Bistable Hofmann-Type Fe\textsuperscript{II} Spin-Crossover Two-Dimensional Polymers of 4-Alkyldisulfanylpyridine for Prospective Grafting of Monolayers on Metallic Surfaces

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ABSTRACT: Aiming at investigating the suitability of Hofmann-type two-dimensional (2D) coordination polymers \{Fe\textsuperscript{II}(L_{ax})\textsubscript{2}[M\textsuperscript{II}(CN)\textsubscript{4}]\} to be processed as single monolayers and probed as spin crossover (SCO) junctions in spintronic devices, the synthesis and characterization of the M\textsuperscript{II} derivatives (M\textsuperscript{II} = Pd and Pt) with sulfur-rich axial ligands (L_{ax} = 4-methyl- and 4-ethyl-disulfanylpyridine) have been conducted. The thermal dependence of the magnetic and calorimetric properties confirmed the occurrence of strong cooperative SCO behavior in the temperature interval of 100–225 K, featuring hysteresis loops 44 and 32.5 K/21 K wide for Pt\textsuperscript{II}-methyl and Pt\textsuperscript{II}/Pd\textsuperscript{II}-ethyl derivatives, while the Pd\textsuperscript{II}-methyl derivative undergoes a much less cooperative multistep SCO. Excluding Pt\textsuperscript{II}-methyl, the remaining compounds display light-induced excited spin-state trapping at 10 K with \(T_{\text{LIESST}}\) temperatures in the range of 50–70 K. Single-crystal studies performed in the temperature interval 100–250 K confirmed the layered structure and the occurrence of complete transformation between the high- and low-spin states of the Fe\textsuperscript{II} center for the four compounds. Strong positional disorder seems to be the source of elastic frustration driving the multistep SCO observed for the Pd\textsuperscript{II}-methyl derivative. It is expected that the peripheral disulfanyl groups will favor anchoring and growing of the monolayer on gold substrates and optimal electron transport in the device.

INTRODUCTION

Bistable molecular materials with switchable properties are appealing candidates for developing technological applications, e.g., sensors for information storage. Iron(II) spin crossover (SCO) complexes afford excellent examples of molecular bistability, because they reversibly switch between the high-spin (HS, \(t_{2g}^3 e_{g}^2\)) and low-spin (LS, \(t_{2g}^6 e_{g}^0\)) electronic states in response to a variety of external stimuli such as temperature, pressure, light, adsorption of analytes or extrinsic phase transitions. This is particularly true when the spin changing centers are strongly coupled to each other, since the spin state change manifests cooperatively conferring hysteretic behavior (memory effect) to the magnetic, optical, structural, mechanical, and electric properties associated with the material.

The SCO research is a very active and multidisciplinary field that spans in many complementary directions. The synthesis and characterization of interesting mononuclear, polynuclear, and one-dimensional to three-dimensional (1D–3D) polymeric SCO systems has increased exponentially during the last two decades, affording new SCO behaviors which, in turn, have inspired new sophisticated physical techniques and theoretical models. To engineer new multifunctional materials where the SCO synchronically interplays with other relevant physicochemical properties—e.g., porosity (host–guest chemistry), liquid crystalline properties, crystal-to-crystal phase transitions, luminescence or chirality—in a synergetic fashion in the same crystal is one of the fundamental goals in the field. This requires a rational design of the synthesis at macrosopic scale and precise control of essential elusive SCO parameters, such as critical temperature \(T_{1/2}\), abruptness, hysteresis width, and completeness. Relevant achievements of this strategy include the combination of SCO and nonlinear optical properties, electronic conduction, electroluminescence, fluorescence, liquid-crystalline properties, porosity, molecular recognition, photoswitchable magnets, chirality, room-temperature photoisomers and reactions.

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etc. The ultimate goal is the construction of sensing materials capable of acting as switches in response to changes of ambient conditions (temperature, humidity, chemical contaminants, etc.). Furthermore, the potential implementation of SCO materials into electronic and spintronic devices is a new concept of paramount importance that has fuelled sophisticated studies aiming at controlling the electron transport (charge and spin) processing SCO materials as ultrathin films on surfaces.

