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**$S = \frac{1}{2}$ Heterospin Frustration in a Metal–Fullerene-Bonded Semiconductive
Antiferromagnet**

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Abstract

Lithium-ion-encapsulated fullerenes ($\text{Li}^+@C_{60}$) are 3D superatoms with rich oxidative states. However, no current studies have reported $\text{Li}^+@C_{60}$ as ligands. Here, we report a conductive and magnetically frustrated metal–fullerene-bonded framework $\{[\text{Cu}_4(\text{Li}^+@C_{60})(\text{L})(\text{py})_4](\text{NTf}_2)(\text{hexane})_n\}$ (**1**) prepared from redox-active dinuclear metal complex $\text{Cu}_2(\text{L})(\text{py})_4$ and lithium-ion-encapsulated fullerene salt ($\text{Li}^+@C_{60})(\text{NTf}_2^-)$, where ligand L denotes 1,2,4,5-tetrakis(methanesulfonamido)benzene, py pyridine, and NTf_2^- the bis(trifluoromethane)sulfonamide anion. Electron donor $\text{Cu}_2(\text{L})(\text{py})_2$ bonds to acceptor $\text{Li}^+@C_{60}$ via eight Cu–C bonds. Cu–C bond formation stems from spontaneous charge transfer (CT) between $\text{Cu}_2(\text{L})(\text{py})_4$ and ($\text{Li}^+@C_{60})(\text{NTf}_2^-)$ by removing the two-terminal py molecules, yielding triplet ground state $[\text{Cu}_2(\text{L})(\text{py})_2]^+(\text{Li}^+@C_{60}^-)$, evidenced by absorption and electron paramagnetic resonance (EPR) spectra, magnetic properties, and quantum chemical calculations. Moreover, $\text{Li}^+@C_{60}^-$ radicals ($S = 1/2$) and Cu^{2+} ions ($S = 1/2$) interact antiferromagnetically in triangular spin lattices in the absence of long-range magnetic ordering up to 1.8 K; thus, compound **1** is a potential candidate for an $S = 1/2$ quantum spin liquid.

Introduction

Since the pure form of the lithium-ion-encapsulated fullerene salt

$[\text{Li}^+@\text{C}_{60}](\text{SbCl}_6)$ was isolated and structurally determined by X-ray diffraction analysis in 2010,¹ studies on this smallest endohedral metallofullerene (EMF) have taken precedence over photoinduced electron transfer (ET) in noncovalent donor–acceptor (D–A) complexes,^{2–4} covalent metal complexes,⁵ organic photovoltaics,⁶ and molecular electronics⁷ over the past decade because of the salt’s unique structure and electronic properties relative to pristine C_{60} .^{8–11} Although the optical bandgap (E_g) is very close to that of pristine C_{60} , the lowest unoccupied molecular orbital (LUMO) of $\text{Li}^+@\text{C}_{60}$ has been observed to decline significantly to -3.90 eV with an initial reduction potential at -0.39 V *versus* Fc/Fc^+ in *o*-dichlorobenzene (*o*-DCB).¹ Furthermore, the oxidation state of $\text{Li}^+@\text{C}_{60}$ can be easily tuned from $1+$ to $3-$ by external chemical stimuli to realise various electronic states.¹ Therefore, this compound has been widely used as a π -electron acceptor owing to the small reorganisation energy required, which leads to highly delocalised π -electrons over a 3D sphere.^{3, 4} It is easy to deduce that $\text{Li}^+@\text{C}_{60}$ can be doped by alkali metals to produce high-temperature superconductors in imitation of M_3C_{60} superconductors ($\text{M} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$) with three electrons accommodated in the triply degenerated LUMO.^{12–15} In particular, the emergence of $\text{Li}^+@\text{C}_{60}^-$ requires milder chemical oxidant than for C_{60}^- . Such a low reduction potential provides many opportunities for coordination chemistry. According to the Mulliken theory,^{16–19} the formation of the CT complex requires efficient orbital overlap between the highest occupied molecular orbital (HOMO) of D and the LUMO of A. The CT interactions in the ground state increase with decrease in the energy difference between the HOMO of D and LUMO

of A. In this regard, Martin and co-workers reported several CT complexes between comparatively strong electron donors such as π -extended tetrathiafulvalene derivatives and fullerenes.^{20, 21} Additionally, Yamada et al. observed a triplet charge-separated state by laser-exciting a curved π -surface donor and $\text{Li}^+@\text{C}_{60}$ in solution.³

Although C_{60} is an ideal ligand to realise topological architectures owing to its isotropic coordination environment,²² to date, no candidates have been reported for the experimental realisation of electrically conductive and magnetically frustrated solids based on $\text{Li}^+@\text{C}_{60}$. On the other hand, the $S = \frac{1}{2}$ electronic system holds promise for exploring interesting quantum phenomena such as unconventional superconductivity²³⁻²⁶ and quantum spin liquids (QSLs) which are commonly observed in triangular or kagomé lattices.²⁷⁻³³ Herein, we selected an electronically active donor, $\text{Cu}_2(\text{L})(\text{py})_4$, and a 3D charge-tuneable metallofullerene, $\text{Li}^+@\text{C}_{60}$, as both the ligand and electron acceptor to construct a conductive and spin-frustrated framework based on the Mulliken theory.

