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Thomas Groizard, Nick Papior, Boris Le Guennic, Vincent Robert, Mikael Kepenekian. Enhanced Cooperativity in Supported Spin-Crossover Metal-Organic Frameworks. *Journal of Physical Chemistry Letters*, 2017, 8 (14), pp.3415-3420. 10.1021/acs.jpcllett.7b01248 . hal-01578535

HAL Id: hal-01578535

<https://univ-rennes.hal.science/hal-01578535>

Submitted on 5 Dec 2017

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Enhanced Cooperativity in Supported Spin-Crossover Metal-Organic Frameworks

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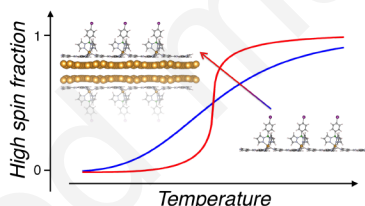
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Abstract

The impact of surface deposition on cooperativity is explored in Au(111) supported self-assembled metal-organic frameworks (MOF) based on Fe(II) ions. Using a thermodynamic model, we first demonstrate that dimensionality reduction combined with deposition on a metal surface are likely to deeply enhance the spin-crossover cooperativity, going from $\gamma_{3D} = 16$ K for the bulk material to $\gamma_{2D}^{supp} = 386$ K for its 2D supported derivative. Based on density functional theory, we then elucidate the electronic structure of a promising Fe-based MOF. A chemical strategy is proposed to turn a weakly interacting magnetic system into a strongly cooperative spin-crossover monolayer with $\gamma_{MOF}^{Au(111)} = 83$ K. These results open a promising route to the fabrication of cooperative materials based on SCO Fe(II) platforms.

Table of Contents Graphical Abstract



Molecular electronics originally proposed in the 1950s and reinvigorated by the founding proposition of Aviram and Ratner¹ has led to intense activity on the study of electronic transport through single molecules, supported by the advent of scanning tunneling microscopy (STM) and break junction setups.^{2,3} More recently, molecules entered the field of spintronics, *i.e.* the control and manipulation of spins,⁴ and gave birth to molecular spintronics,^{5–8} where the working principle of the targeted devices relies on bistability. Molecular bistability has been best served by molecular magnetism with two distinct families: spin-crossover (SCO) compounds and single molecule magnets (SMM).^{9,10} Whereas SMM display bistability at rather low temperatures,^{9,10} higher temperature regimes are reached for SCO materials.¹¹

In order to bridge the gap between functional molecules and practical devices, one has to deposit the objects on a surface while retaining the bistability property. With respect to the intense activity in the field of adsorbed SMM,^{8,12–15} SCO supported compounds have received much less attention. It is only recently that supported examples have emerged, starting from 3-dimensional (3D) materials with thin-films grown on gold.^{11,16,17} 0D systems followed based on single SCO molecules,^{18–24} or molecular junctions.²⁵ However, 2D monolayer organized networks exhibiting SCO behavior have not been reported so far. Not only should low-dimensional SCO patterns offer new insights into the spin transition phenomenon, but such organized networks may also offer the opportunity to control the intermolecular interactions dictating the collective behavior of transiting centers (*a.k.a.* cooperativity).²⁶

With this goal in mind, a promising route might come from the use of self-assembled metal-organic framework (MOF).²⁷ Indeed, magnetic couplings²⁸ were reported in several 2D MOF based on 3d ions such as Fe,^{29,30} Ni,³¹ Mn^{32,33} or Cu.³⁴ Recently, Umbach *et al.* have investigated a Au(111)-supported MOF based on Fe(II) ions and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (T4PT) ligand.³⁰ Interestingly, in addition to the observation of a weakly ferromagnetic behaviour, the speculated structure of the system consists in FeN₆ units, an archetype arrangement of SCO systems.³⁵

In this letter, we use a model based on Fe(II) transiting unit to investigate the effect of dimensionality reduction and surface deposition. Our thermodynamic model shows that a metallic

substrate is likely to enhance cooperativity by an order of magnitude. In the light of these findings, we then perform calculations based on density functional theory (DFT) to establish the structure of the synthetic Fe-T4PT MOF supported on a Au(111) surface.³⁰ We show that the most stable structure consists of FeN₃Au₃ units rather than on the expected FeN₆ building blocks. Beyond the interpretation of experimental results, a chemical modification of the ligand is proposed to generate a FeN₆ candidate for spin-crossover behavior. Finally, we demonstrate that the Au(111) surface is likely to drive the original weakly-coupled system into a highly cooperative material.

