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Publication Date

2023-02-01

DOI

10.1016/j.matchemphys.2022.127276

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# Perturbing the spin state and conduction of Fe (II) spin crossover complexes with TCNQ

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## Abstract

We investigated modifications driven by 7,7,8,8-tetracyanoquinodimethane (TCNQ) to the spin state configuration of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  co-crystal and both spin state and electric conductivity of the mixture of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  and TCNQ. The  $\text{Fe}^{2+}$  site in the  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  co-crystal has a sizable orbital moment. During X-ray absorption measurements, the iron ion is partially excited to the high spin state and strong surface effects are indicated. Mixing TCNQ with the  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  spin crossover complex leads to a molecular combination with increased conductivity and drift carrier lifetimes.  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  thin films with TCNQ, grown using dimethylformamide (DMF), are to great extent locked mainly in the low spin (LS) state across a broad temperature range and exhibit drift carrier lifetimes approaching 0.5 s. When deposited onto a ferroelectric polyvinylidene fluoride thin film substrate,  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ , shows enhanced transistor carrier mobility, likely associated with the increasing cationic character of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  thin films with TCNQ.

## Introduction

While organic electronics has become increasingly attractive as a route to developing flexible nonvolatile memory devices [1–9], molecular spin crossover (SCO) materials

with transition metal ions show considerable promise for non-volatile memory devices [9,10]. Molecular spin crossover (SCO) materials exhibit magnetic bistability due to a reversible transition between low spin (LS) and high spin (HS) states that can be triggered by external stimuli, such as pressure, temperature, magnetic field, light, and X-ray irradiation, or by adding guest molecules [11–15]. Critical for prospective applications is the realization of voltage-controlled isothermal spin state switching in SCO molecular films and a non-volatile conductance change in heteromolecular structures with a molecular ferroelectric [16,17]. This conductance and spin state change introduces a facile "read" to a device based on molecular ferroelectric polarization reversal [10,16,17]. Although very convenient, there are complications with this voltage controlled read and write mechanism, i.e., a large on-state resistance that hinders a favourable comparison with the silicon technology [10]. Several molecular SCO systems with low resistivity have been reported [10,18]. The challenge is, though, to synthesize molecular SCO thin films with significantly lower impedance [10].

Combining polar molecules with SCO complexes is a way to achieve SCO materials with altered properties, particularly, affecting the temperature and abruptness of the spin state transition [19,20]. Adding polyaniline to the SCO complex  $[\text{Fe}(\text{Htrz})_2(\text{trz})(\text{BF}_4)]$  was shown to result in a significant increase in the conductivity [21], with a strong dependence on the polyaniline concentration [21] and choice of polyaniline [22]. Aside from polyaniline, the organic acceptor molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) also shows promise for providing a route toward low-impedance SCO materials [18,23–30]. Due to its strong electron-acceptor character, TCNQ increases the cationic character of the SCO [18,31] molecule and lowers the resistance, especially when introduced as fractionally charged anions, i.e.  $\text{TCNQ}^{\delta-}$  ( $0 < \delta < 1$ ) [18,23–28]. Several recent studies have reported co-crystallization of SCO cations with TCNQ anions [18,23,24,27], and the addition of TCNQ is frequently seen to affect the spin transition and conductivity in molecular materials.

Given the very limited number of studies investigating the change in charge carrier properties of potential device related spin cross over molecular thin films, we studied two different Fe(II) SCO complexes that include TCNQ as an additive: a  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$  co-crystal described previously [23,32] and a  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  complex in a matrix mixture with neutral TCNQ. The co-crystallization with TCNQ anions [23] makes the  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$  crystal highly conductive and opens a route to topologically protected currents in the transistor geometry, because of loss of inversion symmetry. The much investigated  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  SCO molecule has been used as a molecular transistor channel conductor in heteromolecular transistor structures that make effective nonvolatile memory devices [16,17], albeit with significant impedance [10]. Here, we show that adding TCNQ to a Fe(II) molecular SCO system reduces the impedance despite locking  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  in the low spin state. The majority charge carriers appear to be holes, yielding a p-channel transistor.

