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1 Direct Observation of Charge Transfer and
2 Magnetism in Fe₄Co₄ Cyanide Bridged Molecular
3 Cubes

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16 **ABSTRACT**

17 We have studied the zero-dimensional cubane molecular correspondent of a Prussian blue
18 analogue Cs-Fe₄Co₄ at low temperature and high magnetic field by means of L-edge X-ray
19 absorption spectroscopy and X-ray magnetic circular dichroism. We probe the magnetic and
20 electronic structures of Fe and Co separately upon light irradiation, which allows us to observe
21 directly the electron transfer coupled to a spin transition (ETCST) phenomenon within the
22 molecular cubes and to investigate the nature of the metastable photoexcited state. From our
23 results we estimate a lower bound for the intramolecular Fe-Co exchange coupling of $J \gtrsim$
24 -0.5 cm^{-1} with the negative sign denoting antiferromagnetic coupling.

25 **TOC GRAPHICS.**

26

27 **KEYWORDS.** Photomagnetism, Prussian blue analogues, Charge transfer, Cyanometalates,
28 XMCD, XAS

29

30 The photocontrol of the magnetic and optical properties of switchable compounds is of great
31 interest in view of possible implementations as sensors, optical switches or memories in organic
32 electronics devices.¹⁻⁷ FeCo Prussian Blue Analogues⁸ (PBAs) are excellent candidate materials
33 exhibiting a photoinduced metastable state as reported in the inorganic
34 $K_{0.2}Co_{1.4}[Fe(CN)_6] \cdot 6.9H_2O$ PBA.⁹ At the origin of the substantial changes of the magnetic
35 properties in these three-dimensional networks of metallic ions connected by cyanide ligands,
36 there is a metal-to-metal electron transfer within the Fe-CN-Co pairs associated with a spin
37 transition of the Co ions, known as the electron transfer coupled to spin transition (ETCST)
38 phenomenon.^{10,11} The ground state is formed from pairs of Co and Fe ions both in the t_{2g}^6
39 configuration. After the ETCST, in the excited state the formerly diamagnetic ($Co^{III}, t_{2g}^6, S =$
40 $0) - (Fe^{II}, t_{2g}^6, S = 0)$ pairs are converted to the paramagnetic ($Co^{II}, t_{2g}^5 e_g^2, S = 3/2) - (Fe^{III}, t_{2g}^5, S$
41 $= 1/2)$ ones. A schematic representation of the ETCST process in FeCo 3D-PBA is depicted
42 Figure 1a.

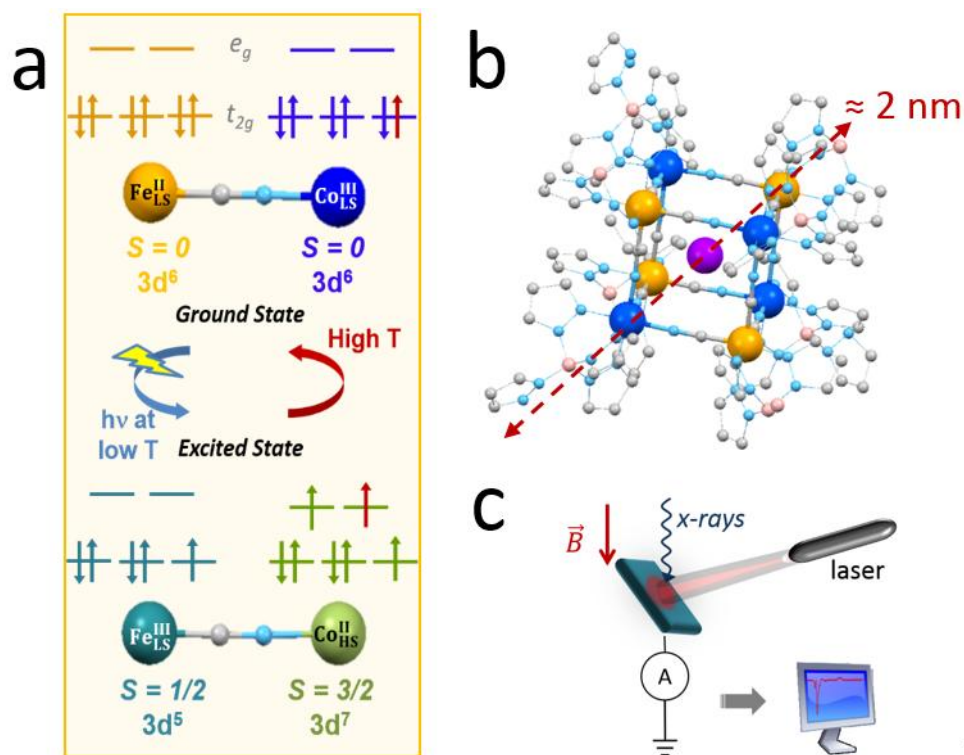
43 Lately, cyanide-bridged FeCo systems have attracted a renewed attention when the light-
44 induced magnetic properties of PBAs were successfully transferred to discrete molecular FeCo
45 models. First demonstrations include the report of thermally-induced ETCST in a Fe_2Co_3
46 pentanuclear complex¹² and the photomagnetic effect in a zero-dimensional molecular cube of
47 Fe_4Co_4 was reported for the first time a decade ago.¹³ Since then, the many advantages of
48 transferring the photomagnetic properties to zero-dimensional molecular systems were
49 corroborated.¹⁴⁻²⁰ These include less structural complexity than in 3D-PBAs facilitating
50 rationalization and optimization of their magnetic properties, the availability of single crystals
51 and good solubility. Similar to 3D-PBA, the light-induced properties of the molecular systems
52 are also attributed to the mechanism of ETCST.

