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Manipulation of the molecular spin crossover transition of $\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})$ by addition of polar molecules

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Abstract

The addition of various dipolar molecules is shown to affect the temperature dependence of the spin state occupancy of the much studied spin crossover Fe(II) complex, $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ (pz = pyrazol-1-yl, bipy = 2,2'-bipyridine). Specifically, the addition of benzimidazole results in a re-entrant spin crossover transition, i.e. the spin state starts in the mostly low spin state, then high spin state occupancy increases, and finally the high spin state occupancy decreases with increasing temperature. This behavior contrasts with that observed when the highly polar \square -benzoquinonemonoimine zwitterion $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$ was mixed with $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$, which resulted in locking $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ largely into a low spin state while addition of the ethyl derivative $\text{C}_6\text{H}_2(\cdots\text{NHC}_2\text{H}_5)_2(\cdots\text{O})_2$ did not appear to perturb the spin crossover transition of $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$.

Keywords: Spin Crossover metal organic molecules, X-ray absorption spectroscopy, dipolar heteromolecular molecular interactions, re-entrant transition

1. Introduction

The spin crossover (SCO) complex $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ (pz = pyrazol-1-yl, bipy = 2,2'-bipyridine) typically adopts a high spin state configuration above ca. 160 K and a diamagnetic low spin state at lower temperatures [1-7], although this spin crossover transition temperature can be shifted to lower temperatures by an incident X-ray flux [6]. Recently, it has been established that (i) the nature of the substrate interface [8], (ii) intermolecular coordination [8], or (iii) added dipolar zwitterions, like $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$ [9], will modify the energy barriers to the molecular spin crossover transition. In this respect, the spin crossover complex $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ exhibits remarkable tunability with regard to the spin crossover transition, even to the point of changing the hysteretic behavior [8].

In particular, it has been observed that upon addition of the highly polar π -benzoquinonemonoimine zwitterion $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$, the spin state may be locked, resulting in the LS state persisting at room temperature [7,9]. Remarkably, this allows for the SCO complex locked in a low spin (LS) state to transition to a high spin (HS) state, at room temperature when exposed to incident soft X-rays, facilitating a spin crossover well above the typically allowed temperatures [7,9]. Obviously, this poses the question of whether it is the strong dipole provided by any π -benzoquinonemonoimine zwitterion of the type $\text{C}_6\text{H}_2(\cdots\text{NHR})_2(\cdots\text{O})_2$, that results in locking the molecular spin state of a complex like $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$, or whether interactions specific to the zwitterion where R = H are at work, as suggested by theory [7]. Furthermore, if entropic factors are considered and were to affect the nature of the spin crossover transition, as do local intermolecular coordination, then new phenomena should occur through combination with other polar molecules, as we show here.

2. Experimental Section

The $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ complex was synthesized using published methods [2], and

subsequently combined with various zwitterionic polar molecules by weighting both powders and mixing them together in the desired molar ratios. In this work, we have used either $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ alone or $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ mixed with $\text{C}_6\text{H}_2(\cdots\text{NHR})_2(\cdots\text{O})_2$ (R = H, C₂H₅) or with benzimidazole in a molar ratio of 1:2. The π -benzoquinonemonoimine zwitterions $\text{C}_6\text{H}_2(\cdots\text{NHR})_2(\cdots\text{O})_2$ (R = H, C₂H₅) were synthesized as described elsewhere [10-13]. Benzimidazole was purchased from Sigma-Aldrich (98% purity) and used as received. The mixtures were immersed in isopropyl alcohol and placed in an ultrasonic bath for 60 min resulting in complete solution formation of the molecular mixtures. The samples were subsequently dried, and their powders were spread on conducting tape and loaded into an ultra-high vacuum environment for X-ray absorption spectroscopy (XAS) measurements.

