Addressing the Magnetic Properties of Sub-Monolayers of Molecular Nanomagnets by X-ray Magnetic Circular Dichroism

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Abstract

We report on a comparative study of electronic and magnetic properties of Mn₆ molecular nanomagnets grafted on gold surface. Two derivatives with spin – ground state 4 and 12 have been functionalized with 3 – tp – CO₂[−] (3 – thiophene carboxylate, tpc) ligands and characterized as thick films (TFs) as well as sub-monolayers (sMLs) by synchrotron – based techniques. X – ray absorption spectroscopy at the Mn – L_{2,3} edges shows the modification of the spectral lineshape in the sMLs with respect to the TFs suggesting that the local symmetry at the Mn sites changes once the molecules are deposited on gold surface. In spite of this the expected Mn^{III} oxidation state is preserved. X – ray magnetic circular dichroism (XMCD) spectra show that the total magnetic moment is only given by spin part because of the quenched orbital moment. Moreover, variable temperature variable field (VTVH) XMCD spectra reveal an effective decrease of the Mn spin moment for both derivatives deposited on gold surface.

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Introduction

Among the several objects which can be realised in nanomagnetism, Molecular Nanomagnets (MNMs) have recently attracted much interest because of their potential application as molecular devices¹⁻⁸. They combine large spin – ground state with large and negative magnetic anisotropy giving rise to an anisotropy energy barrier leading to slow relaxation of the magnetization at low temperatures⁹. In principle these properties might be used to store information in an individual molecular unit, although it has been hindered so far by two main issues. Firstly, the superparamagnetic blocking temperature is still too low because, in the most fortunate cases (e.g. Mn_{12} ¹⁰), it reaches only 2 – 3 K^{9,11,12}. This issue might be overcome by larger values of the spin – ground state and magnetic anisotropy, the latter being extremely difficult to achieve by controlled synthesis. Secondly, the retention of magnetic properties at the molecular level following the deposition of spatially isolated MNMs on substrates is far to be achieved¹³. The interaction with surfaces may modify the intrinsic properties of molecules leading to the reduction of the magnetic core and the removal of the hysteresis loop as already observed for Mn_{12} on gold¹⁴⁻¹⁶.

Recently a step forward towards the enhance of the anisotropy barrier was carried out with the synthesis of MNMs with general formula $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{R} - \text{sao})_6(\text{O}_2\text{CR}')_2\text{L}_{4-6}]$, (in short Mn_6) where R = H, Me or Et, R' = H, Me, Ph etc., L = EtOH, H₂O, MeOH and saoH_2 is salicylaldoxime. Milios *et al*¹⁷⁻¹⁹ proved that the use of derivatised oxime ligands and bulky carboxylates deliberately increases the value of the spin – ground state of Mn_6 – based systems from spin $S = 4$ to $S = 12$ in a stepwise fashion, and in – so – doing enhances the energy barrier for magnetization reversal (U_{eff}) establishing a new record of 86.4 K. The representative core of the $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{sao})_6(\text{O}_2\text{CR}')_2(\text{ROH})_4]$ derivative^{20,21} contains a non-planar $[\text{Mn}^{\text{III}}_6(\mu_3 - \text{O}^{2-})_2(\mu_2 - \text{OR})_2]^{12+}$ unit of two off – set, stacked $[\text{Mn}^{\text{III}}_3(\mu_3 - \text{O}^{2-})]^{7+}$ triangular subunits linked by two central oximato O – atoms (Figure 1, left panel). This class of compounds shows a ferromagnetic (FM) exchange interaction between the two antiferromagnetically (AF) coupled $[\text{Mn}^{\text{III}}_3]$ triangles leading to $S = 4$ spin – ground state²². A number of important structural changes leading to different values of S and U_{eff} take place in the related complexes $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{R} - \text{sao})_6(\text{O}_2\text{CR}')_2(\text{EtOH})_4(\text{H}_2\text{O})_2]$ with R = Et, Me, Ph²³, where the increased steric bulk and non – planarity of the R – sao^{2-} ligands cause a shortening (by ~ 1 Å) of the phenolato oxygen – square pyramidal Mn distance and a severe twisting of the Mn – N – O – Mn moieties within each Mn^{III}_3 sub – unit (Figure 1, right panel). The structural changes force a switch in the dominant magnetic exchange interactions from AF to FM, thus stabilizing $S = 12$ spin – ground state^{19,23}. However, all these derivatives are characterized by weak exchange interaction ($J < 1 \text{ cm}^{-1}$), leading to the population of low – lying excited states ($S = 11, 10, \dots$). This makes feasible their participation in the relaxation by