In our approach, an $S = \frac{1}{2}$ electronic framework $\{[\text{Cu}_4(\text{Li}^+@\text{C}_{60})(\text{L})(\text{py})_4](\text{NTf}_2)(\text{hexane})\}_n$ (**1**) is isolated by constructing the donor and acceptor. The donor is bonded to the acceptor via Cu–C bonds. It is noteworthy that the HOMO of $\text{Cu}_2(\text{L})(\text{py})_4$ has the equivalent energy level of the LUMO of $\text{Li}^+@\text{C}_{60}$, thereby facilitating CT interactions in the ground state. From our calculations, we found that the d_{xz} orbitals of the Cu ions in $\text{Cu}_2(\text{L})(\text{py})_4$ are delocalised and strongly coupled with the $\text{N}(p_z)$ orbitals (π -electrons) of the ligand, thereby yielding delocalised electrons in the HOMO. In **1**, the four-terminal d_{xz}

orbitals of Cu ions coordinate with one $\text{Li}^+@\text{C}_{60}$ cage and the remaining four Cu ions coordinate with the next $\text{Li}^+@\text{C}_{60}$ cage to form an infinitely scaled 1D chain structure. The four $\text{Cu}(\text{L})(\text{py})$ sites transfer a single electron into the $\text{Li}^+@\text{C}_{60}$ cage, and the resulting four Cu^{2+} ($S = \frac{1}{2}$) ions and $\text{Li}^+@\text{C}_{60}^-$ ($S = \frac{1}{2}$) interact with each other and exhibit magnetic frustration in a triangular-like lattice. To the best of our knowledge, our study is the first to demonstrate long-range electrical conductivity (σ) and spin frustration using $\text{Li}^+@\text{C}_{60}$ superatoms in such a bonded D–A-type framework.

Results and discussion

Metal-fullerene bonded donor-acceptor-type framework. Compound **1** crystallises in the triclinic $P\bar{1}$ space group with the unit-cell dimensionality of $a = 9.9959(2)$ Å, $b = 13.3083(3)$ Å, $c = 19.7024(4)$ Å, $\alpha = 77.327(2)^\circ$, $\beta = 76.571(2)^\circ$, and $\gamma = 69.498(2)^\circ$. One $\text{Li}^+@\text{C}_{60}$ cage coordinates with four Cu ions from four $\text{Cu}_2(\text{L})(\text{py})_2$ molecules (Figure 1a), and the remaining four Cu ions coordinate with the next $\text{Li}^+@\text{C}_{60}$ cage to afford infinite 1D ladder-like structures along the b -axis (Figure 1d). Each Cu ion exhibits an equivalent of five coordination numbers (two Cu–C and three Cu–N bonds) in a distorted trigonal bipyramid geometry (Figure 1b). The rectangular plane formed by the four Cu ions perfectly divides the C_{60} cage into two (Figure S1), and the shell-like Li^+ ion is off-centred and localised above or below the Cu plane with thermal ellipsoids at 50% probability. Similar Li^+ -ion arrangements are also observed in the other forms of $\text{Li}^+@\text{C}_{60}$ salts.^{34,35} The inner Li^+ ion coordinates with the six-carbon ring with Li–C bond lengths in the range of 2.246–2.368 Å, which are

consistent with the reported results.^{36, 5} The encapsulated Li^+ ions should strengthen the π back-bonding from the transition-metal centre to the fullerene cage;⁵ however, the Cu ions do not coordinate with the rings of the six-carbon (pink atoms in Figure 1b) owing to the highly symmetrical array of the four Cu ions. The benzene ring of the ligand is distorted (Figure S2), and the bond patterns indicate the loss of aromaticity (Figure 1c). On the other hand, the hexane molecules are trapped inside the squared structure of $[\text{Cu}_2(\text{L})(\text{py})_3(\text{Li}^+@C_{60})]_2$ and strongly disordered along two lines (Figure S3). Close to the square structure, the NTf_2^- molecules interact electrostatically with ligands through hydrogen bonds. Inside the ladder chain, the $\pi \cdots \pi$ distance (r_π) between the two $\text{Li}^+@C_{60}$ cages is 6.5 Å (Figure 1d), indicating well-separated π electrons along the b -axis. The 1D ladder structures self-stack along the a -axis to form 2D interacting nanosheets with r_π of 3.19 Å (Figure 1e). Finally, the 3D electronic framework is established by a number of hydrogen bonds in the bc plane and strong $\pi \cdots \pi$ interactions along the a -axis (Figure 2).