Two-dimensional (2D) Hofmann-type FeII coordination polymers with general formula \( \{ \text{Fe}^{II}(L_{ax})_{2}[\text{M}^{II}(\text{CN})_{4}] \} \) represent an important source of SCO compounds, where \( \text{M}^{II} = \text{Pt}^{II}, \text{Pd}^{II}, \) or \( \text{Ni}^{II} \) and \( L_{ax} \) is a terminal monotopic axial ligand based on 2-pyridine/2-pyridine-like and triazole rings. The \( \text{Fe}^{II} \) ions are equatorially connected through square-planar \( \{\text{M}^{II}(\text{CN})_{4}\} \) anionic metalloligands affording robust infinite \( \{\text{Fe}^{II}(\text{M}^{II}(\text{CN})_{4})\} \) layers that are the origin of the cooperativity typically exhibited by these compounds. The layers stack on top each other interdigitating the axial ligands \( L_{ax} \) whose nature (length, donor–acceptor substituents, etc.) plays an important role in the modulation of the cooperativity through changes in the interlayer spacing and flexibility of the layers (corrugation), factors that may influence the inclusion of guest molecules.

It has recently been shown that 2D Hofmann-type coordination polymers can be processed as ultrathin films under mild conditions (RT) by applying the layer-by-layer (LbL) methodology,16–18 at variance of the homologous 3D derivatives, which require very low temperatures.19–25 Processing of these materials as ultrathin films is a requirement to keep small electrode separation in vertical transport devices to ensure a functional current flow, but, obviously, it can seriously compromise the SCO properties. For example, synchrotron XAS studies showed that, for film thicknesses above ca. 12 nm, the 2D coordination polymer \( \{ \text{Fe}^{II}(\text{pyridine})_{2}[\text{Pt}^{II}(\text{CN})_{4}] \} \) presents a cooperative SCO behavior similar to that observed for the microcrystalline sample.17 However, below this threshold value, the cooperativity and completeness of the spin transition are exponentially attenuated since the films lose cohesion conferring to its structure a high degree of mosaicity constituted of practically unconnected nanoislands. The nature of the axial ligand and its dramatic influence on the coalescence of the thin film deposited on Au substrates has also been investigated for two new 2D Hofmann compounds \( \{ \text{Fe}^{II}(\text{pyrimidine})_{2}[\text{Pt}^{II}(\text{CN})_{4}] \} \) and \( \{ \text{Fe}^{II}(\text{isoquinoline})_{2}[\text{Pt}^{II}(\text{CN})_{4}] \} \), together with their transport properties.18

In the search for new FeII Hofmann-type 2D coordination polymers, here, we report on the preparation, structural characterization, and spin crossover properties of four complexes generically formulated \( \{ \text{Fe}^{II}(\text{pyS}_{2}R)_{2}[\text{M}^{II}(\text{CN})_{4}] \} \) (MpyS2R, where \( \text{M}^{II} = \text{Pt}, \text{Pd} \) and \( R = \text{Me}, \text{Et} \)), where the axial organic ligand pyS2R is 4-methyl/ethyldisulfanylpyridine (R = Me, Et). In contrast to the mentioned above multilayer studies based of the LPE technique, the axially coordinated pyridine ligand functionalized in 4-position with a reactive alkylsulfanyl group opens the possibility to process the resulting 2D coordination polymers as robust single monolayer arrays of elastically coupled SCO centers deposited on suitable surfaces to be probed as SCO junctions. This approach was inspired by a relevant pioneer work by Mallek et al. about the growth of ultrathin films of the porous 3D Hofmann clathrate \( \{ \text{Ni}(4,4'-\text{bipyrindine})[\text{Pt}(\text{CN})_{4}] \} \) anchored through a monolayer of 4-pyridyl ethylidisulfide on gold substrates.20 A similar strategy has recently led to the production of molecular monolayers prepared by simple immersion of the substrate in highly diluted solutions of mononuclear FeII SCO complexes on gold substrates and successfully tested as spintronic devices.26

### RESULTS

**Synthesis.** All the samples MpyS2R (where \( M = \text{Pt}, \text{Pd} \) and \( R = \text{Me}, \text{Et} \)) were prepared as single crystals from slow diffusion techniques in water–methanol solutions (see the Experimental Section). According to chemical and thermoravimetric analyses (see Figure S1 in the Supporting Information), the single crystals resulted to be unsolvated and decompose above 420 K.

