Supporting Information

Magnetic Ordering in Gold Nanoclusters

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1. Computational Details

The NWChem package is employed to simulate individual MPC, using Perdew-Burke-Ernzerhof (PBE), its hybrid PBE0 extension, or the hybrid B3LYP exchange-correlation (xc) functionals and a large basis set of triple-zeta-plus-polarization quality [Au/16s10p7d2f, C/5s3p2d1f, S/5s5p2d1f, H/3s1p], with spin-orbit coupling effects treated in the zeroth-order relativistic approximation (ZORA) within the van Wullen formalism. In the main text, orbital energies are reported as averages over \( \alpha/\beta \) (spin majority/minority) values. Given the order of magnitude of magnetic interactions in these computationally demanding systems, comparison with previous literature is in order, thus we have validated our numerical approach by comparing with the DFT/PBE results on the \( \text{Au}_{25}(\text{SCH}_3)_{18}^- \) anion. In the absence of SO coupling, our calculations predict two high-lying HOMO and HOMO-1 orbitals separated by 0.04 eV from a lower-lying HOMO-2 orbital; on a qualitative basis, this degeneracy breaking is in keeping with previous calculations. After introduction of SO coupling and crystal distortion, the HOMO-1 becomes lower in energy by 0.12 eV with respect to the HOMO, and the energy of HOMO-2 becomes lower than that of the HOMO-1 by 0.15 eV. As further consistency and accuracy tests, by performing DFT/PBE calculations on the \( \text{Au}_{25}(\text{SCH}_3)_{18}^0 \)-crystal model using the two plane-wave codes Abinit and Quantum Espresso, we found orbital-energy schemes with differences no larger than 0.02 eV with respect to that predicted by the homologous DFT/PBE NWChem calculations. It is worth noting that the SO coupling predicted by using the PBE xc-functional is 0.07 eV, which compares well with that predicted by the B3LYP xc-functional, i.e., 0.08 eV; the SO coupling in this system is thus robust with respect to the quality of the DFT description. The OPENMX package using the Local Density Approximation (LDA) was finally used to assess the effect of the transformation of \( \text{Au}_{25}(\text{SCPh})_{18}^0 \)-crystal into \( \text{Au}_{25}(\text{SCH}_3)_{18}^0 \)-crystal on the HOMO orbital energies. We find negligible changes, no larger than 0.01 eV (e.g., by including the SO coupling, the splitting of the HOMO/HOMO-1/HOMO-2 energies - cf Figure 9 - at the DFT/LDA level are 0.10 eV.
and 0.11 eV for the \(\text{Au}_{25}(\text{SCH}_3)_{18}^0\)-crystal model and 0.11 eV and 0.12 for the \(\text{Au}_{25}(\text{SC}2\text{Ph})_{18}^0\)-crystal model), which validates the use of the methyl-simplified model.

The OPENMX package\(^{S14}\) using the Local Density Approximation (LDA)\(^{S15}\) is also used in the solid-state non-spin-collinear calculations. In the periodic solid-state calculations on the \(\text{Au}_{25}(\text{SC}2\text{Ph})_{18}^0\)-crystal model there are 4 \(\text{Au}_{25}(\text{SC}2\text{Ph})_{18}^0\) MPCs and thus 1396 atoms in the unit cell. This system is very computationally demanding and thus only the LDA was affordable with our computational resources. We performed DFT non-spin-collinear calculations using the OPENMX code and the LDA xc-functional with the Ceperley-Alder parameterization.\(^{S15}\) SO coupling was incorporated through norm conserving j-dependent pseudo-potentials\(^{S16}\) and the orbital wave functions were expanded onto a linear combination of multiple pseudo-atomic orbital basis functions,\(^{S17}\) employing [2s,2p,2d] optimized radial functions for Au, [2s,2p] for S and C, and [1s] for H.

