][\text{NTf}_2]$ (Figure S2).

Two other ILs, $[\text{N}_{112\text{GlyA}8}]\text{Br}$ and $[\text{N}_{112\text{Hex}8}]\text{Br}$, were also prepared as control compounds (see Figure 1). The cations in these possess the same design features of the ammonium and amide groups in $[\text{N}_{112\text{GA}8}]\text{Br}$, except the number of OH groups are reduced to either one or none, thereby reducing the potential for good coordination to Co^{2+} .

The addition of $\text{Co}(\text{NTf}_2)_2$ to the binary mixture of $[\text{N}_{112\text{GA}8}]\text{Br}$ and $[\text{N}_{2224}][\text{NTf}_2]$ at room temperature generated a pink solution, suggesting a predominance of octahedrally coordinated cobalt(II) ions at this temperature. This changed progressively to

predominantly tetrahedral coordination on warming to 90 °C, Figure 2a. The colour change is supported by changes in the electronic absorption spectra recorded over this temperature range, Figure 2b. Temperature dependent spectra reveal a steady increase in the four bands in the region between 620 nm and 740 nm on warming, and these are assigned to tetrahedrally coordinated species. This is accompanied by a decrease in the broad absorption at 540 nm, which is attributed to the octahedral component and the relationship is underscored by the isosbestic point at 550 nm.

In contrast to the thermochromic behaviour of Co^{2+} in $[\text{N}_{112\text{GA}8}]\text{Br}/[\text{N}_{2224}][\text{NTf}_2]$, the control ionic liquids, $[\text{N}_{112\text{GlyA}8}]\text{Br}$ and $[\text{N}_{112\text{Hex}8}]\text{Br}$ with Co^{2+} displayed blue colour at room temperature, with no visible or spectroscopic change detected on warming to higher temperatures (Figures S5–S6). This proves the essentiality of the sugar moiety in $[\text{N}_{112\text{GA}8}]\text{Br}$ for coordination to Co^{2+} resulting thermochromism. Hence all above observations are in line with the hypothesis that the OH groups on the $[\text{N}_{112\text{GA}8}]^+$ cation are essential for the thermally-dependent multiple binding modes with Co^{2+} .

It was possible to map the changing equilibrium by following the intensity of the band at 725 nm over the temperature range 8–90 °C, Figure 2c. The onset of a plateau at 59 ± 1 °C indicates full conversion to the tetrahedral assembly in the upper temperature regime, while the octahedral species dominates below 15 °C. The value of 59 °C was obtained by extrapolation and corresponds to the point of intersection of the two straight lines derived from the linear regression of the two sections of the plot (*i.e.* from 15 °C to 60 °C and from 65 °C to 90 °C) and also corresponds to the visible change of the colour of the solution as observed by eye (Figure S7).

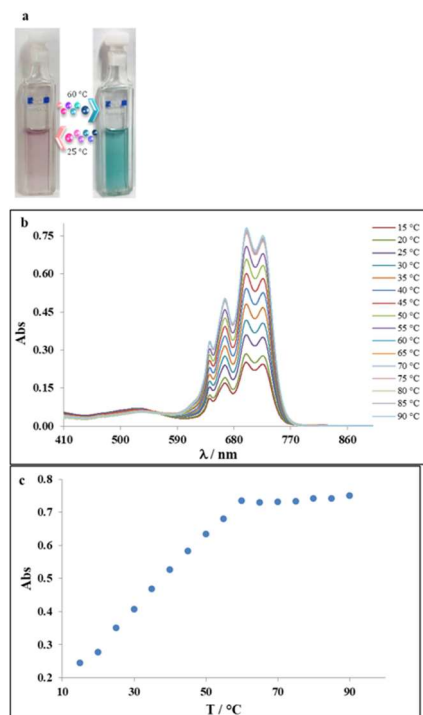


Figure 2. a) view of 0.062 M solution of $\text{Co}(\text{NTf}_2)_2$ and $[\text{N}_{112\text{GA}8}]\text{Br}$ in $[\text{N}_{2224}][\text{NTf}_2]$ at 25 °C (pink) and 60 °C (blue); b) UV-vis spectra of same solution over the temperature range 15 – 90 °C; c) plot showing temperature dependence of absorption at 725 nm.

The characteristic bands are in line with those observed in other thermochromic cobalt(II) complexes, allowing for adjustments to the ligand structure.^{12,16,17} The system reported here shows stable and

reversible thermochromism after several heating/cooling cycles, and the behaviour persists even after two months of storage (Figure S8).