53 The characterizations of the metal-to-metal electron transfer processes are typically
54 performed indirectly using magnetometry or X-ray structural analysis. In this respect, X-ray
55 absorption spectroscopy (XAS) is a very powerful technique able to clarify the electronic
56 structure of transition metals, including valence and spin states and crystal-field splitting by a
57 direct observation of the $2p \rightarrow 3d$ dipole allowed transitions at the $L_{2,3}$ edges. The technique has
58 been indeed successfully applied to examine the light-induced excited spin state trapping
59 (LIESST) in spin-crossover complexes and PBA.²¹⁻²⁴ The direct observation of the ETCST
60 properties to the photomagnetic molecular complexes was reported by Sekine *et al.* who have
61 investigated the thermal and X-ray induced conversion in Fe_2Co_2 cyanide bridge molecular
62 squares using K-edge XAS.²⁵ Very recently, Fatima *et al.* have evidenced the occurrence of the
63 thermal and light-induced electron transfer in a FeCo dinuclear complex using L-edge XAS and
64 XMCD electron transfer.²⁶ Another important unknown is the nature of the Fe-Co magnetic
65 coupling in the photoinduced paramagnetic state of the molecular systems. While in 3D-PBA an
66 antiferromagnetic coupling between the Co_{HS}^{II} and the Fe_{LS}^{III} was reported,²⁷ calculations on
67 paramagnetic 1D FeCo chains²⁸ and on 0D FeCo square complexes²⁹ have demonstrated that
68 intramolecular ferromagnetic exchange pathways may dominate in the lower dimensional
69 systems.

70 In this study, we employ L-edge XAS and X-ray Magnetic Circular Dichroism (XMCD)
71 to examine the photomagnetic process in the discrete molecular heterocubane
72 $Cs \llbracket \{ [Fe^{II}(Tp)(CN)_3]_4 [Co^{III}(^{pz}Tp)]_3 [Co^{II}(^{pz}Tp)] \} \rrbracket \cdot 12CH_3CN$ cluster³⁰ (Tp = hydrotris(pyrazol-1-
73 yl)borate; ^{pz}Tp = tetra(pyrazol-1-yl)borate), from here on referred to as Cs-Fe₄Co₄. This system
74 is the true zero-dimensional model of the Cs-FeCo 3D-PBA. Besides, the remarkable stability of
75 these cubic molecules in solution allows to envision different solution processes for the surface

76 deposition of these materials, which is of extreme importance for applications in molecular
77 electronics or spintronics devices. Taking advantage of the elemental selectivity of XAS, we
78 follow the changes of the electronic structure of Fe and Co upon photoexcitation proving the
79 concurrent electron transfer between these ions as well as the Co spin state change. Furthermore,
80 we resolve the exact compositions of the ground state and of the metastable excited state with the
81 support of ligand-field multiplet (LFM) calculations. To the best of our knowledge, we report for
82 the first time an XMCD study of the photoinduced-excited state in a Fe_4Co_4 cubane system. We
83 exploit the magnetic sensitivity of XMCD as a local probe of the magnetic moments of the Fe
84 and Co ions and to obtain insight into the magnetic coupling between the metallic centers in Cs-
85 Fe_4Co_4 .

