Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary information

Investigation of light-induced electron-transfer-coupled spin transition in a cyanide-bridged [Co_2Fe_2] complex by X-ray diffraction and absorption measurements

Yoshihiro Sekine,[a] Masayuki Nihei,[a] Reiji Kumai,[b] Hironori Nakao,[b] Youici Murakami[b] and Hiroki Oshio*[a]

[a]Graduate School of Pure and Applied Sciences, University of Tsukuba, Tennodai 1-1-1, Tsukuba, Ibaraki 305-8571, Japan

[b]Photon Factory and Condensed Matter Research Center, Institute of Materials Structures Sciences, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

Email: oshio@chem.tsukuba.ac.jp

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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 equipped with a CCD type area detector. A full sphere of data was collected with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). 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 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** before and after light irradiation 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]

Table S1. Crystallographic parameters of **1**

	24 K[a] before 808 nm irradiation	24 K[b] after 808 nm irradiation
Formula	$C_{110}H_{148}B_2Co_2F_{12}Fe_2N_{26}O_2P_2$	
Mr [g mol^{-1}]	1.299	1.214
Space group	Monoclinic *C*2/*c*	Monoclinic *C*2/*c*
a [Å]	24.682(4)	24.56(3)
b [Å]	18.626(3)	19.67(2)
c [Å]	29.150(5)	29.88(4)
β [°]	113.266(2)	114.159(18)
V [Å^3]	12311(4)	13170(28)
Z	4	4
λ [Å]	0.71073	0.71073
μ [mm^{-1}]	0.597	0.558
Reflection Collected	27381	24967
Independent reflections	9975	9672
*R*1 ($I>2\sigma I$)	0.0729	0.1295
*wR*2 ($I>2\sigma I$)	0.2028	0.3066
GOF on F^2	1.027	1040

[a] See Ref.[3]. [b] this work.

Table S2. Selected coordination bond lengths (Å)

	24 K[a] before 808 nm irradiation	24 K[b] after 808 nm irradiation
Fe−C1	1.877(5)	1.916(15)
Fe−C2	1.861(6)	1.923(18)
Fe−C3	1.898(6)	1.936(13)
Fe−N4	2.046(5)	2.002(12)
Fe−N6	2.044(5)	2.019(12)
Fe−N8	2.034(5)	2.002(10)
Fe−C, N (average)	**1.960(5)**	**1.966(14)**
Co−N1	1.888(4)	2.093(12)
Co−N2	1.898(5)	2.105(13)
Co−N10	1.939(5)	2.149(10)
Co−N11	1.944(5)	2.130(9)
Co−N12	1.917(5)	2.127(10)
Co−N13	1.931(4)	2.112(9)
Co−N (average)	**1.920(5)**	**2.119(10)**

[a] See Ref. [3]. [b] This work.

Table S3. Selected coordination angle around metal ions (°)

	24 K[a] before 808 nm irradiation	24 K[b] after 808 nm irradiation
C1−Fe−C2	86.2(2)	85.0(5)
C1−Fe−C3	86.4(2)	85.6(5)
C2−Fe−C3	88.9(2)	86.7(5)
C1−Fe−N6	95.2(2)	91.9(5)
C1−Fe−N8	94.9(2)	92.4(4)
C2−Fe−N4	91.7(2)	93.0(5)
C2−Fe−N8	91.0(2)	90.8(5)
C3−Fe−N4	89.0(2)	90.1(5)
C3−Fe−N6	93.4(2)	92.7(5)
C4−Fe−N6	87.08(18)	90.1(5)
C4−Fe−N8	89.71(19)	91.9(4)
C6−Fe−N8	86.60(18)	89.7(4)
N1−Co−N2	94.16(19)	97.0(4)
N1−Co−N11	93.50(19)	94.2(4)
N1−Co−N12	90.48(19)	92.1(4)
N1−Co−N13	89.42(18)	92.8(4)
N2−Co−N10	86.84(19)	85.8(5)
N2−Co−N11	86.93(19)	89.2(4)
N2−Co−N13	93.27(19)	93.5(4)
N10−Co−N11	82.75(19)	78.3(4)
N10−Co−N12	88.81(19)	86.1(4)
N10−Co−N13	94.33(19)	95.2(4)
N11−Co−N12	96.95(19)	99.4(4)
N12−Co−N13	82.61(19)	76.7(4)

[a] See Ref.[3]. [b] This work.