**Spin Crossover Properties.** Figure 1 shows the magnetic and photomagnetic properties of the title compounds in the form of the product \( \chi_M(T) vs T \) at which the populations of the HS and LS state are practically fully populated. The pro

![Figure 1. Magnetic and photomagnetic properties of MpyS2Me (M = Pt (a), Pd (b)) and MpyS2Et (M = Pt (c), Pd (d)). Cooling, heating and photoswitching processes are represented in blue, red, and green, respectively.](https://doi.org/10.1021/acs.inorgchem.1c01010)
232 K; however, below this temperature, it decreases gradually in a succession of slightly marked steps, reaching a value of 0.15 cm³ K/mol at 100 K. Except for the lower step, which shows a small hysteresis between 130 K and 138 K, the cooling−heating profiles are practically superposed. The corresponding characteristic $T_{1/2}$ temperature is 170 K. The SCO profile for the $\text{MpyS}_2\text{Et}$ derivatives is similar to that of $\text{PtpyS}_2\text{Me}$, featuring strong cooperative hysteretic behaviors with $T_{1/2}$ temperatures 121.5 and 154.0 K ($\Delta T = 32.5$ K) for $\text{M} = \text{Pt}$ and 111.0 and 132.0 K ($\Delta T = 21.0$ K) for $\text{M} = \text{Pd}$, in the cooling and heating modes, respectively.

Photogeneration of the fully populated metastable HS* state, the so-called “light-induced excited spin state trapping (LIESST)” experiment, was performed by irradiating microcrystalline samples of the title compounds with green light ($\lambda = 532$ nm) at 10 K. Under these conditions, all the samples but $\text{PtpyS}_2\text{Me}$ display the LIESST effect and saturate at $\chi_M T$ values of 2.08 cm³ K/mol for $\text{PdpyS}_2\text{Me}$ and 2.80 cm³ K/mol for $\text{MpyS}_2\text{Et}$ ($\text{M} = \text{Pt}, \text{Pd}$). Subsequently, the light was switched off and the temperature increased at a rate of 0.3 K/min inducing a gradual increase of $\chi_M T$ to a value of 2.36 cm³ K/mol at 26 K for $\text{PdpyS}_2\text{Me}$ and 3.54 cm³ K/mol at ca. 48 K for $\text{MpyS}_2\text{Et}$ ($\text{M} = \text{Pt}, \text{Pd}$), which corresponds to ca. 64% and 96% of the maximum value observed at 300 K, respectively. This increase in $\chi_M T$ reflects the thermal population of different microstates originated from the zero-field splitting of the HS* spin state. At higher temperatures, $\chi_M T$ decreases rapidly until joining the thermal SCO curve at ca. 65 K ($\text{PdpyS}_2\text{Me}$), 69 K ($\text{PtpyS}_2\text{Et}$), and 76 K($\text{PdpyS}_2\text{Et}$), indicating that the metastable HS* state has relaxed back to the stable LS state. The corresponding $T_{\text{LIESST}}$ temperatures, evaluated as $\partial(\chi_M T)/\partial T$, are 50.0 K ($\text{PdpyS}_2\text{Me}$) and 68−70 K ($\text{MpyS}_2\text{Et}$, $\text{M} = \text{Pt}, \text{Pd}$). These temperatures are consistent with the inverse-energy-gap law, i.e., the metastability of the photogenerated HS* species decreases as the stability of the LS increases, namely as $T_{1/2}$ increases.

The SCO behavior was also investigated through the thermal dependence of the heat capacity at constant pressure, $\Delta C_p$, for $\text{MpyS}_2\text{Me}$ ($\text{M} = \text{Pt}, \text{Pd}$) (Figure 2). The low SCO temperatures observed for both ethyl derivatives prevented us to evaluate their thermodynamic parameters. The average enthalpy $\Delta H$ and entropy variations $\Delta S$ ($= \Delta H/T_{1/2}$) are, respectively, 16.12 kJ/mol and 79.84 J/K mol for $\text{PtpyS}_2\text{Me}$ and 7.68 kJ/mol and 45.18 J/K mol for $\text{PdpyS}_2\text{Me}$. The $\Delta H$ and $\Delta S$ values found for $\text{PtpyS}_2\text{Me}$ are comparable to those reported for similar Hofmann-type coordination polymers with comparable cooperative SCO. However, for $\text{PdpyS}_2\text{Me}$ these values are considerably smaller due to the fact that ca.
Selected Bond Lengths and Angles for MpyS₂Me (M = Pd, Pt)