From a thermodynamic point of view, the low-spin (LS) to high-spin (HS) transition displays an overall entropy increase resulting from (i) the spin change (from LS, $S = 0$ to HS, $S = 2$ in the case of Fe(II) ions), and (ii) the weakening of the metal-ligand bond strength (vibrational contribution). As a consequence, for the transition to occur the enthalpy change must be positive as well. This quantity can be approximated by the electronic adiabatic energy difference ΔE_{adia} , *i.e.* the energetic difference between the HS and LS states each taken at its optimized geometry, accessible from quantum chemistry calculations. Naturally, weak ligand fields that favor HS over LS as the ground-state are not suitable for SCO. In the same way, too strong ligand fields will lead to a blocked LS state. For Fe(II)-based compounds, ΔE_{adia} is traditionally of the order of 100 meV when room-temperature transition is observed.

In addition, the steepness of the transition phenomenon is characteristic of the extent of cooperativity, a much more difficult quantity to retrieve from calculations. Indeed, interactions between transiting units can be mediated by phonon coupling, electron-phonon coupling^{36,37} and driven by the Madelung field modulation in the crystal.^{26,38}

In the following, we inspect changes in charge distribution resulting from dimensionality reduction and surface deposition. To that purpose, let us briefly recall the so-called polarization contribution.³⁸ In a mean-field scheme, the molar Gibbs free energy G of a mixture of spin transiting centers as a function of the HS molar fraction x reads

$$G(x, T) = G_{ni} - TS_{mix} + G_{pol}$$

where $G_{ni} = xG_{HS} + (1 - x)G_{LS}$ is the free energy of non-interacting sites. S_{mix} is the entropy of mixing $-R(x\ln(x) + (1 - x)\ln(1 - x))$. G_{pol} arises from the electrostatic potentials generated by the rest of the transiting sites and possibly the metallic surface at the position of (i) Fe ions (V_{LS} , V_{HS}), and (ii) ligands (v_{LS} , v_{HS}).^{26,38} This contribution G_{pol} to the Gibbs free energy reads :

$$G_{pol} = \gamma x(1 - x)$$

$$\text{with } \gamma = \Delta Q(\delta V_{HS} - \delta V_{LS})$$

where $\Delta Q = Q_{HS} - Q_{LS}$ is the charge variation on the Fe center. δV_{HS} and δV_{LS} are the potential differences between metal and ligand positions in the HS and LS state, respectively.

In order to modulate the dimensionality of the materials, let us consider a model system consisting in neutral Fe(II) units in a typical N_6 environment. $\text{Fe}(\text{NCH})_4(\text{NCS})_2$ units are formed from a formally Fe^{2+} ion surrounded by four neutral NCH and two thiocyanate NCS^- ligands. Charges are extracted from *ab initio* calculations,²⁶ and summarized in Table 1 along with the geometrical parameters defining the hypothetical 3D cubic crystal structure.

Table 1: Fe-Fe and Fe-N distances (in Å) of the cubic model structure of built with $\text{Fe}(\text{NCH})_4(\text{NCS})_2$ units, and corresponding point charges (atomic units) on Fe (Q) and ligands (q) for both LS ($S = 0$) and HS ($S = 2$) states.²⁶

Spin state	d(Fe-Fe)	d(Fe-N)	Q	q_N	q_{NCS}
LS	11.75	2.00	+1.44	-0.18	-0.36
HS	12.00	2.20	+1.92	-0.24	-0.48

Starting from such a $\text{Fe}(\text{NCH})_4(\text{NCS})_2$ unit, we built three different environments. First, we considered a 3D network, then a free-standing network, and finally a 2D network supported on a metallic surface. ΔE_{adia} and ΔS are chosen to establish a critical temperature $T_{1/2}$ equal to 200 K. Let us stress that these parameters naturally affect the shape of the transition but not the γ value. From the values given in Table 1, the 3D network exhibits a weak cooperativity with $\gamma_{3D} = 16$ K and a smooth transition is observed (Figure 1).