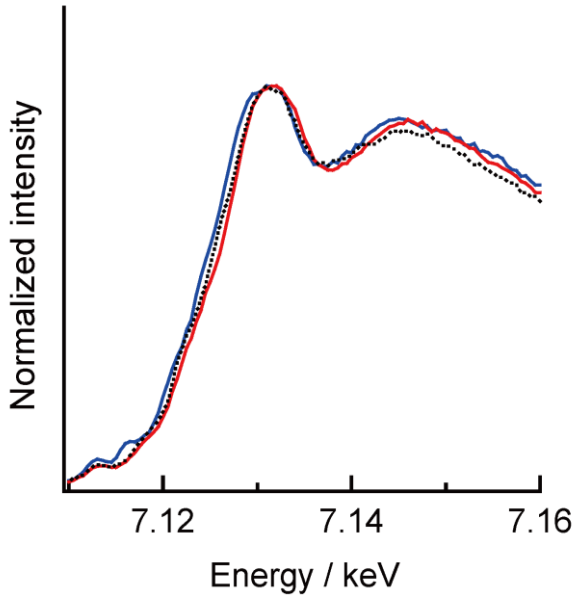

Fig. S1 Fe K-edge XAS spectra before (blue) and after (red) visible-light-irradiation at 808 nm at 15 K. The black dashed line represents thermally generated HS state.

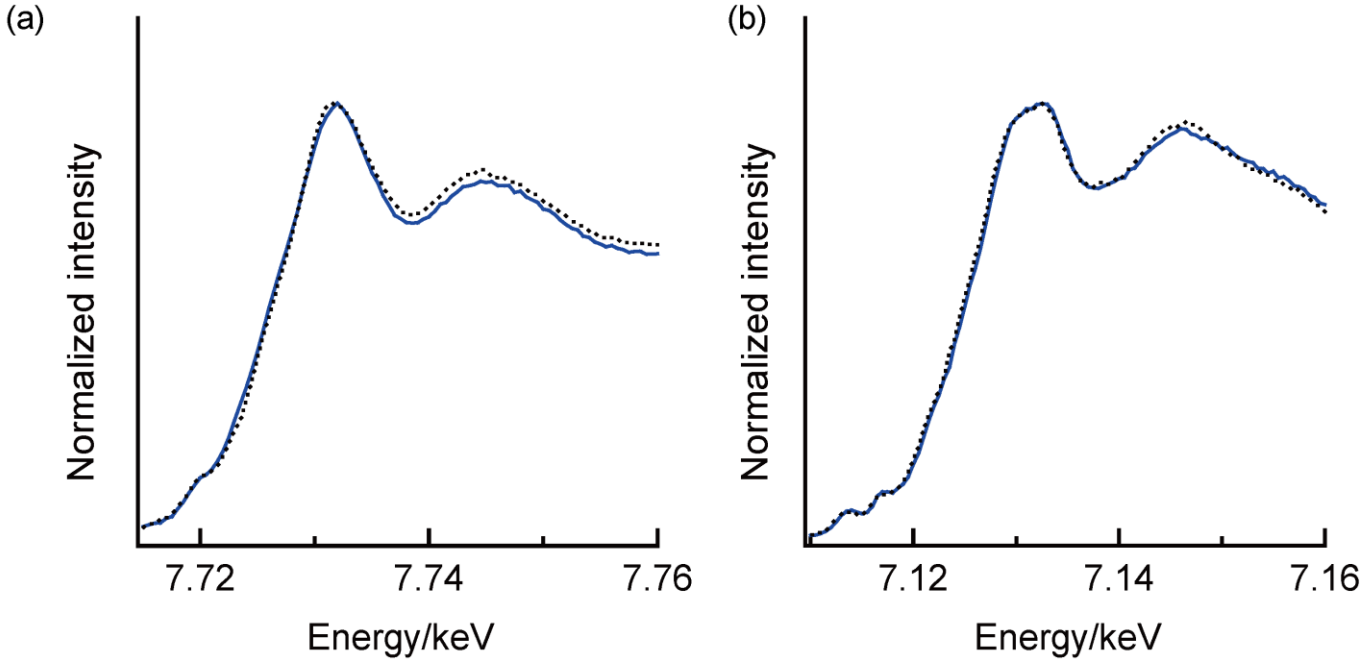

Fig. S2 (a) Co K-edge and (b) Fe K-edge XAS spectra before (blue solid line) and after (black dashed line) visible-light irradiation at 808 nm at 100 K.

References

1 Sheldrick, G. M. *SADABS*s: *An Empirical Absorption Correction Program*, Bruker Analytica X-ray Systems, Madison, WI, 1996.
2 S. Sakai, *KEK Report*, 1990, 90-16.
3 Y. Sekine, M. Nihei, R. Kumai, H. Nakao. Y. Murakami, H. Oshio, *Chem*. *Comm*., **2014**, *50*, 4050.