Supplementary Text

Numerical calculation for the second moment of $^1$H NMR spectra

We calculated the $^1$H NMR spectra and estimated $\langle \Delta f^2 \rangle_m$, using the numerical method described in the Materials and Methods in the main text. Because the $^1$H NMR spectra at high temperatures above $T_{MI}$ is determined by the $^1$H-$^1$H nuclear dipolar interactions, the spectral shape is sensitive to the structural conformation of the ethylene end groups of ET molecule. Here we used the crystal structure of the isostructural sister compound $\kappa$-Hg-Cl at 100 K (25) because the low-temperature structure of the ethylene groups in $\kappa$-Hg-Br is not available. As 85% of the ethylene groups were reported to be frozen to the staggered conformation in $\kappa$-Hg-Cl at 100 K (25), we assumed the staggered conformation throughout the simulations. The total spectrum for an ET molecule consists of the 16 lines from the inequivalent four pairs of protons. We assumed the Gaussian shape $g(f)$, where the HWHM is given by $(\ln 2)^{1/2}s$ with the natural width $s$, and $I_n g(f - f_{n0})$, where $f_{n0}$ and $I_n$ are the central position and its intensity of line $n$ determined by Eqns. (5–8) and (9–12) in the Materials and Methods, respectively.
For $m_{\text{local}} = 0$, the spectral shape is determined solely by the dipole interactions between a pair of $^1$H nuclear spins and the natural width, $s$. Figure S1 compares the experimental spectra at 98.5 K in 6.00 T and the simulated spectra obtained for various $s$ values. The simulated spectra with a small value of $s$ have more than two peaks different from the experimental bell-shaped spectra very probably by the following reason. The present simulations consider only the dipolar interactions between the nearest-neighboring $^1$H nuclear spins to be simplified. The relative distance of nearest- and next-nearest-neighboring protons are 1.6 and 2.3 Å (25), respectively, and thus the next-nearest-neighboring and further $^1$H-$^1$H dipolar interactions should cause additional broadening. In reality, the broadening of $s = 10$ kHz gives the simple bell-shaped spectrum, which reproduces the experimental spectra. The simulated and experimental values of $\langle \Delta f^2 \rangle^{1/2}$ are 16.5 and 14.4 kHz, respectively, which well coincide with each other. Note that the value of $s$ is irrelevant to the estimation of the local moment size because, as seen later, the value of $\langle \Delta f^2 \rangle_m^{1/2}$ is independent of $s$. Furthermore, we used the $\kappa$-Hg-Cl structure because the low-temperature structure of ethylene conformation in $\kappa$-Hg-Br was not known. If it is known, the simulation might be more improved to reproduce the experimental spectra.

Figure S2 shows the moment configurations considered in the present work. As representatives of the possible staggered moment configurations, we considered two simple colinear configurations where local moments point parallel ("AFM I" in Fig. S2B) and perpendicular ("AFM II" in Fig. S2C) to the applied magnetic field. We considered both the ferromagnetic (i) and antiferromagnetic (ii) interlayer configurations, because the sign of the interlayer interaction ("AFM II" in Fig. S2C) to the applied magnetic field. We considered both the ferromagnetic (i) and antiferromagnetic (ii) interlayer configurations, because the sign of the interlayer interaction depending on the compound (14) was not known in the present compound. For the configuration "AFM I", we approximated all the local moments to have the same $m_{\text{local}}$ for simplicity. For the configuration "AFM II" in Fig. S2C, we put the in-plane sublattice moments on the two inequivalent dimers in a layer, $m_1$ and $m_2$ as

$$m_1 = m_{\text{local}}(e_b \sin \theta + e'_c \cos \theta),$$

$$m_2 = m_{\text{local}}(e_b \sin(\theta + \pi) + e'_c \cos(\theta + \pi)),$$

where $e_b$ is the unit vector of $b$ axis and $e'_c$ is the unit vector of $c$ axis projected to the plane perpendicular to $a$ axis; $e_c = e_a \cos \beta + e'_c \sin \beta$ with the angle between $a$ and $c$ axes, $\beta = 90.266^\circ$ (25).