quantum tunnelling of the magnetisation, which results in a reduction of the energy barrier. This problem has been successfully solved by further replacement of the carboxylates via simple metathesis type reactions that produces identical cores except for the Mn – N – O – Mn torsion angles (α_v) which are modified according to the steric bulk of the ligand. The complexes with the largest torsion angles show an increase in the magnitude of the pairwise exchange parameter (J) and an increase in the effective U_{eff} up to 86.4 K^{19,23}, i.e. notably higher than that of Mn₁₂ – ac (61 K)².

In our previous work²⁴, we already succeeded in self – assembling of two Mn₆ derivatives [Mn^{III}₆O₂(sao)₆(O₂C – tp – 3)₂(EtOH)₄] (**1**) and [Mn^{III}₆O₂(Et – sao)₆(O₂C – tpc – 3)₂(EtOH)₄(H₂O)₂] (**2**) on Au(111) surface. The spin – ground state of these compounds is $S = 4$ and $S = 12$, respectively. For both compounds, the functionalization is made by two 3 – tp – CO₂[–] units pointing in opposite direction and being perpendicular to the molecular plane with the sulphur atoms in outermost position on the thiophene ring (Figure 1, top panel). This favours the direct grafting on gold surface by covalent bond with the molecular axis which should be preferentially normal to the surface. The investigation carried out by means of scanning tunnelling microscopy (STM), shown in Figure 1, and X-ray photoemission spectroscopy (XPS), suggests that Mn₆ molecules preserve their integrity when deposited by liquid phase. The electronic structure of Mn₆ on gold surface was also studied by means of resonant photoemission spectroscopy (ResPES) at the Mn L_3 edge aimed to single out the Mn – 3d derived states in the valence band²⁵. Moreover, magnetic measurements on powder pellets clearly showed that the 3 – tp – CO₂[–] functionalisation does not significantly alter the magnetic properties of both compounds²⁴.

The magnetic characterization of grafted MNMs is the key point which needs to be addressed. Unfortunately standard magnetometry techniques do not have enough sensitivity for detecting the magnetism of sub – monolayer quantities of grafted clusters. In terms of high resolution and element selectivity, X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) are excellent tools. The analysis of isotropic XAS spectra at the $L_{2,3}$ edges of transition metals provides unambiguous information about the oxidation state and local symmetries of the selected chemical element. On the other hand, XMCD directly probes the local spin and orbital magnetic moments as well as the sign of the exchange interactions. In particular cases, the application of the XMCD sum rules allows the quantification of the orbital and magnetic moments in an element – specific way. Herein we address the structural, electronic and magnetic properties of the sub – monolayers (sMLs) and thick films (TFs) of **1** and **2** by means of XAS and XMCD measurements in order to elucidate how the molecular properties are affected after the deposition on surface.

Experiment

The TFs of the Mn_6 – tpc derivatives **1** and **2**, and those of the pristine Mn_6 – benz compounds, $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_2(\text{sao})_6(\text{EtOH})_4]$ and $[\text{Mn}_6\text{O}_2(\text{O}_2\text{CPh})_2(\text{Et} - \text{sao})_6(\text{EtOH})_6]$, were obtained by drop-cast procedure on a highly ordered pyrolytic graphite (HOPG) substrate. The sML samples were prepared by immersion of flame annealed gold on mica surface in a 1 mM solution of the derivatives **1** and **2** in CH_2Cl_2 for 10 min. After the adsorption process the samples were rinsed with proper solvent in order to remove the excess of molecular layers and quickly introduced into the sample chamber^{26,27}. Solvent used, deposition time and solution concentration were optimized in order to get homogeneous sML distribution of isolated molecules. STM was used to check that the desired two – dimensional distribution of nanometric entities was actually achieved (Figure 1)²⁴.

