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## Direct Observation of Charge Transfer and Magnetism in Fe<sub>4</sub> Co<sub>4</sub> Cyanide-Bridged Molecular Cubes

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1 Direct Observation of Charge Transfer and  
2 Magnetism in Fe<sub>4</sub>Co<sub>4</sub> Cyanide Bridged Molecular  
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15

16 **ABSTRACT**

17 We have studied the zero-dimensional cubane molecular correspondent of a Prussian blue  
18 analogue Cs-Fe<sub>4</sub>Co<sub>4</sub> 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  $-0.5 \text{ cm}^{-1}$  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.<sup>1-7</sup> FeCo Prussian Blue Analogues<sup>8</sup> (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.<sup>9</sup> 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.<sup>10,11</sup> 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.

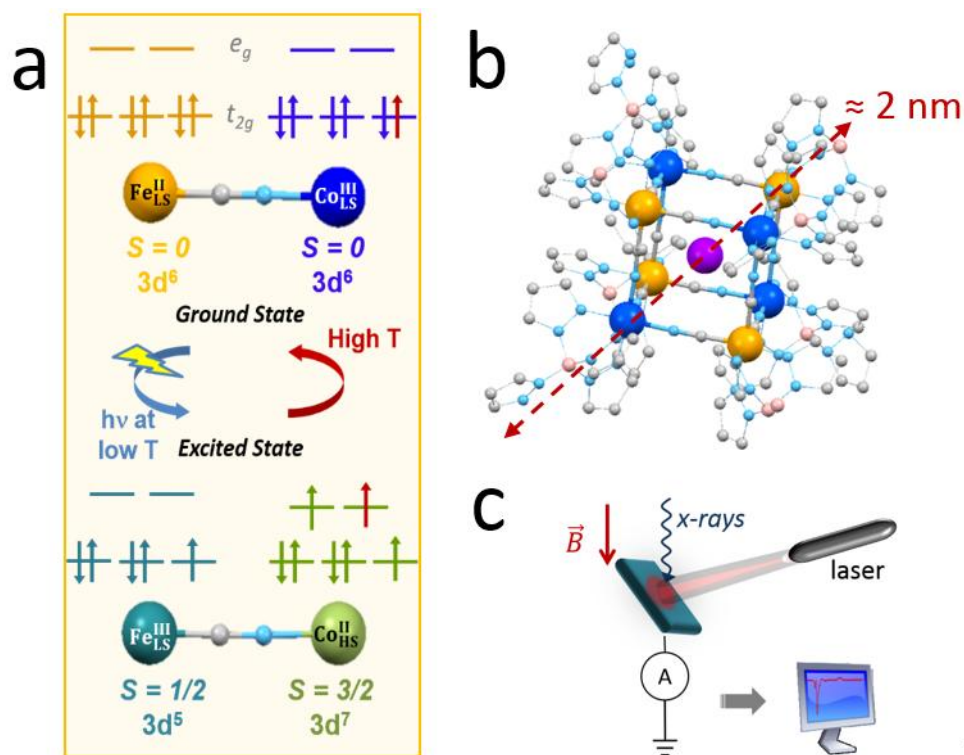
43 Lately, cyanide-bridged FeCo systems have attracted a renewed attention when the light-  
44 induced magnetic properties of PBAs were successfully transferred to discrete molecular FeCo  
45 models. First demonstrations include the report of thermally-induced ETCST in a  $Fe_2Co_3$   
46 pentanuclear complex<sup>12</sup> and the photomagnetic effect in a zero-dimensional molecular cube of  
47  $Fe_4Co_4$  was reported for the first time a decade ago.<sup>13</sup> Since then, the many advantages of  
48 transferring the photomagnetic properties to zero-dimensional molecular systems were  
49 corroborated.<sup>14-20</sup> 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.<sup>21-24</sup> 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.<sup>25</sup> 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.<sup>26</sup> 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,<sup>27</sup> calculations on  
67 paramagnetic 1D FeCo chains<sup>28</sup> and on 0D FeCo square complexes<sup>29</sup> 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  $Cs \llbracket \{ [Fe^{II}(Tp)(CN)_3]_4 [Co^{III}(^{pz}Tp)]_3 [Co^{II}(^{pz}Tp)] \} \rrbracket \cdot 12CH_3CN$  cluster<sup>30</sup> (Tp = hydrotris(pyrazol-1-  
73 yl)borate; <sup>pz</sup>Tp = tetra(pyrazol-1-yl)borate), from here on referred to as  $Cs-Fe_4Co_4$ . 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  $\text{Fe}_4\text{Co}_4$  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  $\text{Fe}_4\text{Co}_4$ .

