Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Article pubs.acs.org/IC

Guest-Adaptable Spin Crossover Properties in a Dinuclear Species **Underpinned by Supramolecular Interactions**

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Supporting Information

ABSTRACT: Molecular crystals with guest-adaptable crystalline structures and properties are comparatively rare owing to their inherent reduced structural stability and malleability to support molecular variation. To overcome this intrinsic challenge, here we introduce structural stabilizing supramolecular interactions into a dinuclear material and henceforth demonstrate a dynamic structural and spin crossover property interchange between solvated (A·3MeOH) and desolvated $(\hat{A} \cdot \emptyset)$ products $(\hat{A} =$ $[Fe^{II}_{2}(o-NTrz)_{5}(NCS)_{4}];$ 4-(o-nitrobenzyl)imino-1,2,4-triazole). Relatively uncommon for molecular species, the guest molecules in A·3MeOH are evolved $(A \cdot \emptyset)$ via a single-crystal to single-crystal transformation with affiliated phase transition resulting in a reversible transformation from one- to two-step spin crossover (SCO) transition character. We additionally present the water-saturated product $(A \cdot 3H_2O)$, which distinctly shows an abrupt one-step SCO character with a 22 K wide thermal hysteresis loop. Detailed structure-property analysis highlights that the substantial structural



malleability and guest-adaptable SCO properties of this dinuclear species are afforded by the supportive, yet flexible, supramolecular interaction pathways derived from the ligand functionalization.

INTRODUCTION

Porous materials, including metal-organic frameworks (MOFs), coordination polymers (PCPs) and organic frameworks, are intensely investigated for their ability to absorb molecular guests,¹ often with concomitant guest-triggered modulation to physical properties.² In cases where guest induced physical or chemical changes occur, such as color or luminescence variation, molecular sensing opportunities arise.³ Somewhat counterintuitively, nonporous materials such as molecular materials can also act as molecular sponges;⁴ however, examples are relatively rare as guest removal and replacement chiefly results in lattice collapse due to the absence of the long-range structural supports that are intrinsically present in MOFs and PCPs.³ Indeed, one substantial driver for actively developing the field of functional molecular materials is their inherent structural malleability, which in turn may lead to enhanced structural and property modification.⁶

Of the various examples of guest-triggered structure and property variation thus far reported, those with spin-state adaptable metal ions are important candidates.⁷ It is wellestablished that spin crossover (SCO) activity is extremely sensitive to local structure variation, whereby even subtle lattice change occurring alongside guest interchange can confer substantial magnetic, color and structure variation. While this inherent platform for host-guest sensing has been intensely investigated in SCO-PCPs,^{2a,d,8} it has been somewhat less extensively exploited in molecular crystals.4b,c,e-h,9 Notable

examples include $[Fe(bpp)(H_2L)](ClO_4)_2$ (guest) (bpp = 2,6bis(pyrazol-3-yl)pyridine, $H_2L = 2,6$ -bis(5-(2-methoxyphenyl)pyrazol-3-yl)pyridine)), and $[Fe^{II}_2(L)_2(CH_3CN)_4](BF_4)_4$. $2CH_3CN$ (L = 4-(4-methylphenyl)-3-(3-pyridazinyl)-5-pyridyl-4H-1,2,4-triazole), both showing vapochromism and on-off SCO switching with guest modulation.^{4e,f} Alongside this, highlighting the substantial adaptability of nonporous complex to structural transformations, several independent studies show a dynamic guest-induced conversion from discrete to 1D chain structures.4f,h,9j

In conjunction with using molecular variation to induce onoff molecular switching, various studies on SCO-PCPs have illustrated that guest-manipulation is a powerful tool to tune SCO character more subtly by for example inducing multistep switching exchange.^{8d,g-k',9i} Given that such diversity is apparent in traditional porous materials, herein we show that such dynamic, guest-induced SCO switching can also be observed in molecular materials. For this study, we focus on the dinuclear species $[Fe_2(R-trz)_5(NCX)_4]^{10}$ (Scheme 1), which alongside analogous trinuclear species,¹¹ are rapidly attracting attention as readily attainable structural protypes of the widely acclaimed, highly cooperative triazole-containing 1D chains of the type $[Fe^{II}(R-trz)_3]A_2$ (R-trz = R-1,2,4-triazole; A = anion).¹² To date, as for practically all dinuclear SCO species,¹³ spin transitions with comparable cooperativity