Figure S3A shows the calculated spectra varied with the local moment $m_{\text{local}}$ on an ET dimer for the AFM I-(i) configuration (Fig. S2B) for an example. The square root of the second moment of spectrum, $\langle \Delta f^2 \rangle^{1/2}$, is monotonically increase as $m_{\text{local}}$ increases (Fig. S3B). To evaluate the magnitudes of local moments in $\kappa$-Hg-Br with reference to the simulations, we calculated the coefficient, $a$, relating the linewidth $\langle \Delta f^2 \rangle_m^{1/2}$ and the size of the moment $m_{\text{local}}$ in the form of $\langle \Delta f^2 \rangle_m^{1/2} = am_{\text{local}}$ for each spin configuration; given the pattern of the spin configuration, the simulated $\langle \Delta f^2 \rangle_m^{1/2}$, determined by the second moment of the spectrum subtracted by that of the spectrum for $m_{\text{local}} = 0$, is proportional to the size of the local spin moments, $m_{\text{local}}$ (Fig. S3C).

The values of $\langle \Delta f^2 \rangle_m^{1/2}$ are independent on $s$ as seen in Fig. S3C, where the results obtained using the delta function as $g(f)$ ($s = 0$ kHz in Fig. S3C) are also plotted, and are in a perfect agreement with the standard deviation of $\gamma \delta H_f$ for eight protons in an ET molecule.

We also did simulations for the possible case with intradimer spin density imbalanced. Table S1 summarizes the values of $a$ estimated for each configuration.
Recovery curves of $^1$H nuclear magnetization

Figure S4A shows the recovery curves of $^1$H nuclear magnetization measured at various temperatures below $T_{MI}$ in a magnetic field of 6.00 T. The recovery curves show bending at low temperatures, indicating the developing inhomogeneity in the nuclear spin lattice relaxation rate $1/T_1$, most visible around 7–10 K. To compare the bending nature of the recovery curves at different temperatures, we plot the relaxation curve of $1 - M(t)/M(\infty)$ versus $t/T_1$ at 6 T for different temperatures in Fig. S4B, where $t/T_1$ is a time normalized to $T_1$ determined by the fit to the data of $1 - M(t)/M(\infty)$ with the Kohlrausch function, $\exp[-(t/T_1)^\beta]$, with the exponent $\beta$ characterizing the degree of inhomogeneity (see also Fig. 6A). At high temperatures, the relaxation curve is close to the single exponential function, $1 - M(t)/M(\infty) = \exp(t/T_1)$, as expected for a homogeneous relaxation. On cooling, the recovery curves gradually deviate from the single exponential function and approach the form, $1 - M(t)/M(\infty) = \exp[-(t/T_1)^{0.5}]$. Figures S4C, S4D and S4E show the results for the applied magnetic fields of 3.66, 1.00 and 0.30 T, respectively. In each magnetic field, the temperature dependence of the recovery curve is similar to those in 6.00 T, as seen in that of $\beta$ in Fig. 6A.

BPP analysis

Using $1/T_1$ around $T_{peak}$, we fitted Eq. (1) in the main text:

$$\frac{1}{T_1} \sim \gamma^2 \hbar^2 \frac{\tau_c(T)}{1 + (2\pi f_0)^2 \tau_c(T)^2}$$

as well as Eq. (2) in the main text:

$$\frac{1}{T_1} = \int_{-\infty}^{+\infty} \langle H_{loc}(0) H_{loc}(\tau) \rangle \cos(2\pi f_0 \tau) d\tau$$

with the expanded exponential correlation function $\langle H_{loc}(0) H_{loc}(\tau) \rangle \propto \exp[-(|\tau|/\tau_c)^\alpha]$ (38, 39), which is identical to Eqn. (1) in the $\alpha = 1$ limit. In both cases, we assumed the Arrhenius-type correlation time $\tau_c$ in the form of $\tau_c = \tau_0 \exp(E_a/k_BT)$, where $\tau_0$, $E_a$, $k_B$ and $T$ denote the correlation time in a high-temperature limit, activation energy, Boltzmann constant and temperature, respectively. The best fits for each magnetic field are shown in Figs. S5A–S5D. The $1/T_1$ measured in different magnetic fields are reproduced well especially at temperatures above $T_{peak}$ and appear reproduced better in a wide temperature range if the expanded BPP model is employed. The best fitting parameters are summarized in Figs. S5E–S5G. Both fittings yielded similar field (frequency) dependence of $\gamma \sqrt{\hbar^2}$ and $E_a$. The activation energy $E_a$ obtained by the fitting is in the range of 20–80 K and 40–100 K for the BPP and expanded BPP models, respectively. Remarkably, in either case, $E_a$ is larger by one order of magnitude than the Zeeman energy and decreases as the applied field strength increases. These results strongly indicate that the magnetic slowing down in $\kappa$-Hg-Br is rather intrinsic, unlikely originating from impurity or isolated spins.