Figure 1. Crystal structure of 1. **a**, Thermal ellipsoid drawing of the unit-cell crystal structure at 120 K. One $\text{Li}^+@C_{60}$ cage coordinates with four $\text{Cu}_2(\text{L})(\text{py})_3$ via Cu–C bonds. The Cu-ion coordination number is five. The NTf_2^- anion locates at the unit-cell corner; the hexane molecule is disordered and locates near the fullerene cage. **b**, Coordination environment of $[\text{Cu}(\text{N})_3]_4(\text{Li}^+@C_{60})$, with coordinated bond lengths and distances between Cu ions, units of $\text{\AA}$. **c**, Bond patterns of $\text{Cu}_2(\text{L})$. **d**, 1D ladder-like structure along the *b*-axis in the *bc* plane (anion NTf_2^- and hexane molecules are omitted). One $\text{Li}^+@C_{60}$ cage coordinates with four Cu ions, and the remaining four-terminal Cu ions coordinate with the adjacent $\text{Li}^+@C_{60}$ cage to form a 1D ladder-like structure. Distance r_π between adjacent $\text{Li}^+@C_{60}$ cages is $6.5 \text{ \AA}$. The Li atoms are off-centred and polarised above/below the Cu plane. **e**, Top view of the 1D ladder-like structure in the *ac* plane. Each structure stacks along the *a*-axis to form a 2D interacting sheet with intermolecular distance $= 3.19 \text{ \AA}$ between two $\text{Li}^+@C_{60}$ cages. Colour code: Cu (blue), sulphur (yellow), oxygen (red), nitrogen (pastel cyan), carbon (black/pink in Figures b, d, and e). Hydrogen atoms are omitted for clarity.

Figure 2. Packing structure. Perspective view of packing structure of **1** along the *bc* plane. Counter anion NTf₂⁻ and hexane molecules are omitted for clarity. The arrows represent the spins of Cu²⁺ ions.

Spontaneous charge transfer between Cu₂(L)(py)₄ and (Li⁺@C₆₀)(NTf₂) by precise control of the redox-activities. Figure 3a shows the CV plot with respect to Fc/Fc⁺. Four reversible redox processes with the first and second oxidation potentials are observed at -0.36 and -0.04 V, respectively. Meanwhile, the first and second reduction potentials are observed at -0.92 and -1.08 V, respectively. The potential at -0.36 V corresponds to the first oxidation process of Cu₂(L)(py)₄ to [Cu₂(L)(py)₄]⁺. In this regard, Aoyagi et al. reported that the first reduction process from Li⁺@C₆₀ to Li⁺@C₆₀⁻ occurs at -0.39 eV in *o*-DCB versus Fc/Fc⁺.¹ Consequently, the HOMO energy level of Cu₂(L)(py)₄ can be simply treated as equivalent to the LUMO energy level of Li⁺@C₆₀ if the dissolution-free energy effect is ignored (Figure 3b). According to the Mulliken theory, ET from Cu₂(L)(py)₄

(donor) to $\text{Li}^+@C_{60}$ (acceptor) can spontaneously occur without external energy to generate a triplet ground state $[\text{Cu}_2(\text{L})(\text{py})_4]^+[\text{Li}^+@C_{60}^-]$. The solution-state absorption spectra in Figure 3c evidence this mechanism. $(\text{Li}^+@C_{60})(\text{NTf}_2)$ does not show any absorption band from 750–1500 nm whereas $\text{Cu}_2(\text{L})(\text{py})_4$ shows a strong and broad band at 920 nm. Once the two pristine molecules are mixed in *o*-DCB, two new bands at 886 and 1032 nm are observed, strongly indicating that $\text{Li}^+@C_{60}^-$ is generated.³⁷ Moreover, the strong band at 920 nm in $\text{Cu}_2(\text{L})(\text{py})_4$ vanishes from the mixed solution, strongly indicating ET occurrence. The solid-state absorption spectrum of **1** shows several broad absorption bands at 1.30, 1.91, 2.42, and 3.48 eV (Figure S4), where the band at 1.30 eV extends to the IR region (inset of Figure S4), which indicates that **1** has a small optical bandgap (E_g). Figure 3d shows the Tauc plot of the Kubelka–Munk-transformed spectrum, with $E_g = 0.57$ eV, as obtained from a linear fit to the low-energy onset of absorption. However, it is difficult to assign the $\text{Li}^+@C_{60}^-$ band owing to absorption-band superpositions. Nevertheless, the generated $\text{Li}^+@C_{60}^-$ can be detected by the EPR spectra. Figure 3e shows the temperature dependence of the EPR spectra of **1** for 3.5–300 K with all spectra showing two EPR active bands. At the lower magnetic field, parallel $g_{\parallel}$ values of 2.45(3), 2.32(1), and perpendicular $g_{\perp}$ value of 2.09(1) are observed at 300 K. The g values and peak-to-peak linewidth, $\Delta H_{\text{pp}} = 217.5(4)$ G, are entirely consistent with the Cu^{2+} ion ($S = 1/2$).^{38, 39} Another weak signal observed near the Cu^{2+} signal with $g = 2.0008(3)$ and $\Delta H_{\text{pp}} = 8.1(2)$ G, signifies the presence of electronically active $\text{Li}^+@C_{60}^-$ radical.^{40, 37, 3} However, it is difficult to assign significant interactions between Cu^{2+} ions and $\text{Li}^+@C_{60}^-$ radical

