Temperature dependence of spherical electron transfer in a nanosized [Fe$_{14}$] complex

Wei Huang$^1$, Shuqi Wu$^2$, Xiangwei Gu$^1$, Yao Li$^1$, Atsushi Okazawa$^3$, Norimichi Kojima$^4$, Shinya Hayami$^5$, Michael L. Baker$^6,7$, Peter Bencok$^8$, Mariko Noguchi$^9,12$, Yuji Miyazaki$^9$, Motohiro Nakano$^9$, Takumi Nakanishi$^2$, Shinji Kanegawa$^2$, Yuji Inagaki$^{10}$, Tatsuya Kawae$^{10}$, Gui-Lin Zhuang$^{11}$, Yoshihito Shiota$^2$, Kazunari Yoshizawa$^2$, Dayu Wu$^{1*}$ & Osamu Sato$^{2*}$

The study of transition metal clusters exhibiting fast electron hopping or delocalization remains challenging, because intermetallic communications mediated through bridging ligands are normally weak. Herein, we report the synthesis of a nanosized complex, [Fe(Tp)$^-$]$\text{CN}_3\text{H}_2\text{O}$[Fe(H$_2$O)(DMSO)$_6$]$_8$ (abbreviated as [Fe$_{14}$], Tp$^-$, hydrotris(pyrazolyl)borate; DMSO, dimethyl sulfoxide), which has a fluctuating valence due to two mobile d-electrons in its atomic layer shell. The rate of electron transfer of [Fe$_{14}$] complex demonstrates the Arrhenius-type temperature dependence in the nanosized spheric surface, wherein high-spin centers are ferromagnetically coupled, producing an $S=14$ ground state. The electron-hopping rate at room temperature is faster than the time scale of Mössbauer measurements ($<10^{-8}$ s). Partial reduction of N-terminal high spin Fe$^{II}$ sites and electron mediation ability of CN ligands lead to the observation of both an extensive electron transfer and magnetic coupling properties in a precisely atomic layered shell structure of a nanosized [Fe$_{14}$] complex.

$^1$Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Advanced Catalysis & Green Manufacturing Collaborative Innovation Center, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China. $^2$Institute for Materials Chemistry and Engineering & IRCCS, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. $^3$Department of Basic Science, Graduation School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan. $^4$Toyota Physical and Chemical Research Institute, Yokomichi, Nagakute, Aichi 480-1192, Japan. $^5$Department of Chemistry, Graduate School of Science and Technology and Institute of Pulsed Power Science (IPPS), Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan. $^6$The School of Chemistry, The University of Manchester, Manchester M13 9PL, UK. $^7$The School of Chemistry, The University of Manchester at Harwell, Didcot OX11 0FA, UK. $^8$Diamond Light Source, Science Division, Didcot OX11 ODE, UK. $^9$Research Center for Structural Thermodynamics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan. $^{10}$Department of Applied Quantum Physics, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. $^{11}$Institute of Industrial Catalysis, College of Chemical Engineering, State Key Lab Breeding Base of Green-Chemical Synthesis Technology, Zhejiang University of Technology, Hangzhou 310032, China. $^{12}$Present address: Department of Chemistry, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan. *email: wudy@cczu.edu.cn; sato@cm.kyushu-u.ac.jp
To date, numerous nanosized transition metal complexes have been synthesized, which can be predetermined to have various fascinating structures via molecular self-assembly process. One of the challenges in realizing their functions is the introduction of fast electron transfer over a long distance that ubiquitously occurs in chemical and biological systems. The low-nuclearity compounds have been intensively investigated as intramolecular electron transfer systems. The recent interesting work on the [Fe] mixed-valence compound exhibited changes in the electron transfer rate observable by Mössbauer spectroscopy with a ferromagnetic S = 9/2 ground state. It is still challenging to isolate nanoarchitectures where electron transfer occurs over more metal centers, toward revealing extraordinary spectral and electronic behavior. In the absence of intermetallic coupling in high-nuclearity complexes, the recent interesting work on the [Fe2]V mixed-valence compound can demonstrate the coexistence of electron transfer and magnetism at both high and low temperatures. Considering its isomer shift (IS) of 0.07−0.15 mm s−1 and quadrupole splitting (QS) of ~0.45 mm s−1, the additional doublet can be assigned to FeII−FeII in the [Fe(Tp)(CN)3] unit. The result indicates that the reactant, [FeII(Tp)(CN)3]−, is completely reduced to [FeII(Tp)(CN)3]2− during the formation of [Fe14]. Furthermore, a comparison of the Mössbauer spectra of [Fe14] and [Fe5Fe7] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range. The Mössbauer spectra of [Fe14] and [Fe857Fe6] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range. The Mössbauer spectra of [Fe14] and [Fe857Fe6] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range. The Mössbauer spectra of [Fe14] and [Fe857Fe6] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range. The Mössbauer spectra of [Fe14] and [Fe857Fe6] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range. The Mössbauer spectra of [Fe14] and [Fe857Fe6] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range. The Mössbauer spectra of [Fe14] and [Fe857Fe6] indicates that the role of the FeII ions at the A sites remains static (FeII−FeII) across the entire temperature range.
behavior has previously been reported in a mixed-valence trinuclear Fe complex, \([\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}]_3\text{O}(\text{CH}_3\text{COO})(\text{H}_2\text{O})_3\)]_{27}, where the slope of the second-order Doppler shift was calculated as \(6.3 \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}\), comparable to the value of \(5.6(3) \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}\) for \([\text{Fe}_{14}]\). The electron-hopping relaxation model provides a good fit in the temperature range of 164–297 K, with a relaxation time of \(\tau\) as shown in Fig. 2e. A typical Mössbauer time window was observed to range from \(~3 \times 10^{-7}\) to \(~1 \times 10^{-8} \text{ s}\) for the system. Actually, in a previous study using the relaxation model, it was indicated that such dynamics are detectable as spectral changes in the range of \(~6.5 < -\log(\tau/\text{s}) < 8.0\)]_{28}, which is comparable to the case of \([\text{Fe}_{14}]\). The electron-hopping activation energy \((U_{\text{eff}})\) was successfully evaluated using the Arrhenius equation, \(\ln(\tau) = \ln(\tau_0) + U_{\text{eff}}/k_B T\). The best fit of the experimental data yielded \(U_{\text{eff}} = 943(47) \text{ cm}^{-1}\) with a pre-exponential factor of \(\tau_0 = 5.0(16) \times 10^{-11} \text{ s}\). Hence, the temperature dependence of the rates of intramolecular electron transfer in the Mössbauer spectroscopic analysis clearly demonstrated that six B-site Fe ions form a class II mixed-valence system according to the Robin–Day classification\[^{29}\]. Electronic spectroscopy in the domain of intervalence transitions exhibits a wide peak centered at 11,100 \text{ cm}^{-1} (900 nm) with a pronounced absorption tail due to the superposition of adjacent IVCT (Fe\text{II}-CN-Fe\text{II}) and remote IVCT (Fe\text{II}-NC-Fe\text{II}-CN-Fe\text{III}), as indicated in the reported cyanide-bridged systems with N-terminal mixed-valence state\[^{24,30,31}\]. (Supplementary Fig. 3)