To provide further quantitative data on the spin delocalization in the solid state, we report that for the global minimum (z-axis) spin configuration (cf Figure 10) the atomic percentages of spin moment on the Au, S, C, and H atoms are 72.91, 22.84, 3.26, and 0.99, respectively, whereas the atomic percentages of spin moment on the Au, S, C, and H atoms are 62.58, 31.38, 4.65, and 1.39, respectively, for the local (x-axis) minimum, \(i.e.,\) somewhat larger values on the C and H atoms with respect to the global (z-axis) minimum.

2. EPR Simulations

Cw-EPR applied to paramagnetic systems is one of the most accurate ways to determine the g-tensor components that characterize the Zeeman interaction of the unpaired electron spins with the external field. Figure S3a shows the cw-EPR spectra of \(\text{Au}_{25}(\text{SC}2\text{Ph})_{18}^0\) in dichloromethane solution recorded at different temperatures, together with their simulations. The spectra were simulated by assuming a distribution of randomly oriented \(S = 1/2\) spin centers characterized by an anisotropic g-tensor \((g = 2.56, 2.36, 1.82)\) and an anisotropic hyperfine tensor \((71, 142, 50\ \text{MHz})\) with 13 magnetically
equivalent $^{197}$Au ($I = 3/2$) nuclei. A Lorentzian lineshape, with a peak-to-peak linewidth of 200 G, was used. Simulations were carried out using the EasySpin toolbox working on the MatLab 7.12 software platform.\textsuperscript{518}

In a conventional EPR spectrometer, the signal-to-noise ratio is improved greatly by the field modulation and the narrow-band amplification of the detected signal. Typically the resulting EPR signal is rectified and resembles the first derivative of an absorption line. The EPR signal can be integrated to obtain the corresponding EPR absorption spectrum, and further integration yields the so-called double integrated EPR intensity ($I_{\text{EPR}}$). The latter is proportional to the magnetic susceptibility $\chi_m$ of the sample therefore $I_{\text{EPR}}$ values obtained at different temperatures provide an experimental estimate of the temperature dependence of $\chi_m$.

Paramagnetism is a property exhibited by substances containing unpaired electrons. Paramagnetic susceptibilities, however, are dependent on temperature. To a first approximation, the susceptibility $\chi_m$ varies inversely with temperature according to the Curie Law. There are many situations in which the Curie law is not strictly obeyed. Sources of deviations can be the exchange and other inter-clusters dipole-dipole interactions. This behavior can be approximately expressed by a small modification of the Curie law, \textit{i.e.}, the Curie-Weiss law. Figure S3b shows the plot of $I_{\text{EPR}}^{-1}$ as a function of temperature for 2 mM Au$_{25}$(SC$_2$Ph)$_{18}$ in frozen dichloromethane solution. Calculations of $I_{\text{EPR}}$ values were carried out by performing the numerical integration of the EPR simulations (red traces in the Figure S3a) and calculating areas under the obtained EPR absorption spectra. Figure 1 and Figure 2 show the same analysis carried out for the Au$_{25}$(SC$_2$Ph)$_{18}$ amorphous film. In comparison with spectra of Au$_{25}$(SC$_2$Ph)$_{18}$ in frozen solution, the main spectral features of the Au$_{25}$(SC$_2$Ph)$_{18}$ film are similar, except for the requirement of including a Gaussian distribution for the y and z components of the $g$-tensor in the simulations. Other important differences can be noted. In particular, a less severe line broadening due to spin relaxation mechanisms is present in the film, as the EPR signals are still observable up to 160 K. Additionally and particularly important, a significant deviation from the Curie law is evident in the dependence of the $I_{\text{EPR}}^{-1}$ on
temperature (Figure 2). These analyses reveal that exchange and other inter-clusters dipole-dipole interaction effects can be sensitively detected by cw-EPR particularly by monitoring the spectral distribution of $g$ and the $I_{\text{EPR}}$ dependence on $T$.