|                  | MpyS₂Me, 120 K | MpyS₂Me, 250 K | MpyS₂Me, 120 K | MpyS₂Me, 250 K |
|------------------|----------------|----------------|----------------|----------------|
| **Selected Bond Lengths [Å]** |               |                |                |                |
| Fe−N(1)         | 1.987(3)       | 2.219(5)       | 1.992(14)      | 2.23(3)        |
| Fe−N(2)         | 1.942(3)       | 2.132(4)       | 1.943(14)      | 2.13(2)        |
| Fe−N(3)         | 1.943(3)       | 2.137(4)       | 1.945(14)      | 2.11(2)        |
| Pd−C(1)         | 1.991(3)       | 1.991(4)       |                |                |
| Pd−C(2)         | 1.992(3)       | 1.988(5)       |                |                |
| Pr−C(1)         |                | 1.975(17)      | 1.97(2)        |                |
| Pr−C(2)         |                | 1.978(17)      | 1.93(2)        |                |
| C(1)−N(2)       | 1.149(4)       | 1.131(7)       | 1.15(3)        | 1.16(3)        |
| C(2)−N(3)       | 1.153(5)       | 1.130(7)       | 1.15(3)        | 1.21(3)        |
| **Selected Bond Angles (°)** |               |                |                |                |
| N(1)−Fe−N(2)    | 90.06(12)      | 90.1(2)        | 90.7(6)        | 91.6(11)       |
| N(1)−Fe−N(3)    | 90.13(12)      | 90.0(2)        | 90.5(6)        | 91.0(11)       |
| N(2)−Fe−N(3)    | 90.01(10)      | 90.04(14)      | 91.0(6)        | 90.2(6)        |
| Σ⁹⁻         | 0.8            | 0.56           | 8.8            | 11.2           |
| C(1)−N(2)−Fe    | 179.8(2)       | 179.7(5)       | 178(2)         | 169(2)         |
| C(2)−N(3)−Fe    | 179.8(3)       | 179.9(5)       | 177(2)         | 178(2)         |

27% of the SCO occurs out of the temperature window of our calorimeter, an extrapolation to 100% gives ΔH = 10.5 kJ/mol and ΔS = 62 J/Kmol (see also Figure S2 in the Supporting Information). These extrapolated values are still smaller than those observed for PpyS₂Me but consistent with the much less cooperative gradual SCO and lower T_{1/2} temperature of the homologous Pd derivative. The T_{1/2} values obtained from the calorimetric measures are virtually the same than those obtained from magnetism (see Figure S2). As it can be seen from Figure 2, the surprisingly distinct nature of both SCO behaviors, hysteretic versus multistepped, are clearly reflected in the ΔCp vs T plots.

Single-Crystal Structure Analysis. Structure of MpyS₂Me. The crystal structure of MpyS₂Me (M = Pt and Pd) was investigated at 120 and 250 K; it turned out to be isostructural and crystallized in the triclinic P1 space group. A selection of relevant crystallographic data for MpyS₂Me (M = Pt, Pd) is given in Table S1 in the Supporting Information. At 120 K, the structure is characterized by a crystallographically unique FeII site lying in an inversion center de 120 K, the structure is characterized by a crystallographically unique FeII site lying in an inversion center. Two 2D layers in which the equatorial planes of the [FeIIN₆] and [PtII(CN)₄]²⁻ centers are strictly coplanar (Figure 3, right). Two consecutive layers interdigitate in such a way that the pyS₂Me axial ligands of one layer point toward the center of the square windows of the adjacent layers, with the distance between the [FeII²][MII(CN)₄]₂⁻ layers being equal to 10.36 Å (M = Pt) and 10.75 Å (M = Pd). The S−S−CH₃ tails display positional disorder in two equivalent positions for the Pt derivative while the disorder is considerably more severe for the Pd derivative also involving the pyridine groups (see Figure S3 in the Supporting Information). At 250 K, the structures are essentially the same, being the most significant differences, with respect to those at 120 K, the increase of the (Fe−N) bond length by 0.2 Å and the change of color of the crystals to yellow. Both facts are perfectly consistent with the full population of the FeII HS state in agreement with the magnetic data. In addition, the change to the HS state in the Pt derivative is accompanied by a small degree of corrugation. The angle defined between the equatorial FeIIN₄ and the [PtII(CN)₄]²⁻ square planes is 7.64°. Consistently, the Fe−N₂−C₁ angle decreases 9° from 178(2)° in the LS state until 169(2)° in the HS state. In addition, the separation of two consecutive [Fe₂M₂]ₙ layers increases by 0.38 Å until 10.74 Å. In contrast, the layers remain perfectly flat for the Pd derivative while the separation between consecutive layers increases by 0.2 Å until 10.95 Å (see Figure S2).