Received: September 24, 2018

Scheme 1. Structures⁴



^{*a*}(a) Dinuclear $[Fe_2(R-trz)_5(NCS)_4]$ core structure; (b) *o*-NTrz, 4-(*o*-nitrobenzyl)imino-1,2,4-triazole (blue: N–Fe binding groups, red: functionality).

to polymeric species are yet to be reported in this family. Here, in the parallel pursuit of improved communication pathways and increased lattice stability to guest sorption/desorption, we include specific ligand functionalization (Scheme 1:red) to induce supportive, flexible and long-range supramolecular interaction pathways. By this approach, we show substantial structural malleability to molecular guests, as supported by these supramolecular interactions, and a diverse assortment of guest-induced SCO properties embodied in the one dinuclear moiety; this includes one- and two-step transitions, and strong spin-state switching cooperativity in the form of an abrupt and hysteretic one-step transition.

EXPERIMENTAL SECTION

General Procedures. All reagents were commercially available and were used as received. Iron(II) perchlorate was handled carefully and in small amounts to avoid any potential explosions.

Ligand Synthesis. 4-Amino-4*H*-1,2,4-triazole (1.5 g, 17.8 mmol) and 2-nitrobenzaldehyde (3.3 g, 22 mmol) were dissolved in ethanol (50 mL). Concentrated sulfuric acid (0.3 mL) was added, and the solution was heated to reflux for 24 h. Upon cooling, the solution was concentrated, and the product precipitated on ice. The precipitate was filtered and washed with distilled water (10 mL), then isopropanol (10 mL), yielding 4-(*o*-nitrobenzyl)imino-1,2,4-triazole (*o*-NTrz) as a pale-yellow powder (2.6 g, 67%). Mp 126 °C. Elemental Analysis (%): C 49.77, H 3.25, N 32.25; found: C 49.62, H 3.30, N 32.11. ¹H NMR (300 MHz, MeOD): 9.40 (1H, s), 9.10 (1H, s), 8.22 (1H, dd, *J* = 7.9, 0.6) 8.17 (1H, dd, *J* = 7.5, 1.2), 7.88 (1H, td, *J* = 7.5, 0.6), 7.81 (1H, td, 7.9, 1.2). ESI-MS (*m*/*z*) calcd: 217.06. Found: 217.04.

3MeOH) and $[Fe_2(\mu \text{-}o\text{-}NTrz)_3(o\text{-}NTrz)_2(NCS)_4]\cdot 3H_2O$ ($A\cdot 3H_2O$). Sodium thiocyanate (30 mg, 0.37 mmol), iron(II) perchlorate hexahydrate (31 mg, 0.85 mmol), and ascorbic acid (5-10 mg) were dissolved in methanol (2 mL). This solution was added dropwise to a separately prepared solution of o-NTrz (96 mg, 0.44 mmol) dissolved in methanol (5 mL). Red block-shaped crystals of A· 3MeOH formed over several days (ca. 90% yield; Figure S1a). Orange rodlike crystals of A·3H₂O (Figure S1b) cocrystallize alongside A· 3MeOH (major product (~75%): A·3MeOH; minor product (~25%): $\mathbf{A} \cdot 3\mathbf{H}_2\mathbf{O}$). The IR spectra of both phases (and $\mathbf{A} \cdot \mathbf{\emptyset}$) are identical. IR (cm⁻¹): 2084 (s), 1526 (s), 1347 (s), 1176 (w), 1061 (s), 853 (w), 791 (w), 742 (w), 624 (s). Pure samples of A·3MeOH and A·3H₂O were subsequently prepared by seeding freshly prepared reaction solutions with the respective phase. Phase purity and solvent content for these two phases was determined by a combination of thermogravimetric analysis, powder X-ray diffraction and single crystal X-ray diffraction. Elemental analysis was conducted on these phases, but the results were not conducive for proving phase purity, as although crystals of A-3MeOH are relatively stable in solution, exposure to air over time results in desolvation (A· \emptyset see below) and crystals of A·3H₂O dissolve in solution over a period of days and are not stable as dry crystals.

 $[Fe_2(\mu-o-NTrz)_3(o-NTrz)_2(NCS)_4]$ (**A**·Ø). Crystals of **A**·3MeOH were dried under dynamic vacuum for 72 h, producing orange-yellow

crystals of **A**·Ø (100% yield; Figure S1c). Elemental Analysis (%): C 41.16, H 2.47, N 28.41, S 8.97. Found: C 41.00, H 2.56, N 28.32, S 8.77.