## Experimental

[Fe(3-bpp)<sub>2</sub>](TCNQ)<sub>2</sub> [23] (Figure 1a) and [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] [33] were synthesized as discussed in the literature. The synthesis of [Fe(qsal)<sub>2</sub>][TCNQ<sub>2</sub>] was adapted from two similar molecules [29,30] using a Li(TCNQ) precursor [34,35] and [Fe(qsal)<sub>2</sub>]Cl [36]. The Li(TCNQ) precursor was fabricated according to [34,35] where TCNQ in anhydrous acetonitrile was brought to a boil and then added to a boiling solution lithium iodide acetonitrile. The synthesis of [Fe(qsal)<sub>2</sub>]Cl was from 8-aminoquinoline and salicylaldehyde in methanol followed by the addition of FeCl<sub>3</sub> and triethylamine, as in [36]. The [Fe(qsal)<sub>2</sub>]Cl and LiTCNQ were then combined acetonitrile to form the [Fe(qsal)<sub>2</sub>][TCNQ<sub>2</sub>]. The [Fe(qsal)<sub>2</sub>][TCNQ<sub>2</sub>] studies were done to confirm the influence of PVDF as a substrate on an Fe(III) complex with TCNQ. More of the characterization of [Fe(qsal)<sub>2</sub>][TCNQ<sub>2</sub>] will be reported in future studies. [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] and TCNQ were mixed in a 1:1 ratio and dissolved in DMF prior to drop-casting. Both TCNQ and DMF were purchased from Sigma Aldrich. The organic field-effect transistor (OFET) chips were acquired from the Fraunhofer Institute for Photonics. The spacing of the interdigitated electrodes is 2.5 μm and the thickness of the dielectric layer is about 230 nm.

X-ray absorption spectroscopy (XAS) was done at the Advanced Light Source (ALS, beamline 6.3.1) at Lawrence Berkeley National Laboratory (Berkeley, CA) using total electron yield and right-handed circularly polarized X-rays. X-ray magnetic circular dichroism (XMCD) spectroscopy was carried out at beamline 4.0.2 at the ALS using also the total electron yield. A magnetic field of 3.6 T/μ<sub>0</sub> was applied normal to the plane of the thin-film sample. Since this field is insufficient to align and saturate the magnetic moment, the measured values for the spin and orbital moments are a mere fraction of the actual Fe (II) moments. The measurements were performed in the temperature range of 130 K to 250 K. At each temperature, samples were equilibrated for 10 to 15 minutes. The [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] with TCNQ solution was drop-cast on a HOPG substrate and the [Fe(3-bpp)<sub>2</sub>](TCNQ)<sub>2</sub> co-crystal was crushed into powder and attached to a carbon tape.

Thin films of [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] combined with TCNQ were fabricated on OFET chips with and without polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) film and prepared by drop-casting. The PVDF-HFP thin film is about 10 nm thick and was deposited onto the substrate using the Langmuir-Blodgett technique after established methods [37]. The PVDF-HFP pellets were obtained from Sigma Aldrich and dissolved in acetone to create a 0.05% by weight solution. This solution was then drop casted onto a subphase of ultrapure 18 MΩ water and the acetone was allowed to evaporate leaving behind a PVDF-HFP monolayer. The monolayer was transferred to the Fraunhofer substrate at a rate of 1.9 mm/s and allowed to dry completely between layers. Transport

measurements were conducted using a 4200A-SCS parameter analyser and cryogenic Lakeshore probe station. We found the challenges of making a uniform molecular thin film, from solution, presently insurmountable as the  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  favors co-crystallization and does not form a thin film suitable for electrical transport measurements. Üngör et al. [23] reported electrical resistance measurements, however, from  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  single crystals using a four-probe. A 2nd-order Savitzky-Golay (SG) filter was applied to the data to create Figure 1c and Figure 2a. A 7-point SG and 25-point SG were used for resonance and non-resonance regions respectively so that absorption features can be retained even with the smoothing. The filtered data presented with unprocessed data.

### Spin-crossover monitored by X-ray absorption spectroscopy

One benchmark for tracking the spin transition is the change in magnetic susceptibility ( $\chi$ ) as a function of the temperature (T) [11,38]. The magnetic susceptibility of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  shows an abrupt spin transition with a thermal hysteresis of 9 K when using a heating and cooling rate of 2 K/min (Figure 1b). This observation compares well with the temperature-induced SCO reported by Üngör et al. [23] who also showed that the HS state observed at higher temperatures can be trapped by flash cooling to 10 K.