Sample dependence of the results of dc magnetic susceptibility and $^1$H NMR measurements

We measured the temperature dependences of $M/H$ for different samples: (#1) a single crystal weighing 0.31 mg (used for the $^1$H NMR measurements described in the main text),
an assembly of four pieces of single crystals weighing 2.06 mg in total (used for the dc magnetization measurements described in the main text),

an assembly of several tens pieces of single crystals weighing 12.56 mg in total (used for the ac magnetization measurements described in the main text)

a single crystal weighing 0.98 mg picked up from #2, all of which were synthesized in Chernoglova. In the samples #2 and #4, the central double-bonded carbons in the ET molecule are enriched by $^{13}C$ isotopes (Fig. 1C).

As seen in Fig. S6, the temperature dependence of $M/H$ in applied fields of 1.00 and 0.10 T nearly parallel to $a$-axis is nearly reproduced by all the above samples.

We conducted $^1H$ NMR measurements on another single crystal (#5) (Fig. S7). The sample #5 was too small to measure its weight but its volume was ~2% of that of the crystal #1. The low-temperature spectrum of #5 (Fig. S7A) shares the feature of #1 in that both are continuous and broad indicating the inhomogeneities in local fields. Although the detail of the spectral shape is slightly different, the temperature dependence of $\langle \Delta f^2 \rangle^{1/2}$ for #5 is in good agreement with that for #1 as shown in Fig. S7B. The relaxation rate, $1/T_1$, also makes no meaningful difference between samples #1 and #5.

As described above, we did not find significant sample dependence in the dc magnetic susceptibilities and $^1H$ NMR results of the crystals used in the present work.

**Field-cooled and zero-field-cooled dc magnetic susceptibility and cooling-rate dependence**

Figure S8 shows the temperature dependence of dc magnetic susceptibility $M/H$ of the samples #2 (Figs. S8A and S8B) and #3 (Figs. S8C and S8D) measured in 1.00 T (Figs. S8A and S8C) and 0.10 T (Figs. S8B and S8D). In either sample, the field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities showed no meaningful differences in both magnetic fields of 1.00 and 0.10 T although $M/H$ at low temperatures below ~40 K in 1.00 T measured in slow cooling at 0.02 K/min are slightly larger by < 15% than $M/H$ measured in cooling at 0.2 K/min.

**DC magnetic susceptibility above and below the metal-insulator transition at $T_{MI}$**

The dc magnetic susceptibility shows an abrupt increase on cooling across $T_{MI}$. This has been recognized as a jump in the paramagnetic susceptibility, not an appearance of a spontaneous magnetization. We confirmed this by measuring the $M-H$ curves of the samples #2 and #3 at temperatures above and below $T_{MI}$. Figs. S9A and S9B unambiguously demonstrate that the magnetization is linear to the applied field even in the zero-field limit above and below $T_{MI}$.

**Mean-field analysis of dc magnetization**

The present observations are reminiscent of the superparamagnetic systems (41–47), where spins form large clusters. In such cases, the Langevin description of magnetization $M(H, T)$ (41,42) is commonly used for characterizing the magnetic behavior. To analyze the present dc magnetization data from this point of view, we employed the Langevin function in the form of $M(T) = M_s L(\alpha)$, where

$$L(\alpha) = \coth(\alpha) - \frac{1}{\alpha}$$

with
\[ \alpha = \frac{\mu H}{k_B T} + 3 \frac{T_0}{T} M_s', \]

and fitted it to the \( M-T \) curves of the sample #2 below 80 K in Fig. 4. The parameters, \( \mu, M_s \) and \( T_0 \), denote the magnetic moment per cluster, saturation moment and mean-field Curie-Weiss temperature, respectively. The fitted results to the \( M(T) \) curves are displayed in Fig. S10 and those for the \( M(H) \) curves are shown in Fig. S11.