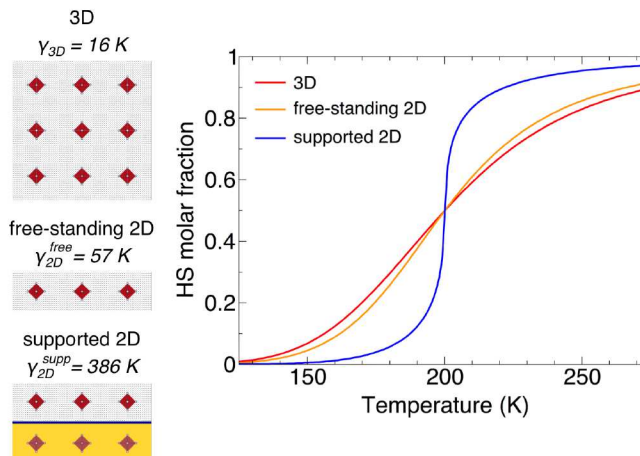


Figure 1: Simulated temperature-induced spin-crossover for the model FeN₆ units organized in (i) a 3D network, (ii) a free-standing 2D network, and (iii) a 2D network supported on a metallic surface generating mirror charges. ΔE_{adia} is 140 meV and ΔS is set to 0.70 meV/K leading to a critical temperature $T_{1/2}$ of 200 K. Deposition on a surface leads to a large increase of the polarization-induced cooperativity and, thus, to a more abrupt transition.

Upon 3D to 2D dimension reduction, the cooperativity is moderately increased by a factor of 3.5 with $\gamma_{2D}^{free} = 57\text{ K}$. Formally, half of the point charges generating the Madelung field were set to zero when moving to this free standing 2D network. The presence of a metallic surface is likely to change this state of affairs. From elementary electrostatics, each charge above the equipotential metallic surface generates a mirror charge within the bulk. Quite remarkably, the cooperativity parameter is enhanced to $\gamma_{2D}^{supp} = 386\text{ K}$. As a main conclusion, the polarization induced by the proximity of a metallic surface drives the system into a highly cooperative regime, featured by an amplification factor $\gamma_{2D}^{supp} / \gamma_{3D}$ for cooperativity larger than 20.

Naturally, our model is likely to exaggerate polarization effects. Indeed, the limited size of the ligands concentrates the charge variation, with respect to more realistic ligands, and therefore might artificially amplify the role of the surface. To support these findings obtained on a simplified model, we assess its robustness with a synthetic Fe(II)-based MOF self-assembled on Au(111).³⁰ First, structural and electronic information are explored from DFT calculations, conducted using the SIESTA code (details are provided in Supporting Information).^{39,40} Out of atomically resolved STM topographic images, Umbach *et al.* have been able to propose a structure for the monolayer formed from the sublimation of T4PT molecules and Fe atoms.³⁰ It consists in three μ^1 -T4PT