86 The neutral cyanide-bridged Fe_4Co_4 cage encapsulating a Cs^+ ion is depicted in **Figure**
87 **1b**. Details about the synthesis, magnetic and structural characterization of Cs- Fe_4Co_4 can be
88 found in ref. 30.



89

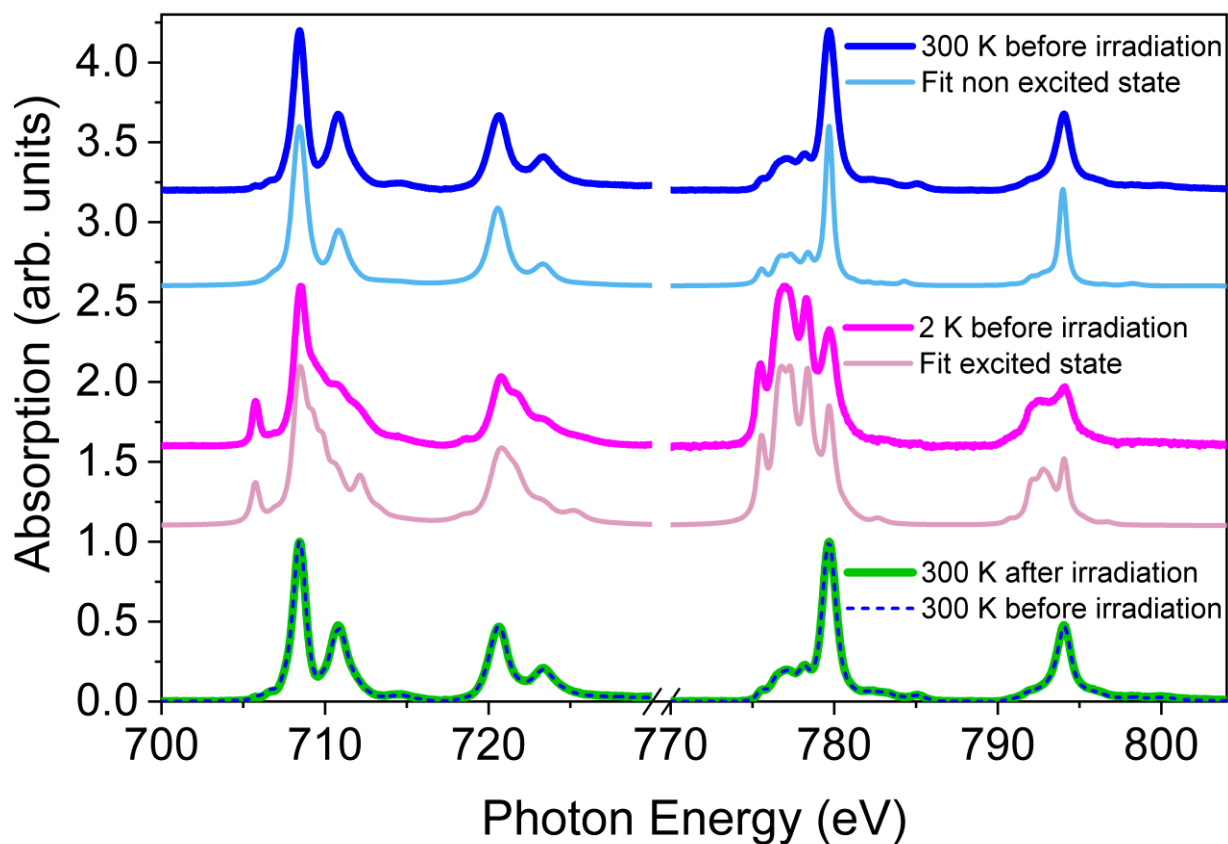
90 **Figure 1.** (a) Schematic representation of the ETCST process in FeCo 3D-PBA. (b) Scheme of the XAS and XMCD
 91 experimental geometry (c) Ball-and-stick representation of Cs-Fe₄Co₄. Hydrogen atoms, solvent molecules, and Cs bonds are
 92 omitted for clarity. Color code: iron: orange, cobalt: blue, cesium: purple, nitrogen: light blue, carbon: grey, boron: pink. The
 93 scale bar has a length of XXX nm.