The crystal structure was additionally analyzed to probe whether a temperature-induced charge separation occurs in \([\text{Fe}_{14}]\) at lower temperature, that is, 25 K, a temperature at which the electrons should be completely frozen \((\tau \sim 10^{13} \text{ s})\) according to aforementioned Arrhenius equation. However, no crystallographic differences in the coordination environment of the B-site Fe ions were observed between the structures at low and room temperature. At 25 K, the B-site Fe ions stay at the crystallographically identical sites in the unit cell as in the case of the RT (room temperature) structure. Therefore, although two Fe\text{II} are expected to be located in the trans positions of the [Fe\text{II}] octahedron to minimize Coulombic repulsion, the positions of the Fe\text{II} atoms cannot be assigned by X-ray diffraction. This is mostly due to the random distribution of the localized electrons at six B-site ions in the lattice. Thus, the charges at each B-site Fe virtually hold site occupation factors of 0.333 for Fe\text{II} and 0.667 for Fe\text{III}, respectively. The heat capacity of \([\text{Fe}_{14}]\) under zero field at \(7–300 \text{ K}\) was investigated (Fig. 3a). No distinct anomaly was observed in the heat capacity data, further indicating no first- or second-order phase transition. The observation is consistent with the thermal dependence of the rate of intramolecular electron transfer as indicated in the Mössbauer spectra.