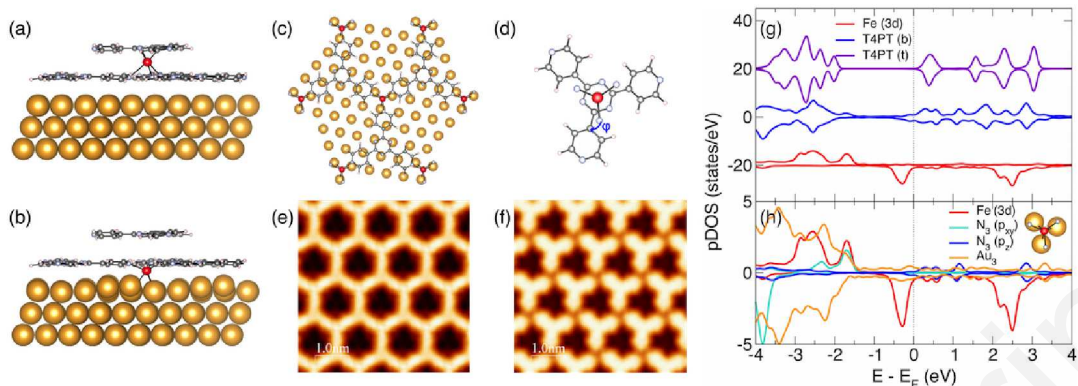


Figure 2: (a) Side view of the starting geometry for Fe-T4PT on top of Au(111). Each Fe(II) ion is bound to three T4PT molecules of the bottom layer and a supplementary T4PT from the top layer. Fe(II) ions lie above the bottom organic layer. Au, Fe, N, C and H atoms are depicted in yellow, red, blue, gray and pale pink, respectively. (b) Side view of the DFT optimized geometry. Fe(II) ions move into Au(111) hollow sites. (c) Top view of the Fe-T4PT bottom layer. (d) Top view of the second T4PT layer. For clarity, the Fe center and the bonded N atoms are displayed. The top T4PT molecule forms an angle $\phi = 26^\circ$ with the first layer. Simulated constant current STM images at (e) 0.10 V and (f) 2.0 V. (g) pDOS on the Fe 3d orbitals (red line), the bottom T4PT layer (blue) and the top T4PT layer (violet). The top T4PT layer does not exhibit any hybridization. (h) pDOS on Fe 3d orbitals (red), on $2p_x$ and $2p_y$ orbitals of the N atoms of the T4PT bottom layer neighboring Fe (blue) and the neighboring Au atoms (orange) that form the hollow site occupied by the Fe(II) ion (red). The inset shows the iron ion and its coordination sphere.

ligands pointing at one Fe(II) ion and a second layer of η^3 -T4PT ligands with the central triazine moiety of T4PT lying on top of the iron center (Figure 2a). However, the optimized structure unambiguously leads to a different scenario. The Fe(II) ion moves away from the second organic layer and occupies a hollow site of the Au(111) surface (Figure 2b-d) with Fe-Au distances of 2.76 Å, Fe-N bond lengths of 2.14 Å with the bottom layer (see Figure S1 and Table S1 in Supporting Information), while the Fe-N distances with the second triazine layer are larger than 4 Å. Therefore, the system does not present itself as an expected octahedral FeN_6 coordination sphere but rather as a trigonal prismatic FeAu_3N_3 one. Trigonal prismatic geometry is well known in Fe(II) complexes. In particular, it is often observed when a geometric constraint is imposed, *e.g.* by macrocycle ligands.^{41,42} Here, the constraints is imposed by the periodicity of the hybrid network (Fe-T4PT and Au(111)). This optimized structure leads to STM simulated images that compare well with the experimental ones (Figure 2e,f).³⁰ A low bias constant current image highlights the first layer, while a higher bias reveals the position of the second layer.

The computed Bader charge for Fe (+1.76 e^-) is compatible with a +II formal oxidation state.

This is confirmed by the analysis of the density of states (DOS, Figure 2g). The iron levels are typical of a HS Fe(II) ion with five electrons occupying the spin-up $3d$ levels, while a single one lies in the spin-down $3d$ levels. This picture is also supported by X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements.³⁰ Around this cationic center, the top T4PT layer shows typical molecular levels with no hybridization either with the bottom organic layer or the metallic center. On the other hand, the bottom layer shows large hybridization with a modest charge transfer ($0.28 e^-$) to the lowest unoccupied molecular orbital (LUMO). The energy ordering is also characteristic of a trigonal prismatic N_3Au_3 ligand field with the HS state more stable by 1.52 eV than the LS solution and the intermediate state ($S = 1$) lying much higher in energy. Therefore, the electronic structure of the Fe(II) ion is best described by a weak trigonal prismatic ligand field formed by three Au neighboring atoms and three terminal N atoms of the T4PT bottom layer.