94

95 A solution of Cs-Fe₄Co₄ in dichloromethane ($c \sim 1$ mM) was sprayed onto a gold-coated silicon
 96 substrate to obtain a homogeneous and clearly visible film of molecular deposit after the
 97 evaporation of the solvent indicating a film thickness much larger than the probing depth of the
 98 total electron yield (TEY) detection of a few nanometers. No additional capping was used and a
 99 comparison of the XAS recorded on a polycrystalline sample revealed that the molecules are
 100 fully intact in the film (Supporting Information **Figure S1**). These findings are consistent with
 101 the stability of the molecules in solutions as demonstrated in ref. 30. XAS and XMCD spectra
 102 were recorded at the X-Treme beamline of the Swiss Light Source.³¹ The sample was positioned
 103 so that the X-ray beam was incident at an angle of 30° from the sample surface as depicted in
 104 **Figure 1c**. XAS measurements were performed in total electron yield (TEY) mode with the

105 magnetic field applied parallel to the beam propagation direction. A large spot size (0.5×2.5
106 mm^2) and a low photon flux were chosen to avoid radiation damage. The spectra were
107 normalized to the maxima of the Fe or Co L_3 edges after subtraction of the background using a
108 step function to allow a direct comparison with the simulations. A laser ($\lambda = 650 \text{ nm}$) with
109 moderate intensity of $\sim 1 \text{ mW/mm}^2$ was used to photoexcite the molecules for a total of 3 hours.

110 Fe and Co XAS recorded at 300 K before the irradiation and at 2 K after the laser
111 irradiation are shown in **Figure 2**. Initially, the Fe L_3 edge exhibits a double-peak shape. After
112 laser irradiation at 2 K, additional features appear including a broad shoulder at around 710.9 eV
113 and a sharp peak at the lower energy of 705.8 eV. The Co L_3 edge displays one main peak at
114 779.7 eV and smaller contributions at 775.5 eV, 776.9 eV and 778.3 eV before laser irradiation.
115 In contrast, after irradiation the contributions of features at lower energies prevail, while the peak
116 at 779.7 eV is significantly reduced. Upon heating the sample to 300 K after the laser irradiation
117 at low temperature relaxes the molecules to the ground state, since the molecules are trapped in
118 the photoexcited state only up to a few tens of Kelvin. The ground state of $\text{Cs-Fe}_4\text{Co}_4$ is fully
119 recovered as shown by the substantial overlap of the spectra acquired after warming up the
120 sample and the ones recorded before irradiation at low temperature in **Figure 2**. The thermal
121 reversibility which we evidenced by XAS is in good agreement with previous SQUID
122 measurements described in ref 28. Furthermore, it testifies to the absence of damage of the
123 sample by the laser and X-ray irradiation.



124
 125 **Figure 2.** Experimental XAS of the ground and excited states measured at the Fe $L_{2,3}$ edges (700 eV – 740 eV) and Co $L_{2,3}$ edges
 126 (770 eV- 805 eV) of Cs-Fe₄Co₄ and calculated best-fit curves. All fits exhibit a high coefficient of determination $0.81 \leq R^2 \leq$
 127 0.95 .

128 A more precise analysis and understanding of the X-ray spectra of the ground and excited states
 129 is obtained by comparison with theoretical spectra of multiplet features of Fe_{LS}^{III}, Fe_{LS}^{II}, Co_{LS}^{III} and
 130 Co_{HS}^{II} (LS: low spin and HS: high spin). Spectra were calculated using LFM theory as
 131 implemented in the CRISPY software package.³² In the molecular Cs-Fe₄Co₄ cubes, all metal
 132 ions experience a slightly distorted octahedral coordination sphere, with a pseudo C_3 axis along
 133 the boron-metal direction. In order to approximate this distorted octahedral environment, the
 134 calculations are performed using a C_{3v} point symmetry for the metallic ions and the strength of
 135 the crystal field potential is therefore defined using three independent parameters Dq , $D\sigma$ and $D\tau$.
 136 Details of the parameters used are given in the Supporting Information (SI). The simulations of