Powder X-ray Diffraction. Bulk crystalline samples of A·3MeOH and A·3H₂O were carefully ground into a polycrystalline powder in a slurry of methanol and loaded into glass capillaries. The experimental patterns were compared to patterns calculated from single crystal X-ray diffraction data to assess phase purity (Figures S2 and S3).

Thermogravimetric Analysis. Samples of A·3MeOH and A· $3H_2O$ were heated from room temperature to 600 °C at a rate of 1 °C min⁻¹ under a dry N₂ gas flow (20 mL min⁻¹) using a TA Instruments Discovery Thermogravimetric Analyzer (Figures S4 and S5).

Magnetic Susceptibility Measurements. Data were collected on a Quantum Design Versalab System with a vibrating sample magnetometer attachment. Samples were loaded into a polyethylene sample container and sealed with Teflon tape. Measurements were taken continuously with a ramp rate of 2 K min⁻¹ (no overshoot) under a field of 0.3 T, in the range 250–50 K for A·3MeOH and A· $3H_2O$ and 320-50 K for A·Ø. Data were also collected at slower scan rates (1 and 0.5 K min⁻¹; Figures S6 and S7).

Single Crystal X-ray Diffraction. Data were collected on an Agilent SuperNova Dual Source diffractometer employing a Cu K_a radiation source ($\lambda = 1.5418$ Å). Data integration and reduction were performed using CrysAlisPro.¹⁴ Structural solution for all materials was completed within SHELXS-97 and refined using SHELXL-97¹⁵ within the X-SEED user interface.^{16,17} All atoms except those in disordered positions were refined anisotropically, and hydrogen atoms were fixed using the riding model. The occupancies of the disordered structural components (all of which show 2-fold disorder) were refined using free variables. ORTEP representations (50% probability ellipsoids) for all structures are shown in Figures S8-14. Tables S1-S3 contain crystallographic data and refinement details for A·3MeOH, $A \cdot \emptyset$, and $A \cdot 3H_2O$, respectively. Table S4 reports selected parameters for all structures, and Table S5 hydrogen bonding interactions. Figure S15 shows the hydrogen bonding interactions for each complex with reference to Table S5. Figures S15-S17 show representative packing diagrams for A·3MeOH, A·Ø, and A·3H₂O, respectively. CCDC 1502200-1502204 and CCDC 1856712 contain the supplementary crystallographic data.

Variable-temperature single crystal unit cell parameters were collected over the range 250–90 K at 10 K intervals for A·3MeOH and A·Ø. The unit cell parameter and volume evolution are plotted versus temperature in Figure S19.

RESULTS AND DISCUSSION

Synthesis and Characterization. The novel ligand 4-(onitrobenzyl)imino-1,2,4-triazole (o-NTrz, Scheme 1) was prepared by the condensation reaction of 4-amino-4H-1,2,4triazole and 2-nitrobenzaldehyde. Single crystals of $[Fe_2(\mu - o -$ NTrz)₃(o-NTrz)₂(NCS)₄]·3MeOH form over several days from a methanolic solution of iron(II) perchlorate hexahydrate, sodium thiocyanate, ascorbic acid, and o-NTrz. Two guest-variant phases of the dinuclear species, A·3MeOH and A· $3H_2O$, cocrystallize under these conditions; with A·3MeOH the major product (ca. 75:25 for $A \cdot 3MeOH: A \cdot 3H_2O$). The solvatomorphs can be visually distinguished by color and crystal morphology; A·3MeOH forms as dark-red blocks and A·3H₂O as orange elongated blocks (Figure S1). Attempts to form the latter phase in neat water or water:methanol solutions were unsuccessful. Notably, once formed, the crystals of A-3H₂O redissolve into the methanolic mother liquor over a period of days, so they must be utilized immediately upon crystallization. However, once redissolved, pure phases of either A·3MeOH or A·3H₂O can be reformed from the same solution with crystal seeding. The A·3MeOH crystals are stable in solution.



Figure 1. Variable-temperature magnetic susceptibility measurement for (a) \mathbf{A} ·3MeOH, (b) \mathbf{A} ·Ø, and (c) \mathbf{A} ·3H₂O (250–50–250 K; sweep mode; scan rate: 2 K min⁻¹). Inset: Spin-state per dinuclear unit at the indicated plateau region, as determined by structural analysis (Fe–Fe; HS: gold; LS: purple).

