Supplementary information

X-ray Induced Phase Transition by Selective Excitation of Heterometal ions in a Cyanide-bridged Fe-Co Molecular Square

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Physical measurements

Crystal structural analyses

A single crystal of 1 was mounted on the top of a glass capillary coated with apiezon grease. Diffraction data were collected at 24 K using a Bruker SMART APEX II diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) equipped with a CCD type area detector. The data frames were integrated using the SAINT program and merged to give a unique data set for structure determination. An absorption correction was performed using SADABS.¹ The synchrotron-based X-ray diffractometer measurements for 1 were conducted at 14 K using a diffractometer installed at BL-8A at the Photon Factory, KEK, Tsukuba. The wavelength of the incident synchrotron X-ray beam, monochromated by a Si (111) double-crystal monochromator, was set to 1.0000 Å and the scattered X-rays were detected using an IP area detector. The Bragg reflection intensities were measured in a full-sphere of reciprocal space in the range $2\theta < 74^{\circ}$. The PROCESS-AUTO program (RIGAKU) was used for cell refinement and data reduction.

The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares methods using SHELXTL package (Bruker Analytical X-ray systems). Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystallographic parameters for 1 under all conditions are summarized in Table S1.

XAS measurements

A single crystal of 1 coated with apiezon grease was mounted on the top of glass capillary and was fixed using epoxy resin. The XAS measurements were conducted at BL-8A at the Photon Factory, KEK, Tsukuba. The spectra were measured by the fluorescence method, in which the intensity of fluorescent X-rays from the sample was detected by a silicon drift detector (SDD) and the X-ray energy was calibrated using standard Fe foil.² The XAS spectra after X-ray irradiations were deconvoluted using the spectra for the thermally generated HS and LS states. The results of the analyses are likely to have an associated error of a few percent, resulting from a combination of the equipment resolution, the slight variability in the experimental conditions and the non-statistical normalization process.

	24 K ^[a]	14 K ^[b]	
	before irradiation	after X-ray irradiation	
Formula	$C_{110}H_{148}B_2Co_2F_{12}Fe_2N_{26}O_2P_2$		
Mr [g mol ⁻¹]	1.299	1.250	
Space group	Monoclinic C2/c	Monoclinic C2/c	
<i>a</i> [Å]	24.682(4)	24.639(2)	
<i>b</i> [Å]	18.626(3)	19.1926(16)	
<i>c</i> [Å]	29.150(5)	29.908(2)	
$\beta[\degree]$	113.266(2)	115.207(2)	
V[Å ³]	12311(4)	12796.4(18)	
Z	4	4	
λ [Å]	0.71073	1.0000	
μ [mm ⁻¹]	0.597	1.418	
Reflection Collected	27381	19994	
Independent reflections	9975	9517	
<i>R</i> 1 (<i>I</i> >2σ <i>I</i>)	0.0729	0.1070	
wR2 (I>2σI)	0.2028	0.3193	
GOF on F^2	1.027	1.446	

Table S1. Crystallographic paramet	ers of 1
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[a] Measured using conventional X-ray source (Mo-K α). [b] Measured using synchrotron radiation.

	24 K ^[a]	14 K ^[b]	330 K ^[a,c]
	before irradiation	after X-ray irradiation	
Fe-C1	1.877(5)	1.899(8)	1.917(5)
Fe-C2	1.861(6)	1.903(5)	1.929(5)
Fe-C3	1.898(6)	1.915(8)	1.928(6)
Fe-N4	2.046(5)	2.015(5)	1.995(4)
Fe-N6	2.044(5)	2.044(5)	2.003(4)
Fe-N8	2.034(5)	2.039(5)	2.011(4)
Fe-C, N (average)	<u>1.960(5)</u>	<u>1.969(6)</u>	<u>1.964(5)</u>
Co-N1	1.888(4)	2.014(6)	2.068(4)
Co-N2	1.898(5)	2.010(4)	2.100(4)
Co-N10	1.939(5)	2.065(5)	2.150(4)
Co-N11	1.944(5)	2.049(5)	2.122(4)
Co-N12	1.917(5)	2.050(5)	2.122(4)
Co-N13	1.931(4)	2.044(5)	2.119(4)
Co-N (average)	1.920(5)	2.039(5)	2.113(4)

Table S2. Selected coordination bond lengths (Å)

[a] Measured using conventional X-ray source (Mo-Kα). [b] Measured using synchrotron radiation. [c] See Ref.[3].



Fig. S1 (a) Co K-edge and (b) Fe K-edge spectra at 330 K (red) and 15 K (blue).



Fig. S2 (a) Co K-edge and (b) Fe K-edge spectra before (blue) and after (red) X-ray irradiation at 7.725 keV for 270 mins.



Fig. S3 (a) Co K-edge and (b) Fe K-edge XAS spectra before (blue solid line) and after (black dashed line) X-ray irradiation at 7.725 keV at 100 K.



Fig. S4 Ortep diagram of cation **1** before irradiation at 24 K. The *tert*-butyl groups on bpy* were omitted for clarity. Thermal ellipsoids are displayed at 30 % probability.



Fig. S5 Ortep diagram of cation 1 after X-ray irradiation at 7.725 keV at 14 K. The *tert*-butyl groups on bpy* were omitted for clarity. Thermal ellipsoids are displayed at 30 % probability.



Fig. S6 The Co K-edge XAS spectrum after X-ray irradiation at 7.725 keV for 270 mins (black solid line) with calculated spectrum (green dash line).



Fig. S7 Time course of the Co K-edge XAS spectra (black line) upon X-ray irradiation at (a) 7.129 keV, (b)

7.725 keV and (c) 12.40 keV.	The deconvoluted HS and LS spectra	(red and blue line) were displayed.
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7 120 koV 7 725 koV 12 40 koV					
7.129 KeV		7.723 Ke v		12.40 KCV	
Time / mins	HS fraction	Time / mins	HS fraction	Time / mins	HS fraction
120	0.38	30	0.38	30	0.65
360	0.52	60	0.60	60	0.75
540	0.48	110	0.74	120	0.85
600	0.48	270	0.90	210	0.92

Table S3. Time course of the HS fractions upon X-ray irradiation.



Fig. S8 (a) Co K-edge and (b) Fe K-edge XAS spectra before (blue solid line) and after (black dashed line) X-ray irradiation at 12.40 keV at 100 K.

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Fig. S9 Cyclic voltammogram of (a) **1** at 200 K in butyronitrile, (b) $[Co^{III}_2Fe^{II}_2(CN)_6(tp)_2(dtbbpy)_4](PF_6)_2 \cdot 4H_2O$ in MeCN at 293 K (see ref. 3f).



Fig. S10. The energy orbital of the Fe-Co system in the LS state ([Fe^{II}_{LS2}Co^{III}_{LS2}]).



Fig. S11 Time course of the HS fraction upon X-ray irradiation to the metastable HS* state at 7.129 keV.

References

- 1 Sheldrick, G. M. SADABSs: An Empirical Absorption Correction Program, Bruker Analytica X-ray Systems, Madison, WI, 1996.
- 2 S. Sakai, KEK Report, 1990, 90-16.
- 3 M. Nihei, Y. Sekine, N. Suganami, K. Nakazawa, A. Nakao, H. Nakao, Y. Murakami, H. Oshio, *J. Am. Chem. Soc.* 2011, **133**, 3592.