The thermochromic O_h - T_d switching in Co^{2+} complexes should also be accompanied by a significant change in the magnetic moment in line with the loss of orbital contribution on switching from the orbital triplet (octahedral) to the orbital singlet (tetrahedral),¹⁸ Figure 3.

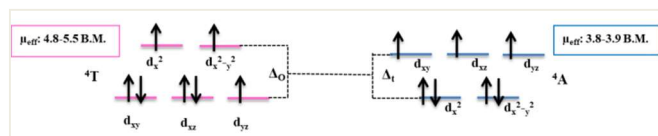


Figure 3. Octahedral and tetrahedral crystal field splitting diagrams for the d^7 configuration with typical observed experimental values of μ_{eff} for each.

1H NMR is a useful method to determine magnetic moment in solution^{19,20} and here the Evans' method was used to determine the magnetic moment across the temperature range of the thermochromic switching, yielding textbook values for the orbital singlet and triplet forms at 70 and 30°C respectively, Table 1 and Figure 4 (Figures S9-S10).

Table 1. Evans method parameters calculated.

T / K	$\mu_{\text{eff}} / \text{B.M.}$
303.15	5.28
313.15	5.07
323.15	4.72
333.15	4.44
343.15	3.90

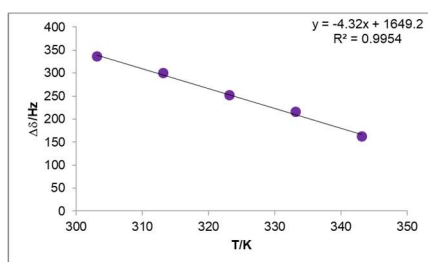


Figure 4. The $\Delta\delta$ is the difference of chemical shifts, operating between the alcohol function relative to the *t*-butanol reference in the capillary, and the same function relative to the *t*-butanol in the solution.

By containing the change in coordination number within the ionic liquid, the only input required to effect the change in moment is temperature, *i.e.* the ionic liquid acts as a magnetic thermometer with orbital contribution stored and released on demand. This is very

convenient, as alternative routes to change coordination number in cobalt(II) necessitate physical addition of competing ligands to alter the equilibrium, in contrast to the simple thermal switching demonstrated here.

Further NMR analysis, using the spin of the ^{59}Co nucleus to track the electronic environment, clearly supports the change in coordination number detected using other methods. ^{59}Co spectra of $Co(NTf_2)_2$ and $[N_1 1 2GA 8]Br$ in $[N_2 2 2 4][NTf_2]$ collected in warming mode, over the temperature range 20 – 90 °C, are shown in Figure 5a with a plot of chemical shift versus temperature in Figure 5b.

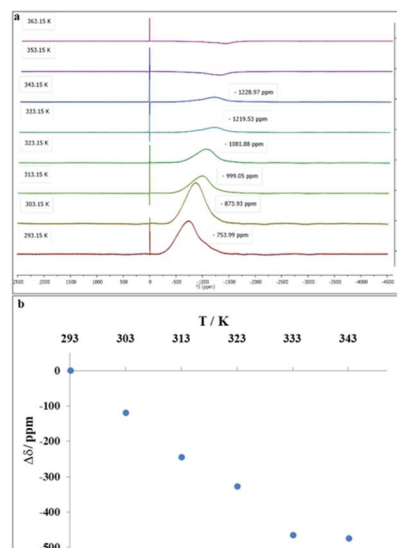


Figure 5. a) Variable temperature ^{59}Co NMR spectra of $Co(NTf_2)_2$ and $[N_1 1 2GA 8]Br$ in $[N_2 2 2 4][NTf_2]$; * = reference $K_3[Co(CN)_6]$ dissolved in D_2O and placed in a silica capillary; b) plot of change in chemical shift versus temperature.

Chemical shifts were measured relative to the diamagnetic external standard $K_3[Co(CN)_6]$ (0 ppm), for which the formal charge on cobalt is 3+. The chemical shift of the hexacyanocobaltate standard also shows a temperature dependence, as has been reported by Freeman *et al.*, with a temperature coefficient of 6.2 Hz/°C.²¹ Although it would be possible to correct the spectra for the drift in the standard, the changes in the chemical shifts of our system are so large that this was deemed not to be necessary to probe the coordination change. Indeed, the frequency values of the signal under investigation are three orders of magnitude larger than the changes to the reference signal. Since the percentage changes for the reference signal are calculated to be between 0.11 to 0.25 %, no corrections to the chemical shift of the sample were included.

The changes in position and intensity of the ^{59}Co resonance, between 20 – 90 °C, suggest more than one environment for the ion over this temperature range, Figure 5a.