Structure of MpyS₂Et. The crystal structures of MpyS₂Et, M = Pt and Pd, were investigated at 100 and 250 K turning out to be isostructural. At 100 K, the red crystals of both derivatives display a monoclinic I2/m unit cell that changes to monoclinic C2/m at 250 K, where the crystals are yellow (see Table S2). Table 2 contains a selection of significant bond lengths and angles including the angular distortion parameter Σ⁹⁻. The asymmetric unit contains one slightly distorted [FeIIN₆] octahedral site defined by two distinct pyS₂Et axial ligands coordinated, respectively, via N1 and N2 and two distinct [M(CN)₄]²⁻ groups coordinated, respectively, via N3 and N4 (Figure 4). The two pyridine rings of pyS₂Et and the FeII center lie in a reflection plane which bisects the equatorial N₃−Fe−N₃' and N₄−Fe−N₄' angles. At 250 K, both FeII centers in a fully populated LS state, whereas, at 120 K, both average bond lengths increase by 0.20−0.21 Å attaining typical values for the
Table 2. Selected Bond Lengths and Angles for MpyS2Et (M = Pd, Pt)

|                | PdpyS2Et, 100 K | PdpyS2Et, 250 K | PpyS2Et, 100 K | PpyS2Et, 250 K |
|----------------|----------------|----------------|---------------|---------------|
| **Selected Bond Lengths [Å]** |                  |                |               |               |
| Fe–N(1)        | 2.001(5)       | 2.218(8)       | 1.997(7)      | 2.205(7)      |
| Fe–N(2)        | 2.017(5)       | 2.237(9)       | 2.004(6)      | 2.202(9)      |
| Fe–N(3)        | 1.946(4)       | 2.170(5)       | 1.940(5)      | 2.162(5)      |
| Fe–N(4)        | 1.948(4)       | 2.140(5)       | 1.944(5)      | 2.133(5)      |
| Pd(1)–C(1)     | 1.992(4)       | 1.987(7)       |               |               |
| Pd(2)–C(2)     | 2.003(5)       | 2.005(6)       |               |               |
| Pr(1)–C(1)     |                | 1.98(5)        | 1.98(5)       |               |
| Pr(2)–C(2)     |                | 1.989(5)       | 1.99(5)       |               |
| C(1)–N(3)      | 1.146(5)       | 1.145(8)       | 1.160(7)      | 1.142(6)      |
| C(2)–N(4)      | 1.146(5)       | 1.126(8)       | 1.159(7)      | 1.141(7)      |
| **Selected Bond Angles [°]**          |                  |                |               |               |
| N(1)–Fe–N(3)   | 91.29(14)      | 90.7(2)        | 91.4(2)       | 90.5(2)       |
| N(1)–Fe–N(4)   | 90.72(14)      | 91.3(2)        | 90.6(2)       | 91.2(2)       |
| N(2)–Fe–N(3)   | 86.83(14)      | 86.7(2)        | 86.6(2)       | 86.6(2)       |
| N(2)–Fe–N(4)   | 91.18(14)      | 91.2(2)        | 91.5(2)       | 91.7(2)       |
| N(3)–Fe–N(4)   | 88.43(14)      | 88.3(2)        | 88.3(2)       | 88.5(2)       |
| N(3)–Fe–N(4)   | 91.9(2)        | 90.4(3)        | 92.0(3)       | 92.2(3)       |
| N(4)–Fe–N(4)   | 91.2(2)        | 93.0(3)        | 91.3(3)       | 92.7(3)       |
| N(1)–Fe–N(3)   | 91.96          | 19.8           | 20.5          | 19.5          |
| N(1)–Fe–N(3)   | 169.7(4)       | 158.8(6)       | 169.3(4)      | 160.3(5)      |
| C(1)–N(3)–Fe   | 178.0(3)       | 177.7(6)       | 178.1(4)      | 177.1(5)      |

