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COMMUNICATION

Electrospray Ionization: an efficient approach to deposit polymetallic molecular switches onto gold surfaces

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Electrospray ionization (EI) deposition is proven efficient in obtaining monolayers of a polymetallic charge transfer complex onto gold surfaces. The molecule's integrity is monitored by PM-IRRAS and XPS. This approach broadens the perspective of molecular magnetic switches' deposition, which is currently dominated by thermal evaporation technique of monometallic spin crossover (SCO) complexes.

Molecular switches, which can undergo reversible changes of their electronic properties under external perturbation, are attracting strong research interests because of their potential application in molecule-based nanodevices.^{1–4} In particular, magnetic switches such as spin-crossover,⁵ charge-transfer⁶ and valence tautomeric complexes,⁷ whose spin-state can be controlled by light, pressure, temperature, electric and magnetic fields, open opportunities in molecular spintronics.⁸ In this context, strong efforts have been devoted to the deposition of these complexes onto surfaces as this can represent a first stage in the device's construction. Over the last decade, the vacuum thermal evaporation has stood out as the dominant approach for the deposition of molecular multilayers, monolayers or sub-monolayers of neutral monometallic spin-crossover complexes onto various substrates. Some of these studies led to the creation of interesting nano-electronic devices.^{9,10} However, the vacuum evaporation (*via* sublimation) approach successfully used for SCO complexes can hardly be extended to heavier and charged polymetallic complexes because large molecules can disassemble during the process or form aggregates on the surface. In such cases, wet chemistry approaches (such as drop casting, spin coating) can be used, and

they usually lead to thin films of micro/nano-metric size. However, wet-deposition approaches require coping with the ubiquitous presence of organic contaminants on the inorganic solid surfaces, which is due to their high surface energy.¹¹ In particular, the omnipresence of the adventitious contaminants considerably limits the selectivity of the characterization of the organic adlayer of interest.¹² More sophisticated methods have to be used to target (sub)monolayer of mono/polymetallic magnetic switches on surfaces. For example, polymetallic photomagnetic charge transfer complexes were deposited onto surfaces using the Langmuir-Blodgett method,¹³ while self-assembled monolayers of valence tautomeric complexes could be obtained by functionalizing a ligand with an anchoring group.¹⁴ Overall, these examples of successful monolayer deposition remain scarce although the properties of the polymetallic complexes are very attractive. In fact, besides showing multi-responsive behaviour¹⁵ like the SCO complexes, we recently showed that some charge transfer switches also exhibit a multi-redox flexibility,^{16,17} which make them attractive for the design of charge-storage molecule-based devices.^{3,18} In particular photomagnetic cyanide-bridged $A\{Fe_4Co_4\}$ cubes can show up to nine reversibly accessible redox states (A is an inserted alkali ion).¹⁹ The search for reliable routes for depositing these polymetallic functional molecules is crucial to fully explore their potential in molecular electronics. In this context, we decided to explore the electrospray ionisation (EI). Indeed, EI was already proven efficient for depositing either organic molecules,²⁰ peptides,²¹ SCO and magnetic complexes^{22,23} or even single molecule magnets onto surfaces.^{24,25} Here EI was successfully applied to deposit a soluble and robust $Cs\{Fe_4Co_4\}$ molecular switch as (sub)-monolayer.

The investigated complex, of formula $Cs\{[Fe(Tp)(CN)_3]_4[Co(T^{Ph}Tp)]_4\}ClO_4$ (noted from now $Cs\{Fe_4Co_4\}$) is an octametallic cubic cage where cyanide ligands act as edges (Fig. 1). It is obtained by the self-assembly of the $[Fe^{III}(Tp)(CN)_3]^-$ precursor (Tp = hydrotris(pyrazolyl)borate)) with $Co^{II}(ClO_4)_2$ and $CsClO_4$ salts and a blocking ligand of the Tp family, where the