XAS measurements at the Mn $L_{2,3}$ edges were carried out at the ID08 Dragon beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) in Total Electron Yield (TEY) detection mode and normalized to the incident photon flux. The photon source was an Apple II undulator delivering a high flux (10^{13} photons/s) of ~ 100 % of circularly polarized light.

The sML samples were fixed to a molybdenum sample holder by means of tantalum wires to ensure a proper thermal and electrical contact, and transferred into a liquid – helium cryomagnet kept under UHV (10^{-10} mbar). The direction of both impinging beam and magnetic field generated by superconducting coils are perpendicular to the sample surface (z – axis). The XMCD spectrum is the difference between XAS spectra taken with the helicity of the incident photon (**P**) antiparallel ($\sigma^{\uparrow\downarrow}$) and parallel ($\sigma^{\uparrow\uparrow}$) to the field direction and normalized to the isotropic edge height. To avoid systematic errors, $\sigma^{\uparrow\downarrow}$ ($\sigma^{\uparrow\uparrow}$) absorption spectrum was obtained by averaging a set of spectra recorded with the field orientated parallel and anti – parallel to the photons direction²⁸. The beam flux was attenuated by more than 1 order of magnitude in order to avoid sample damaging induced by radiation exposure. In these conditions the spectra never showed any sign of degradation during the experiment.

Results and Discussion

XAS spectra taken with right ($\sigma^{\uparrow\uparrow}$) and left ($\sigma^{\uparrow\downarrow}$) circularly polarized light and the relative XMCD signal ($\sigma^{\uparrow\downarrow} - \sigma^{\uparrow\uparrow}$) at the Mn – $L_{2,3}$ edges for the TF of **1** and **2** are shown in Figure 2 and compared with the analogous Mn_6 – benz derivatives (the pristine not functionalized compounds) with spin 4 and 12 (see experimental section). The 2p core hole spin – orbit interaction splits the spectrum in two parts, corresponding to L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$) levels with a separation of about 11 eV. The L_2 edge features are more broadened than the L_3 edge, owing to the increased probability of the Coster –

Kronig Auger decay channel. Hereafter we focus only on L_3 fine structure. The L_3 level is further split into the t_{2g} and e_g sub – bands by the octahedral ligand field. The fine structure of the absorption edges is due to a combination of the electron – electron interaction within the Mn ions, the crystal field felt by the Mn ions and the hybridization of Mn_{3d} , O_{2p} and N_{2p} orbitals. The strong similarity between the XAS and XMCD spectra of TF – benz and TF – tpc compounds clearly suggests that the tpc functionalization does not significantly affect the electronic and magnetic properties at the Mn sites.

In Figure 3 the isotropic Mn – $L_{2,3}$ absorption spectra for the TFs and sMLs of **1** and **2** are compared with a series of reference Mn – oxide compounds. The absorption spectra of the TFs **1** and **2** have almost identical lineshape suggesting that the Mn ions present the same local symmetries and comparable crystal field intensities in the two complexes. Indeed the overall site geometry extracted from crystallographic data of the Mn ions in **1** and **2** is the same²⁴. The local symmetry of each Mn ion (Figure 1) is represented by a distorted octahedron with six apical atoms, five O atoms and one N atom. The main difference is that all the Mn ions are six-coordinated in **2**, while four Mn ions are six – coordinated and the other two are five – coordinated in **1** (one apical oxygen is missing, Figure 1). Despite the obvious inequality of N and O, the very similar bond lengths and angles around the magnetic ion leads to an almost perfect equivalence of the four in – plane atoms. On the other hand, their average apical – in – plane distance ratio is 1.17 for **1** and 1.19 for **2** with a percentage difference of only 1.4 %. In general, such small variations of the local symmetry around the selected chemical element cannot be observed in XAS spectra. For instance, in the case of other Mn – based complexes reported by Noh *et al*²⁹, no significant variation of the spectral lineshape was found for changes below 6% in the apical – in – plane ratio.