Fe II in the HS state [2.166(9) and 2.179(9) Å, respectively]. The ΣFe parameter is small (~20°) and remains almost constant upon SCO. There are two crystallographically distinct [MII(CN)4]2− groups and two pairs of them connect each FeII center to four equivalent atoms defining an irregularly corrugated layer. Indeed, at 100 K, the angle defined between the [MII(CN)4]2−/[MII(CN)4]2− squares and the equatorial plane of the FeII center is, respectively, 4.04°/4.24° and 20.47°/21.40° and increase by ca. 36° up to 6.22°–6.56° and 32.25°–35.82° for M = Pt/Pd at 250 K. The change of this angle occurs through the Fe–N3–C1, which decrease 10.9° (Pd) and 9° (Pt) when moving from the LS to the HS state. The separation between two consecutive the layers, measured from the average plane defined by M1 and M2, is very similar for the two derivatives and practically does not change with temperature (11.15–11.52 Å).

### DISCUSSION

Since the first SCO Hofmann type 2D coordination polymer {FeII(pyridine)2[MII(CN)4]2}, MII = Ni,30 and its isostructural PdII and PtII counterparts31 were reported, this family of compounds has been steadily growing until recently (see refs 2d, g, 14, 15, 18). Despite their high insolubility, their synthesis based on formal replacement of the axial pyridines with homologous N-donor ligands can be addressed in a straightforward manner to obtain samples constituted exclusively of single crystals by employing liquid–liquid slow diffusion techniques, which is the safest way to get pure samples with reliable SCO properties for this type of compounds. The strong cooperative SCO behavior featuring well-shaped symmetric hysteresis loops expressed by many of these compounds is likely the most appealing aspect, which explains the interest and growth of this family of compounds. This cooperativity seems to be originated mainly from the robust nature of the {FeII[MII(CN)4]2}n layers where all SCO centers are strongly coupled. Indeed, most of the [FeII(L)2[MII(CN)4]2] compounds show hysteresis widths ranging in the interval of 10–30 K, but it has been also reported hysteresis close to 40 K15b or even larger (50–65 K).15b It is reasonable to consider that the nature of the axial ligands and included guest molecules play an important role in the modulation of the observed cooperativity, however, this is a fact that generally has not obvious rationalization. In addition, it is also worth noting that the hysteresis width seems not to be correlated with the length of the axial ligand, namely, with the separation between the {FeII[MII(CN)4]2}n layers. For example, interdigitation of the relatively long ligands L = 4-styrylpyridine (n = 0.5) and 4-(2-phenylethyl)pyridine (n = 0) in [FeII(L)2(PtII(CN)4)2]·nMeOH separates the

Figure 4. (Left) Molecular fragment of PtpyS2Et showing the atom numbering of the asymmetric unit. (Right) Packing of three consecutive layers (only one of the two possible orientations of the –S–S–Et moiety is shown.)
{Fe\textsuperscript{II}[Pt\textsuperscript{IV}(CN)\textsubscript{4}]} layers by ca. 13.85 Å and although both compounds display sharp SCO transitions they lack of hysteretic behavior.\textsuperscript{32b} In contrast, the closely related axial ligands L = 3-phenylazo-pyridine and 4-phenylazopyridine in \{Fe\textsuperscript{II}(L)\textsubscript{2}[Pd\textsuperscript{IV}(CN)\textsubscript{4}]}\textsuperscript{3+} with similar interdigitation induce abrupt hysteretic spin transitions with $\Delta T_{1/2} = 12$ and 17 K, respectively.\textsuperscript{32c} An additional difficulty when dealing with this type of compounds is that the spin crossover nature ($T_{1/2}$, $\Delta T_{1/2}$, complete, abruptness, etc.) may be strongly affected by the degree of crystallinity. A relevant example has been recently observed for \{Fe\textsuperscript{II}(pyridine)\textsubscript{2}[Pt\textsuperscript{IV}(CN)\textsubscript{4}]} (separation between layers \{Fe\textsuperscript{II}[Pt\textsuperscript{IV}(CN)\textsubscript{4}]}\textsuperscript{3+}.\textsuperscript{7a} In its precipitated microcrystalline form, it displays a SCO centered at 212 K with a hysteresis 8 K wide, which is characterized by a remarkable residual fraction (15%–19%) of inactive HS centers. In contrast, the same compound exclusively constituted of single crystals shows a complete well-shaped SCO centered at 234 K and a hysteresis 42 K wide (see Figure S4 in the Supporting Information).\textsuperscript{17} Rapid precipitation of these highly insoluble compounds usually produces microcrystalline samples consisting of submicrometric/nanometric crystallites, dramatically influencing the SCO via the increase of crystal defects, and hence consisting of the residual HS molar fraction in the LS phase, which, in turn, is reflected on a decrease of the $T_{1/2}$ of cooperativity ($\Delta T_{1/2}$) and completeness of the SCO.