The crystal structure of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$ , determined from X-ray diffraction (XRD), reveals an average Fe-N bond lengths of 2.080 Å, 2.090 Å, and 2.167 Å at 90 K, 100 K, and 250 K, respectively [23]. The larger metal-to-ligand bond lengths in SCO complexes are associated with the conversion to the HS state [39], in agreement with the aforementioned magnetic behaviour of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$ . However, while the magnetic data suggest a nearly complete LS state below 105 K, the Fe-N bond lengths observed at 90 K and 100 K indicate a considerable HS fraction under an X-ray fluence (the average Fe-N bond length expected for the LS state is 2.00 Å). The fraction of HS state occupancy, estimated as 40% at 90 K and 45% at 100 K, was hypothesized to stem from X-ray induced excited spin state trapping (XIESST) [11]. The material also shows a temperature-induced excited spin-state trapping (TIESST) effect at low temperatures, the first reported for any SCO complex combined with TCNQ [23]. The so-called TIESST state remains stable at low temperatures but decays rapidly to the ground LS state when the temperature exceeds 75 K. Further heating to 300 K and cooling to 5 K at 2 K/min follow the pathway of the hysteretic thermally induced spin transition observed upon initial cooling.

To confirm the presence of XIESST, we performed XAS on  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  co-crystals (Figure 1c). The electronic transition from fully occupied Fe  $2p$  orbitals to partially unoccupied  $3d$  orbitals, measured by the  $L$ -edge XAS, indicates the weighted empty Fe  $3d$  orbitals. Based on the ligand field theory, the  $3d$  orbitals split in two energy states,  $t_{2g}$  and  $e_g$  [11–15]. Six  $\text{Fe}^{2+}$   $3d$  electrons occupy three  $t_{2g}$  orbitals in pairs in the LS state, resulting the two  $e_g$  orbitals empty. In the HS state, two electrons are promoted from

$t_{2g}$  to  $e_g$ , leaving both sets of orbitals partially filled/depopulated [11–15]. For  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$ , the excitations to the  $e_g$  and  $t_{2g}$  orbitals are observed at 708 eV and 706 eV, respectively, similar to the XAS transitions observed in other SCO systems [40–48]. The XAS spectra in Figure 1c were taken at temperatures ranging from 50 K to 250 K. The system has a HS state fraction of 0.55 at 50 K which decreases to 0.35 at 60 K, and then increases to above 0.5 as the temperature increases to 250 K. This is distinct from magnetic susceptibility data which shows a nearly complete LS state below 100 K and a complete HS state above 120 K (Figure 1b). Some SCO systems reveal light-induced excited spin-state trapping (LIESST) upon irradiation at low temperatures and return to the LS state with increasing temperature [49–51]. By analogy with the LIESST effect, X-rays can trap the spin state at low temperatures leading to the XIESST effect that is typically suppressed at high temperatures. The XAS spectra (Figure 1c) show a similar effect. The modest variation of HS fractions at different temperatures (Figure 1d) is consistent with the negligible change in the HS fraction found by Üngör et al. [23] using an average Fe-N bond length determined by XRD. The fluence of X-ray from XRD and X-ray absorption could enhance the high spin state occupancy even below the spin state transition temperature.