Thermogravimetry on A·3MeOH and A·3H₂O reveal substantially distinct guest evolution, dinuclear stability, and decomposition pathways. For A·3MeOH, three methanol molecules are evolved together below ca. 100 °C. However, for A·3H₂O, two water molecules are desorbed below 100 °C and removal of the third requires heating to ca. 150 °C (Figures S4 and S5). Thermogravimetry furthermore reveals that the A·3MeOH apohost phase $(A \cdot \emptyset)$ is present over the temperature range 100-220 °C, whereas decomposition occurs soon after guest desorption from A·3H₂O. Methanol desorption from A·3MeOH occurs via a single-crystal to singlecrystal transformation and with a color change from dark-red to orange-yellow (Figure S1). This process is reversible via exposure of $\mathbf{A} \cdot \mathbf{\emptyset}$ to methanol vapor or neat methanol, although with loss of monocrystallinity. Water molecule removal from $A \cdot 3H_2O$ results in irreversible sample degradation.

Dynamic Spin Crossover Properties. Temperaturedependent magnetic susceptibility measurements were performed on A·3MeOH, A· \emptyset and A·3H₂O revealing a broad diversity of SCO transition profile characteristics (Figure 1).

For A·3MeOH (Figure 1a) at 250 K, the $\chi_M T$ value of 6.64 cm K mol⁻¹ is consistent with two HS Fe^{II} ions per dinuclear unit. These values remain constant until 200 K, below which there is a gradual decrease in $\chi_M T$ values to ca. 150 K followed by a more abrupt decrease to 115 K. Below approximately 100 K, the $\chi_M T$ values remain constant at ca. 0.25 cm K mol⁻¹, consistent with two LS Fe^{II} ions per dinuclear unit. Negligible thermal hysteresis is observed over the cooling and heating modes, and the SCO profile is insensitive to collection scan rate. The gradual, complete one-step SCO transition for A·3MeOH shows a transition temperature $(T_{1/2})$ of 135 K.

For A·Ø (Figure 1b), between 250 and 200 K the $\chi_{\rm M}T$ values remain constant at 6.80 cm K mol⁻¹, consistent with two HS Fe^{II} ions per dinuclear unit. Over the range of 200-175 K, the $\chi_{\rm M}T$ values decrease rapidly to 3.39 cm K mol⁻¹ and then again to 0.25 cm K mol⁻¹ over the range of 175–125 K. The $\chi_M T$ values at the subtle intermediate plateau (ca. 175 K) are consistent with a 1:1 HS/LS ratio of Fe^{II} sites. The $\chi_{\rm M}T$ values below approximately 100 K remain constant at ca. 0.25 cm K mol⁻¹, consistent with LS Fe^{II} ions. Narrow thermal hysteresis is observed over the heating and cooling profiles which shows a subtle scan rate dependence (Figure S6). The complete, two-step SCO transition of $A \cdot Ø$ (2 K min⁻¹) is characterized by $T_{1/2(1)\downarrow\uparrow}$: 181, 185 K and $T_{1/2(2)\downarrow\uparrow}$: 141, 148 K, with narrow hysteresis ($\Delta T_{(1)}$: 4 K, $\Delta T_{(2)}$: 7 K). This is the first evidence of a complete two-step SCO in the [Fe2(R $trz)_5(NCX)_4$ family.¹⁰

For $A \cdot 3H_2O$ (Figure 1c), with cooling the $\chi_M T$ values remain constant at ca. 6.74 cm K mol⁻¹ between 250 and 160 K, consistent with two HS Fe^{II} ions per dinuclear unit. Below 160 K, the $\chi_M T$ values decrease abruptly to 0.78 cm K mol⁻¹, indicating a complete, one-step conversion to LS Fe^{II} ions. The $\chi_M T$ values remain constant at this value below 130 K. A wide thermal hysteresis loop is observed over the cooling and heating cycles which shows subtle thermal scan rate dependence (Figure S7). The complete and hysteretic one-step SCO transition of $A \cdot 3H_2O$ (2 K min⁻¹) is characterized by $T_{1/2\downarrow\uparrow}$: 150, 172 K, ΔT : 22 K. This is the first evidence of strong cooperativity in the [Fe₂(R-trz)₅(NCX)₄] family and among the widest thermal hysteresis reported thus far for a dinuclear complex.¹⁰

Structure of A-3MeOH. Variable-temperature single crystal X-ray diffraction unit cell data were collected on A-3MeOH at 10 K intervals over the temperature range 250 to 90 K revealing a primitive monoclinic symmetry $(P2_1/c)$ over the entire one-step SCO profile. A plot of the unit cell evolution versus temperature maps the gradual one-step spin transition observed by magnetic susceptibility (Figure S19).