The molecular mixtures leave the core moieties intact as indicated by the Raman (Figure 1), infra-red spectroscopy (Figure 2) and X-ray diffraction. The admixture of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, with the zwitterionic p -benzoquinonemonoimine $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$, in the molar ratio of 1:2, showing Raman (Figure 1b) and IR absorption (Figure 2c) features of each component. The admixture of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, with benzimidazole, in the molar ratio of 1:2, also shows the IR absorption (Figure 2c) features of each component, and the spectroscopic signatures of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, in Figure 2a are clearly evident in Figure 2b. While the Raman, IR spectroscopy and XRD show the core moieties remain intact, we cannot exclude the formation of new molecular complexes though hydrogen bonding, as suggested in [7], or through the formation of more strongly, i.e. covalently, bonded species.

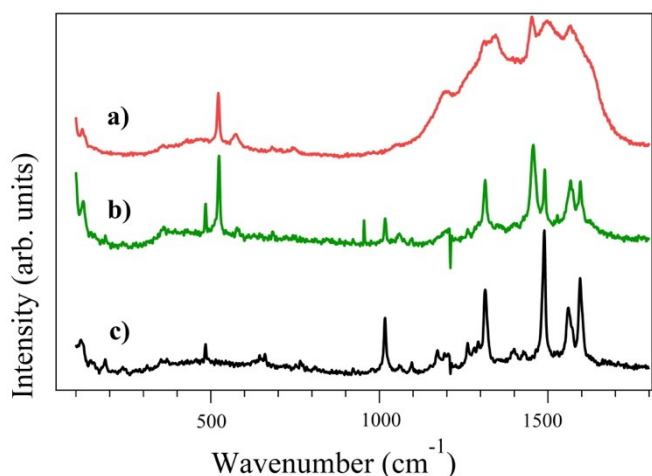


Figure 1. The experimental Raman spectra of the spin-crossover molecule $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (c-black), with the zwitterionic *p*-benzoquinonemonoimine $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$, (a-red), with the admixture of the two, in the molar ratio of 1:2, showing Raman features of each component (b-green).

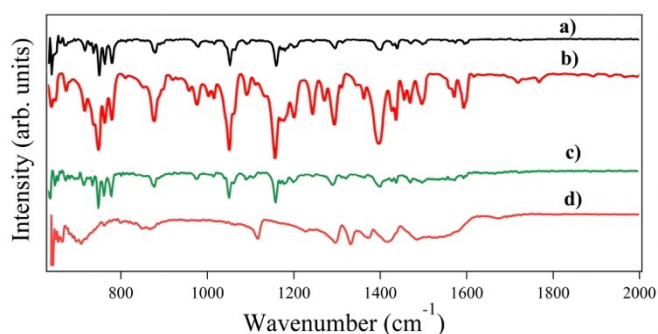


Figure 2. The experimental infra-red absorption spectra of the spin-crossover molecule $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (a), $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$ (d), the admixture of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ and $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$ in the molar ratio of 1:2 (c), and the admixture of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ and benzimidazole in the molar ratio of 1:2 (b), with the latter mixtures showing the IR absorption features of each component.

The XAS measurements of the Fe absorption of the L_3 and L_2 edges were performed at the Advanced Light Source bending magnet beamline 6.3.1 at Lawrence Berkeley National Laboratory [14], with a nominal photon flux of ca. 1.65×10^5 photons/s/ μm^2 . X-ray absorption

spectra were collected in the total electron yield (TEY) mode, at the absorption of the Fe L_3 edge. In the TEY mode, the XAS data were recorded by measuring the compensation current from ground to the sample, proportional to the TEY from the sample. One problem faced in these specific X-ray absorption experiments is that the X-rays initiate a spin state change for $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ on many dielectric substrates upon sufficiently long exposure times, as discussed elsewhere [6,7,9,15]. Consequently, the influence of the X-ray excitation should be kept as low as possible while absorption data must be acquired rapidly, so as to avoid having the measured spin state occupancy to be too strongly affected by the measurement process. In the case of the studies reported here, the XAS spectra have degraded energy resolution due to the need for rapid data acquisition so as to acquire spin state transition rates. The typical Fe L_3 -edge spectrum was acquired within ca. 17 s, as in previous studies [7,8,15]. Temperatures reported in the measurements were stabilized within ± 1 K.