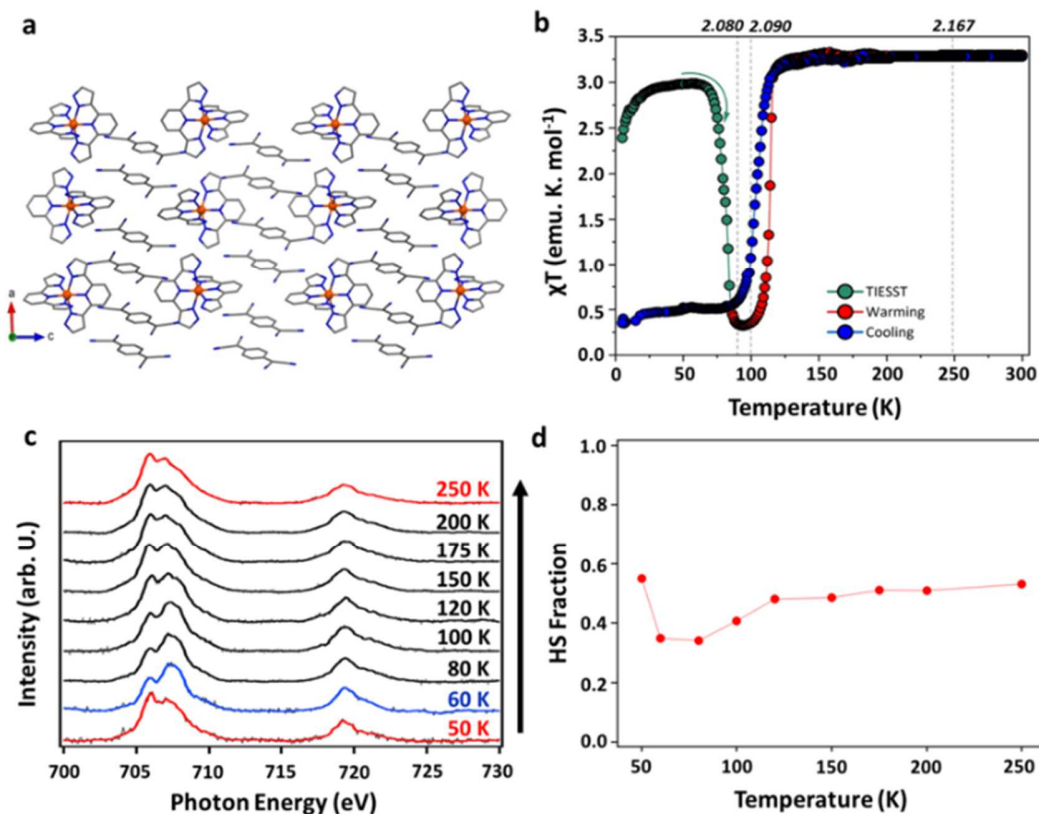


Figure 1: (a) Crystal structure of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  (Fe = orange, N = blue and C = grey) and (b) temperature-dependent  $\chi T$  product of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  (the average Fe–N bond lengths at 90 K, 100 K, and 250 K are indicated by numbers in the top of the plot). (c) Temperature-dependent X-ray absorption spectra of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  (with the filtered data in bold). d) HS fraction extracted from c).

The data presented in Figure 1d do raise a question as to why the fraction of the high spin state does not reach 1.0 above 120 K, as expected from the magnetic measurements [18,23,31]. Although this could indicate some damage of the sample through, e.g., by long-term X-ray exposure, our samples are very stable in our experiments with nearly complete spin transition observed in magnetic measurements even after prolonged storage. Nevertheless, even small crystallites can exhibit surface effects [47,48,52], so that the surface can exhibit a different LS/HS occupancy ratio than the bulk [48,52,53]. XAS taken in the total electron yield mode, as was done here, is quite surface sensitive and thus can provide an indication of spin state that differs substantially from the bulk [47,48,52,53]. Yet the possibility of the surface affecting the electronic structure needs to be recognized [48,52,53], as this can influence the transport properties of the thin film limit.

Chirality effects in molecules arise from mirror symmetry breaking due to large spin-orbital coupling and prevail in SCO materials. Mirror symmetry could be lost during molecular deposition on the substrate, the off-center location of the TCNQ, or the imperfect octahedral coordination of the Fe(II), inducing chirality effects, as seen with several amino acids on surfaces [54,55]. Chirality effects, for example resulting from a loss of inversion symmetry at the top layer of a crystallite, may lead to less successful X-ray excitation of some  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  to the high spin state and could result in the observed high spin state occupancy that is smaller between 60 K and 110 K, if circularly polarized light is used.

In this scenario, it is likely that circularly polarized light preferentially excites some  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  species over the others. This contributes to the incomplete spin state transition observed by XAS. While several reports on soft XESST underlined the central role of secondary electrons in the excitation process [56,57], secondary electron mediated excitations are not expected to be very sensitive to the helicity of circularly polarized light. Overall, the XMCD results indicate that there is imperfect chirality compensation, regardless of the origin. We acknowledge this chiral effect could be due to the lack of center of symmetry at the surface. Several studies have been done on these chirality effects on the SCO materials [58–60]. As a single layer of the  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  co-crystal has no inversion symmetry [23,31], the surface interface ensures that there is spin orbit coupling and chiral properties at the  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  to vacuum interface. The  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  crystal appears to exhibit incomplete chirality compensation which was observed by XMCD measurements.