Our description is further confirmed by the inspection of magnetic properties. Indeed, Figure S1-a shows the calculated ground-state spin-density of the Fe-T4PT network on Au(111), suggesting parallel alignment of spins localized on Fe ions. XMCD measurements have indeed shown a weak ferromagnetic coupling between iron centers, featuring a critical temperature T_c of 1.8 K.³⁰ Based on the optimized structure, we performed a detailed inspection of the magnetic coupling (see Supporting Information for the complete description of our investigation) that reveals the respective roles of the surface-mediated RKKY interaction and of the T4PT linker. The resulting ferromagnetic coupling $J = 0.51$ K is in agreement with experimental findings strengthening our conviction that our description of the electronic structure is correct.

At this stage, the negative energy difference between HS and LS states ($\Delta E_{\text{adia}} = -1.52$ eV) is not compatible with SCO behaviour. Thus, the prerequisites for the generation of bistable devices are definitely not fulfilled. However, our calculations show that the T4PT top layer is only weakly bound to the bottom one and therefore can be substituted by other molecules with stronger binding energy to the Fe(II) ion. We felt that chemical modification of the organic part might restore the N_6 coordination sphere around the Fe(II) centers and shift ΔE_{adia} to positive values. Indeed,

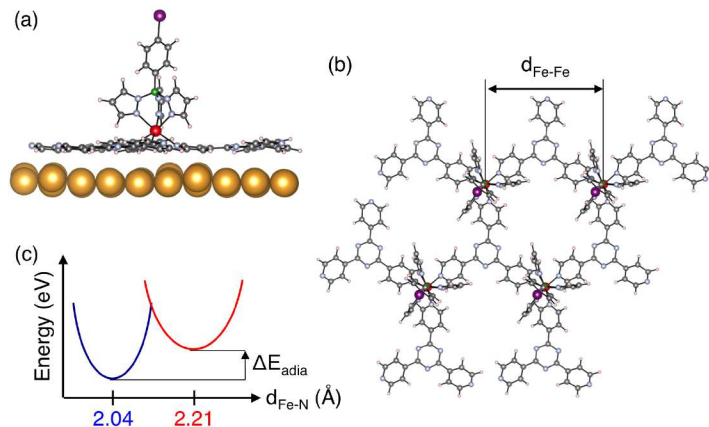


Figure 3: (a) Optimized structure of Fe(T4PT)(*p*-IC₆H₄)B(pz)₃ on Au(111). For clarity, only one gold layer is displayed. (b) Top view of the optimized free-standing Fe(T4PT)(*p*-IC₆H₄)B(pz)₃ network. The Fe-Fe distance is optimized with respect to the spin value. (c) Schematic energetics, ΔE_{adia} is positive, a prerequisite for spin-crossover.

molecular magnetism has produced a wealth of ligands with the ability to modulate the energetics. Then, we intended to examine the impact of surface deposition of the modified Fe(II)-based MOF. Here, we restrict our study to two tridentate N-terminated ligands. As a first guess, we consider the 1,4,7-trimethyl-1,4,7-triazacyclononane (tacn) ligand, known to generate Fe(II) compounds exhibiting temperature-induced SCO.⁴³ As hopped, the iron center leaves the gold hollow site and a N₆ coordination sphere is restored after DFT geometry optimization. A similar picture holds for tris(pyrazolyl)-borate (*p*-IC₆H₄)B(pz)₃ ligand (Figure 3a), a well-known negatively-charged ligand in SCO chemistry.^{44,45}

In this first step, we have conserved the original periodicity of the network imposed by the commensuration with the Au(111) surface. In that configuration, Fe-T4PT distances (≈ 2.15 Å) are too large to stabilize the LS state. However, since the Fe ion is not bound to the Au hollow site anymore and that the T4PT is weakly adsorbed to the substrate, there is no reason for the MOF to conserve the same periodicity. From a computational perspective, it is not affordable to vary the periodicity of the MOF network while keeping the gold substrate fixed. Thus, we considered the free-standing Fe(T4PT)(tacn) and Fe(T4PT)(*p*-IC₆H₄)B(pz)₃ 2D structures and optimized the atomic positions as well as the unit cell vectors (Figure 3b) for the HS and LS states.