To calculate the spectrum of the Au$_{25}$(SC$_2$Ph)$_{18}$ film, we wrote a code with Matlab. The Eigen energies were found by diagonalization of the Hamiltonian matrix (equation 3) at different fields corresponding to the experimental field values. The resonance fields were obtained, which are the fields that match the EPR resonance condition at the experimental frequency of ~9.4 GHz. Boltzmann populations were considered and Gaussian lineshapes were used with a linewidth of 4 G. Since the amorphous film consists of an ensemble of randomly oriented clusters, the spectrum was calculated by integration over all the possible orientations. The best fit was obtained using a $g_e$ value of 1.9, slightly lower than the usual 2.0023 value, and this attributed to a scalar relativistic mass effect. The initial values of the parameters used during the fitting process were taken from previously reported energy splitting values.$^{10}$ The lineshapes were best simulated by introducing a distribution of $D$ values ($D = 0.6 \pm 0.4$ eV), which is the equivalent of introducing a distribution of $g$ in the aforementioned simulations performed with the Easyspin routines. The spectrum of the monocrystal was simulated by using two Lorentzian lines, one with $g = 2.70$ and a linewidth of 50 G, and another with $g = 2.79$, a linewidth of 20 G and a slight inhomogeneous broadening due to $g$ distribution ($\pm 0.01$).
3. Figures

Figure S1. Images of the solid samples inside the EPR tubes: (a) film, (b) single crystal, (c) microcrystals, (d) collection of single crystals. For reference, the backgrounds are 1 mm graph papers. The single crystals were collected from those electrocrystallized on a 0.7 mm diameter gold-wire electrode (e).
Figure S2. cw-EPR spectra of \( \text{Au}_{25} (\text{SC2Ph})_{18} \) at 10 K. The red trace shows a 2 mM dichloromethane solution, whereas the blue trace pertains to the film. For the sake of better comparison, the spectra were corrected for the signal of the EPR cavity and normalized on the maximum intensity.
Figure S3. (a) cw-EPR spectra of 2 mM $\text{Au}_{25}(\text{SC2Ph})_{18}^0$ in dichloromethane (black traces) at different temperatures (K), and corresponding simulations (red traces). (b) Plot of $I_{\text{EPR}}^{-1}$ (inverse of the doubly integrated EPR signal) as a function of temperature.
Figure S4. cw-EPR spectrum (black) for a Au$_{25}$(SC2Ph)$_{18}^0$ single crystal at 10 K. The simulations correspond to: (red) two Lorentzian lines with $g$ factors of 2.79 and 2.70; (blue) $g = 2.79$; (green) $g = 2.70$. 
Figure S5. Hysteresis cw-EPR experiment for a Au$_{25}$(SC$_2$Ph)$_{18}$ single crystal at 10 K. The direction and trace color of the three scans are indicated.
Figure S6. Hysteresis cw-EPR experiments for a Au$_{25}$(SC2Ph)$_{18}$ single crystal in frozen MeCN at 5 K. Graph (a) and (b) were taken at 0 and 90° rotation of the EPR tube, respectively.
Figure S7. Temperature (K) effect on the cw-EPR spectrum of a group of 10 single crystals of Au$_{25}$(SC2Ph)$_{18}^0$. 
Figure S8. Temperature (K) effect on the cw-EPR spectrum of a group of 10 single crystals of $\text{Au}_{25}(\text{SC2Ph})_{18}^0$ immobilized by frozen acetonitrile.
Figure S9. Hysteresis cw-EPR experiment for a group of 10 single crystals of $\text{Au}_{25}(\text{SC2Ph})_{18}^0$ at 5 K. The direction and trace color of the three scans are indicated.
Figure S10. Hysteresis cw-EPR experiment for a group of 10 single crystals of Au$_{25}$(SC2Ph)$_{18}^0$ immobilized by frozen acetonitrile at 5 K. The direction and trace color of the three scans are indicated.
Figure S11. Example of the effect of the rest time on the hysteresis experiment carried out at 20 K for the Au_{25}(SC2Ph)_{18}^{0} microcrystals. The two downward scans correspond to 30 min (red) and 60 min rest time (blue) after the upward scan (black).
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