The fits to the \( M(T) \) data in magnetic fields of 6.00 and 3.66 T yield the average number of spins per cluster, \( N = \mu M_s \), of 52 and 75 spins/cluster, respectively. Below 20 K, the temperature dependence of magnetization slightly deviates from the Langevin curve probably because the present spin system remains paramagnetic even below the mean-field \( T_c \) (Fig. 5 and Fig. S10) unlike in the conventional superparamagnetic systems that show inhomogeneous ordering or freezing below \( T_c \). Such paramagnetic feature is more prominent in lower fields, where magnetization does not sufficiently grow. It may explain the anomalous field dependence of the resultant fitted values of \( \mu \) and \( M_s \), in the low field region (Fig. S10E). The fitting to the \( M(H) \) data was performed with the Langevin function of \( M(H) = \alpha \mathcal{L}(\alpha) \) with

\[ \alpha = \frac{\mu H}{k_B T}. \]

The resultant fitted values of \( \mu \) are strongly temperature-dependent (Fig. S11F), again pointing to the behavior out of the conventional superparamagnetism. However, at low temperatures where the moment is largely field-induced, the \( \mu \) and \( M_s \) values obtained for the sample 2 are consistent with those of the fitting to \( M(T) \) at high fields and yield the numbers of spins \( N \) of 57 and 86 spins/cluster for 2 K and 3 K, respectively, similar to the values obtained above. We also analyzed the \( M(H) \) of the sample #3 (Fig. S12); the \( N \) value was 52 spins/cluster for 1.8 K.

In summary, the whole data are not consistently explained by the model of superparamagnetism with fixed parameter values, suggesting that the present system is distinguished from the conventional superparamagnetic systems. However, at the high-field and low-temperature region where magnetization is largely induced by magnetic field, the fitting is roughly self-consistent. We consider that the high-field, low-temperature fittings capture the profile of spin clusters in the present system.

**Field-induced moments in the presence of the DM interaction**

To verify if the DM interaction explains the field-induced magnetism in \( \kappa-\text{Hg-Br} \), we simulated the uniform and staggered moments in the presence of the DM interaction under magnetic fields within the molecular-field theory, following Ref. (J2). We considered the \( S = 1/2 \) antiferromagnetic (AFM) Heisenberg model on a two-dimensional square lattice in the \( xy \) plane described by

\[ \mathcal{H} = J \sum_{\langle i,j \rangle} S_i \cdot S_j + g \mu_B \sum_i S_i \cdot H_i + \sum_{\langle i,j \rangle} D_{ij} \cdot (S_i \times S_j), \quad \text{(S3)} \]

where \( S_i \) and \( H_i \) are the spin operator and the external magnetic field at site \( i \), respectively. The nearest-neighbor exchange interaction and DM vector are denoted as \( J \) and \( D_{ij} \). If \( H_i = D_{ij} = 0 \), the system exhibits the Néel order with a wave-number vector of \( (\pi, \pi) \) to form the two sublattices, + and −, with the same magnitude of the moments. For simplicity, we assumed that \( D_{ij} \) is parallel to the \( z \)-axis. The uniform external magnetic field \( H(0) \) is set to be parallel to the \( y \)-axis.

The effective fields at the sublattices + and −, \( H_{c,\text{eff}} \) and \( H_{\text{eff}} \), are written as
\[
H^{\text{eff}}_{\pm} = -\frac{ZJ}{(g\mu_B)^2}(M_\pm) - \frac{Z}{(g\mu_B)^2}\langle M_\pm \rangle \times D + H_i,
\]

(S4)

\[
H^{\text{eff}} = -\frac{ZJ}{(g\mu_B)^2}(M_+) - \frac{Z}{(g\mu_B)^2} D \times \langle M_+ \rangle + H_i
\]

(S5)

with the number of nearest-neighboring sites \(Z = 4\), the DM vector \(D = (0, 0, -D)\), the external magnetic field \(H_i = (0, H(0), 0)\). Here \(\langle M_+ \rangle \) (\(\langle M_- \rangle\)) denotes the averaged moment of the sublattice + (−).