While the XAS spectra of TFs **1** and **2** are almost identical, most interestingly the sMLs **1** and **2** (Figure 3) show sensible discrepancy at the L_3 edge with respect to the corresponding TFs, the L_2 edge being quite similar. Notably, these modifications are identical for both **1** and **2** suggesting that the same kind of perturbation affects the two differently functionalized compounds when the Mn_6 molecules are deposited on gold surface. We will show in the following discussion, based on comparison of XAS spectra with those of reference manganese oxide compounds, that these modifications can be ascribed to a local structural modification of the grafted clusters, when they are deposited on the substrate.

The absorption spectra of MnO (Mn^{II}), Mn_2O_3 (Mn^{III}) and MnO_2 (Mn^{IV}) presented in Figure 3 as references were measured at the same time and in the same experimental conditions with the Mn_6 derivatives. Particular attention was paid for the energy alignment of all the spectra plotted in Figure 3. The main spectral features are labelled from A to E to facilitate the comparison. For both TFs and sMLs the Mn^{III} components (B, C and D) are dominant while the Mn^{IV} (E) is negligible. By comparing

the shapes of MnO (Mn^{II}) and Mn₂O₃ (Mn^{III}) spectra with those of the TFs, we can safely conclude that the fraction of reduced Mn^{II} ions must be extremely small.

The superimposition of normalized XAS and XMCD spectra taken for Mn₆–tpc TFs and sMLs reported in Figure 4 allows a more accurate analysis. Four features (A, B, C and D) can be easily distinguished at the Mn *L*₃ edge. Two highest features B and D with comparable intensity are visible in TFs, while only D is dominant in sMLs. B and C are much higher in TFs, conversely A is higher in the sMLs. This suggests an apparent transfer of spectral weights from B and C to A in sMLs with respect to TFs which can be explained in terms of a structural modification of the Mn sites. The comparison between XMCD spectra also shows features at the same energy of A, B, C and D. The decrease of the feature B gives evidence for a reduction of the magnetic moment associated with the Mn^{III} ions, as will be discussed later.

In general, the interpretation of absorption and dichroic spectra is not trivial because the lineshape changes drastically with the strength of the crystal field and spin – orbit interaction. Notwithstanding, the origin of the spectral differences between TFs and sMLs can be explained looking at the well – known Mn^{III} based reference systems. In Figure 5 the isotropic Mn – *L*_{2,3} absorption spectra of the Mn₆–tpc TFs are compared with those of the Piedmontite³⁰ and the ZnMn₂O₄²⁹, whereas the spectra of the sMLs with those of the Mn^{III}₂O₃ and ZnGa₁Mn₁O₄²⁹. The similarity between the Piedmontite, ZnMn₂O₄, and TFs absorption spectra let us suppose that the Mn ions posses large tetragonal distortions (i.e. Jahn – Teller distortion) as well known for polycrystalline spinel manganite oxides. This is also confirmed by the strong distortion of ZnMn₂O₄ (apical – in – plane ratio of 1.18) comparable to those of Mn₆ TFs **1** and **2** (apical – in – plane ratio of 1.17 – 1.19 respectively). Conversely, the XAS spectra of the ZnGa₁Mn₁O₄ and in particular of the Mn₂O₃ (Mn^{III}) with almost perfect octahedral symmetry (apical – in – plane ratio of 1.06) are more similar to the Mn₆ – sMLs. This suggests that the absorption of the 3 – tp – CO₂[–] functionalized Mn₆ clusters on gold surface induces a structural modification of the Mn sites reducing the elongation of the O – Mn – O axes, with respect to the bulk conditions, leading to an almost octahedral symmetry. This distortion could be ascribed to the interaction with gold and / or due to the lack of the isotropic interactions with all the surrounding molecules. Notably, this mechanism occurs without affecting the oxidation state of the Mn ions because the absorption spectra of the Mn₆ – sMLs and Mn₂O₃ are almost identical, as evidenced by their comparison presented in Figure 6 upper panel.