In the present study, the SCO behavior has been investigated for samples exclusively constituted of single crystals. Except for PdpyS\textsubscript{2}Me, the SCO behavior of the title compounds MpyS\textsubscript{2}R (R = Me, Et; M = Pd, Pt) retain the general features described for other Hofmann-type 2D coordination polymers. Compound PtpyS\textsubscript{2}Me undergoes a particularly strong cooperative transition with a hysteresis $\Delta T = 44$ K wide, which, despite an interlayer distance increase of $\sim 2$–3 Å, because of the presence of the flexible $\sim$S–S–CH\textsubscript{2} moieties, it is virtually the same than the SCO observed for single crystals of \{Fe\textsuperscript{II}(pyridine)\textsubscript{2}[Pt\textsuperscript{IV}(CN)\textsubscript{4}]}\textsuperscript{3+}. The only noticeable difference is observed for the average $T_{1/2}$ of the series, which is 32 K less than that observed for the pyridine derivative. This result also supports the idea mentioned above that separation between the layers does not substantially affect the cooperativity.

Replacement of the methyl group by the ethyl group in MpyS\textsubscript{2}R does not change significantly the separation between the layers but involves a considerable decrease in $T_{1/2}$ from 202 K to 138 K (64 K) for the Pt derivative. This fact could tentatively be correlated with a higher corrugation of the layers in the ethyl derivatives. This fact is clearly reflected in the decrease from 180° of one of the two Fe–N–C–Pt moieties. For PtpyS\textsubscript{2}Me, the angle Fe–N2–C1(Pt) is 168.5°, while the equivalent angle for PtpyS\textsubscript{2}Et, Fe–N3–C1(Pt), is 158.8°, both in the HS state, and they change to 170.6° and 169.6° in the LS state, respectively. Obviously, the larger misalignment of the N–C–Pt moiety, with respect to the 3d orbitals of Fe\textsuperscript{II} in the ethyl derivative, must necessarily decrease the $\sigma$ and $\pi$ overlaps, thereby decreasing the ligand field felt by the Fe\textsuperscript{II} centers. Another important difference pointing to the same direction is that the angular distortion $\Sigma^{Fe}$ (see Tables 1 and 2) is significantly larger for PtpyS\textsubscript{2}Et than for its methyl counterpart.

Surprisingly, even though both MpyS\textsubscript{2}Me (M = Pd, Pt) compounds are isostuctural, their SCO properties are drastically different to each other. The Pd derivative shows a relatively gradual multistep behavior (ca. 6 steps) separated by very narrow plateaus, while the Pt derivative displays a sharp cooperative spin transition with large hysteresis. The most significant structural difference between them is the occurrence of positional disorder of the pyridine and S–S–CH\textsubscript{2} groups over four orientations in the Pd derivative, which remains in the HS and LS states. This behavior is reminiscent of that found, among others, for the 2D coordination polymer \{Fe\textsuperscript{II}[Hg\textsuperscript{II}(SCN)\textsubscript{4}](4,4’-bipy)\textsubscript{3}\} where a sequence of different phases characterized by distinct HS/LS fractions and symmetry breaking results from competition between SCO and structural 4,4’-bipy ligand ordering. For this system, it was possible to identify a correlation between the internal dihedral angle adopted by the 4,4’-bipy ligand and each particular step (spin state phase) as being responsible for the observed multistability.\textsuperscript{33} From a phenomenological point of view, thermally induced multistep SCO behavior is associated with elastic frustration,\textsuperscript{3b,c} namely, the occurrence of subtle balances between opposed intermolecular interactions that drive the HS ↔ LS transformation in fractional steps consistent with different concentrations of HS and LS centers (with or without ordering). For PdpyS\textsubscript{2}Me, the more conspicuous positional disorder may be the source of subtle balances between interlayer interactions and/or distortions of the \{FeN\textsubscript{4}\} centers. However, to precisely identify the structural constraints favoring the steps, is for most of the known multistep SCO examples a major difficulty in particular when the steps are poorly defined.