We obtained the molecular-field solutions by assuming \(\langle M_+ \rangle\| H^{\text{eff}} \rangle \) and \(\langle M_- \rangle\| H^{\text{eff}} \rangle \). Due to the presence of non-zero Zeeman and DM interactions, \(\langle M_+ \rangle \) and \(\langle M_- \rangle \) pointing in the \(xy\)-plane are not mutually parallel but symmetric across the y-axis. Below, we discuss the solutions using the basis of \(M(0) = \langle M_+ \rangle + \langle M_- \rangle \rangle/2\) and \(M(Q) = \langle M_+ \rangle - \langle M_- \rangle \rangle/2\), which represent uniform and staggered moments along the y- and x- axes, respectively.

Throughout the simulations, the exchange interaction was set to \(J = 8\) K so that it coincides the peak temperature in 1/\(T_1\). When \(H(0) = 0\), the non-zero \(M(Q)\) emerges below \(T_N \sim (J^2 + D^2)^{1/2}\) and \(M(0)\) also becomes finite below \(T_N\) only when \(D \neq 0\). In the non-zero \(H(0)\), \(M(0)\) seemingly follows the Curie-Weiss’ law in the nominal paramagnetic state at high temperatures for \(D \leq J\) (Figs. S13A–C). The apparent Weiss temperatures of the \(M(0)\) behavior in 40–60 K under 0.30 T for \(D = 0.08, 0.8\), and 8.0 K are \(\Theta_w = -8.0, -8.0\), and \(-2.4\) K, respectively. For a fixed \(D\) satisfying \(D \leq J\), the inverse of the uniform magnetic susceptibility, \(\{M(0)/H(0)\}^{-1}\) is less dependent on \(H(0)\) at high temperatures above \(-20\) K and the sign \(\Theta_w\) was always negative for \(H(0)\) up to 6.0 T. These numerical results qualitatively differ from the experimental behavior of uniform magnetic susceptibility showing a positive \(\Theta_w\) value of \(-20\) K (Fig. 4F), whereas both of the calculated staggered moment, \(M(Q)\), and the experimental local moment evaluated from \(\langle \Delta f^2 \rangle_{m}^{1/2}\) have a positive \(\Theta_w\) temperature (Figs. S13D–F and Fig. 4E). Thus, the observed behaviors of the uniform and staggered magnetizations cannot be coherently explained by the simple model including antiferromagnetic exchange interaction and the DM interaction.

Comparison of the \(^1H\) NMR data of \(\kappa-(ET)_2\)Hg(SCN)$_2$Br to other \(\kappa\)-type ET compounds