If the modifications in the XAS spectrum lead to different structural and electronic properties, those in the XMCD reflect the deviations of the magnetic properties. Comparison of the XMCD spectra (Figure 6 bottom panel) highlights that sMLs **1** and **2** are very similar to Mn₂O₃ and once again rather

different from MnO also in the magnetic behaviour. Since no significant Mn^{II} component is visible in the sMLs we can conclude that a large fraction of Mn_6 molecules have been deposited on Au surface preserving the Mn^{III} oxidation state; unlike the case for Mn_{12} – ac where a systematic reduction of the magnetic core occurs after the adsorption on gold^{15,16,31,32}. The sharp feature B of the reference compound Mn_2O_3 is observed in both TFs and sMLs with different intensities. Ghigna³³ and Voss¹⁶ observed the peak B in the Mn_{12} – biph spectrum and they assigned it to different crystal symmetry or to a poor single crystal quality. Because in sMLs and TFs the molecules are not aligned in the same direction like in single crystals we suggest that B reflects local symmetries of the Mn sites.

The application of the XMCD spin moment sum rule for Mn^{III} is unfeasible because the $L_{2,3}$ edges overlap due to the strong spin – orbit coupling and it is also complicated by the determination of the magnetic dipole operator (T_z)^{34,35,36}. Conversely, the orbital moment sum rule still holds and by definition it is proportional to the integral of the XMCD signal through the $L_{2,3}$ edges³⁴. The XMCD integral curves reported in Figure 4 vanish for both TFs and sMLs of **1** and **2** giving evidence for quenched orbital moment. Hence, the total magnetic moment possesses only spin contribution. Since the orbital moment is quenched for all TFs (– benz and – tpc), we conclude that neither the functionalization nor the deposition on gold surface affects the degree of quenching of the orbital momentum at the Mn sites. Variable temperature variable field (VTVH) XMCD signal (%) at the L_3 edge for the TFs and sMLs of **1** and **2** are plotted in Figure 7. The uncertainty is estimated to be 20 % of the corresponding maximum values. The comparison between TFs and sMLs shows that: (i) as expected the dichroic signal of the TF **2** is more intense with respect to the TF **1** in agreement with the nominal values of their spin; (ii) the dichroic signal for the TFs and sMLs decreases with increasing temperature from 10 to 25 K due to the increased thermal fluctuation of the spin magnetic moments, (iii) upon the increase of the temperature the dichroic signal in the sMLs decreases with respect to the TFs from 30 % at 10 K to 50 % at 25 K. Because the error bars of the TFs and sMLs isothermal curves do not overlap, the Mn^{III} spin magnetic moment shows an effective decrease. According with the results of XAS measurements (Figure 4) this can be explained in terms of structural changes of the Mn local environment when they are grafted on gold surface in sMLs compounds. In fact such changes may lead to different relative distances and angles between Mn ions and to the modification of the Mn – Mn exchange couplings with respect to the corresponding TFs. The origin of such structural changes can be ascribed to the molecule – gold surface interactions and / or to the lack of the isotropic interactions with all the surrounding molecules. In fact, in the TFs the molecules are packed and unless the first layer, the molecules probed by XMCD in TEY mode are surrounded by others. Hence isotropic molecule – molecule interactions are expected while interactions with the surface do not play any role

because the TFs are deposited on poor reactive HOPG surface and also because of the small sampling depth of the TEY mode (2 – 3 molecular layers) with respect to the TFs thickness. In the sMLs the molecules are surrounded by the surface on bottom, free space on top and molecules in the plane (Figure 1). Then local and molecular symmetries are driven by anisotropic molecule – molecule and molecule – surface interactions. Other effects such as preferential orientation of the molecular easy axis of the magnetisation in the plane of the surface, and high – spin to low – spin transitions driven by a competition between the inter – atomic exchange couplings and the crystal field strength must be considered. If the molecular easy axis lies preferentially in the plane of the surface, then the variable field XMCD signal is expected to be lower than the relative TFs because the magnetic field is applied perpendicular to the surface and along the molecular hard axis. This can be proven only with further studies based on grazing incident XMCD experiment although STM studies were in favour with preferential molecular axis perpendicular to the surface²⁴. The transition of Mn^{III} ions from high – spin to low – spin can be also disregarded because the XAS lineshape for both sMLs and TFs **1** and **2** have a well – defined multiplet structure, which is a clear fingerprint of localized 3d orbital with high – spin state. Conversely, itinerant systems with low – spin state are characterized by smooth XAS spectral lineshape^{37,38}.