86         The neutral cyanide-bridged  $\text{Fe}_4\text{Co}_4$  cage encapsulating a  $\text{Cs}^+$  ion is depicted in **Figure**  
87 **1b**. Details about the synthesis, magnetic and structural characterization of Cs- $\text{Fe}_4\text{Co}_4$  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-Fe<sub>4</sub>Co<sub>4</sub>. 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.

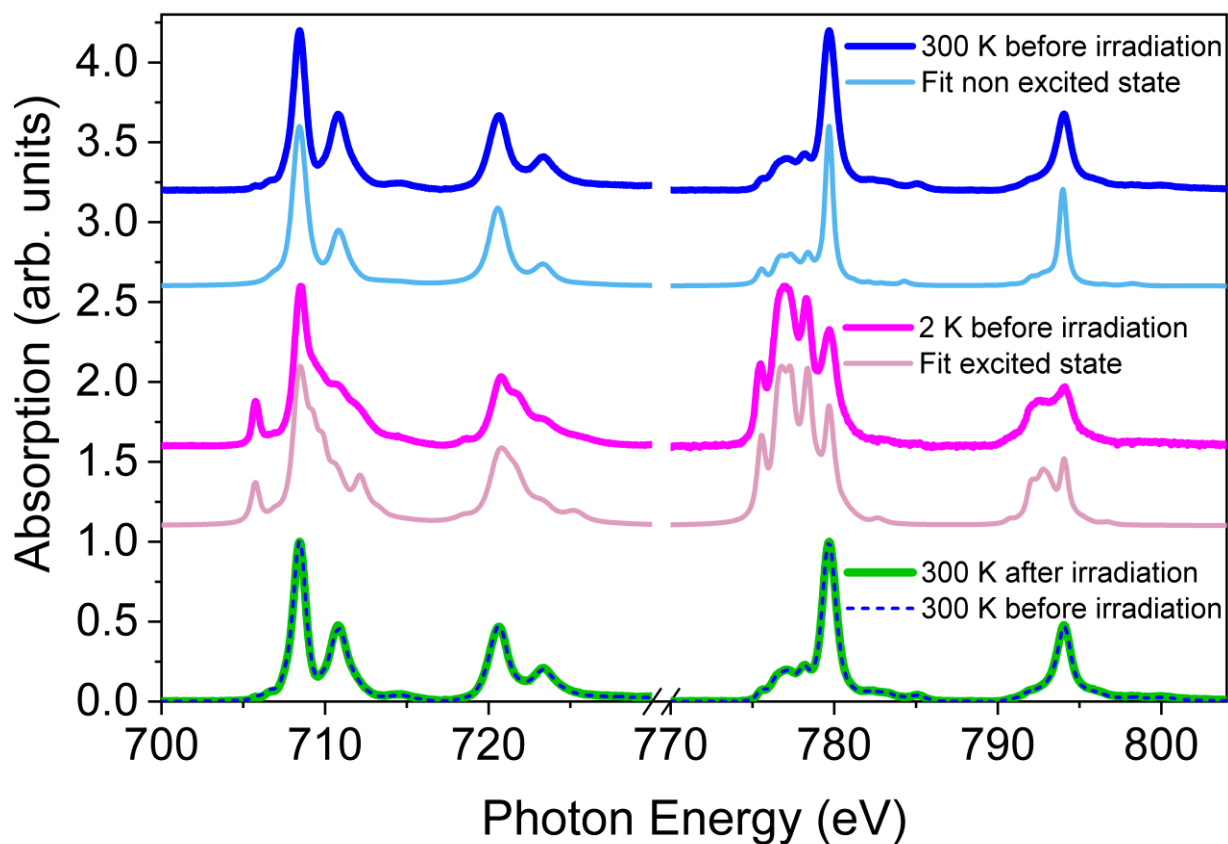
94

95 A solution of Cs-Fe<sub>4</sub>Co<sub>4</sub> 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.<sup>31</sup> 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 ( $0.5 \times 2.5$   
106  $\text{mm}^2$ ) 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-Fe<sub>4</sub>Co<sub>4</sub> 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<sub>LS</sub><sup>III</sup>, Fe<sub>LS</sub><sup>II</sup>, Co<sub>LS</sub><sup>III</sup> and  