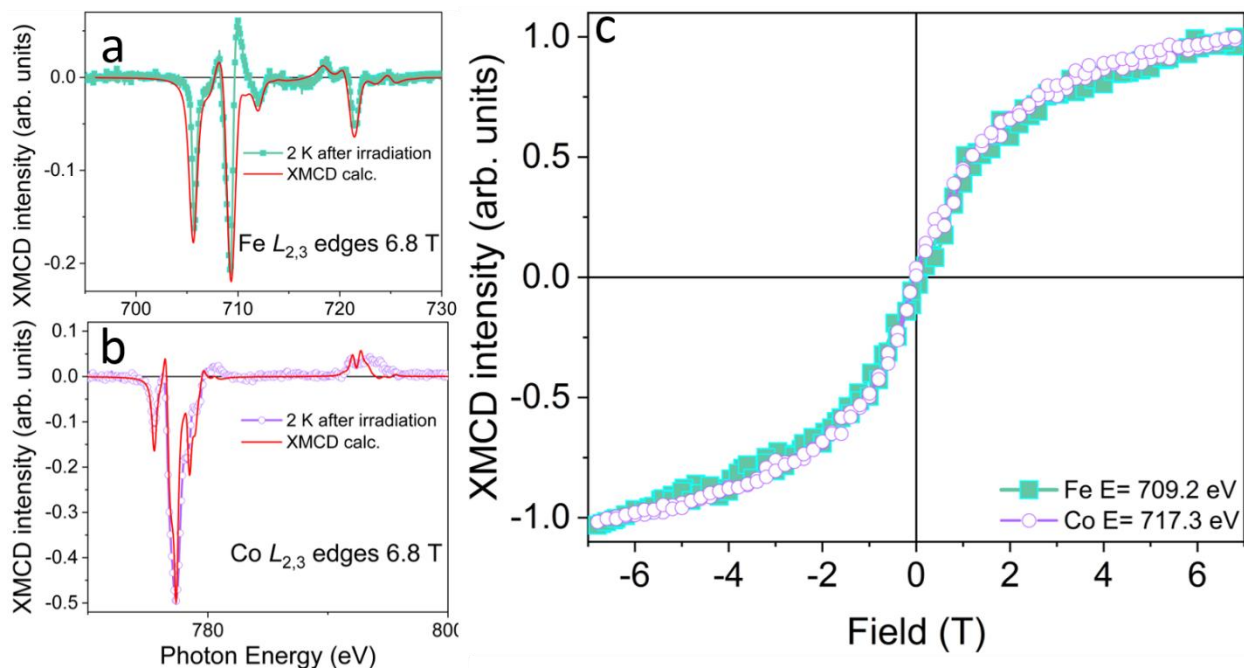
137 the Fe L-edge spectra were performed in order to match the ones of the mononuclear reference
138 complexes $K_2[Fe^{II}(Tp)(CN)_3]$ and $NBu_4[Fe^{III}(Tp)(CN)_3]$ (see Supporting Information **Figures S2**
139 **and S3** possessing well-known oxidation numbers. The best-fit calculations of the X-ray spectra
140 are presented in **Figure S4**. The best simulation of $K_2[Fe^{II}(Tp)(CN)_3]$ is obtained for Fe^{II} ions
141 with relatively strong cubic crystal field of 2.8 eV consistent with a LS state. To reproduce the
142 spectral shape of Fe_{LS}^{III} , the same parameters reported for the precursor $[TpFe^{III}CN_3]$ by Jafri and
143 co-workers are used (10 $Dq = 2.8$ eV; $D\sigma = 0.07$ eV, $D\tau = 0.12$ eV). The Fe L-edge spectrum
144 measured on Cs- Fe_4Co_4 at 300 K before photoexcitation plotted in **Figure 2** is manifestly very
145 similar to the simulations obtained for Fe_{LS}^{II} . In contrast, the peak at 705.2 eV is the signature of
146 Fe_{LS}^{III} , which is observed in the excited state of Cs- Fe_4Co_4 . This peak is known to originate from
147 the $2p^6t_{2g}^5 \rightarrow 2p^5t_{2g}^6$ transitions that are absent in the Fe_{LS}^{II} configuration.¹¹

148 Concerning the Co spectra, the peaks centered at 775.8 eV, 776.8 eV and 778.2 eV are
149 fingerprints of Co^{II} in a sixfold coordination environment, while the signature of Co^{III} is
150 characterized by peaks at 779.7 eV and 783.1 eV. The features corresponding to Co^{III} are shifted
151 toward higher energies due to the shortening of the Co-ligand bonds as compared to Co^{II}. This
152 well-defined separation in energy allows the comparison of the respective spectral features. The
153 results obtained on the mononuclear reference compounds for Co^{II} and Co^{III} are presented and
154 discussed in the SI **Figure S3**. The contributions of Co^{II} are well modeled using the C_{3v}
155 symmetry which takes into account the deviation from the octahedral symmetry because of the
156 non-equivalent ligands. A weak crystal field of $10 Dq = 0.11 \text{ eV}$ is found for the Co^{II} ions, in
157 agreement with the axial distortion factor ($\Delta = -922 \text{ cm}^{-1}$) previously reported and compatible
158 with the expected HS state. In contrast, the best simulation in the case of the Co^{III} ions
159 corresponds to the higher $10Dq$ potential value of 0.5 eV consistent with a LS state.