from the EPR spectra, probably owing to the superposition of the two characterised bands, but the spectra demonstrate that spontaneous ET occurs from $\text{Cu}_2\text{L}(\text{py})_4$ to $\text{Li}^+\text{@C}_{60}$ and **1** remains in a triplet ground state up to 3.5 K.

Figure 3. Spectroscopic spectra. **a**, Cyclic voltammogram (–2.0 V to 0.8 V versus Fc/Fc⁺) of $\text{Cu}_2\text{L}(\text{py})_4$ in *o*-DCB with 0.1 M TBAPF₆ as the supporting electrolyte. The pale blue dot at $E = -0.39$ eV represents the first reduction potential from $\text{Li}^+\text{@C}_{60}$ to $\text{Li}^+\text{@C}_{60}^-$. **b**, Schematic of charge transfer interactions of HOMO and LUMO orbital energies between $\text{Cu}_2\text{L}(\text{py})_4$ and $\text{Li}^+\text{@C}_{60}$ calculated from the cyclic voltammogram. The HOMO energy level of $\text{Cu}_2\text{L}(\text{py})_4$ is identical to the LUMO energy level of $\text{Li}^+\text{@C}_{60}$, indicating strong CT interactions. **c**, In-situ solution-state UV-Vis-NIR absorption spectra at room temperature. **d**, Tauc plot of room-temperature diffuse reflectance UV-vis-NIR spectra of **1** from 0.05 to 3.3 eV, obtained via Kubelka–Munk transforms ($F(R)$) for indirect allowed transition. The optical bandgap is determined as 0.57 eV by the linear fit (orange dots) of absorption onset in the NIR energy region. **e**, First-derivative solid-state X-band absorption EPR spectra of **1** for 3.5–300 K.

Electrical conductivity. The black colour of the single-crystals with metallic surfaces indicates that **1** could be electrically conductive. Figure 4 shows the temperature dependence of σ in the range of 250–300 K, obtained with a two-probe dc method. The σ value at 300 K is $(4.4\text{--}8.2) \times 10^{-5} \text{ S cm}^{-1}$ based on measuring several single-crystals. Parameter σ decreases with temperature reduction, indicating that **1** behaves as a semiconductor. The activation energy (E_a) is determined to be 0.44 eV as per the Arrhenius function. To date, this is the first report on a $\text{Li}^+@C_{60}$ -based conductive coordination polymer with a small energy gap.

Figure 4. Temperature dependence of σ of **1.** Temperature dependence of σ for single-crystals obtained by using a two-probe method in the range of 250–300 K.

$S = \frac{1}{2}$ heterospin frustration between Cu^{2+} and $\text{Li}^+@C_{60}^-$ in the ladder-like chains. The intensity of main peaks in the EPR spectra mimics the thermal dependence of the magnetic susceptibility (χ). The χ – T plot of **1** does not show any magnetic phase transition from 1.8 to 300 K under 1 T (Figure 5a) and 4 T fields

(Figure S5), thereby indicating no long-range magnetic ordering. In addition, no sign of a spin-glass state is observed in the rectangular Cu lattices, as there is no deviation between the zero-field-cooled (ZFC) and field-cooled (FC) measurements. This suggests that $\text{Li}^+@\text{C}_{60}^-$ radicals are involved in the magnetic reactions. Fitting the χ^{-1} to the Curie–Weiss law at high temperatures ($T > 175$ K) yields a large negative Curie–Weiss temperature, $\theta_{\text{cw}} = -305$ K (inset of Figure 5a), suggesting strong antiferromagnetic (AF) interactions between the spins. Even the fitted low-temperature χ^{-1} ($T = 1.8\text{--}10$ K) results in a $\theta_{\text{cw}} = -1.8$ K, indicating significant AF interactions. The χT value at 300 K is $1.836 \text{ cm}^3 \text{ K mol}^{-1}$ (Figure S6), which follows the theoretical prediction of four Cu^{2+} ions and one $\text{Li}^+@\text{C}_{60}^-$ radical per unit ($\chi T_{\text{calc}} = 0.375 \times 5 = 1.875 \text{ cm}^3 \text{ K mol}^{-1}$). The rapid decrease in χT with temperature reduction indicates that AF exchange interactions are dominant. In addition, the magnetic-field dependence of magnetisation from 1.8–300 K does not show any visible hysteresis loops (Figure 5b).