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proton linked to the boron in Tp is replaced by a thiophene-aryl group (noted $\text{T}^{\text{Ph}}\text{Tp}$). As observed in our previous studies on similar cages, a metal-to-metal charge transfer occurs in solution.¹⁹ The cubic molecule is thus isolated here in its $\text{Cs}\{\text{Fe}^{\text{II}}_4\text{Co}^{\text{III}}_4\}$ diamagnetic state, as shown by the magnetic measurements and the NMR data (see ESI). In these cubic complexes, the central caesium ion occupies the cubic cavity and interacts with the twelve cyanide edges, conferring a remarkable stability to the polymetallic complex. It was not possible to obtain single crystal suitable for X-ray diffraction, however the actual molecule composition was checked by elemental analysis, ^1H , ^{13}C (1D and 2D) and ^{133}Cs NMR (details in ESI). For example, the ^{133}Cs NMR spectrum shows a unique peak corresponding to the inserted alkali ion. Finally, the high-resolution mass spectrometry experiment shows a molecular

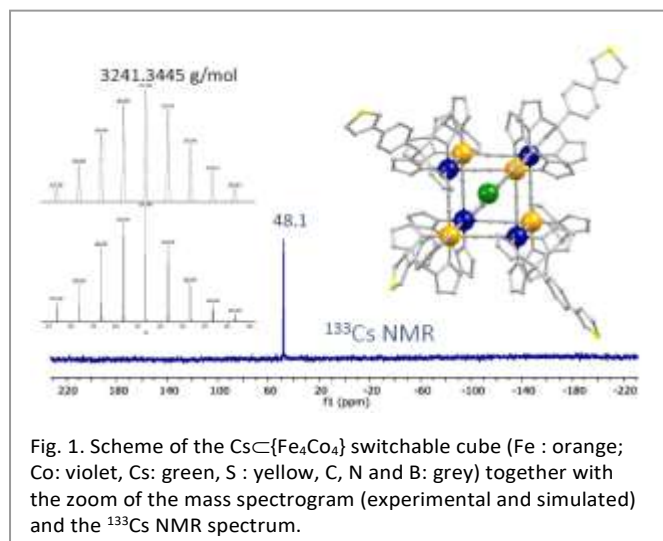


Fig. 1. Scheme of the $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ switchable cube (Fe : orange; Co: violet, Cs: green, S : yellow, C, N and B: grey) together with the zoom of the mass spectrogram (experimental and simulated) and the ^{133}Cs NMR spectrum.

peak at 3241.3 g/mol whose isotopic pattern perfectly matches with the simulated one (Fig. S1, details in ESI).

The deposition of $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ molecules on a (111) gold substrate through EI was performed from a solution in 1,2-dichloroethane at 5.10^{-4} M, as described in the ESI. During EI deposition, the partial pressure in the main chamber was around 10^{-7} Torr. In these experimental conditions (solvent and concentration), the molecules were shown to preserve their molecular structure as demonstrated by the comparison of the infrared spectroscopy studies and the XPS analyses on the bulk and on the surface.

The infrared (IR) spectroscopy is a well-adapted technique for the structural and electronic characterization of cyanido-based coordination complexes.²⁶ Actually, the cyanide stretching vibration, ν_{CN} , which shows strong absorption in an unpopulated region of the IR spectra (between 2000- 2300 cm^{-1}), is very sensitive to both the metal oxidation state and the coordination mode of the cyanide ligand. For example, ν_{CN} vibration of non-bridging $\text{Fe}^{\text{II}}\text{-CN}$ moieties typically occurs below ca. 2080 cm^{-1} while bridging ones occurs up to ca. 2135 cm^{-1} . In the present case the IR spectrum of the $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ cube recorded on a crystalline powder (Fig. 2B) features two intense cyanide stretching vibrations at 2104 and 2124 cm^{-1} , which are associated to the $\text{Fe}^{\text{II}}\text{-C}\equiv\text{N-Co}^{\text{III}}$ linkages. These stretching vibrations are actually very close to those observed in related