Full-sphere single crystal data were collected at 250 and 90 K (Tables S1 and S4), representative of the high and low temperature plateaus of the gradual one-step spin transition. Structural analyses reveal an entire dinuclear complex in the asymmetric unit, thus defining two crystallographically unique Fe^{II} sites, [Fe1–Fe2] (Figure 2a). The Fe–N bond lengths at 250 K ($d_{\text{Fe-N}}$: [2.172(6), 2.166(5) Å]) and 90 K ($d_{\text{Fe-N}}$: [1.972(6), 1.967(6) Å]) highlight a complete [HS–HS] to [LS–LS] transition of both Fe^{II} sites.^{7d}

The crystalline lattice is propagated by a dense supramolecular interaction network comprised of both dinuclear... dinuclear and dinuclear...MeOH interactions (Figure 2a; Table S4). Notably, the methanol molecules participate in a collection of interactions with the nitro-groups alongside other aromatic interactions, as illustrated in Figure 2b. Various other dinuclear...dinuclear interactions are present, in most case involving the nitro-groups (for example, see Figure 2b).

Overall, the presence of a one-step spin transition for A-3MeOH is somewhat counterintuitive given the existence of two crystallographically distinct Fe^{II} sites; notably, however, this has been similarly observed in $[Fe_2(bzCl_2trz)_5(NCS)_4]$ · H₂O (bzCl_2trz = 2,5-dichloride-4-phenylimino-1,2,4-trizole) and $[Fe_2(napthtrz)_5(NCSe)_4]$ ·2DMF·2H₂O (napthtrz = naphthylimino-1,2,4-triazole).^{10e,f} In the majority of cases, SCO ion distinction results in some form of multistep switching behavior, including trapped [HS–LS] species such as observed in the related dinuclear $[Fe_2(bztrz)_5(NCS)_2]$ ·xMeOH (bztrz =



Figure 2. (a) Structural representation of an entire dinuclear moiety of A·3MeOH, which has two distinct Fe^{II} sites per dinuclear unit, [Fe1–Fe2]; various dinuclear…dinuclear (red) and dinuclear…methanol (blue) supramolecular interactions. (b) Guest-removal (A·Ø) occurs via a singlecrystal to single-crystal transformation with the phase transition introducing a C_2 axis ($P2_1/n \rightarrow C2/c$) and dynamic ligand rotation (inset); single unique Fe^{II} site per dinuclear, [Fe1–Fe1']; relevant dinuclear…dinuclear (red) supramolecular interactions. Hydrogen atoms, third MeOH molecule, and secondary ligand disorder not shown.

4-phenylimino-1,2,4-triazole).^{10d} This suggests that this system is best rationalized as one in which the intermolecular interactions provide insufficient cooperativity between dinuclear units to sharpen the transition to the point where individual transitions of inequivalent Fe sites (or dinuclear two-step behavior resulting from intramolecular cooperativity stabilizing a local HS-LS state) become thermally resolved. An alternative interpretation is that each dinuclear unit undergoes a cooperative HS-HS to LS-LS intramolecular transition that overrides the Fe^{II} site inequivalence, but that weak intermolecular cooperativity broadens this transition; however, we can largely discount this possibility due to the observation of two-step behavior in $\mathbf{A} \cdot \mathbf{\emptyset}$, as discussed below. Probing the structure of A·3MeOH reveals several notable distinctions to the inner and outer coordination sphere of Fe1 and Fe2 which support a magneto-structural rationalization. First, the HS state phase shows a mild but clear difference in the octahedral distortion about Fe1 and Fe2 ($\Sigma = 29.7$ and 23.9° , respectively).7d This distortive difference is readily accounted for by the prominent variance to supramolecular interactions about the Fe1 and Fe2 outer coordination sphere. Most notably, Fe1 is surrounded by more dinuclear---methanol interactions than is Fe2 (Figure 2a). Furthermore, while the SCO behavior is overall one-step, an underlying two-step behavior exists comprised of distinct regions of more gradual (i.e., ~200-150 K) and abrupt (i.e., ~150-125 K) spin-state transition pathways (Figure 1a). Such behavior is not uncommon,¹⁸ and here likely indicates that a fraction of the Fe^{II} sites initiate a HS to LS transition, perhaps in this case related to the presence of disorder at some of the nitro oxygen atom sites and their related interactions,^{18b,c} and once the LS concentration is sufficiently high, the remainder of the transition occurs in a more cooperative fashion. The driving force for this is likely an enhancement of communication pathways with LS doping due to compression of dinuclear... dinuclear and dinuclear...MeOH interactions. Alongside this, the LS state appears to show substantially reduced strain over the short Fe…N-N…Fe bridge, as evidenced by the reduced difference in octahedral distortion between the two Fe^{II} site in each dinuclear in the LS state ($\Delta \Sigma_{\text{Fe1-Fe2}} = 5.8^{\circ}$ at 250 K; $\Delta \Sigma_{\text{Fe1-Fe2}} = 0.8^{\circ}$ at 90 K) indicating it is the preferred phase.^{7d}