 130 Co<sub>HS</sub><sup>II</sup> (LS: low spin and HS: high spin). Spectra were calculated using LFM theory as  
 131 implemented in the CRISPY software package.<sup>32</sup> In the molecular Cs-Fe<sub>4</sub>Co<sub>4</sub> 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

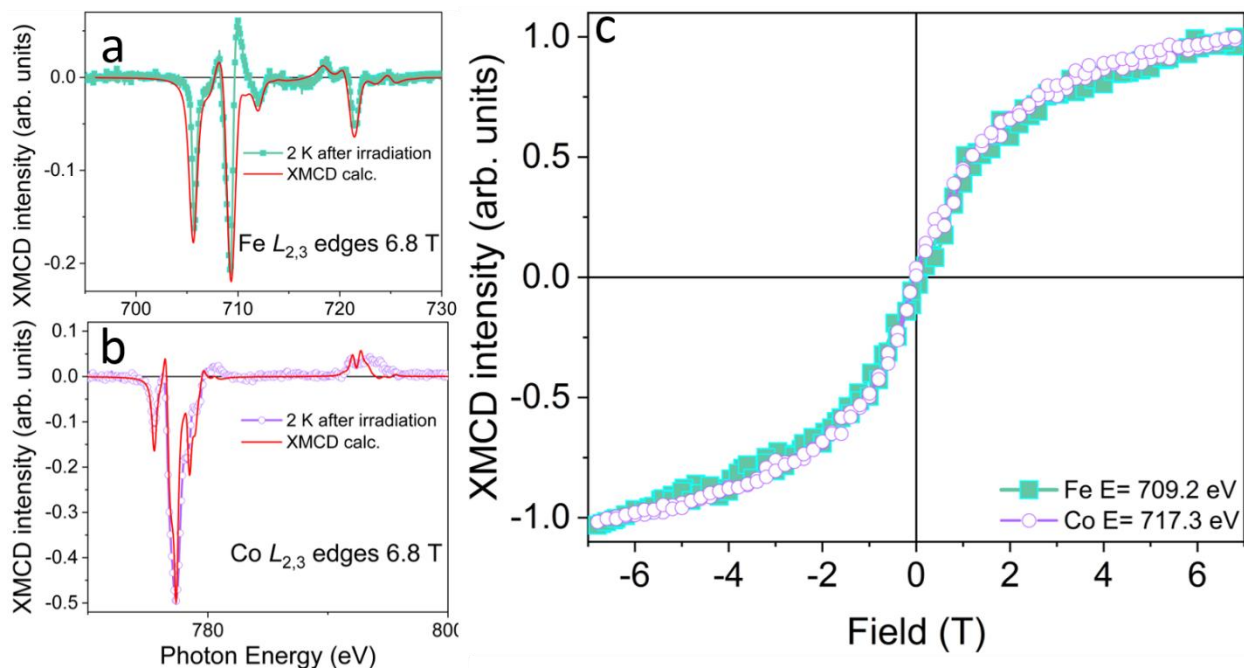
137 the Fe L-edge spectra were performed in order to match the ones of the mononuclear reference  
138 complexes  $K_2[Fe^{II}(Tp)(CN)_3]$  and  $NBu_4[Fe^{III}(Tp)(CN)_3]$  (see Supporting Information **Figures S2**  
139 **and S3** possessing well-known oxidation numbers. The best-fit calculations 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.<sup>11</sup>

