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Solvent Vapor-Induced Polarity and Ferroelectricity Switching

type

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Vapor-induced crystal to crystal transformation between nonpolar [Fe(sap)(acac)(sol)] (H_2 sap = 2-salicylideneaminophenol, acac = acethylacetate, sol = MeOH, pyridine) and polar [Fe(sap)(acac)(DMSO)] was demonstrated. It provides an example of switchable ferroelectric behaviour attributted to the structural phase transition triggered by solvent vapour.

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The development of flexible responsive systems with high structural order, as represented by the concept of "soft crystals", has received much recent attention.¹ In contrast to conventional hard crystals, such systems exhibit some flexibility and are typically able to respond to particular macroscopic stimuli, such as exposure to vapor as well as to physical rubbing.² Such responses may include changes in optical properties such as luminescence. Obtaining a deep understanding of such systems clearly provides the basis for the development of new sophisticated responsive materials. Several such vapor-induced functional switching systems have been reported. These were shown to exhibit facile structural transformations in response to specific vapor stimuli, that led to reversible luminescent properties, colours and spin-state changes.³

The development of functional switching molecules that exhibit bistability with respect to ferroelectric, ferromagnetic and spin crossover (SCO) properties has attracted considerable interest for use in new functional devices that include memory devices and sensors.⁴ For example, Miyasaka and coworkers have reported that a reversible magnetic change is associated with solvation/desolvation cycles for a "magnetic sponge" of Cl₃PhCO₂⁻ = 2,3,5-trichlorobenzoate; TCNQMe₂ = 2,5-dimethyl-7,7,8,8-tetracyanoguinodimethane; DCM = dichloromethane).⁵ Reports describing the switching of ferroelectric properties are extremely limited compared to those describing the switching of magnetic properties. Xiong and coworkers have reported the reversible switching of the ferroelectric and SCO behaviour of the mononuclear iron(II) complex, $[Fe(bpp)_2](isonic)_2 \cdot 2H_2O$ (bpp = 2,6-bis(pyrazol-3-yl)pyridine; isonic = isonicotinate) on hydration/dehydration.⁶ This was attributed to changes in the complex's hydrogen bonding network (and polarity) following the absorption/desorption of lattice water. While such a functional switching system induced by absorption/desorption of guest molecules is an attractive candidate for use in the construction of molecular devices, the synthesis of new systems of this type clearly remains challenging.

[{Ru₂(O₂CPh-2,3,5-Cl₃)₄}₂(TCNQMe₂)]·4DCM

In the present study, we have focused on investigating mononuclear iron(III) complexes of type [Fe(sap)(acac)(sol)] $(H_2 sap = 2-salicylideneaminophenol; acac = acetylacetate and$ sol = MeOH (1), DMSO (2), pyridine (3)) incorporating a substitution-prone coordination site. In this context it is well established that six-coordinated octahedral metal complexes in which a coordination site is occupied by a solvent molecule show a propensity for solvent ligand exchange with a second solvent having a higher coordination ability, giving rise to the prospect that polarity-dependent solvatochromism may occur.⁷ Herein, we report the occurrence of ferroelectric behaviour and solvent vapor-induced polarity switching involving mononuclear iron(III) complexes of type [Fe(sap)(acac)(sol)] (sol = MeOH (1), DMSO (2), pyridine (3)): in each of these the coordinated solvent corresponds to a substitution prone coordination site (Scheme 1).

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Electronic Supplementary Information (ESI) available: Experimental sections, Crystallographic data, PXRD, TGA, DSC, SHG, Dielectric properties. See DOI: 10.1039/x0xx00000x

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Scheme 1 Solvent vapor-induced structural transformations for 1-3.

[Fe(sap)(acac)(MeOH)] (1) was synthesized by mixing Fe(acac)₃ with H₂sap in methanol in a 1:1 molar ratio to yield the product as a brown powder (Fig. S1, ESI[†]). Black plate-like single crystals were obtained on recrystallizing the powder from MeOH/CH₂Cl₂ (see the Supporting Information, ESI[†]). [Fe(sap)(acac)(DMSO)] (2) was obtained by recrystallizing 1 from MeOH/CH₂Cl₂/DMSO, resulting in a mixture of two crystalline polymorphs: quartz-like (2a) and block shape (2b) products (Fig. S2, ESI[†]). The pyridine-substituted complex, [Fe(sap)(acac)(py)]·0.5py (3) was synthesized by recrystallizing 1 from MeOH/pyridine. 1, 2a, 2b and 3 were each characterized by elemental analysis and single-crystal X-ray diffraction (XRD) measurements.