3. Discussion

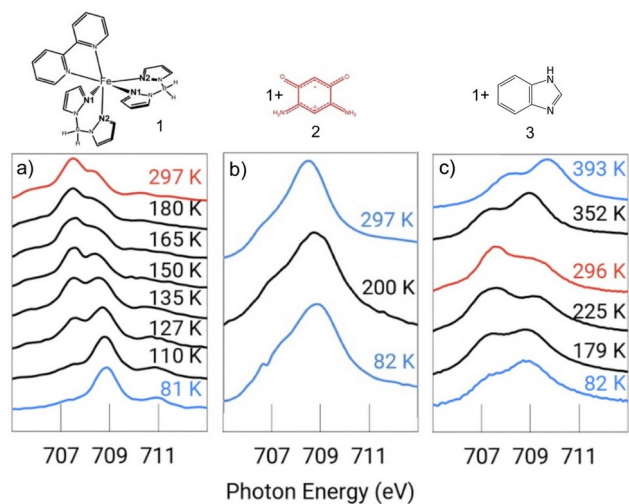
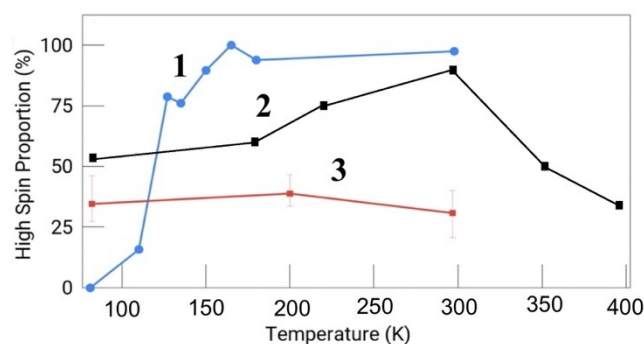


Figure 3. The temperature dependent X-ray absorption spectroscopies of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ mixed with various polar molecules in a 1:2 molar ratio. a) the



temperature dependence of the spin crossover complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ alone, where spectra associated with the low spin (LS) state are highlighted in blue, while those associated with the high spin (HS) state are colored red. b) the temperature dependence of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combined with the \square -benzoquinonemonoimine, indicating dominant retention of low spin state occupancy. c) the temperature dependence of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combined with benzimidazole, showing a shift to low spin state occupancy, then to high spin state occupancy, then a significant return to low spin state occupancy with increasing temperature.

The spin state occupancy of the Fe(II) complex $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ may be extracted from the X-ray absorption spectra. In the low spin (LS) state of $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$, the 3d electrons occupy the t_{2g} orbitals in pairs, leaving the e_g orbitals empty. This is generally observed in the Fe L_3 edge ($2p_{3/2}$) X-ray absorption spectra as a major feature at a photon energy around 708 to 709 eV (Figures 3, blue curves). The high spin (HS) state occupancy, upon heating, is reflected by clear differences in the XAS spectra, as indicated in Figure 3 (red curves), leaving t_{2g} vacancies, with associated XAS peaks at 706.5 eV. We have used the "empty t_{2g} / empty e_g " ratio, as extracted from the typical XAS spectra of the representative $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ HS state (Figure 3a, red) and LS state (Figure 1a, blue), as an empirical approximation of molecules in the HS state at a given temperature [6-9,15-18].