To elucidate such strong exchange coupling in **1**, we consider Figure 5c and Figure 2, which show the spin arrangements in a ladder-like structure with four Cu^{2+} ions positioned at the corner of the rectangular plane and one $\text{Li}^+@\text{C}_{60}^-$ at the centre. In this magnetic pattern, owing to symmetry, one Cu^{2+} ion magnetically interacts with three adjacent Cu^{2+} ions (J_{12} , J_{13} , J_{23} , and J_{14}), which are magnetically linked by the $\text{Li}^+@\text{C}_{60}^-$ radical (J_{12} , J_{13} and J_{23}) and ligand (J_{14}). Moreover, the Cu^{2+} ion interacts with $\text{Li}^+@\text{C}_{60}^-$ ($J_{\text{Cu-C}_{60}}$) via Cu–C bonds and the central $\text{Li}^+@\text{C}_{60}^-$ interacts with the adjacent $\text{Li}^+@\text{C}_{60}^-$ via $\pi \cdots \pi$ stacking (a -axis). Such complicated and competitive

interactions lead to a magnetically frustrated ground state. To obtain the J values, we calculated spin Hamiltonian $\hat{H}$ and eigenvalues E using equations (1) and (2), respectively, by considering the possible exchange coupling:

$$S_T = S_{Cu1} + S_{Cu2} + S_{Cu3} + S_{Cu4} + S_{C_{60}}, S_{1234} = S_{Cu1} + S_{Cu2} + S_{Cu3} + S_{Cu4}, S_{12C_{60}} = S_{Cu1} + S_{Cu2} + S_{C_{60}}, S_{C_{60}C_{60}^-} = S_{C_{60}} + S_{C_{60}^-}.$$

$$\hat{H} = -2J(\hat{S}_{Cu1} \cdot \hat{S}_{Cu2} + \hat{S}_{Cu1} \cdot \hat{S}_{Cu3} + \hat{S}_{Cu1} \cdot \hat{S}_{Cu4} + \hat{S}_{Cu2} \cdot \hat{S}_{Cu3}) - 2J_{Cu-C_{60}}(\hat{S}_{Cu} \cdot \hat{S}_{C_{60}}) - 2J_{C_{60}^-C_{60}}(\hat{S}_{C_{60}} \cdot \hat{S}_{C_{60}^-}) \quad (1)$$

$$E = -J[(S_T(S_T + 1) - S_{1234}(S_{1234} + 1) - S_{12C_{60}}(S_{12C_{60}} + 1) - S_{C_{60}^-C_{60}}(S_{C_{60}^-C_{60}} + 1))] - J_{1234}[S_{1234}(S_{1234} + 1)] - J_{12C_{60}}[S_{12C_{60}}(S_{12C_{60}} + 1)] - J_{C_{60}C_{60}^-}[S_{C_{60}C_{60}^-}(S_{C_{60}C_{60}^-} + 1)] - J_{23}[S_{23}(S_{23} + 1)] \quad (2)$$

The five effective exchange coupling parameters of $J_{12}/k_B = -191.5$ K, $J_{13}/k_B = -93.4$ K, $J_{14}/k_B = -23.5$ K, $J_{23}/k_B = +39.9$ K, and $J_{Cu-C_{60}}/k_B = -264.8$ K with $g_{Cu} = 2.48(2)$ were obtained after the best fit. The magnetic interactions are fairly anisotropic.

Similar J values can also be calculated via the mean-field solution with the equation:

$$\theta_{cw} = -nJS(S + 1)/3k_B, \text{ where } k_B \text{ denotes the Boltzmann constant and } n \text{ the}$$

coordination number. Assuming only the nearest-neighbouring exchange interactions

(J) of $n = 5$, we obtain $J/k_B = -248.9$ K, which is consistent with the fitted $J_{Cu-C_{60}}/k_B$

value. The negative J_{12} , J_{13} , and $J_{Cu-C_{60}}$ values confirm that any two neighbouring spins

are AF coupled. Therefore, in this rectangular spin lattice, composed of several

triangular lattices (such as $\Delta Cu_1 Cu_2 C_{60}^-$ and $\Delta Cu_1 Cu_3 C_{60}^-$), we can observe the five

spins exhibiting competing interactions. Frustration parameter⁴¹ $f = (-\theta_{cw}/T_N)$ is >168

($T_N < 1.8$ K), indicating that **1** has a highly frustrated ground state. Such a frustrated

lattice leads to inner Li^+ ions locating far away from the four coordinated Cu^{2+} ions.