148 Concerning the Co spectra, the peaks centered at 775.8 eV, 776.8 eV and 778.2 eV are  
149 fingerprints of Co<sup>II</sup> in a sixfold coordination environment, while the signature of Co<sup>III</sup> is  
150 characterized by peaks at 779.7 eV and 783.1 eV. The features corresponding to Co<sup>III</sup> are shifted  
151 toward higher energies due to the shortening of the Co-ligand bonds as compared to Co<sup>II</sup>. 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<sup>II</sup> and Co<sup>III</sup> are presented and  
154 discussed in the SI **Figure S3**. The contributions of Co<sup>II</sup> are well modeled using the C3v  
155 symmetry which takes into account the deviation from the octahedral symmetry because of the  
156 non-equivalent ligands. A weak crystal field of  $10 Dq = 0.11$  eV is found for the Co<sup>II</sup> ions, in  
157 agreement with the axial distortion factor ( $\Delta = -922$  cm<sup>-1</sup>) previously reported and compatible  
158 with the expected HS state. In contrast, the best simulation in the case of the Co<sup>III</sup> 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 Fe<sub>4</sub>Co<sub>4</sub> 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<sup>II</sup><sub>HS</sub> and Fe<sup>III</sup><sub>LS</sub> compared to  
164 the ground state at room temperature, which mainly includes Co<sup>III</sup><sub>LS</sub> and Fe<sup>II</sup><sub>LS</sub>. The signatures of  
165 Co<sup>III</sup><sub>LS</sub> and Fe<sup>II</sup><sub>LS</sub> 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<sup>II</sup> ions in the ground state which implies the presence of Fe<sup>II</sup> ions in the excited  
168 state.

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

171 fit the measurements obtained for Cs-Fe<sub>4</sub>Co<sub>4</sub>. We find 100% of Fe<sub>LS</sub><sup>II</sup> and a mix of 16±1% of  
172 Co<sub>HS</sub><sup>II</sup> and 84±1 % of Co<sub>LS</sub><sup>III</sup> in the ground state. The amount of Co<sup>II</sup> in the ground state is lower  
173 than the 25% that were previously reported.<sup>30</sup> 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<sub>LS</sub><sup>II</sup> + 48±1 % Fe<sub>LS</sub><sup>III</sup> on the one hand and 64±1 % of Co<sub>HS</sub><sup>II</sup> +  
176 36±1 % of Co<sub>LS</sub><sup>III</sup> 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<sub>LS</sub><sup>III</sup> are transformed into Co<sub>HS</sub><sup>II</sup> while  
178 48±1 % of the initial Fe<sub>LS</sub><sup>II</sup> ions in the ground state are oxidized toward Fe<sub>LS</sub><sup>III</sup> 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<sup>II</sup> and Fe<sup>III</sup> 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,<sup>18</sup> and/or the presence  
188 of Co<sup>II</sup> 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-Fe<sub>4</sub>Co<sub>4</sub> cages. XMCD spectra were recorded on  
 195 the Cs-Fe<sub>4</sub>Co<sub>4</sub> 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<sup>II</sup>. 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<sup>II</sup><sub>HS</sub> in line with  
 200 the XAS analysis of the ground state. After laser irradiation at 2 K, the magnetic state of Cs-  
 201 Fe<sub>4</sub>Co<sub>4</sub> is considerably modified as shown by the XMCD signals reported in **Figure 3a-b**.  
 202 Indeed, a significant XMCD signal is detected from Fe<sup>III</sup><sub>LS</sub> together with a strong XMCD  
 203 contribution of Co<sup>II</sup><sub>HS</sub>, 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<sub>3v</sub>

205 point symmetry for  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  (note that we did not obtain any XMCD signal for the  
206 calculations described above while performed for  $\text{Fe}^{2+}$  and  $\text{Co}^{3+}$  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-Fe<sub>4</sub>Co<sub>4</sub> 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 Fe<sub>4</sub>Co<sub>4</sub> 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<sup>III</sup> and Co<sup>II</sup> spectral features during laser irradiation.

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