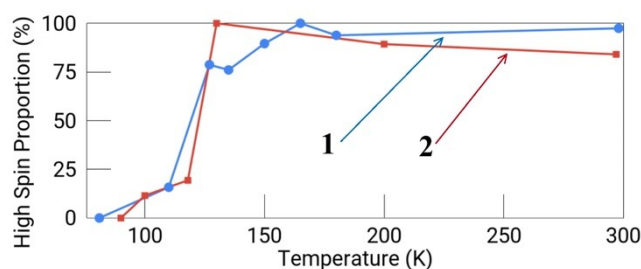
Figure 4. The temperature-dependent high spin state fraction of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ mixed with various polar molecules in a 1:2 molar ratio, extracted from the X-ray absorption spectra. The temperature dependence of the spin crossover complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ alone (curve 1-blue) is plotted along with the temperature dependence of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combined with the \square -benzoquinonemonoimine (curve 3-red), and the temperature dependence of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combined with benzimidazole (curve 2-black).

3.1 Locking and nonlocking dipolar additives

As seen in Figure 3b, and as noted elsewhere [7,9], addition of the \square -benzoquinonemonoimine

zwitterion $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$ will "freeze" or "lock" the spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ so that the expected changes in spin state, with increasing temperature, are not observed. Indeed, as plotted in Figure 4, addition of this zwitterion will typically leave $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ mostly in the LS state, with only about 1/3 of the sample powder in HS state occupancy, independent of temperature. This locking of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ spin state, in the largely low spin state, is also evident in magnetometry, as reported elsewhere [7].

We note that not all \square -benzoquinonemonoimine zwitterions will "freeze" or "lock" the spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ independent of temperature. The addition of the ethyl-substituted \square -benzoquinonemonoimine zwitterion $\text{C}_6\text{H}_2(\cdots\text{NHC}_2\text{H}_5)_2(\cdots\text{O})_2$, for instance, does little to "freeze" or "lock" the spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ and the spin crossover transition remains largely unperturbed, as is evident in the temperature-dependent spin state occupancies plotted in Figure 5. This finding suggests that any argument of spin state locking in the investigated Fe-II complexes, based on dipole-dipole interactions alone, is too simplistic. The different influence of the different \square -benzoquinonemonoimine zwitterions, on the spin crossover transition of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, points to more complex interactions between spin crossover complexes and these dipolar additives. We can infer, from this comparison,



that the ethyl group on the one \square -benzoquinonemonoimine zwitterion creates steric effects that inhibit the interactions that cause the "locking" of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ spin state. These interactions could well include the formation of new molecular complexes though hydrogen bonding as suggested in [7].

Figure 5. The temperature-dependent high spin state fraction of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ alone

(curve 1-blue) compared the temperature dependence of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combined with the ethyl substituted \square -benzoquinonemonoimine $\text{C}_6\text{H}_2(\cdots\text{NHC}_2\text{H}_5)_2(\cdots\text{O})_2$ (curve 2-red).

3.2 Indications of a re-entrant spin crossover transition

Interestingly, when benzimidazole, another polar molecule but with a smaller dipole moment of about 3.6 D [19] compared to the benzoquinonemonoimine zwitterions (ca. 10 D), is mixed with the spin crossover complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, an unusual temperature dependence was observed. The typical spin crossover transition (Figure 1a) is no longer observed, but rather the high spin (HS) state occupancy is seen to increase with increasing temperature (Figure 1c), then the high spin (HS) state occupancy peaks at around room temperature, and then declines with further increase in temperature, as plotted in Figure 4 (black curve). The XAS spectroscopic signature, at the Fe $2p_{3/2}$ at 82 K and at 393 K are nearly identical, for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, when combined with benzimidazole, we find that the tetragonal ligand field is not significantly different between high and low temperature, otherwise the spectroscopic signature of the molecule would change. This behavior is fully reversible and observable in subsequent cooling and heating cycles. This reversibility and the fact that thin films, of the intact and unfragment molecular species, are formed by the evaporation of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ in the region of 400 K and above [2,3,5,7,8,16], tend to exclude that fragmentation of the core moieties is the cause of the results for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, combined with benzimidazole, as seen in Figure 4.