Fig. 1 Packing structures of [Fe(sap)(acac)(MeOH)] (1) and [Fe(sap)(acac)(DMSO)]
(2b). Color code: orange, Fe; red, O; blue, N; grey, C; yellow, S. Hydrogen atoms are omitted for clarity.

The single-crystal X-ray structural analyses of **1**, **2a**, **2b** and **3** were carried out at 123 or 298 K. Crystallographic data and selected bond lengths are displayed in Tables S1 and S2 (ESI[†]). **1** crystallized in the triclinic non-polar space group *P*-1. The structure of **1** is in accordance with the previously reported structure (Table. S1, ESI[†]).⁸ The iron(III) centre has a NO₅-donor coordination sphere with distorted octahedral geometry. The metal centre has a NO₃-donor set coordinated equatorially

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arising from the H₂sap and acac ligands (Fig. S3, ESI;), while the axial positions are occupied by O,O' Idonorsoform academid MeOH. The Fe-O and Fe-N bond lengths for 1 at 123 K are agreed well with values observed for typical high-spin iron(III) ion in octahedral environments.9 Complexes 2a and 2b have similar structures to 1 except that the central iron(III) in 2 is coordinated by a DMSO molecule rather than a MeOH molecule as in 1; both structures belong to the monoclinic polar space group Cc (Fig. 1 and Figs. S5-S8, ESI⁺). 2a and 2b form polymorphic crystals displaying different lattice parameters that are attributed to the presence of slightly different intermolecular interactions (Table S1, Fig. S9, ESI⁺). The crystal structure of **2b** is in accordance with the previously reported structure.¹⁰ The respective crystals can be distinguished by their different morphologies and crystal sizes (Fig. S2, ESI[†]). Although 3 crystallized in the monoclinic nonpolar space group $P2_1/n$ with a similar molecular structure to 1, the asymmetric unit incorporates half of a lattice pyridine molecule (Figs. S10 and S11, ESI[†]).

When the methanol-containing complex **1** was exposed to DMSO or pyridine as vapours for 1 day, then in each case the initial PXRD pattern for **1** changed completely to the patterns obtained directly for **2b** and **3**, respectively (Fig. 2). Clearly this result is in accord with the coordinated MeOH in **1** having exchanged with DMSO or pyridine upon exposure to the DMSO or pyridine atmospheres. In addition, by undertaking time-dependent PXRD measurements during the uptake of DMSO enabled the time-dependent structural transformations to be followed (Fig. S12, ESI†). The observed PXRD pattern for **1** after exposing to DMSO vapor for 1 day indicated that a mixture of **2a** and **2b** was present. Further exposure to DMSO vapor for 5 days resulted in a change to a simpler PXRD pattern which corresponded to the pattern for **2b** (Fig. S13, ESI†).



Fig. 2 PXRD patterns for 1 (red), 2b (blue), 3 (pink) and 1 after exposure to DMSO and pyridine vapours (black).

In the case where **2b** was exposed to MeOH vapor, the PXRD pattern for **2b** did not change even after the exposure had continued for 5 days in agreement with the coordination ability of a MeOH being lower than DMSO.