The temperature dependent XMCD spectra of  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  were recorded in the presence of a magnetic field of  $3.6 \text{ T}/\mu_0$ . The XMCD signal decreases with temperature (Figure 2b). Figure 2c shows the spin and orbital moments, calculated using the sum rules [61] and the integrals of the XAS and XMCD signals (Figures 2a and 2b). We observe a slight increment in the spin moment as the temperature increases from 130 K to 170 K and a possible decrease in the orbital moment with increasing temperature. The latter trend is due to enhanced molecular dynamic motion. It is generally expected that for a moment paramagnet, the spin moment would decrease with increasing temperature but in this study, we see little evidence of a significant incremental change in the spin moment with temperature. The increased spin moment with increasing temperature is more difficult to understand and further investigation is indicated.

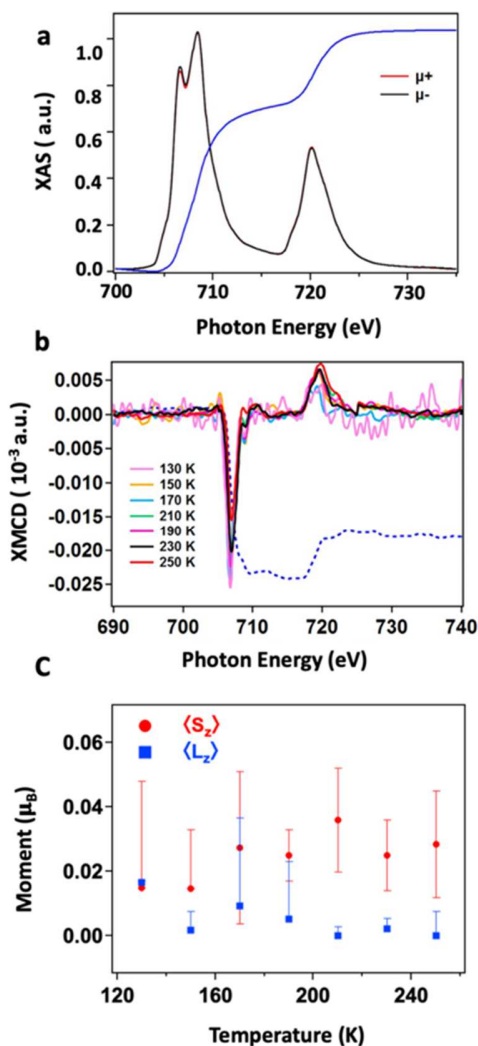




Figure 2: (a) X-ray absorption spectra and (b) temperature dependent XMCD contrast taken for  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$  powder near the Fe  $L$  edges. (c) Calculated spin and orbital moment with respect to temperature

Adding TCNQ to  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  or growing  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  thin films from solution lock  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  largely in the LS state. Figure 3 shows the Fe  $2p$  ( $L$ -edge) XAS data of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  and pure  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  thin films. With increasing temperature, both  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  (Figure 3a) and  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  (Figure 3b) are mostly locked in the LS state. This indicates that the solvent removal process affects the packing of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  molecules by 'freezing' the thin film largely into the LS state. While it is known that adding polar molecules can lock the spin state [20], the solvent can play an important role too. This is consistent with previous reports that the addition or removal of solvent molecules can alter the nature of the spin transition [62,63].