In this subsection, we compare the \(^1H\) NMR characteristics of \(\kappa\)-Hg-Br with those of a spin-glass system and an impurity- or defect-containing spin singlet system. \(\kappa\)-Cu-Cl is an antiferromagnet with a commensurate magnetic order as indicated by a discrete \(^1H\) NMR line splitting (inset of Fig. S14). It is known that X-ray irradiation to this system induces molecular defects and collapses the pristine AFM long-range order, resulting in a glassy spin-frozen state (57). The temperature dependences of the spectral width and relaxation rate, 1/\(T_1\), in \(\kappa\)-Hg-Br is quite different from those in the X-ray irradiated \(\kappa\)-Cu-Cl; the spectral broadening of \(\kappa\)-Hg-Br begins at much higher temperatures than the 1/\(T_1\) peak temperature whereas the spectral broadening of the X-ray irradiated \(\kappa\)-Cu-Cl begins nearly at the same temperature as the 1/\(T_1\) peak temperature (Fig. S14), as expected for conventional spin glasses. In addition, the 1/\(T_1\) peak value of \(\kappa\)-Hg-Br is two orders of magnitude larger than that of the X-ray irradiated \(\kappa\)-Cu-Cl, accentuating the enhanced moment fluctuations in \(\kappa\)-Hg-Br. The 1/\(T_1\) behavior of \(\kappa\)-Hg-Br is also distinct from the impurity-dominated 1/\(T_1\) behavior of the isostructural charge ordered insulator \(\kappa\)-Hg-Cl, which shows a peak in 1/\(T_1\) around 5 K, and it is considered to originate from impurities in a charge-ordered singlet background. The difference of the 1/\(T_1\) behavior between \(\kappa\)-Hg-Br and \(\kappa\)-Hg-Cl is obvious in its temperature profile and magnitude (the lower panel of
Fig. S14). Furthermore, as revealed by the BPP analysis described in an early subsection, the activation energy of $1/T_1$ for $\kappa$-Hg-Br is 40–100 K (Fig. S5F), which is far larger than the Zeeman energy for $S = 1/2$ whereas the activation energy in $\kappa$-Hg-Cl was reported to accord with the Zeeman energy (40). Thus, the NMR characteristics of $\kappa$-Hg-Br are qualitatively different from the spin-glass behavior and the impurity-dominated behavior observed in analogous systems.
Fig. S1. Simulation of $^1$H NMR spectra at high temperatures. Simulated spectra varied with the natural width $s$ and the experimentally obtained $^1$H NMR spectrum at 98.5 K in 6.00 T.
Fig. S2. Moment configurations for the simulations of $^1$H NMR spectra. Moment configurations considered in the spectral simulations in the present work. The solid line rectangles and dashed lines represent the unit cell and the glide $ac'$ plane, respectively.
Fig. S3. Simulation of $^1$H NMR spectra for AFM I configuration. (A) Simulated spectra for AFM I moment configuration using $\kappa$-Hg-Cl crystal structure (25). The intradimer spin-density disproportionation was assumed to be 0.5:0.5. (B, C) The $\langle \Delta f^2 \rangle^{1/2}$ (B) and $\langle \Delta f^2 \rangle_{m}^{1/2}$ (C) of the simulated spectra for various sizes of local moment, $m_{local}$. The “standard dev. of local fields” is the standard deviations of the hyperfine fields $\gamma\delta H_{ji}$ at the considered eight protons in an ET molecule.
Fig. S4. $^1$H nuclear magnetization recovery curves. (A) Recovery curves of $^1$H nuclear magnetization at various temperatures in the magnetic field of 6.00 T. The solid curves are the results of the fit of the Kohlrausch function to the entire recovery curve. (B–E) Recovery curves of the nuclear magnetization plotted against $t/T_1$ above 7 K in the fields of (B) 6.00, (C) 3.66, (D) 1.00 and (E) 0.30 T. The broken lines and solid curves represent the functions of $\exp(-t/T_1)$ and $\exp[-(t/T_1)^{0.5}]$, respectively.
Fig. S5. BPP analysis of $^1$H NMR nuclear spin-lattice relaxation. (A–D) The plots of $1/T_1$ versus inverse temperature, $1/T$. The broken and solid curves are the best fitted curves of Eqn. (1) and Eqn. (2) using the expanded exponential correlation function, respectively. The best fitted parameters are summarized in (E–G). The open squares and triangles are the results of the fits of Eqns. (1) and (2), respectively. In (E), the values of $\gamma \sqrt{\hbar^2}$ obtained from the analysis using the method described in the main text are plotted as closed circles.
Fig. S6. Sample dependence of dc magnetic susceptibility. Sample dependence of dc magnetic susceptibility $M/H$ measured in cooling in applied magnetic fields of (A) 1.00 and (B) 0.10 T nearly parallel to $a$-axis. The typical cooling rate was 0.2 K/min.
Fig. S7. **Sample dependence of $^1$H NMR spectra and relaxation rate.** Sample dependence of the results of $^1$H NMR for single crystals #1 and #5 in a magnetic field of 3.66 T applied nearly parallel to $a$-axis. (A) $^1$H NMR spectra at 5 K. (B) Square root of second moment of the spectrum, $\langle \Delta f^2 \rangle^{1/2}$. (C) Temperature dependence of $1/T_1$ obtained by the Kohlrausch fits to the recovery curves.
Fig. S8. Cooling-rate dependence of dc magnetic susceptibility under zero-field-cooled and field-cooled conditions. Temperature dependence of $M/H$ of the sample #2 [(A) and (B)] and #3 [(C) and (D)] measured in 1.00 T [(A) and (C)] and 0.10 T [(B) and (D)].
Fig. S9. DC magnetization versus magnetic field above and below the metal-insulator transition temperature. (A) $M$-$H$ curves of the sample #2 at 100 K and 80 K. (B) $M$-$H$ curves of the sample #3 at 100 K and 50 K.
Fig. S10. Fitting of a model of superparamagnetism to $M$-$T$ curves of the sample #2. The fits of the Langevin function of $M(T) = M_s \mathcal{L}(\alpha)$ to the $M$-$T$ curves of the sample #2 in Fig. 4 in the main text. The best fits are shown by the solid curves in (A–D). The fitted values for $M_s$, $\mu/\mu_B$ and $T_0$ for each applied magnetic field are plotted in (E) and (F).
Fig. S11. Fitting a model of superparamagnetism to $M$-$H$ curves of the sample #2. The fits of the Langevin function $M(H) = M_s \mathcal{L}(\alpha)$ to $M$-$H$ curves of the sample #2 in Fig. 4 in the main text. The best fits are shown by the solid curves in (A–E). The fitted values for $M_s$ and $\mu/\mu_B$ are plotted in (F).
Fig. S12. Fitting of a model of superparamagnetism to $M$-$H$ curves of the sample #3. The fits of the Langevin function $M(H) = M_s \mathcal{L}(\alpha)$ to $M$-$H$ curves of the sample #3. The best fits are shown by the solid curves in (A–F). The fitted values for $M_s$ and $\mu/\mu_B$ are plotted in (G).
Fig. S13. Mean-field calculations of magnetic-field-induced uniform and staggered moments of an antiferromagnetic Heisenberg model with the DM interaction. The plots of the inverse of the calculated uniform and staggered magnetization divided by the external magnetic field, (A–C) \([M(0)/H(0)]^{-1}\) and (D–F) \([M(Q)/H(0)]^{-1}\) versus temperature in various external magnetic fields in the presence of the DM interaction, respectively. The solid lines are the Curie-Weiss fits in the temperature range between 40 and 60 K.
Fig. S14. Comparison of $\kappa$-Hg-Br with a spin glass system, X-ray-irradiated $\kappa$-Cu-Cl, and an impurity-containing spin singlet system, $\kappa$-Hg-Cl, in $^1$H NMR characteristics.