Dynamic Guest Removal (A·Ø). Molecular methanol evacuation from A·3MeOH occurs via a single-crystal to single-crystal transformation from primitive monoclinic $(P2_1/n)$ to *C*-centered monoclinic (C2/c) for A·Ø. This increase in

symmetry imposes a C_2 axis through the center of the dinuclear unit, resulting in only half a dinuclear moiety in the asymmetric unit (Figure 2b). Consequentially, the two unique Fe^{II} sites observed for A·3MeOH ([Fe1–Fe2]) convert to a single crystallographically distinct Fe^{II} site in A·Ø ([Fe1–Fe1']; Figure 2b).

Variable-temperature single crystal X-ray diffraction unit cell data collected on $\mathbf{A} \cdot \mathbf{\emptyset}$ at 10 K intervals over the temperature range of 250–90 K reveal a retention of the monoclinic C symmetry (C2/c) over the entire two-step spin transition. Importantly, a plot of the unit cell evolution versus temperature clearly shows a two-step character consistent with that observed by magnetic susceptibility (Figure S19).

Full sphere single crystal data were collected at 250, 150, and 90 K (Tables S2 and S4), representative of the high, intermediate and low temperature plateau of the two-step spin transition. Structural analyses reveal a systematic decrease in average apparent Fe1-N bond lengths ($d_{\text{Fe-N}}$: 2.167(11), 2.035(9) and 1.966(10) Å, at 250, 150, and 90 K, respectively) with the 250 and 90 K lengths, confirming a complete HS to LS transition (Figure 1b).^{7d} The Fe–N bond lengths at 150 K are intermediate in length, indicating a 1:1 mix of HS/LS and LS/HS sites (Figure 1b). This result confirms that within each dinuclear unit local order of the type [HS-LS] and [LS-HS] exists, but without long-range order conferred throughout the crystal lattice. We can discount the other possible spin-state distribution of pairs of [HS-HS] and [LS-LS] dimers¹⁹ on two grounds: This would result in unit cell doubling or the emergence of a lower crystalline symmetry if 3D long-range ordered or diffuse scattering if associated with lower dimensional and/or short-range order;²⁰ this would likely result in distinctly different local intramolecular Fe---Fe distances, leading to a pronounced elongation of the Fe site atomic displacement parameter in the intermediate phase, which is not seen (see Figure S10).

A significant outcome of the increased symmetry in $\mathbf{A} \cdot \mathbf{O}$ is that one of the three $\mu_{1,2}$ -bridging ligands is centered over the C_2 axis, resulting in 2-fold disorder of the ligand (Figure 2b). The most substantial consequence of this disorder is the presence of the peripheral NO₂ group in two opposing positions in equal ratios (Figure 2b). For this to transpire, concomitant with methanol removal 50% of the disordered μ o-NTrz ligands would need to undergo a solid-state rotation as depicted in Figure 2. Considering this molecular rotation,²¹ it is notable for the guest removal process to proceed in a singlecrystal to single-crystal manner. The preserved crystallinity is undoubtably due to the structural stabilizing platform provided by the facile replacement of dinuclear···methanol interactions in A·3MeOH with new dinuclear···dinuclear interactions, as illustrated in Figure 2. Providing evidence of the intrinsic role that the inclusion of the nitro-groups plays in providing structure adaptability to chemical perturbation, all the new dinuclear···dinuclear interactions are all formed utilizing the nitro-groups (Figure 2b).