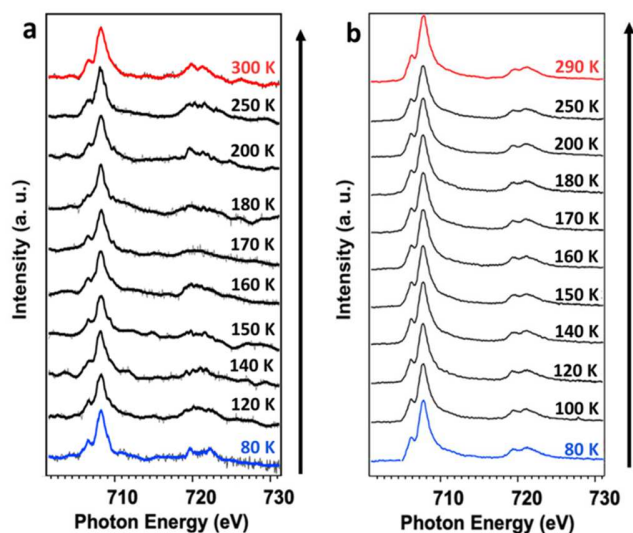


Figure 3: X-ray absorption spectra with increasing temperature for (a)  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  (with the filtered data in bold) and (b) pure  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  film. In both cases, the spin state remains largely unaffected by the temperature change.

The challenges associated with the inclusion of interstitial solvent molecules have been highlighted in recent reports on the co-crystallization of SCO cation  $[\text{Fe}(3\text{-bpp})_2]^{2+}$  (3-bpp = 2,6-bis(pyrazol-3-yl)pyridine) with the  $\text{TCNQ}^{\delta-}$  anions. [23,31] Different

charges of the  $\text{TCNQ}^{\delta-}$  ( $0 < \delta \leq 1$ ) and varying interstitial solvent content alter the SCO temperature, thermal hysteresis, and conductivity. Among these materials,  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2 \cdot 3\text{MeCN}$  has been shown to undergo complete desolvation without the loss of crystallinity. Moreover, the desolvated complex,  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$ , exhibits an abrupt SCO with the transition temperature of 106 K upon cooling and 117 K upon warming [23]. Comparing XAS of both complexes demonstrates a spin transition for  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$  even though it is photoactive and a locked LS state without apparent spin transition for  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  combined with TCNQ.

### Transport properties for composites of $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ and TCNQ

Conductivity measurement at room temperature of  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$  shows a conductance of  $10^{-6} \text{ S cm}^{-1}$  [23]. Such low conductivity is due to the dimerization of integer charged  $\text{TCNQ}^-$  anions [23]. Current and capacitance measurements of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  with the addition of TCNQ are shown in Figure 4. Mixing TCNQ with  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  enhances the conductivity (Figure 4a) of the LS state compared with pure  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  (Figure S1) and reduces the resistance to about  $10^4 \text{ } \Omega \cdot \text{cm}$ . For a two terminal diode like device based on pure  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  the resistivity can be estimated as about  $10^6 \text{ } \Omega \cdot \text{cm}$  (off-state, LS state) and about  $10^3 \text{ } \Omega \cdot \text{cm}$  (on-state, HS state) [10]. As mentioned in the introduction, prospective non-volatile molecular memory device, based on SCO complexes, requires a spin state switching between two spin states at room temperature without either being locked.

Using these current and capacitance measurements, the drift carrier lifetime  $\tau$  was calculated [64–70]

$$\tau = \frac{\left( \left( \left( \frac{C_D \omega \sqrt{2}}{G_0} \right)^2 + 1 \right)^2 - 1 \right)^{\frac{1}{2}}}{\omega},$$

with the conductance  $G_0 = dI/dV$  and the frequency-dependent diffusion capacitance

$$C_D = \frac{G_0}{\omega \sqrt{2}} \left( \sqrt{1 + \omega^2 \tau^2} - 1 \right)^{\frac{1}{2}}.$$

The drift carrier lifetime (Figure 4c) is in the sub seconds range and indicates a longer recombination time in  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  with TCNQ.

Even though  $[\text{Fe}(3\text{-bpp})_2](\text{TCNQ})_2$  shows a clear spin transition, it has low conductivity at room temperature [23]. However  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})] + \text{TCNQ}$  shows high conductivity at room temperature even though the spin state is locked at LS state. Even more remarkable is the very long drift carrier lifetimes. Since adding TCNQ enhances the conductivity of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  thin films, even though the spin state is locked in the LS state, it offers the possibility to develop an organic non-volatile memory device.