160 The straightforward comparison of typical spectral features of both Fe and Co ions in Cs-
161 Fe₄Co₄ as visible in **Figure 2**, along with the LFM calculations described in the above, yields
162 clear evidence of the occurrence of the light-induced excited state at 2 K. The spectra obtained
163 after irradiation with the laser show an increase of the signatures of Co^{II}_{HS} and Fe^{III}_{LS} compared to
164 the ground state at room temperature, which mainly includes Co^{III}_{LS} and Fe^{II}_{LS}. The signatures of
165 Co^{III}_{LS} and Fe^{II}_{LS} in the excited state do not disappear completely, which indicates that the
166 conversion is not complete for both Fe and Co ions. This is expected because of the initial
167 presence of Co^{II} ions in the ground state which implies the presence of Fe^{II} ions in the excited
168 state.

169 In order to extract quantitative information about the relative amount of Co^{II}/Co^{III} and
170 Fe^{II}/Fe^{III}, linear combinations presented in **Figure 2** of the modeled spectra are used to visually

171 fit the measurements obtained for Cs-Fe₄Co₄. We find 100% of Fe_{LS}^{II} and a mix of 16±1% of
172 Co_{HS}^{II} and 84±1 % of Co_{LS}^{III} in the ground state. The amount of Co^{II} in the ground state is lower
173 than the 25% that were previously reported.³⁰ Due to the probing depth of TEY of a few
174 nanometers, this result can be interpreted in terms of surface oxidation of part of the cubes. The
175 excited state is composed of 52±1 % Fe_{LS}^{II} + 48±1 % Fe_{LS}^{III} on the one hand and 64±1 % of Co_{HS}^{II} +
176 36±1 % of Co_{LS}^{III} on the other hand (see SI **Figures S4 and S5**). From the compositions of the
177 ground and excited states we conclude that 48±1 % of Co_{LS}^{III} are transformed into Co_{HS}^{II} while
178 48±1 % of the initial Fe_{LS}^{II} ions in the ground state are oxidized toward Fe_{LS}^{III} during the three
179 hours of laser irradiation. These findings are perfectly consistent, and they demonstrate the
180 concomitance of the Fe oxidation with the Co reduction. This is further supported by the
181 observation of the XAS changes during the irradiation process. **Figure S5** in the SI shows the
182 comparison of the variation of Co^{II} and Fe^{III} in time during laser irradiation, revealing similar
183 time constants for Co and Fe extracted from monoexponential fits. Altogether, these results show
184 that only a charge transfer between the Fe and the Co ions associated with a Co spin transition
185 can be at the origin of the simultaneous transformation. **Figure S5** indicates that the conversion
186 is not complete after 3 hours of irradiation. This may be due to the 650 nm wavelength deviating
187 from 800 nm for which a full conversion was reported in these compounds,¹⁸ and/or the presence
188 of Co^{II} in the ground state preventing the electron-transfer of 16% of the Co-CN-Fe pairs.



189

190 **Figure 3.** Experimental and calculated XMCD spectra measured after laser excitation at 2 K (a) at the Fe $L_{2,3}$ edges and (b) at the
 191 Co $L_{2,3}$ edges in a magnetic field of 6.8 T and at 2 K. Symbols and solid lines denote experimental data and calculations,
 192 respectively. (c) Experimental, element specific and normalized $M(H)$ curves extracted from XMCD are plotted as symbols.