To elucidate the electron-hopping behavior in the \([\text{Fe}_{14}]\) complex, temperature-dependent infrared (IR) spectroscopic measurements were carried out at 78–350 K. The IR spectrum of \([\text{Fe}_{14}]\) at 78 K exhibits several strong \(v_{\text{CN}}\) stretches at 2101, 2078, 2068, 2053, and 2042 \text{ cm}^{-1} (Fig. 3b), indicative of the Fe\text{II}-Is species bound to the C terminal of a cyanide bridge and both Fe\text{II} and Fe\text{III} to the terminal N atom. Notably, only two \(v_{\text{CN}}\) stretching bands were observed in the same region for a previously reported \([\text{Fe}_{12}]\) cluster, \([([\text{Fe}(\text{Tp})(\text{CN}))_2][\text{Fe}(\text{H}_2\text{O})_2]_6][\text{Fe}(\text{dpp})]_2\).
(H2O)12(CF3SO3)6·18H2O \((dpp = 1,3$\text{-}$di(4$\text{-}$pyridyl)propane), wherein the valence$\text{-}$trapped FeII$\text{-}$ls$\text{--}$CN$\text{--}$FeIII$\text{-}$hs structure was preserved across the whole temperature range\(^{32}\) (Supplementary Fig. 4). Furthermore, the \(\nu\) CN stretching frequency in Prussian blue with a FeII$\text{-}$ls$\text{--}$CN$\text{--}$FeIII$\text{-}$hs structure has been previously observed to be slightly higher compared with that in Prussian white with a FeII$\text{-}$ls$\text{--}$CN$\text{--}$FeII$\text{-}$hs structure\(^{33}\). The additional \(\nu\) CN stretching bands for \([\text{Fe}_{14}]\), which lack in \([\text{Fe}_{42}]\), indicates the presence of a FeII$\text{-}$ls$\text{--}$CN$\text{--}$FeIII$\text{-}$hs and FeII$\text{-}$ls$\text{--}$CN$\text{--}$FeII$\text{-}$hs mixed linkage, by in situ Fourier$\text{-}$transform infrared spectroscopy. These results mean that the electron$\text{-}$hopping rate is slower than the time scale of the IR technique \(\left(10^{-12}$–$10^{-13}$ \(s\)\)\(^{34}\).

Iron L$\text{-}$edge X$\text{-}$ray absorption spectra (XAS) were measured between 3.5 and 300 K to further characterize the electronic structure (Fig. 3c). Spin$\text{--}$orbit coupling of the \(2p^6\) final state \(\left(2p^6\ 3d^{10} \rightarrow 2p^5\ 3d^{10} + 1\right)\) leads to the splitting of \(L_{2,3}\) edges into \(L_1 (J = 3/2)\) and \(L_2 (J = 1/2)\) absorption regions, which are separated in energy by \(~12\) eV. The \(L_1\) and \(L_2\) absorption edges of \([\text{Fe}_{14}]\) were found to have maxima at 708.5 and 722 eV, respectively. The \([\text{Fe}_{14}]\) L edge includes overlapping contributions from the A and B sites. The XAS spectra measured between 3.5 and 300 K are identical, confirming that there is no resolvable change in the local Fe coordination symmetry or crystal field splitting at the A or B sites between the low$\text{-}$ and high$\text{-}$temperature states.

Fig. 2 Mössbauer spectra analysis of the valence and spin state of the Fe ions. a$-$b Zero$\text{-}$field \(^{57}\text{Fe}\) Mössbauer spectra of a natural isotopic \([\text{Fe}_{14}]\) and a \(^{57}\text{Fe}\)$\text{--}$enriched sample on the N$\text{-}$terminal B site, \([\text{Fe}_{8}\text{^{57}\text{Fe}_{6}}]\), at selected temperatures with fits considering the electron hopping between FeII$\text{-}$hs and FeIII$\text{-}$hs (purple area), FeIII$\text{-}$hs (green area), FeII$\text{-}$hs (orange area), and FeII$\text{-}$ls (striped yellow area). c Schematic of the valence behavior on the crystallographically equivalent B site in the Mössbauer time window. d Quadrupole splitting (QS) and isomer shift (IS) as a function of the temperature in the Mössbauer spectra. The values of FeII$\text{-}$hs (green) and FeIII$\text{-}$hs (orange) are determined from the \(^{57}\text{Fe}\)$\text{--}$enriched sample, whereas those of FeII$\text{-}$ls (striped yellow area) are determined from the natural sample. e Temperature dependence of the relaxation time \(\tau\) of the electron hopping between FeIII$\text{-}$hs and FeII$\text{-}$hs in the temperature window of 164$-$297 K. The error bars were estimated as the respective deviations having the deference of the reduced chi$\text{-}$square value \(\left(\Delta\chi^2\right)\) within 2, considering the parameter correlations in the fitting. The red line represents the Arrhenius fitting in the high$\text{-}$temperature region.
Furthermore, no temperature-induced changes in the spectra were observed for the \( K \text{Fe}_{14} \text{Fe}_{13} \) emission spectroscopy and high-resolution K-edge X-ray absorption near-edge structure measurements (Supplementary Fig. 5). The lack of evidence for the thermal transition by these techniques indicates that the electron-hopping rate is slower than the time scale of the X-ray spectroscopy measurements (\( 10^{-14} \text{ to } 10^{-15} \text{s} \)). A comparison of the \( [\text{Fe}_{14}] \) L-edge XAS data with the monomeric references \( [\text{Fe}^{III}(\text{Tp})(\text{CN})_{3}] \) and \( [\text{Fe}^{II}(\text{Tp})(\text{CN})_{3}] \) indicates that the valences of the eight A sites are diamagnetic \( \text{Fe}^{II}-\text{ls}^{35-38} \), confirming the Mössbauer assignment.