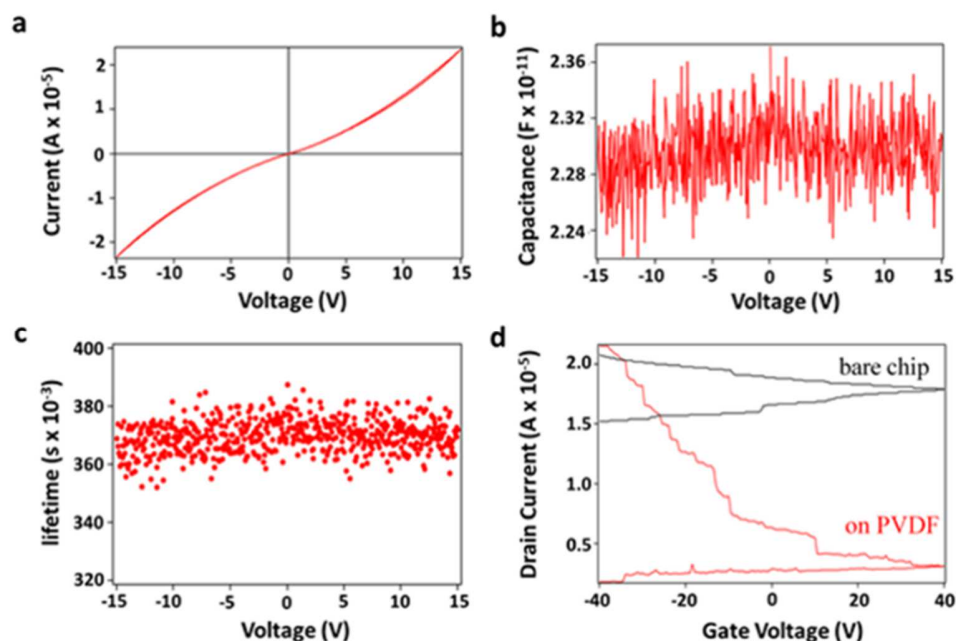


Figure 4 : Electronic transport properties of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  composite thin films. (a) Current-voltage and (b) capacitance-voltage curves at room temperature. (c) Drift carrier lifetime and (d) transistor curves, taken at  $V_{\text{DS}} = 15 \text{ V}$  for  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  composite film on bare chip compared to  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  plus TCNQ composite film deposited on ferroelectric PVDF (red).

To explore the potential of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})] + \text{TCNQ}$  composite thin films for transistor elements, a thin film was deposited on an organic field-effect transistor chip (Figure 4d). Measurements were taken with a constant drain-source voltage ( $V_{\text{ds}}$ ) of 15 V. The drain current shape indicates charge trapping of holes and electrons and this charge trapping is not equal.

The current versus voltage,  $I(V)$ , and capacitance versus voltage,  $C(V)$ , measurements for the  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})] + \text{TCNQ}$  composite thin film were compared to the  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})] + \text{TCNQ}$  composite thin film deposited on polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP), a molecular ferroelectric. The conductivity of composite thin film of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  plus TCNQ deposited on PVDF-HFP is higher (Figure S2) compared to the  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  plus TCNQ composite thin film alone. The PVDF-HFP substrate layer may affect the electron density at the  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  interface as a result of the strong PVDF electric dipole moments [37,71]. This ferroelectric polymer tends to adopt a preferential polarization direction [72] that could well enhance this redistribution of charge population effect. This interface with this organic ferroelectric does appear to affect the whole  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]+\text{TCNQ}$  film, as there is a significant enhancement of the conductivity.

The transistor measurements also show that the current for [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] with TCNQ deposited on PVDF-HFP is higher compared to the [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] with TCNQ composite thin film alone, although both show similar transistor transfer curves. If we consider the slope of the two curves, deposited on bare chip (black) and PVDF-HFP (red), the slope is higher when the PVDF-HFP dielectric layer is used in the transistor. This indicates that the adjacent layer of PVDF-HFP makes the Fe<sup>2+</sup> complex more cationic. The drain current decreases with increasing the gate voltage from negative to positive voltage suggesting that the hole carrier concentration dominates over the electron carrier concentration.

From the I(V) and C(V) measurements for the [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] plus TCNQ, the drift carrier lifetime calculated for the [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] combined with TCNQ composite thin film deposited on PVDF-HFP is also higher compared to the [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] thin TCNQ alone consistent with the enhanced conductivity of [[Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] with TCNQ composite thin film deposited on PVDF-HFP compared to the [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] plus TCNQ composite thin film alone.