$\{\text{Fe}^{\text{II}}_2\text{Co}^{\text{III}}_2\}$ square complexes (at 2109 and 2126 cm^{-1}).²⁷ Interestingly, the IR pattern measured *in-situ* by PM-IRRAS after EI deposition on Au(111) substrate (Fig. 2C) reveals a spectral feature identical to that of the cubes prior to deposition. The two contributions of cyanide bridges are observed at 2109 and

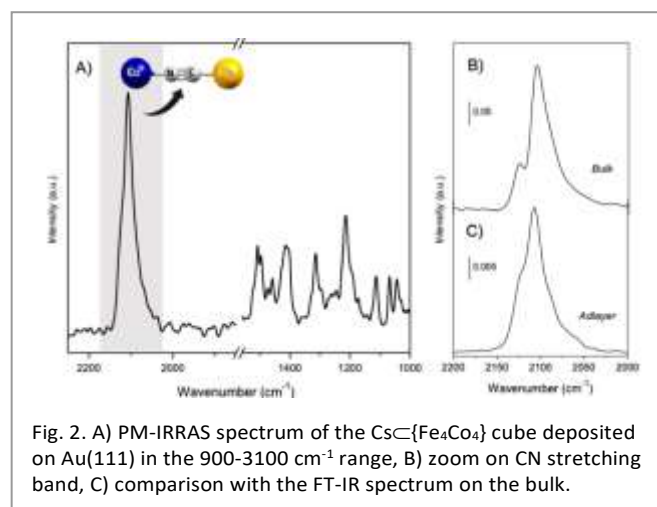


Fig. 2. A) PM-IRRAS spectrum of the $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ cube deposited on Au(111) in the 900-3100 cm^{-1} range, B) zoom on CN stretching band, C) comparison with the FT-IR spectrum on the bulk.

2124 cm^{-1} , indicating that their chemical/electronic environment is preserved in the adsorbed state.

The Fe(II) oxidation state in the bulk sample is also confirmed by the $\nu\{\text{B-H}\}$ stretching at 2483 cm^{-1} (Fig. 2A), which is typical of the $[\text{Fe}^{\text{II}}(\text{Tp})(\text{CN})_3]$ moieties and which contrasts with that of the $[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]$ generally observed above 2500 cm^{-1} (for example at ca. 2509 cm^{-1} in the $\text{Bu}_4\text{N}[\text{Fe}^{\text{III}}(\text{Tp})(\text{CN})_3]$ precursor).

The integrity of the cubic cages once deposited onto surfaces was also checked by the XPS study (Fig. 3). Analyses were first performed on the $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ bulk. Figure 3 displays the expected Co 2p Fe 2p and Cs 3d peaks constituting the molecular cage. The Co 2p doublet shows a Co 2p_{3/2} peak with a single contribution at 783.0 eV, and a distance between the Co 2p_{3/2} and Co 2p_{1/2} peaks equal to 15.0 eV (Fig. 3A). This is consistent with the occurrence of the Co(III) oxidation state, as reported for other organometallic complexes.²⁸ The main Fe 2p_{3/2} contribution shows a narrow peak (FWHM = 1.1 eV) at 708.9 eV (Fig. 3B), which is assigned to Fe(II) compounds.²⁹ The two times less intense Fe 2p_{1/2} peak (~721.7 eV) overlaps with the Cs 3d_{5/2} peak but both contributions remain distinguishable. All these spectral features are fully consistent with the electronic states expected for Co, Fe and Cs elements.