**Magnetic properties.** To assess the magnetic properties of \( [\text{Fe}_{14}] \), variable-temperature direct current magnetic susceptibility data were collected. Figure 4a shows that at 300 K the \( \chi_M T \) value is 27.45 cm\(^3\) K mol\(^{-1}\). Upon a decrease in the temperature, the \( \chi_M T \) value shows a steady increase, before beginning to abruptly increase at ca. 30 K with a maximum of 59.17 cm\(^3\) K mol\(^{-1}\) at 3.5 K. This magnetic behavior suggests an overall ferromagnetic intramolecular exchange for \( [\text{Fe}_{14}] \). The data in the range of 300–10 K can be fitted to the Curie–Weiss law, yielding \( C = 27.17 \text{ cm}^3 \text{K mol}^{-1} \) and \( \theta = 2.95 \text{ K} \). This \( C \) value is comparable to the contribution from two \( S = 2 \text{ Fe}^{II}-\text{ls} \), four \( S = 5/2 \text{ Fe}^{III}-\text{hs} \), and eight \( S = 0 \text{ Fe}^{II}-\text{ls} \) centers in total for an individual \( [\text{Fe}_{14}] \) complex, which is further supported by the evaluated experimental magnetic entropy 87.1 J K\(^{-1}\) mol\(^{-1}\) \( \approx R \ln(5^2 \times 6^8) \) (86.4 J K\(^{-1}\) mol\(^{-1}\), expected magnetic entropy). The positive Weiss constant suggests an intramolecular ferromagnetic interaction\(^{39}\). Density functional theoretical (DFT) calculations revealed that the spin density is mainly concentrated on the six B-site Fe ions (avg. spin value of 3.535) rather than the A-site Fe ions (avg. spin value of 0.232) (Supplementary Fig. 6), which is consistent with the experimental observations. To determine the spin ground state of \( [\text{Fe}_{14}] \), magnetization data were collected and were plotted as reduced magnetization (\( M/N_{\text{Fe}} \)) vs. applied field in the range of 0–5 T at 2 K, as shown in Fig. 4b. The onset of magnetization in the applied field is greater than that of six magnetically isolated centers (red line in Fig. 4b) and is closer to the Brillouin curve for one isotropic \( S = 14 \) center (blue line in Fig. 4b). Inclusion of weak ferromagnetic exchange coupling (green line) between B sites suitably reproduces the measured magnetization curve, indicating a ferromagnetic \( S = 14 \) ground state.

The presence of a ferromagnetic interaction was also confirmed using X-ray magnetic circular dichroism (XMCD), a technique that is a probe of magnetization at the atomic level. Since they are diamagnetic, the A-site Fe ions have no XMCD intensity. Hence, the \( [\text{Fe}_{14}] \) XMCD spectrum provides direct spectroscopic access to only the B-site Fe ions. The left and right circularly polarized total fluorescence yield (TFY) detected XAS at 3.5 K, and 14 T is shown in Fig. 4c, alongside the XMCD spectra at various applied magnetic fields. At 3.5 K, the B sites are in the valence-trapped state in a ratio of 4:2 (\( \text{Fe}^{III} \text{ vs. Fe}^{II} \)). The onset of the \( L_3 \) edge for the octahedral Fe\(^{II}\)-hs component is known to be lower in energy than that of Fe\(^{III}\)-hs by ~1 to 2 eV. Hence, the lower energy region of the \( L_3 \) XMCD spectrum is expected to exhibit Fe\(^{II}\)-hs contributions with respect to the higher energy region, which is expected to show Fe\(^{III}\)-hs contributions. The magnitude of the XMCD signal across the \( L_3 \) edge increases monotonically with an applied field indicating that the ferrous and ferric spins at the B sites are ferromagnetically exchange coupled\(^{40}\). (Supplementary Fig. 7) The field dependence of the XMCD data is in accordance with that observed for the superconducting quantum interference device (SQUID) magnetization.

It should be noted that the maximum \( \chi_M T \) at low temperatures is significantly reduced compared to the expected \( \chi_M T \) value for an isolated \( S = 14 \) ground state (~105 cm\(^3\) K mol\(^{-1}\)). (Supplementary Fig. 8) The susceptibility measurements conducted down to 0.5 K exhibits a sharp peak in \( \chi_M \) at 0.8 K (Fig. 4d), showing a...
The heat capacity of [Fe14] from 0 to 9 T in the temperature region of 100 K was investigated. However, the value of such an analysis is limited due to the Heisenberg contribution to the exchange for charge transfer interelectronic Coulombic repulsions, in conjunction with the necessity for the evaluation of electron transfer integrals and the theoretical description of the intramolecular exchange on the atomic layer of [Fe14] requires consideration of the electron delocalization, as described by Mayoh and Day. In practice, this requires the delocalization of the π* orbitals via bridging CN groups. Since the high-spin sites are coordinated by diamagnetic [FeII-I-(Tp)(CN)3], the mechanism of intramolecular ferromagnetic exchange over the atomic layer of [Fe14] necessitates the delocalization of the t2g [FeII-I-(Tp)(CN)3] metal character to B-site t2g orbitals via bridging CN π* orbitals. A theoretical description of the intramolecular exchange on the atomic layer of [Fe14] requires consideration of the electron delocalization, as described by Mayoh and Day. In practice, this requires the evaluation of electron transfer integrals and interelectronic Coulombic repulsions, in conjunction with the Heisenberg contribution to the exchange for charge transfer states. However, the value of such an analysis is limited due to the onset of 3D magnetic ordering at low temperature.