Temperature dependences of $\langle \Delta f^2 \rangle^{1/2}$ (upper panel) and $1/T_1$ (lower panel) of $\kappa$-Hg-Br in 3.66 T (circles) and $\kappa$-Cu-Cl irradiated by X-ray for 50 hours in 3.7 T (triangles) are plotted. The inset compares $^1$H NMR spectra of the pristine $\kappa$-Cu-Cl at 10.3 K (9) (dotted curve), 50-hour X-ray irradiated $\kappa$-Cu-Cl at 9.94 K (57) (solid curve) and $\kappa$-Hg-Br at 10.6 K. The horizontal axis in the inset represents the frequency from the observation frequency, $f - f_0$, for each spectrum. The vertical broken lines represent the $1/T_1$ peak temperature, $T_{\text{peak}}$. In the lower panel, $1/T_1$ of $\kappa$-Hg-Cl at 2.64 T (40) is also plotted. The arrows indicate the metal-insulator transition temperatures in $\kappa$-Hg-Br and $\kappa$-Hg-Cl.
| Intradimer charge disproportionation | 0.5:0.5 | 0.8:0.2 |
|-------------------------------------|---------|---------|
| FM                                 | 194     | 259     |
| AFM I                              |         |         |
| I-(i)                              | 168     | 188     |
| I-(ii)                             | 133     | 162     |
| AFM II                             |         |         |
| II-(i)                             |         |         |
| $\theta_1 = 0^\circ$               | 253     | 270     |
| $\theta_1 = 90^\circ$              | 104     | 121     |
| II-(ii)                            |         |         |
| $\theta_1 = 0^\circ$               | 270     | 286     |
| $\theta_1 = 90^\circ$              | 108     | 124     |

Table S1. The coefficient $a$ in unit of kHz/$\mu_B$ per ET dimer calculated for the moment configurations shown in Fig. S2. The crystal structure of $\kappa$-Hg-Cl at 100 K (25) was used.