While the maximum of the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ high spin (HS) state occupancy is observed to occur at a much higher temperature than any of the mixtures of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ with other dipolar molecules, the trend of increasing and then decreasing high spin state occupancy is suggestive of a re-entrant transition. Although re-entrant transitions are well known [20,21], and have been discussed in the context of antiferromagnets [22,23] for decades, no prior observation nor any indication (to our

knowledge) of a re-entrant spin crossover transition has been reported. Despite its significantly smaller dipole moment, benzimidazole must perturb the intermolecular interactions that affect the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ spin crossover transition. This may be partially attributed to benzimidazole tendency to bind in linear chains with its polarization aligned in the general direction the chains [19,24]. These interactions possibly play a role in preventing the dipoles of individual molecules from destructively interfering with each other. As such, the added benzimidazole could affect the local coordination that has now been demonstrated to affect the spin crossover transition in $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films [8].

As is evident from the very different influence of various \square -benzoquinonemonoimine zwitterions on $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, that the chemical interactions of \square -benzoquinonemonoimine zwitterion $\text{C}_6\text{H}_2(\cdots\text{NH}_2)_2(\cdots\text{O})_2$ and benzimidazole, with $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$, likely differ significantly. It is quite possible that the different additives result in the formation of different molecular complexes, yet leave the core molecular moieties intact. $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ can be evaporated, when heated to 400 K, to grow a thin films of intact molecules [2,3,5,7,8,15,16]. The fact that neither benzimidazole nor $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ sublime from the admixture of both, in the region of 400 K (Figures 3 and 4), suggests that a new molecular complex is indeed formed. This molecular complex, however, does not significantly perturb the IR signatures of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ and benzimidazole (Figure 2b).

In order to unambiguously claim the occurrence of a reentrant SCO transition, other experimental confirmation would be needed. One should remain vigilant to the possible invasiveness of the XPS on the transition of these molecules, owing to the literature on X-ray induced transition to the high spin state for thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ [6,7,9,15]. We are, however, unaware of promotion of a low spin state though X-ray irradiation, necessary to explain the high-temperature behavior.

4. Conclusion

It has been previously shown that the addition of \square -benzoquinonemonoimine zwitterion

$C_6H_2(\cdots NH_2)_2(\cdots O)_2$ may lock the spin state of $[Fe(H_2B(pz)_2)_2(bipy)]$ to a largely low spin state [7]. The set of new results presented here suggest that the electric dipoles provided by polar molecules added to $[Fe(H_2B(pz)_2)_2(bipy)]$, are not the sole contributors to the spin locking effects previously observed, as the addition of the ethyl-substituted π -benzoquinonemonoimine $C_6H_2(\cdots NHC_2H_5)_2(\cdots O)_2$ does not lock the spin state of $[Fe(H_2B(pz)_2)_2(bipy)]$, and the thermal spin crossover transition is retained. While addition of various molecules to a spin crossover complex, like $[Fe(H_2B(pz)_2)_2(bipy)]$, may influence the spin state occupancy and the temperature dependence of the spin state occupancy, its extent of the perturbation of the spin crossover transition clearly depends on the specific molecule added. Further studies using ordered co-crystals are needed to ascertain the changes in molecular structure and local coordination with changing temperature, as well as an investigation, using precision magnetometry, of the local moment under illumination and without, as a function of temperature, in order to better ascertain the influence of an incident X-ray fluence and the role of entropic factors in the absence of a significant perturbation.