In summary, we report on the synthesis and electronic behavior of a nanosize [Fe14] complex with the two-electron, four-hole mixed-valence state. Two extra 3d electrons in the complex are found to hop at N-terminal Fe centers on its atomically thin spheric surface. The valence of the A-site Fe is basically static, while the valence electrons on the B-site Fe exhibit thermal dependence of the rate of intramolecular electron transfer. Furthermore, [Fe14] has a high-spin ground state with S = 14, meaning that the two electrons are hopping around the exchange-coupled atom-layer thin surface. The nanoarchitecture in this work may be useful for application in future molecular electronic and chemical devices using the intermetallic electronic and magnetic interactions in the framework and precise nanospace.

**Methods**

**Synthesis of the [Fe14] complex.** A 2 mL aqueous solution containing 6 μmol of Fe(BF4)2·6H2O was layered over a 2 mL DMF solution containing 8 μmol of Bu4N[Fe(Tp)(CN)3]. A 1 μmol aqueous solution of L-ascorbic acid was utilized as the middle buffer layer under aerobic conditions. Crystals suitable for X-ray diffraction analysis were obtained in a yield of 16% after a week. Anal. calcd. for...
C_{108}H_{128}B_{8}Fe_{14}N_{72}O_{12}S_{6}: C, 35.18; H, 3.50; N, 27.35. Found: C, 35.12; H, 3.52; N, 27.40. The analysis of Fe content in the solid sample of [Fe14] was performed through paramagnetic resonance (HF-EPR) measurements. The experiment result is 21.27 wt.%, which is in good agreement with the calculated value of 21.20 wt.%.

The 57Fe isotopically enriched sample, [Fe57Fe14], was prepared in a similar manner to that of [Fe14], except that the isotopically enriched salt, 57FeCl2·4H2O (96%), was utilized instead of FeCl2·6H2O. Through X-ray diffraction measurements, the crystal structure of the isotopically enriched sample, [Fe57Fe14], was observed to be identical to that of the natural isotopic [Fe14].

X-ray crystal structure determination. X-ray diffraction data at room temperature and 123 K for [Fe14] were collected on a BRUKER APEX-II CCD (Bruker Corp.) equipped with a graphite-monochromated Mo-Kα radiation source (λ = 0.71073 Å)44–47. Diffraction data at 25 K were collected under a cold helium gas stream on a Rigaku HPC X-ray diffractometer, using multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71073 Å). Bragg spots were integrated using the CrysAlisPro program package, and empirical absorption correction (multi-scan) was applied using the SCALE3 ABSPACK program. The structures were solved by direct methods (SHEXL Version 2014/4) using full-matrix least-squares refinement (SHELX). The H atoms were geometrically placed on organic ligands in riding mode, and all of the non-H atoms were anisotropically refined by full-matrix least-squares refinement on F2 using the SHELXTL program48. A summary of the crystallographic data and refinement parameters is presented in Extended Data Table 1.

Computational details. Spin-polarized DFT calculations were carried out using the PWscf module in the Quantum Espresso 6.1 program package50. The exchange and correlation term in the Kohn–Sham equation was approximately treated using the Perdew–Burke–Ernzerhof method in terms of the gradient of the electronic density; i.e., the gradient corrected wave potential (Gradient) was used along with the plane-wave basis set with a kinetic energy cut-off of 310. Ry. The simulation cell of Fe ([TP(CN)4]2-[Fe(H2O)(DMSO)]3), contained 348 atoms in total. Atomic optimizations were carried out, starting from the experimental cell parameters. Integration in the first Brillouin zone for geometry optimizations was performed using 2 × 2 × 2 Monkhorst–Pack sampling48. The SCF (self-consistent field) convergence and the total force convergence were set to be 1.0 × 10−6 (Ry) and 1.0 × 10−2 (Ry/au), respectively. The total magnetization was constrained to be 28.00 Bohr mag per cell. The spin-polarized DFT calculations further provided reliable information as to the charge and the spin state on each iron atom in [Fe14]. The singly occupied electrons at the B-site FeIII components partially delocalizes on the A site FeII ions.