Alongside the various structural distinctions over the A. 3MeOH to A·Ø transformation, guest removal sees a one-step transition converted into a two-step SCO character. As for A. 3MeOH, this is somewhat counterintuitive given that the two crystallographically distinct Fe^{II} sites merge into all equivalent sites in A·Ø. Indeed, equivalent symmetry and disorder was similarly observed for the related dinuclear complex $[Fe_2(saltrz)_5(NCS)_4]$ ·4MeOH (saltrz = N-salicylidene-4-amino-1,2,4-triazole);^{10b} however, in this case an abrupt onestep SCO emerged. Here, the presence of a two-step transition via the stabilization of a short-range ordered [HS-LS] mixedspin state phase is unique. The reasoning for a two-step SCO is not entirely obvious; however, given the most distinct structural difference between A-3MeOH and A- \emptyset is the bridging ligand rotation and associated array of newly formed local interactions, it is likely that the disposition of the NO₂ groups defines the short-range allocation of [HS-LS] or [LS-HS] spin-state assignment distribution and hence the two-step character (i.e., it is likely that the relative spin state configuration correlates with the local orientation of the disordered bridging o-NTrz ligand, although the disorder is such that it is not possible to unambiguously determine the local spin state/ligand configuration). In the case of $[Fe_2(saltrz)_5(NCS)_4]$ ·4MeOH, it is possible that the interaction networks formed by the effective hydrogen bonds of the ligand OH-groups are more efficient, resulting in a cooperative SCO transition of all Fe^{II} sites, bypassing the [HS-LS] state. The observation of thermal hysteresis in both steps of the twostep transition is a point of some interest, in that it indicates the presence of intermolecular lattice cooperativity despite the absence of any apparent ordering of the local HS-LS and LS-HS dinuclear sites (noting that there remains some possibility that domains of local order exist that lie beyond detection by Bragg diffraction). Such cooperativity may be expected to arise if both orientations of the HS-LS unit have a similar ferroelastic influence on their immediate environment, for example through a general volume reduction effect.

Water inclusion (A·H₂O). Structural analysis was conducted at 225 and 100 K (Tables S3 and S4), representative of the high and low temperature plateaus of the abrupt one-step spin transition. At both temperatures, a C-centered monoclinic (C2/c) symmetry exists, akin to A·Ø. Consequently, the asymmetric unit comprises half a dinuclear complex with one crystallographically distinct Fe^{II} site per dinuclear unit. Bond length analysis reveals a systematic decrease in Fe–N bond lengths (d_{Fe-N} : 2.145(9) and 1.974(5) Å, at 225 and 100 K, respectively), consistent with entirely HS and LS dinuclear species (Figure 1c). Likewise, the octahedral distortion parameters of the single Fe^{II} site become more regular over the HS to LS transition ($\Sigma = 18.7(5)$ and 14.0(3)° for 225 and 100 K, respectively).^{7d}

As for A·Ø, the presence of a C_2 axis centered over one of the three $\mu_{1,2}$ -bridging ligands dictates 2-fold disorder of an entire ligand (Figure 3a). The local disposition of these



Figure 3. (a) Structural representation of $\mathbf{A} \cdot 3H_2\mathbf{O}$ showing the dense network of dinuclear...water (blue) and dinuclear...dinuclear (red) interactions. (b) 1D chain of π -stacking interactions (red dashes) between neighboring (shown in gray or color) dinuclear species in $\mathbf{A} \cdot 3H_2\mathbf{O}$.

disordered ligands, and hence nitro-groups is defined by interactions with water molecules which reside in distinct pockets at either, but not both sides of the dinuclear unit. The elegant assembly of dinuclear…water hydrogen bonding interactions between these and other nitro-groups and triazole groups are depicted in Figure 3a. It is apparent that the presence of water molecules in these pockets provides an optimum pathway for neighboring dinuclear species to interact. This compact arrangement facilitates further interactions (dinuclear...dinuclear) between nitro- and triazole groups on neighboring species (Figure 3a). Alongside hydrogen bonding interactions, the crystalline lattice of $A \cdot 3H_2O$ is supported by one-dimensional chains of π -stacking interactions (Figure 3b) between neighboring molecular species. Notably, such π stacking arrays are absent in A·3MeOH and A·Ø and highlight the dense packing afforded by the mutual dinuclear...dinuclear and dinuclear…water interactions in A·3H₂O.

The highly cooperative nature of the spin transition of A-3H₂O is broadly consistent with the presence of the much denser network of intermolecular interactions than is seen in the methanolic and apohost phases. Despite containing locally (but not crystallographically) inequivalent Fe^{II} sites according to the asymmetric bridging ligand conformation (as described above for A·Ø), the observed one-step transition for A·3H₂O indicates that the lattice cooperativity is sufficient to effectively over-ride these local considerations such that stabilization of the intermediate HS–LS state seen in A·Ø no longer occurs; notably, a similar bypassing of anticipated spin state plateau for inequivalent Fe sites has been seen for example, in the highly cooperative dinuclear phase [Fe₂(saltrz)₅(NCS)₂]·4MeOH^{10b} and four-step framework material [Fe₃(saltrz)₆(M(CN)₄)₃]. 8(H₂O).²² Here, we rationalize the two inequivalent

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transitions as occurring within a combined single step, with the wide thermal hysteresis strongly suggesting that it is the increased lattice cooperativity in this phase that is responsible for the simultaneous site switching rather than a coincidental equivalence of ligand field at each local Fe site.