Moreover, because of the pull forces from the eight external Cu–C bonds and six

internal Li–C bonds, the $\text{Li}^+@\text{C}_{60}$ cage is geometrically distorted with the diagonal lengths of 6.4 and 7.1 Å, respectively (Figure S7).

Figure 5. Magnetic properties. **a**, Temperature dependence of magnetic susceptibility product (χ) of **1** in FC, ZFC modes and the corresponding χ^{-1} – T plots (inset figure) under a 1 T field from 1.8–300 K. The black curve represents the best fit for χ by considering the possible exchange interaction between spins. The black dashed line represents the best fit by the Curie–Weiss law. A large negative $\theta_{\text{cw}} = -305$ K is observed, suggesting strong AF exchange interactions. **b**, Magnetic-field dependence of magnetisation of **1** at 1.8, 20, 50, and 300 K. There is no hysteresis loop at these temperatures. **c**, Spin orientations of the Cu^{2+} ions and $\text{Li}^+@\text{C}_{60}^-$ superatoms emerging in the 1D ladder-like magnetic chain; the four Cu ions and $\text{Li}^+@\text{C}_{60}^-$ superatoms are aligned in a triangular-like lattice and antiferromagnetically interact with each other.

Using generalised charge decomposition analysis (GCDA) method to understand

donor-acceptor bonded interactions. To further elucidate the electronic ground states, we first calculated the orbital energy for $\text{Cu}_2(\text{L})(\text{py})_4$ using the TD-DFT method. The calculated absorption spectrum coincides with the experimental data in the range of 300–1500 nm (Figure S8). The strong absorption band at 920 nm (1.35 eV) calculated at 820 nm (1.51 eV) is 100% attributed to ET from the HOMO (Figure 6a) to LUMO (Figure 6b). The electrons are predominantly located at both terminal Cu ions and the central ligand in the HOMO. Our calculations showed strong hybridisation with 58% $d_{xz}(\text{Cu})$ electron density and 25% $p_z(\text{N})$ electron densities, thus indicating that the electrons are delocalised in HOMO. Thus, the electron-intensive $d_{xz}(\text{Cu})$ orbitals are highly capable of donating electrons to the $\text{Li}^+@C_{60}$ cage through Cu–C bonds. The higher energy absorption band at 443 nm (2.80 eV) calculated at 402 nm (3.08 eV) is 78% assigned to ET from HOMO–1 to LUMO+1 (Figure S9).

Figure 6. Orbital calculations and generalised charge decomposition analysis (GCDA) for donor-acceptor

bonded interactions. a, HOMO of $\text{Cu}_2(\text{L})(\text{py})_4$. b, LUMO of $\text{Cu}_2(\text{L})(\text{py})_4$. c, Orbital interaction diagram and

molecular orbitals in α electron form. d, Orbital interaction diagram and molecular orbitals in β electron form. The

black solid lines and dotted lines represent the occupied and virtual orbitals, respectively. The orange and violet

lines represent the contribution to the HOMO and LUMO and other orbitals, respectively. The isovalue for the

electrons is set at 0.02.

To better understand the donor–acceptor bonding interactions, we used GCDA to investigate the electron-transfer amounts from $\text{Cu}_2\text{L}(\text{py})_3$ (by adding a pyridine molecule to the $\text{Cu}_2\text{L}(\text{py})_2$ molecule) to the $\text{Li}^+@C_{60}$ cage and the generation of complex orbitals by the fragments molecular orbitals in such an open-shell system.