Magnetic analysis. The magnetic measurements of the samples were performed using a SQUID (MPMS-5S) magnetometer (Quantum Device Inc., USA). The magnetic susceptibility measurements shown in Fig. 4d were performed using MPMS-XL7AC (Quantum Device Inc., USA) apparatus with a 9 mm diameter 4He insert51. The data were corrected for diamagnetic contributions, calculated using Pascal’s constants52.

Simulation of magnetization. The field dependence of magnetization for [Fe14] follows neither the Brillouin function for an S = 14 spin moment or the sum of uncoupled moments (four S = 5/2 and two S = 2). Inclusion of a weak ferromagnetic exchange interaction, acting between high spin sites was found to reproduce the measured magnetization curve. The magnetization curve was fit assuming one exchange constant J = 0.9 K and g = 2.0, based on the following Hamiltonian:

\[
\hat{H} = -2J(S_1 S_2 + S_1 S_3 + S_2 S_3 + S_1 S_4 + S_2 S_4 + S_3 S_4 + S_1 S_6 + S_2 S_6 + S_3 S_6 + S_4 S_6 + S_5 S_6) + \sum_i \mu_B g_i S_i,
\]

where \(S_i\) and \(S\) represent the S = 2 sites and \(S_1, S_2, S_3, S_4, S_5, S_6\) represent the S = 5/2 sites, \(B\) is the applied magnetic field and \(\mu_B\) is the Bohr magneton. This exchange model neglects the double-exchange component to the Hamiltonian present in Class B systems and effects due to dipolar fields from neighboring molecules. However, this simplified model indicates how the measured curve is consistent with weak ferromagnetic exchange coupling within [Fe14].

57Fe Mössbauer spectroscopy. The 57Fe Mössbauer spectra were measured using a conventional Mössbauer spectrometer (Topologic Systems, Kanagawa, Japan) in transmission mode with a 85Co/Rh γ-ray source. Low-temperature measurements were performed upon a CryoMini/CryoStat cryogenic refrigerator set (Iwatani Industrial Gases, Osaka, Japan). The samples were tightly sealed with silicon grease in an acrylic holder and the spectra were calibrated using α-Fe foil as a reference at room temperature. The spectral fitting was carried out using the MossWin 4.00 program and the full zero-field 57Fe Mössbauer spectra at all investigated temperatures were provided in Supplementary Fig. 10. For the 57Fe in Fe57Fe14 sample, the spectra were analyzed by applying an electron-hopping relaxation model (164–297 K; see Supplementary Method and Supplementary Fig. 11) or two quadrupole doublets (10–144 K). The area ratio was fixed at the ideal value (FeII/FeIII = 1/2) according to the chemical formula in order to avoid overparameterization. Some parameter correlations were found, especially between the linewidth and relaxation rate, through curve fittings of the spectra at 245–297 K. Therefore, the linewidth and IS values for FeII- at the relevant temperatures were fixed using those at 224 K. For the analyses at 10–144 K, the FeII-doublet was regarded as an asymmetric doublet, rising as a result of paramagnetic relaxation because an alternative symmetric doublet was tried but presented no sufficient result. For the natural isotopic sample of [Fe14], the Mössbauer spectra were analyzed using an additional doublet (FeII/FeIII site A) together with the corresponding FeII- and FeII- signals (site B) produced by the fixed parameters obtained from [Fe57Fe14]. Across the entire temperature range, the FeII/FeII- ratio of the sample was maintained at 8/4.

Heat capacity calorimetry. Heat capacity measurements were performed with a laboratory-made adiabatic microcalorimeter in the temperature range of 9–300 K (adiabatic method) and with a PPMS (Quantum Design Inc., USA) in the temperature range 0.68–100 K under magnetic fields of 0–9 T (relaxation method). In the adiabatic calorimetry, 0.06356 g of a polycrystalline sample, which was made by buoyancy correction, was loaded into a 0.09 cm3 gold-plated copper cell and sealed with an indium wire under helium gas atmosphere. Thermometry was performed using a rhodium–iron alloy resistance thermometer (nominal 270Ω, Oxford Instruments) calibrated on the basis of the international temperature scale of 1990 (ITS-90). In the relaxation calorimetry (PPMS), we used buoyancy-corrected 1.0313 mg of a polycrystalline sample formed into a pellet of 2.5 mm in diameter. For the measurements below 10 K, a 4He He was employed56.