Conclusions

The electronic and magnetic properties of functionalised derivatives **1** and **2** belonging to a Mn₆ MNMs family as TFs and sMLs on gold surface have been investigated by XAS and XMCD techniques. The results can be summarised as follows: i) the functionalisation does not affect the properties of the Mn₆ magnetic core as confirmed by the similarity of XAS and XMCD spectra of Mn₆ – benz and Mn₆ – tpc as TFs; ii) a comparative analysis of XAS and XMCD spectra of **1** and **2** as TFs and as sMLs gave evidence for local distortion of Mn environments when Mn₆ clusters were deposited on gold surface; iii) the Mn^{III} oxidation state was preserved in sMLs **1** and **2** encouraging the synthesis of MNMs based on Mn^{III} ions having large magnetic anisotropy; iv) the orbital moment is quenched in the TFs as well as in the sMLs; iv) VTVH XMCD curves of sMLs reveal an effective decrease of the Mn^{III} spin magnetic moment in **1** and **2** with respect to the relative TFs. The main effect responsible for the last result might be interpreted as a consequence of ii) where the origin of the local distortions can be ascribed to the molecule – gold surface interactions and / or to the lack of the isotropic interactions with all the surrounding molecules. In order to distinguish between these two effects, further studies based on Mn₆ clusters deposited on less reactive surfaces like HOPG will be addressed.

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Figure 1

Figure 1: Upper panel: The Mn_6 structures (with 3 – tp – CO_2^- functionalizations) of the derivatives **1** with $S = 4$ (a) and **2** with $S = 12$ (b). The large and medium circles depict the Mn^{III} ions and the S atoms respectively. While dark and clear small circles indicate N and O atoms. The lines link the carbon atoms. H – atoms are omitted for clarity. Lower panel: STM images ($65 \times 65 \text{ nm}^2$) in constant-current mode of the Au(111) surface immersed in a solution of **1** on the left and **2** on the right.

Figure 2

Figure 2. Upper panel: comparison between Mn $L_{2,3}$ XAS spectra, taken on TF samples with left ($\sigma^{\uparrow\downarrow}$) and right ($\sigma^{\uparrow\uparrow}$) circularly polarized light, of Mn_6 – benz and Mn_6 – tpc for both $S = 4$ (left) and $S = 12$ (right). Lower panels: dichroic spectra of Mn_6 – benz and Mn_6 – tpc for both $S = 4$ (left) and $S = 12$ (right). The XMCD integrals (dotted curve) relative to the tpc – functionalized Mn_6 are also reported. All the spectra were taken at 10 K with an applied magnetic field of 5 T.

Figure 3

Figure 3. Comparison between the isotropic Mn – $L_{2,3}$ XAS spectra of the Mn_6 TF and sML **1** and **2**. The absorption spectra of MnO (Mn^{II}), Mn_2O_3 (Mn^{III}) and MnO_2 (Mn^{IV}) are also shown as a references.

Figure 4

Figure 4 Direct comparison between normalized XAS and XMCD spectra of the Mn_6 – tpc $S = 4$ TF (black thick curve) and sML (red dashed curve). The different A, B, C and D features observed for the TF and the sML suggest deviations of the local symmetries (see the text). In the bottom panel the XMCD integrals are also shown.

Figure 5

Figure 5. XAS spectra of Mn₆ – tpc TF are compared with Piedmontite and ZnMn₂O₄ (a), whereas spectra of the Mn₆ – tpc sML are compared with Mn₂O₃ (Mn^{III}) and ZnGa₁Mn₁O₄ (b) [23, 28].

Figure 6

Figure 6 Normalized XAS and percentage XMCD spectra of the Mn₆ – tpc sMLs, S = 4 (dash curve) and S = 12 (solid curve), are compared with the Mn^{III}₂O₃ (dot curve) and the Mn^{II}O (dot dash curve). The different A, B, C and D features observed in the sMLs and in the Mn₂O₃ are indicated (see the text).

Figure 7

Figure 7: Variable temperature variable field XMCD signal (%) measured for the derivatives **1** and **2** as TFs and sMLs .

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