Unfortunately, a negative adiabatic energy difference $\Delta E_{\text{adia}} = -340$ meV is calculated for the

taen ligand. Thus, the HS state remains the ground-state and no SCO behavior can be anticipated. A contrasted scenario is observed when T4PT is substituted by (*p*-IC₆H₄)B(pz)₃. The adiabatic energy difference is much reduced and remains positive, $\Delta E_{\text{adia}} = 140$ meV (Figure 3c). Meanwhile, the equilibrium geometries are characterized by a Fe-N average distance that varies from 2.04 Å (LS) to 2.21 Å (HS) along with a 0.31 Å elongation of the Fe-Fe distance (12.45 to 12.76 Å). All these values are compatible with a typical SCO behavior and the parameters used in the model previously presented (see Table 1).

In order to evaluate the charge redistribution, the network must be placed on top of the Au(111) surface. As the periodicities of both patterns now differ, we used a single unit consisting of one Fe center and its coordination sphere, *i.e.* three T4PT and one (*p*-IC₆H₄)B(pz)₃ ligands, on top of a large gold layer. Out of Bader analysis, the charge redistribution on the Fe center along the transition is calculated $\Delta Q = 0.64$ e⁻. This value is in agreement with the ones estimated⁴⁶ and calculated on molecular FeN₆ SCO compounds.^{26,47} The polarization contribution was then evaluated by using (i) the atomic positions of the free-standing structure, and (ii) the point charges previously determined. The cooperativity parameter γ_{MOF} is found 20 K. This rather weak value in the 3D material is suggestive of a smooth transition phenomenon. In the presence of the metallic gold surface, a $\gamma_{\text{MOF}}^{\text{Au(111)}} = 83$ K value is calculated. Therefore, one can anticipate a much more abrupt transition, the amplification factor $\gamma_{\text{MOF}}^{\text{Au(111)}}/\gamma_{\text{MOF}}$ reaching a noticeable value of 4.15 for a very realistic synthetic system. Our initial model Fe(NCH)₄(NCS)₂ is attractive from its compact form, but may overestimate actual charge reorganizations along spin transition. However, it provides a transferable view on the impact of surface deposition in the suggested Fe(II) T4PT derivative.

In this work, the prime role played by surfaces in the generation of strongly cooperative SCO compounds is established. The extension of a thermodynamic model stresses the importance of the deposition of FeN₆ units on metal substrates. We estimated an enhancement of the cooperativity parameter by a factor larger than 20. To support these views, DFT calculations were performed on a reported MOF supported on a Au(111) surface. The geometry and electronic structure of Fe-T4PT network were characterized and concluded on a HS ground-state excluding any SCO

behavior. Nevertheless, we identified a promising (*p*-IC₆H₄)B(pz)₃ ligand to construct a spin transitioning Au-supported MOF. Quite remarkably, such substitution allows one to satisfy a positive and small enough value (140 meV) for the enthalpy change. Based on this chemical modification, we showed that the deposition on a gold surface induces a significant enhancement of the cooperativity factor. Naturally, our compact model leaves aside various contributions (phonons, solvents, etc.) that are expected to impact on the spin-transition phenomenon and could be advantageously improved in the future.⁴⁸ But the polarization part of cooperativity unambiguously benefits from metal deposition. With the ability to increase cooperativity in a rational way, we believe that supported spin-crossover Fe(II) materials open up a promising route in the long-hoped design of hysteresis behavior. This inspection paves the way to the preparation of supported materials to complement the immense chemical strategies that have been developed in the last three decades.

Acknowledgements

M. K. work is supported by Rennes Métropole through the *Allocation d'installation scientifique* program. N. P. acknowledges financial support from EU H2020 project no. 676598, “MaX: Materials at the eXascale” Center of Excellence in Supercomputing Applications. We thank L. Norel, J.-F. Halet, G. Chastanet and N. Lorente for stimulating discussions.

Supporting Information Available

Computational details, additional structural data, description of the magnetic coupling in Fe(T4PT)/Au(111) and VASP complementary results.

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