X-ray absorption spectra and X-ray magnetic circular dichroism. XAS and XMCD measurements at the Fe L absorption edges (703–740 eV) were measured on beamline I10 at the synchrotron Diamond Light Source of the Harwell Science and Innovation Centre in the United Kingdom. The XMCD spectra were obtained by flipping the helicity of circularly polarized X-rays exhibiting a 100% degree of polarization in the case of fixed applied magnetic fields. The measurements were performed with the temperature of the sample holder being regulated between 3.5 and 300 K. The total electron yield was obtained by measuring the drain current of the sample, whereas the TFY was obtained using a photodiode. The powdered samples of [Fe14] were attached with indium, to a copper sample holder. Radiolyis was controlled through the attenuation of the incident X-ray flux to 7% of the optimized value. Multiple scans were performed at each sample location to maintain control of the radiolysis, which was indicated by an increase in intensity at the low-energy portion of the L3 edge. TFY-detected measurements were found to be less susceptible to radiolysis and were hence adopted for XMCD measurements.

High-frequency electron paramagnetic resonance. High-frequency electron paramagnetic resonance (HF-EPR) measurements were performed on a locally developed spectrometer at the Wuhan National High-magnetic Field Center with a pulsed magnetic field of up to 30 T.

Data availability

The data that support the findings of this study and its Supplementary Information are available from the corresponding author (D.W. or O.S.) upon reasonable request. The X-ray crystallographic coordinates for structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC), under deposition number CCDC 1,878,752–1,878,754. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Received: 18 May 2019; Accepted: 31 October 2019; Published online: 03 December 2019

References

1. Cook, T. R., Zheng, Y.-B. & Stang, P. J. Metal–organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design, synthesis, and functionality of metal–organic materials. Chem. Rev. 113, 734–777 (2013).
2. Fujita, D. et al. Self-assembly of tetravalent goldberg polyhedra from 144 small components. Nature 540, 563–566 (2016).
3. Nitschke, J. R. Systems chemistry: molecular networks come of age. Nature 462, 736–738 (2009).
4. D’Alessandro, D. M. & Keene, F. R. Intervalance charge transfer (IVCT) in trinuclear and tetracanicular complexes of iron, ruthenium, and osmium. Chem. Rev. 106, 2270–2298 (2006).
5. Iiao, J., Long, G. J., Grandjean, F., Beatty, A. M. & Fehlner, T. P. Building blocks for the molecular expression of quantum cellular automata. Isolation
and characterization of a covalently bonded square array of two ferrocene and two terrocene complexes. J. Am. Chem. Soc. 125, 7522–7523 (2003).

6. Dwivek, S. et al. The novel mixed-valence, exchange-coupled, class III dimer [Fe2M(μ-OH)]4+ ([L = N,N′,N′′-trimethyl-1,4,7-triazacyclonane]). J. Chem. Soc. Chem. Commun. 1, 59–62 (1989).

7. Gamelin, D. R., Bominnaar, E. L., Kirk, M. L., Wieghardt, K. & Solomon, E. I. Excited-state contributions to ground-state properties of mixed-valence dimers supported by electronic-structural studies of [Fe2O(OH)](tetramen)_2-related to the Fe2S4+-active sites of plant-type ferredoxins. J. Am. Chem. Soc. 118, 8085–8097 (1996).

8. Glaser, T. et al. Electronic structure of linear thiophenolate-bridged heteronuclear complexes [LFeM]3+ (M = Cr, Co, Fe; n = 1–3): localised vs delocalized models. J. Am. Chem. Soc. 121, 2193–2208 (1999).

9. Suresh, K. K., Meehan, E. F., Snyder, S. & Holm, R. H. A bisnuclear mixed-valence ferromagnetic iron system with an S = 9/2 ground state and valence trapped and detrapped states. J. Am. Chem. Soc. 111, 5501–5502 (1989).

10. Wilson, C. et al. Multi-temperature crystallographic studies of mixed-valence polymeric complexes; valence trapping process in the trinuclear oxo-bridged iron compound, [Fe3O2(O2CCCH3)3]0(C2H4N3). J. Am. Chem. Soc. 122, 11370–11379 (2000).

11. Dong, T. Y., Hendrickson, D. N., Pierpont, C. G. & Moore, M. F. Mixed-valence f6-dihalobiferrocnium salts: the effect of the solid-state environment on electron-transfer rates. J. Am. Chem. Soc. 108, 963–971 (1986).

12. Somerford, M. O., M., N. H., Karen, L. H. & Raymond, E. D. Electron transfer in mixed-valence, oxo-centered, trinuclear iron acetate complexes: effect of statically disordered to dynamically disordered transformation in the solid state. J. Am. Chem. Soc. 106, 7984–7985 (1984).

13. Zhao, Q. L., Harris, T. D. & Betley, T. A. [(H2)2Fe4(NCMe)4]+ (m = 2, 4, 6; n = 1, 2, 2, 3, 4, 6): an electron-transfer series featuring octahedral Fe4 complexes supported by a hexameric ligand platform. J. Am. Chem. Soc. 133, 8293–8306 (2011).

14. Gaudette, A. J. et al. Electron hopping through double-exchange coupling in a mixed-valence diminozouquinone-bridged Fe2 complex. J. Am. Chem. Soc. 137, 12617–12626 (2015).