Figure 6c and 6d show the calculated α and β forms of the orbital interaction

diagrams for the triplet $\text{Cu}_2\text{L}(\text{py})_3\text{Li}^+\text{@C}_{60}$ complex, respectively. The $[\text{Cu}_2\text{L}(\text{py})_3]^+$ fragment was assumed to be a doublet with a positive charge, and the other fragment ($\text{Li}^+\text{@C}_{60}^-$) contained an anionic radical in the C_{60} cage (doublet). We calculated the net CT value as $0.275e^-$ (Table S1) by estimating the difference between electron donation and back-donation between the fragments. The partial CT interactions can be understood as follows: each $\text{Cu}_2(\text{L})(\text{py})_3$ can only transfer $0.25e^-$ to the $\text{Li}^+\text{@C}_{60}$ cage as the $\text{Li}^+\text{@C}_{60}$ cage is coordinated with four $\text{Cu}_2(\text{L})(\text{py})_2$. Thus, the GCDA calculation shows good agreement with the CV and magnetic results. From Figure 6c, we note that the HOMO and LUMO of the complex are quite similar with an energy gap of 0.40 eV in the α form. The small bandgap is due to the significant contributions from HOMO of $\text{Li}^+\text{@C}_{60}$ and LUMO of $\text{Cu}_2(\text{L})(\text{py})_3$. The electron densities are mainly observed on the central ligand and the $\text{Li}^+\text{@C}_{60}$ cage. The HOMO of the complex originates from the mixture of 45% LUMO of $\text{Cu}_2\text{L}(\text{py})_3$ and 32% HOMO and 21% LUMO of $\text{Li}^+\text{@C}_{60}$; similarly, the LUMO is mixed with 52% $\text{Cu}_2\text{L}(\text{py})_3$ LUMO, 33% $\text{Li}^+\text{@C}_{60}$ HOMO, and 12% $\text{Li}^+\text{@C}_{60}$ LUMO. This result indicates that the electrons in the complex's HOMO are solely derived from the HOMO of $\text{Li}^+\text{@C}_{60}$; there is no electron contribution from the occupied $\text{Cu}_2\text{L}(\text{py})_3$ orbitals. Therefore, the complex's orbitals are not strongly mixed by fragments in the α form. In contrast, β electrons exhibit a deeper frontier orbital toward α electrons, indicating that β electrons are more electronically stable. Figure 6d shows that the frontier occupied orbitals of the complex in β form are doubly degenerated, indicating the significant contributions of fullerene orbitals. The electrons in the complex's

HOMO are mainly delocalised on the $\text{Li}^+@C_{60}$ cage and a small fraction in the d_{xz} orbital of Cu ions, and these electrons originate from 11% HOMO, 4% HOMO–1 (Figure S10), 2% HOMO–2 (Figure S11) of $\text{Cu}_2\text{L}(\text{py})_3$, 29% HOMO, 5% HOMO–1 (Figure S12), and 42% HOMO–3 of $\text{Li}^+@C_{60}$. It is worth noting that a large number of delocalised d_{xz} electrons of Cu ions were observed in the HOMO of $\text{Cu}_2\text{L}(\text{py})_3$; however, the number diminished in the complex's HOMO. This result strongly suggests that electrons transferred from $\text{Cu}_2\text{L}(\text{py})_3$ to the $\text{Li}^+@C_{60}$ cage once Cu–C bonds were established. Thus, the bandgap is expected to be small because the orbital interactions between the fragments are strong. However, the calculated bandgap ($\Delta E = 1.17$ eV) is only slightly smaller than that of undoped $\text{Li}^+@C_{60}$ ($\Delta E \sim 1.5$ eV), which is probably caused by the strong onsite Coulomb interactions.

Conclusions

In summary, we succeeded in observing a conductive metal–fullerene-bonded framework with strong spin frustration, constructed by using redox-active $\text{Cu}_2(\text{L})(\text{py})_4$ and $\text{Li}^+@C_{60}$ molecules. Via the precise control of the redox-activities in each species, the chemical bonds between the dinuclear electronic donor and the 3D spherical $\text{Li}^+@C_{60}$ acceptor allow for an interesting $S = \frac{1}{2}$ spin lattice in a 1D ladder-like magnetic chain. The metal–fullerene bond accompanied by CT leads to a strong spin frustration ground state. Such a heterospin system is promising for the development of high-performance molecule-based spintronic devices and can aid in exploring new QSL candidates. Further studies in this direction aim to control the spin dynamics in a

triangular or kagomé network using $\text{Li}^+\text{@C}_{60}$ superatoms.

Methods

Experimental synthesis: A pure form of $(\text{Li}^+\text{@C}_{60})(\text{NTf}_2^-)$ was obtained from Idea International Co., Ltd. Sendai, Japan.

Synthesis of ligand (H_4L = 1,2,4,5-tetrakis(methanesulfonamido)benzene). H_4L was synthesised from the reaction of 1.0 mmol of 1,2,4,5-tetraaminobenzene and 4.0 mmol methylsulfonyl chloride in 40 mL pyridine, and the resulting dark brown solution was stirred continuously for 3 h and then quenched in 15% aq. HCl. The resulting pale brown solid was filtered, washed with distilled water (2×10 mL), and dried at 80°C overnight (yield: 72%). IR in attenuated total reflection (ATR) mode: $\nu(\text{N-H}) = 3250 \text{ cm}^{-1}$; $\nu(\text{CH}_3) = 2933 \text{ cm}^{-1}$; $\nu(\text{S=O}) = 1142 \text{ cm}^{-1}$.