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References

- [1] Moliner N, Salmon L, Capes L, Muñoz M C, Létard J-F, Bousseksou A, Tuchagues J, McGarvey J J, Dennis A C, Castro M, Burriel R and Real J A 2002 *J. Phys. Chem. B* **106** 4276–83
- [2] Palamarciuc T, Oberg J C, El Hallak F, Hirjibehedin C F, Serri M, Heutz S, Létard J-F and Rosa P 2012 *J. Mater. Chem.* **22** 9690
- [3] Pronschinske A, Chen Y, Lewis G F, Shultz D A, Calzolari A, Buongiorno Nardelli M and Dougherty D B 2013 *Nano Lett.* **13** 1429–34
- [4] Real J A, Muñoz M C, Faus J and Solans X 1997 *Inorg. Chem.* **36** 3008–13
- [5] Zhang X, Palamarciuc T, Rosa P, Létard J-F, Doudin B, Zhang Z, Wang J and Dowben P A 2012 *J. Phys. Chem. C* **116** 23291–6
- [6] Zhang X, Mu S, Chastanet G, Daro N, Palamarciuc T, Rosa P, Létard J-F, Liu J, Sterbinsky G E, Arena D A, Etrillard C, Kundys B, Doudin B and Dowben P A 2015 *J. Phys. Chem. C* **119** 16293–302
- [7] Zhang X, Costa P S, Hooper J, Miller D P, N'Diaye A T, Beniwal S, Jiang X, Yin Y, Rosa P, Routaboul L, Gonidec M, Poggini L, Braunstein P, Doudin B, Xu X, Enders A, Zurek E and Dowben P A 2017 *Adv. Mater.* **29** 1702257
- [8] Jiang X, Hao G, Wang X, Mosey A, Zhang X, Yu L, Yost A J,

- Zhang X, DiChiara A D, N'Diaye A T, Cheng X, Zhang J, Cheng R, Xu X and Dowben P A 2019 *J. Phys. Condens. Matter* **31** 315401
- [9] Costa P, Hao G, N'Diaye A T, Routaboul L, Braunstein P, Zhang X, Zhang J, Doudin B, Enders A and Dowben P A 2018 *J. Phys. Condens. Matter* **30** 305503
- [10] Braunstein P, Siri O, Taquet J, Rohmer M-M, Bénard M and Welter R 2003 *J. Am. Chem. Soc.* **125** 12246-56
- [11] Siri O and Braunstein P 2002 *Chem. Commun.* 208-9
- [12] Tamboura F B, Cazin C S J, Pattacini R and Braunstein P 2009 *Eur. J. Org. Chem.* **2009** 3340-50
- [13] Yang Q-Z, Siri O and Braunstein P 2005 *Chem. - A Eur. J.* **11** 7237-46
- [14] Nachimuthu P 2004 *AIP Conference Proceedings* vol 705 (AIP) 454-7
- [15] Zhang X, N'Diaye A T, Jiang X, Zhang X, Yin Y, Chen X, Hong X, Xu X and Dowben P A 2018 *Chem. Commun.* **54** 944-7
- [16] Beniwal S, Zhang X, Mu S, Naim A, Rosa P, Chastanet G, Létard J-F, Liu J, Sterbinsky G E, Arena D A, Dowben P A and Enders A 2016 *J. Phys. Condens. Matter* **28** 206002
- [17] Wäckerlin C, Donati F, Singha A, Baltic R, Decurtins S, Liu S-X, Rusponi S and Dreiser J 2018 *J. Phys. Chem. C* **122** 8202-8
- [18] Warner B, Oberg J C, Gill T G, El Hallak F, Hirjibehedin C F, Serri M, Heutz S, Arrio M-A, Saintavit P, Mannini M, Poneti G, Sessoli R and Rosa P 2013 *J. Phys. Chem. Lett.* **4** 1546-52
- [19] Costa P S, Miller D P, Teeter J D, Beniwal S, Zurek E, Sinitskii A, Hooper J and Enders A 2016 *J. Phys. Chem. C* **120** 5804-9
- [20] Simons B J, Teng B, Zhou S, Zhou L, Chen X, Wu M and Fu H 2014 *Chem. Phys. Lett.* **605-606** 121-5
- [21] Bayor J S, Teng B and Wang L 2018 *PLoS One* **13** e0199459
- [22] Aharony A, Birgeneau R J, Coniglio A, Kastner M A and Stanley H E 1988 *Phys. Rev. Lett.* **60** 1330-3
- [23] Glazman L I and Ioselevich A S 1990 *Zeitschrift für Phys. B Condens. Matter* **80** 133-7
- [24] Zieliński W and Katrusiak A 2013 *Cryst. Growth Des.* **13** 696-700