15. Jiménez, J. R. et al. [Fe(fos)] tetrahedral cage building nanoscopic molecular assemblies through cyanoannulate and alkoxy linkers. Dalton Trans. 45, 17610–17615 (2016).

16. Zener, C. Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with perovskite structure. Phys. Rev. 82, 403–405 (1951).

17. Anderson, P. W. & Hasegawa, H. Considerations on double exchange. Phys. Rev. 100, 675–681 (1955).

18. Blondin, G. & Girerd, J. J. Interplay of electron exchange and electron transfer in metal polynuclear complexes in proteins or chemical models. Chem. Rev. 90, 1359–1376 (1990).

19. Bechlers, B. & Hasegawa, H. Considerations on double exchange. Phys. Rev. 100, 675–681 (1955).

20. Blondin, G. & Girerd, J. J. Interplay of electron exchange and electron transfer in metal polynuclear complexes in proteins or chemical models. Chem. Rev. 90, 1359–1376 (1990).

21. Aubrey, M. L. et al. Electron delocalization and charge mobility as a function of reduction in a metal–organic framework. Nat. Mater. 17, 625–632 (2018).

22. Pieslinger, G. E., Alborés, P., Slep, L. D. & Baraldo, L. M. Class III delocalization in a cyanide-bridged trimetallic mixed-valence complex. Angew. Chem. Int. Ed. 126, 1317–1320 (2014).

23. Roger, G. et al. A mixed-valence mixed-spin Prussian blue-like heptanuclear complex. Angew. Chem. Int. Ed. 39, 2885–2887 (2000).

24. Ma, X. et al. An unusually delocalized mixed-valence state of a cyanometaloid bridged compound induced by thermal electron transfer. Angew. Chem. Int. Ed. 56, 1605–1609 (2017).

25. Nihei, M., Utii, M., Hoshiba, N. & Oshio, H. Cyanide-bridged iron(II,III) cube with multisteped redox behavior. Inorg. Chem. 47, 6106–6108 (2008).

26. Kroto, H. W., Heath, J. R., Obrèen, S. C., Curl, R. F. & Smalley, R. E. C60: Buckminsterfullerene. Nature 318, 163–165 (1985).

27. Blume, M. Stochastic theory of line shape: generalization of the Kubo–Anderson model. Phys. Rev. 174, 351–358 (1968).

28. Dziobkowski, C. T., Wroblewski, J. T. & Brown, D. B. Magnetic and spectroscopic properties of Fe2+3+3O(OC2H4O)2+ L = H2O or C2H4H. Direct observation of the thermal barrier to electron transfer in a mixed-valence complex. Inorg. Chem. 20, 679–684 (1981).

29. Herber, R. H. & Eckel, H. Electron hopping in FO211121 complexes: a Mössbauer relaxation study. Phys. Rev. B 31, 44–41 (1985).

30. Robin, M. B. & Day, P. Mixed valence chemistry—a survey and classification. Adv. Inorg. Chem. Radiochem. 10, 247–422 (1967).

31. Oshio, H. et al. Cyanide-bridged Fe–Fe and Fe–Co molecular squares: Structures, spectral and chemisty of [Fe2O(CN)6]3+ (β-[Fe2(CO)5(CN)3]pyr)[PF6]3, 4H2O, [Fe2(CO)5(CN)3]pyr)[PF6], 3CH2Cl2, 2CH3CN, and [Fe2(CO)5(CN)3]pyr)[PF6], 2CHCl3, 4CH3NO2. Chem. Eur. J. 6, 2523–2530 (2000).

32. Oshio, H., Ohodera, H. & Ito, T. Spectroelectrochemical studies on mixed-valence states in a cyanide-bridged molecular square. RSC Adv., 4[Fe2(OH)6]3+ (β-[Fe2(CO)5(CN)3]pyr)[PF6]3, 4H2O, [Fe2(CO)5(CN)3]pyr)[PF6], 3CH2Cl2, 2CH3CN, and [Fe2(CO)5(CN)3]pyr)[PF6], 2CHCl3, 4CH3NO2. Chem. Eur. J. 6, 2523–2530 (2000).
discussed the results. A.O., S.H. and N.K. undertook the spectra of Mössbauer and fitted the data. M. Noguchi, Y.M. and M. Nakano performed heat capacity measurement. T.N. measured single-crystal structure at low temperature. Y.I. and T.K. performed magnetic experiment at low temperature. G.-L.Z., Y.S. and K.Y. conducted DFT calculation. All the authors discussed the results and commented on the paper.

**Competing interests**
The authors declare no competing interests.

**Additional information**
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-019-13279-y.

**Correspondence** and requests for materials should be addressed to D.W. or O.S.

**Peer review information**
Nature Communications thanks Hiroki Oshio, and other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.