The carrier mobility was calculated for [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] plus TCNQ composite thin film alone and deposited on PVDF-HFP using [73–75]

$$\mu_{eff} = \frac{\partial I_d}{\partial V_G} \frac{L}{W} \frac{1}{V_d C_i}$$

where L and W are channel length and width, respectively, C<sub>i</sub> is the gate dielectric capacitance per unit area, and V<sub>d</sub> is the drain potential. The effective carrier mobility is calculated using the gradient of the transistor curve ( $\partial I_d / \partial V_G$ ) of both [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] combined with TCNQ on the bare chip with an oxide dielectric and on PVDF is 5 x 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 50 x 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. This is low mobility but is higher than the mobility values generally expected for organic electronics and corroborates the scenario of charge trapping and coincides with the higher lifetime obtained for the mixtures on bare chip and on PVDF.

We can generalize the appearance of enhanced conductivity as a result of the polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) substrate. Not only does [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] + TCNQ system exhibit enhanced conductivity on the PVDF derivative, but [Fe{H<sub>2</sub>B(pz)<sub>2</sub>}<sub>2</sub>(bipy)] films by themselves (without TCNQ) exhibit enhanced conductivity when deposited on PVDF-HFP (supplementary materials Figure S3). In fact, this effect of the PVDF-HFP substrate extends to the Fe(III) system [Fe(qsal)<sub>2</sub>][TCNQ<sub>2</sub>]. Although [Fe(qsal)<sub>2</sub>][TCNQ<sub>2</sub>] neither exhibits spin crossover, nor is this molecule an Fe(II) complex (it is Fe(III)) it does show an increment in conductance when deposited on PVDF-HFP (supplementary materials Figure S4). We note that Fe(III) systems can also show enhance conductivity when combined with TCNQ [29].

## Conclusion

In conclusion, the  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  co-crystal exhibits both LIEEST and TIESST like effect during X-ray absorption yet retains a small but clear spin transition with temperature. As measured with XAS, there is an incomplete occupancy of either the LS state or HS state due to photoactivity. The  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  crystal appears to exhibit large surface effects, as have been seen before with spin crossover polymers [48,52], that could influence conductivity in the thin film limit.  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  mixed with TCNQ is locked in the LS state like pure  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  and this may be due to the solvent used to prepare the thin film. The conductivity of  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$  thin films increases with the addition of TCNQ polar molecules despite being locked in the LS state but remains lower than what was previously reported for  $[\text{Fe}(\text{3-bpp})_2](\text{TCNQ})_2$  co-crystals. It is clear that conductivity is enhanced by adding TCNQ polar molecules. The materials challenge here is that the fabrication of molecular spin crossover systems, when combined with TCNQ, it needs to be preserved the spin state change and associated conductance for reliable organic thin film devices. This suggests that while the addition of TCNQ to molecular SCO systems is promising, as seen here, the complications, affecting the spin state transition, resulting from the choice of solvent [62,63] and dipolar molecular additions [19,20] need to be better understood and addressed as this is important when developing a device. In spite of these challenges, what is significant here is that this is one of the few examples (along with [22]) where the majority carrier of a spin crossover complex, with an additive like TCNQ, has definitely been determined to be holes through the fabrication of a transistor. The hole doping of the spin crossover complex, by TCNQ, is not unexpected [18,31], but then the conduction channel is through  $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ , not TCNQ.

### Author contributions

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### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This research was supported by the National Science Foundation through NSF-DMR 2003057 [T. Ekanayaka, E. Mishra, J. P. Phillips, R. Cheng, Md. Z. Zaz, P. A. Dowben], the EPSCoR RII Track-1: Emergent Quantum Materials and Technologies (EQUATE), Award OIA-2044049 [K. A. McElveen, R. Y. Lai and R. Streubel] and a Nebraska EPSCoR FIRST Award #OIA-1557417 [R. Streubel]. Use of the Advanced Light Source, Lawrence Berkeley National Laboratory, was supported by the U.S. Department of Energy (DOE) under contract no. DE-AC02-05CH11231. The synthesis and magnetic characterization of the complex was carried out by the Shatruk group as part of research on the NSF grant CHE-1955754.

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