Synthesis of $\text{Cu}_2(\text{L})(\text{py})_4$. 2.0 mmol $\text{Cu}(\text{acetate})_2$ solid was slowly added to 10 mL H_4L (1.0 mmol) pyridine solution under dry N_2 gas. The resulting pale brown suspension immediately turned into a clear deep-blue solution, which was subsequently stirred for 12 h. Black block-like crystals were obtained by diethyl ether slowly diffused into the above solution (yield: 81%). The crystal structure was determined via single-crystal X-ray diffraction analysis. CCDC number: 2039286.

*Synthesis of $\{[\text{Cu}_4(\text{Li}^+\text{@C}_{60})(\text{L})(\text{py})_4](\text{NTf}_2)(\text{hexane})\}_n$ (**1**).* This experiment was conducted in an argon-filled glovebox. First, 1.0 mg $(\text{Li}^+\text{@C}_{60})(\text{NTf}_2)$ was dissolved in 1 mL dry *o*-DCB, and the resulting pink solution was slowly added to 1.8 mg $\text{Cu}_2(\text{L})(\text{py})_4$ in 10.0 mL *o*-DCB solution. The molar ratio between $(\text{Li}^+\text{@C}_{60})(\text{NTf}_2)$

and $\text{Cu}_2(\text{L})(\text{py})_4$ was 1:2. The mixture solution immediately turned dark brown. It was stirred for 3 h, after which the solution was filtered. Small shiny black crystals with a typical size of $0.04 \times 0.01 \times 0.001$ cm were obtained by slow diffusion with hexane in one week (yield: 33%). CCDC number: 2039740.

Physical characterisation: Single-crystal crystallographic data were collected at 120 K using a Rigaku Saturn 70 CCD diffractometer (Rigaku, Tokyo, Japan) with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) generated by a VariMax microfocus X-ray rotating anode source. The structures were solved by using Olex2 software.⁴² Cyclic voltammetry (CV) was performed using an ALS/HCH Model 620D electrochemical analyser. A glassy carbon (3 mm diameter) electrode was used as the working electrode, a Pt wire was used as the counter electrode, and an Ag/Ag^+ was used as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($\text{TBA} \cdot \text{PF}_6$) in dry *o*-DCB. The solid-state absorption spectra were acquired by compound **1** was embedded in KBr pellets with the use of a Shimadzu UV-3100PC instrument, and subsequently, the pellets were inserted into a transparent sealed cell and protected by argon gas. The solution-state absorption spectra were measured in a sealed plate tube filled with argon gas. The temperature dependence of the solid-state EPR spectra was examined by using the JEOL JES-FA100 device. Magnetic susceptibility measurements were conducted on a polycrystalline sample using a Quantum Design SQUID magnetometer (MPMS-7L). The magnetic susceptibility data were fitted by PHI software.⁴³ The temperature dependence of σ was measured on single-crystals via a two-probe method by using

the Quantum Design PPMS 6000 instrument.

Quantum chemical calculation: Geometry optimisation was performed by using density-functional theory (DFT) at the B3LYP/6-31G(d, p) level for pristine $\text{Cu}_2(\text{L})(\text{py})_4$. The absorption spectrum was calculated for the optimised geometry by using the TD-DFT method at the B3LYP/6-311G(d, p) level. The $\text{Cu}_2(\text{L})(\text{py})_3(\text{Li}^+@C_{60})$ complex was cut from the X-ray structure by adding one pyridine molecule as the terminal ligand, and the resulting structure was optimised by applying DFT at the UB3LYP/6-31G(d, p) level. The optimised structure was decomposed into two fragments, $[\text{Cu}_2(\text{L})(\text{py})_3]^+$ and $\text{Li}^+@C_{60}^-$, for single-point calculation. The generalised charge decomposition analysis (GCDA)⁴⁴ was used for the open-shell form of this complex and the two fragments by applying DFT at the UB3LYP/def2tzvp level. All calculations were performed using Gaussian 16 software,⁴⁵ and the output results were analysed using the Multiwfn program.^{44, 46}

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Additional information

The authors declare no competing interests. Supplementary information is available for this paper at www.nature.com/naturecommunications. Reprints and permission information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to Y.S.

Author contributions

Y.S. conceived and designed the project. Y.S. synthesised, characterised, and analysed

all compounds. M.C. measured the optical spectra. E.K., K.K., and Y.K. provided $(\text{Li}^+@C_{60})(\text{NTf}_2)$ salt. Y.S., T.Y., N.H., and T.A. measured the EPR spectra. Y.S. performed and analysed the GCDA and DT-DFT calculations. Y.S. wrote the paper with input from M.Y., S. T., T.T. and A.O.

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