CONCLUSIONS

In summary, we present the new, molecular material $[Fe^{II}_{2}(o-$ NTrz₅(NCS)₄ in which a flexible network of supramolecular interactions drives a broad array of guest-sensitive dynamic structure and spin-state switching properties. In the past, such guest-sensitive outcomes have predominantly emerged in traditional porous materials such as SCO-PCPs, as the robust framework scaffolds can sustain molecular variation and the pore character can be readily tuned; by this approach, subtle variation to host-host and host-guest interactions have been observed to lead to diverse molecular switching outcomes. We show here that similarly diverse guest-induced SCO variation can manifest in molecular materials when suitable structural stabilizing motifs are in place. Of particular advantage, we illustrate that the inherent flexibility of such supramolecular networks in molecular crystals allows large structural changes to occur while retaining crystalline properties. Highlighting this, the methanolate to guest-free transition occurs via a single-crystal to single-crystal transformation, which involves substantial molecular rearrangement to optimize interactions, including ligand rotation. Further comparison between the structure of these and the water solvated phase illustrates the genuine guest-adaptability of the lattice. Of particular note, the water-solvated phase shows a densification which results in a compact network of hydrogen-bonding and π -stacking opportunities, in particular a 1D π -stacking array. This dense supramolecular interaction network provides superior solidstate communication pathways, ultimately leading to a highly cooperative spin-state propagation, which is a rare occurrence for dinuclear materials. While for this example direct solid-state structural exchange between all three of the phases does not occur, the substantial SCO and structure variability available via a molecular nonporous approach is clearly evident.

Beyond the benefit of allowing structural mobility, the guestdictated, adaptable molecular crystal platform has provided enhanced molecular switching variation via its flexibility. By this approach, we find for the first time that one-step, two-step, and abrupt and hysteretic spin transition behaviors are accessible in the one molecular material due to the extreme sensitivity of SCO to physical environment changes. Indeed, even within the scope of SCO-active PCPs such as broad diversity of SCO properties in the one material is uncommon.^{8g-k}

From a fundamental perspective, among discrete SCO materials, dinuclear species are significant as they represent the most basic prototype of a polymeric species and thus offer insight into the relative effect of directly linking SCO metal sites through coordinative bridges. While one-step ([HS–HS] \leftrightarrow [LS–LS]) and stepwise transitions (i.e., [HS–HS] \leftrightarrow [HS–LS] \leftrightarrow [LS–LS]) are prevalent in this class of materials, strongly cooperative, hysteretic transitions are rare; this is largely owing to the lack of long-range communication capacity outside of each discrete dinuclear species. Here, the presence of a [HS–HS] \leftrightarrow [LS–LS] transition is observed both gradually (methanolate) and very abruptly with pronounced thermal hysteresis (in the hydrate). Furthermore, a thermally hysteretic two-step transition ([HS–HS] \leftrightarrow [HS–LS] \leftrightarrow

[LS–LS]) is observed in the guest-free state. Detailed structural analyses show that the major difference between these guest-substituted dinuclear species is in the complexity and effectiveness of the supramolecular interaction pathways in each phase. This study therefore very effectively illustrates the considerable power of subtle variation in supramolecular interaction pathways to tune and modulate spin-state switching cooperativity profiles.

Collectively, this study demonstrates that there is vast scope to explore the guest-sensitive aptitude of molecular materials which are not typically associated with porosity. Importantly, the strategic introduction of flexible supramolecular interactions provides access to dynamic structural interplay and enhanced guest sensitive switching properties. Future studies will focus on guest and switching diversity in other members of the $[Fe^{II}_2(R-trz)_5(NCS)_4]$ family, which typically support dense interaction networks such as seen here, alongside expansion to other, more complex, guest molecules. From a broader perspective, the information gained here on structural design characteristics suitable for accommodating malleable structures and dynamic properties can readily be applied to many other molecular crystals toward evolving molecular sensing structure and properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02625.

Additional characterization (gravimetry), single crystal, powder X-ray diffraction and magnetic measurements (PDF)

Accession Codes

CCDC 1502200–1502204 and 1856712–1856713 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Fellowship and Discovery Project funding from the Australian Research Council.

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