## CONCLUSIONS

Here, we have described the synthesis, structure, magnetic, photomagnetic, and calorimetric properties of four new Hofmann-type 2D SCO coordination polymers. Three of them show strong cooperative SCO properties, featuring wide thermal hysteresis, in particular compound PpyS\textsubscript{2}Me, while its isostructural Pd counterpart surprisingly displays a multi-stepped transition without hysteresis, most likely due to the occurrence of additional disorder in the structure. The MpyS\textsubscript{2}Et derivatives, which have the lowest $T_{1/2}$ of the series, show complete LIESST effect. In contrast, the LIESST effect is incomplete for PdpyS\textsubscript{2}Me and vanishes completely for PtpyS\textsubscript{2}Me because of their higher $T_{1/2}$ values.

The results here reported correspond to the first step in a more challenging work whose ultimate objective is to graft these Hofmann-type 2D SCO coordination polymers as monolayers on metallic surfaces (e.g., Au) to be probed as junctions for spintronic devices in which the switchable SCO centers can be used to modulate the junction conductance (see Scheme 1). The choice of 4-allylsulfonylpyridines as axial ligands was based on the well-known fact that S atoms ensure appropriate interaction between the molecular wires and the electrodes. Preliminary work on this second objective confirms its feasibility and definitive conclusions will be reported in due time.

## EXPERIMENTAL SECTION

**Materials and Reagents.** Iron(II) tetrafluoroborate hexahydrate, potassium tetracyanoplatinate(II) trihydrate, potassium tetracyanonapalladate(II) hydrate, 4-mercaptopyridine, and methyl methanethiosulfonate were obtained from commercial sources and used as received without further purification. Ethyl methanethiosulfonate was synthesized following a literature procedure.\textsuperscript{34} Synthesis of Methyl/Ethyl[4-(pyridyl)disulfide. The synthesis of methyl-(4-pyridyl)disulfide was performed using a method previously
Low temperatures were obtained with an aluminum block was kept in a drybox under a nitrogen, and stabilized at a temperature of 110 K. The sample holder microcrystalline samples of MpyS₂Me were constituted of single crystals exclusively obtained through slow liquid-to-liquid diffusion methods using a 10-mL-total-volume H-shaped tube. One arm of the tube was filled with a H₂O:MeOH (1:1) solution containing a mixture of 33.7 mg of methylmethanethiosulfonate and 3.46 mg of ethyl(4-pyridyl)disulfide using the noncommercial precursor ethyl methanethiosulfinate. 300 MHz ¹H-NMR, CDCl₃, δ/ppm: 8.47 (2H), 7.45 (2H), 2.77 (2H), 1.32 (3H).

The sample holder microcrystalline samples of MpyS₂Me were obtained after 2 weeks. Elemental analysis: Calculated for PdpyS₂Me [C₁₆H₁₄N₆S₄FePd (580.8) (%): C 33.09; H 2.43; N 14.65. Calculated for PdpyS₂Me [C₁₆H₁₄N₆S₄FePd (580.8) (%): C 30.52; H 2.52; N 13.35. Calculated for PdpyS₂Me [C₁₆H₁₄N₆S₄FePd (580.8) (%): C 35.51; H 2.98; N 13.80. Found (%): C 35.17; H 2.90; N 14.01.

Variable Physical Measurements. Magnetic Measurements. Variable temperature magnetic susceptibility data were collected on an Oxford Diffraction Supernova diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A multiscan absorption correction was performed. The structures were solved by direct methods using SHELXS-2014 and refined by full matrix least-squares on F² using SHELXL-2014. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters. CCDC 2072898 (100 K) and 2072899 (250 K) (PdpyS₂Et); 2072901 (250 K) and 2072902 (129 K) (PdpyS₂Me); 2072900 (100 K) and 2072905 (250 K) (PtpyS₂Et); and 2072903 (120 K) and 2072904 (250 K) (PtpyS₂Me) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01010.

Relevant crystallographic data (Tables S1 and S2); thermogram for MpyS₂Me and MpyS₂Et (M = Pd, Pt) (Figure S1); comparison of the thermal dependence of ΔC_p and (∂χ/∂T)/σT curves for PdpyS₂Me (Figure S2); positional disorder of the pyS₂Me ligands of PdpyS₂Me at 250 K (Figure S3); comparison of the thermal dependence of ΔC_p and (∂χ/∂T)/σT curves for PdpyS₂Me (Figure S4). Accession Codes

CCDC 2072898–2072905 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.

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