Figure 3 also presents typical Co 2p, Fe 2p and Cs 3d peaks constituting the molecular cage recorded on the gold surface after EI deposition. Remarkably, the Co 2p doublet shows a main Co 2p_{3/2} contribution at 783.0 eV and a distance between Co 2p_{3/2} and Co 2p_{1/2} peaks equal to 15.0 eV (Fig. 3C), identical to that observed on the $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ bulk (Fig. 3A). A broad contribution at lower binding energy (781.0 eV) was also observed, accompanied with satellites at higher binding energies (around 788.0 eV). This is likely due to the presence of a small amount of Co(II) compound. Such reduction is possible as this family of $\text{Cs}\{\text{Fe}_4\text{Co}_4\}$ cubes can be obtained either in a diamagnetic state or in a paramagnetic state (as a neutral molecule with one reduced Co(II)).¹⁶ The stabilization of one state or the other depends on the nature of the blocking

ligand.³⁰ The Fe 2p doublet (Fig. 3D) exhibits a main Fe 2p_{3/2} contribution at 708.8 eV identical to that observed the CsC{Fe₄Co₄} bulk (Fig. 3B), thus confirming their assignment to

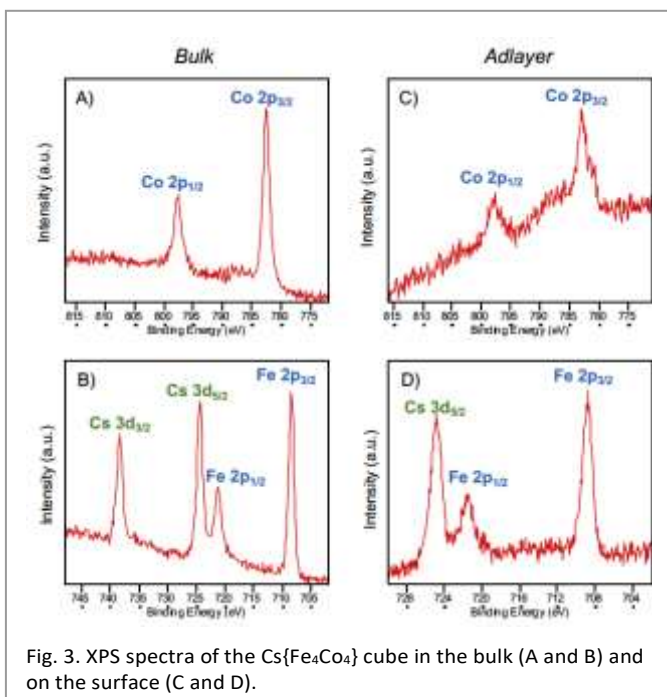


Fig. 3. XPS spectra of the Cs{Fe₄Co₄} cube in the bulk (A and B) and on the surface (C and D).

Fe(II) compounds. Also, Cs 3d_{5/2} (Fig. 3B) shows the typical spectrum due to Cs⁺ species.

XPS Au 4f spectra recorded prior to and after the deposition of CsC{Fe₄Co₄} through EI technique showed significant signal attenuation without any noticeable chemical shift (Fig. S8). This indicates the presence of an adlayer on the gold surface, as expected: by considering the electron inelastic mean free paths (IMFP) calculation detailed in ESI and the attenuation of the Au signal, this yields an adlayer with a mean thickness of about 2.1 nm. This estimate is perfectly consistent with the dimension of CsC{Fe₄Co₄} molecule (*ca.* 15–20 Å) and suggests the formation of a monolayer-like structure on the gold surface.

In summary, the EI technique allowed the deposition of a CsC{Fe₄Co₄} cube, which belongs to a family of photo- and electro-switchable molecules, onto a gold substrate. This approach appears as a straightforward, yet powerful means for the preparation of monolayers of polymetallic molecular switches, while avoiding adventitious organic contaminations. By combining *in-situ* characterization and *ex-situ* analysis in ultra-high vacuum we showed that EI technique preserves the molecular structure of the studied molecules (IR) and the degree of oxidation states of the metals (XPS) in the adsorbed state. EI is thus an alternative to wet-solution approaches that have been previously explored for polymetallic species and the vapour evaporation technique, which is still largely used on monometallic SCO switches. Future studies will aim at (i) evaluating the flexibility of this approach for depositing other polymetallic molecular switches; (ii) investigating the photo-/electro-switching properties of the deposited molecules through advanced physical measurement.

Conflicts of interest

There are no conflicts to declare.

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