193 Beyond the averaged properties provided by SQUID magnetometry, XMCD helps to determine
 194 the local magnetic moments of the ions in the Cs-Fe₄Co₄ cages. XMCD spectra were recorded on
 195 the Cs-Fe₄Co₄ ground state at 200 K, well above the relaxation temperature of the system of ca.
 196 66 K (see **Figure S5**). No XMCD signal is detected at 200 K at the Fe $L_{2,3}$ edges. This is
 197 consistent with the above conclusion that the ground state contains solely LS Fe^{II}. In contrast, at
 198 the Co $L_{2,3}$ edges, a clear dichroic signal of the order of 0.7% with respect to the main edge jump
 199 is detected, confirming that the ground state contains a minor contribution of Co^{II}_{HS} in line with
 200 the XAS analysis of the ground state. After laser irradiation at 2 K, the magnetic state of Cs-
 201 Fe₄Co₄ is considerably modified as shown by the XMCD signals reported in **Figure 3a-b**.
 202 Indeed, a significant XMCD signal is detected from Fe^{III}_{LS} together with a strong XMCD
 203 contribution of Co^{II}_{HS}, leading to 21% and 50% of signal normalized to the main edge jump,
 204 respectively. The intensity of the XMCD is well reproduced by the calculations performed in C_{3v}

205 point symmetry for Fe^{3+} and Co^{2+} (note that we did not obtain any XMCD signal for the
206 calculations described above while performed for Fe^{2+} and Co^{3+} in good agreement with their
207 expecting low spin state). From the calculations of the XMCD signals, we extract for the Fe
208 (respectively for the Co) the orbital angular kinetic momentum $\langle L_z \rangle = XX$ (resp. XX), the spin
209 kinetic momentum $\langle S_z \rangle = XX$ (resp. XX) and the magnetic dipole $\langle T_z \rangle = XX$ (resp. XX). From
210 the comparison of the experimental XMCD signal with the calculated ones with the magnetic
211 field set along the C_{3v} axis one finds that the observed Co and Fe magnetic moments are both
212 oriented parallel to the external magnetic field at 6.8 T. This clearly demonstrates the absence of
213 a significant antiferromagnetic coupling between the metal ions in the paramagnetic excited
214 state. In order to investigate further the magnetic coupling between the ions, we have obtained
215 the field dependent magnetization for both Fe and Co from XMCD, as shown in **Figure 3c** in the
216 paramagnetic excited state. **Figure 3c** shows a superposition of the element-specific
217 magnetization curves $M(H)$ which do not saturate at 6.8 T. This result contrasts with the previous
218 studies which have demonstrated a strong antiferromagnetic coupling between Co and Fe in PBA
219 3D networks. Recently reported XMCD measurements of the dinuclear FeCo complex have led
220 to similar conclusions. A ferromagnetic coupling cannot be excluded, however from the current
221 set of data it is not possible to discriminate between a ferromagnetic Fe-Co exchange interaction
222 and a paramagnetic behavior of the ions with their spins aligned along the direction of the
223 magnetic field applied. Considering the Heisenberg-Dirac Hamiltonian $\hat{H}^{spin} = -J \cdot \vec{S}_{Fe} \cdot \vec{S}_{Co}$ and
224 by comparison with the temperature in the experiment we estimate a lower bound for the Fe-Co
225 superexchange coupling of $J \gtrsim -0.5 \text{ cm}^{-1}$. This can be interpreted in that a very weak
226 antiferromagnetic coupling, no coupling or a ferromagnetic coupling are consistent with our
227 observations. A strong antiferromagnetic coupling can be ruled out.

228 In summary, using L-edge XAS as an element-specific probe of the valence and spin
229 states of Fe and Co ions in Cs-Fe₄Co₄ discrete molecular cubes we have observed directly the
230 concurrent electronic and magnetic changes of both types of ions upon light irradiation. These
231 results demonstrate beyond the shadow of doubt the existence of the light-induced ETCST
232 process and its thermal relaxation in the molecular cages. The XMCD measurements directly
233 reveal a ferromagnetic arrangement of the Fe and Co spins in the photoexcited state at 2 K for all
234 applied magnetic field values. Furthermore, XMCD rules out the possibility of a strong
235 antiferromagnetic coupling. Our study paves the way toward the integration of the present Cs-
236 Fe₄Co₄ cages, featuring excellent photomagnetic properties and a high solubility, into organic
237 electronics devices.

238 ASSOCIATED CONTENT

239 Supporting Information: Crystal field multiplet calculations; best-fit parameters of the LFM
240 calculations; reference spectra of Fe and best fits; reference spectra of Co and best fits; best-fit
241 calculated spectra of the ground state; best-fit calculated spectra of the paramagnetic excited
242 state; time dependence of Fe^{III} and Co^{II} spectral features during laser irradiation.

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