The relationship between change in chemical shift and temperature also matches the profile of the temperature dependence of the electronic absorption at 725 nm, Figure 2c, with a transition temperature of ~60 °C.

The convenient temperature window of the thermochromic behaviour in the liquid state prompted us to consider if the properties could be reproduced in other media which would facilitate incorporation into a future display device. Successful

formation of a thermochromic composite film comprising [bmim]₂[NiCl₄] dissolved in [C₂OHmim][BF₄], with VO₂ nanoparticles in poly(vinylidene fluoride) has already been demonstrated by Jin,⁷ with the VO₂ suggested to impart a colour enhancing effect. A nanocomposite film was also reported to form, by mixing the polymeric ionic liquid poly([ViEtim][NTf₂]) with gold and silver nanorods, with high temperature (~200 °C) thermochromism²² which the authors attributed to both a change in the shape of the nanorods and the colour of the film. A drawback of this approach was that the thermal colour change was not reversible, as the nanorods retained the new shape associated with colour change induced by heating. In general, sensory materials incorporated into polymer films have been demonstrated to be useful in fabricating devices²³ and ILs have been shown to be suitable as components of thermochromic films.^{24,25}

Therefore, we focused on incorporating our Co-IL into the aliphatic polymer matrix poly(methyl methacrylate) (PMMA), and following the thermochromism by UV-vis spectroscopy. This was easily achieved by dissolving the Co-IL mixture with PMMA in dichloromethane followed by careful solvent evaporation to yield a transparent polymer film, Figure 6. The thermochromism observed in the liquid Co-IL was reproducible in the film over the same temperature range, changing gradually from pink at room temperature to blue at 60 °C, Figure 6.



Figure 6. View of PMMA-Co-IL composite film showing colour change from pink (left) to blue (right) after warming on a heating block.

The colour change in the film was also followed by electronic spectroscopy where the changes on warming matched those observed in the liquid, *i.e.* a gradual increase in the bands in the region between 600–800 nm, Figure 7.

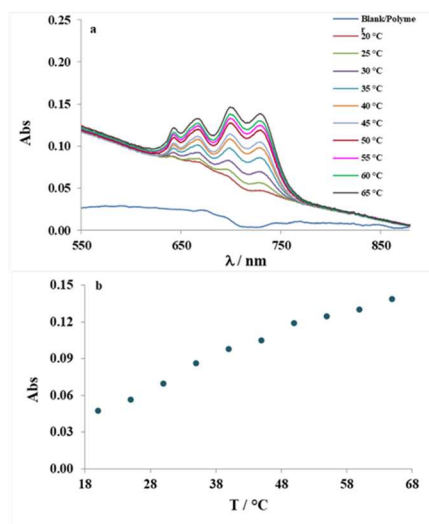


Figure 7. a) UV-vis spectra of PMMA-Co-IL polymer film over the temperature range 20 – 65 °C; b) plot showing temperature dependence of absorption at 725 nm.

As expected, the absorption intensities are lower in the PMMA matrix than in the pure Co-IL liquid and it was more difficult to follow the transition to completion as the maximum temperature attainable on the experimental setup was 65 °C. However, the change in intensity of the band at 725 nm on warming follows the same trend as that of the liquid form, Figure 7b.

Conclusions

In summary, we have assembled a novel thermochromic system using an ionic liquid prepared with a cheap and environmentally sustainable sugar-based ligand coordinated to Co²⁺ which exhibited colour switching, both in solution and in a polymer film, over a convenient temperature range. Reversible switching of the system in liquid form was repeated over 20 cycles with no evidence of fatigue and. The successful incorporation of the function into a polymer film suggests that fabrication into sensory devices as well as the use in windows glazing can be achieved. This hypothesis is supported by the stability of the polymer film for a time of 7 months with no significant change in the performances (Figure S11–12). We have demonstrated that our system is an effective temperature sensor with distinctive optical and magnetic out-puts under different thermal conditions. Moreover, this system is not sensitive to other environmental factors such as moisture and air, operates under ambient conditions and is inherently safe due to its involatility. ⁵⁹Co NMR spectroscopy was demonstrated to be an effective method to monitor changes in the coordination environment of a thermochromic ion for the first time, offering a new detection method to follow temperature fluctuations. In future, the effect of structural changes on the ligand as well as the nature of the “spectator” ionic liquid will be evaluated, both in solution and polymeric film.

Experimental

All experimental data, relevant to this communication, are reported in the electronic supplementary information section.

Conflicts of interest

There are no conflicts of interest to declare.

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Keywords: Thermo-chromism • switchable magnetism • ionic liquids • polymer films •

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