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In order to compare the thermal stability of 2a relative to 2b, the thermogravimetric analysis (TGA) of each of these polymorphs was performed (Fig. S14, ESI⁺). For both complexes, 17% weight loss was observed above ca. 170°C. This shows good agreement with the DMSO content of 2 (17.6%). Following the initial thermal treatment of crystalline 2b at 150°C for 1 h under reduced pressure to remove the coordinated DMSO, the PXRD pattern of the desolvated sample, following its exposure to MeOH vapor, was again measured (Fig. S15, ESI⁺). A relatively fast response to the MeOH vapor was observed; the resulting PXRD pattern corresponded well to the PXRD pattern for 1. Notably, the observed PXRD transformation was found to be reversible; that is, on exposing the above sample to DMSO vapor resulted in regeneration of the original pattern for 2b. Related behaviour was also observed on exposing pyridine-desolvated 3 to MeOH vapor. Again this yielded the PXRD pattern for 1 (Figs. S16 and S17, ESI⁺). On exposing 3 to DMSO vapor or 2b to pyridine vapor, resulted in the PXRD patterns for 2b and 3, respectively (Fig. S18, ESI⁺). Thus in contrast to the case of MeOH vapor, the reversible structural transformations between 2b and 3 are occurred spontaneously without process. The desolvation vapor-induced structural transformations corresponding to the above PXRD changes were also supported by second harmonic generation (SHG) experiments for the respective structures using an excitation wavelength of 1080 nm. A strong SHG intensity was evident at ca 540 nm for 2a and 2b, both of which belong to the polar Cc space group, while no SHG occurred for 1 (Fig. 3a and Fig. S19a, ESI[†]). The exposure of **1** and **3** to DMSO vapor resulted in the expression of polarity along with SHG behaviour (Figs. 3b and S19b, ESI†).



Fig. 3 Results of SHG experiments for (a) 1, 2a and (b) 1 after exposure to DMSO vapor.

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In an attempt to investigate the structural transition behaviour, differential scanning spectroscopycco(DSC) measurements for 2a and 2b were carried out from 125 K to 400 K (Fig. S20, ESI⁺). No peaks were observed over this temperature region, indicating that no structural transitions occurred for either crystal type. We also measured the temperature-dependent dielectric constants for single crystalline samples of 2a and 2b within the frequency range 10 Hz to 1 kHz using inductance capacitance and resistance (LCR) measurements in order to investigate the electric field responses to the phase transitions (Fig. S21, ESI⁺). The dielectric constants of 2a and 2b remained almost unchanged over 300-400 K. These results indicate that no structural transitions occur over this temperature range for both crystal types. The observed behaviour is thus consistent with the results of the DSC analyses mentioned above.

The ferroelectric properties for single crystalline samples of 2a and 2b were studied by analysing polarization vs. electric field (P-E) curves using a TF Analyzer1000. The observed P-E curves for these compounds show well-defined hysteresis loops (Fig. 4). The low leakage currents (10⁻⁸-10⁻⁷ A cm⁻²) further demonstrate that each hysteresis loop originates from the presence of ferroelectricity. At 298 K, the remnant polarizations (P_r) for **2a** and **2b** are 3.2 μ C cm⁻² and 7.5 μ C cm^{-2} , with a coercive field (E_c) of 14.2 kV cm^{-1} and 5.1 kV cm^{-1} , respectively. Because 2a and 2b were structurally stable below ca. 430 K, clear ferroelectric hysteresis loops with the remnant polarization (P_r) values of 1.6 μ C cm⁻² and 7.4 μ C cm⁻², and with coercive fields (E_c) of 10.9 kV cm⁻¹ and 5.5 kV cm⁻¹, were able to be observed respectively, even at 400 K, (Fig. S22, ESI⁺). These results confirm that 2a and 2b exhibit ferroelectric behaviour even under high temperature conditions (up to at least 400 K). Reported examples of molecular ferroelectric systems with high Curie temperatures are quite limited; the above complexes represent new examples of this rare category.11



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Fig. 4 P-E hysteresis loops for (a) **2a** and (b) **2b** with an E \perp C-axis at 298 K (0.1 Hz).

In conclusion, we have demonstrated the occurrence of solvent vapor-induced crystal to crvstal structural transformations between iron(III) complexes of type [Fe(sap)(acac)(sol)] (sol = MeOH (1), DMSO (2), pyridine (3)). This involved the use of a mononuclear iron(III) complex belonging to polar Cc space group which is SHG active. Thus, complexes 2a and 2b exhibit ferroelectric behaviour up to high temperature (at least to 400 K), in part, reflecting both their polarity and their high thermal stabilities. These polymorphs represent new examples of vapor-induced reversible ferroelectric switching systems in which coordinated solvent substitution is the 'trigger' for the corresponding structural rearrangements. The study provides new insights towards solvent-exchange strategies for obtaining new molecular multifunctional materials - not only for achieving ferroelectric switching - but also for solvent-exchange induced spin-state and luminescent switching.

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Conflicts of interest

There are no conflicts to declare.

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A new example of vapor-induced reversible polarity and ferroelectricity switching system has been demonstrated in mononuclear iron(III) complexes.