

SUPPLEMENTARY INFORMATION

Matrix effects on the magnetic properties of a molecular spin triangle embedded in a polymeric film

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Sample preparation and characterization

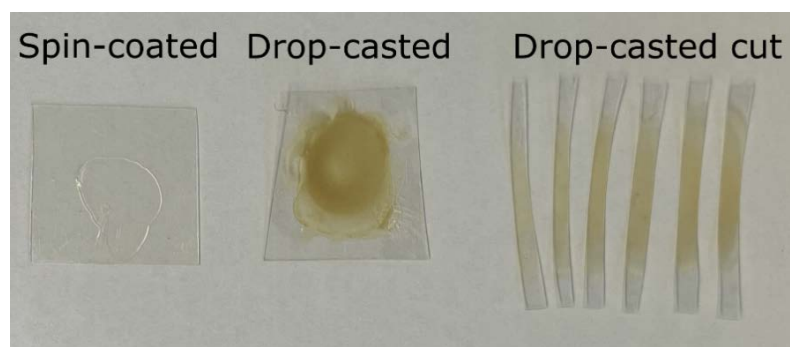


Figure S1. Examples of thin films produced by the different deposition methods: spin-coating and drop-casting. Both types of samples are deposited on a flexible substrate that can be easily cut into strips to fit the EPR tube.

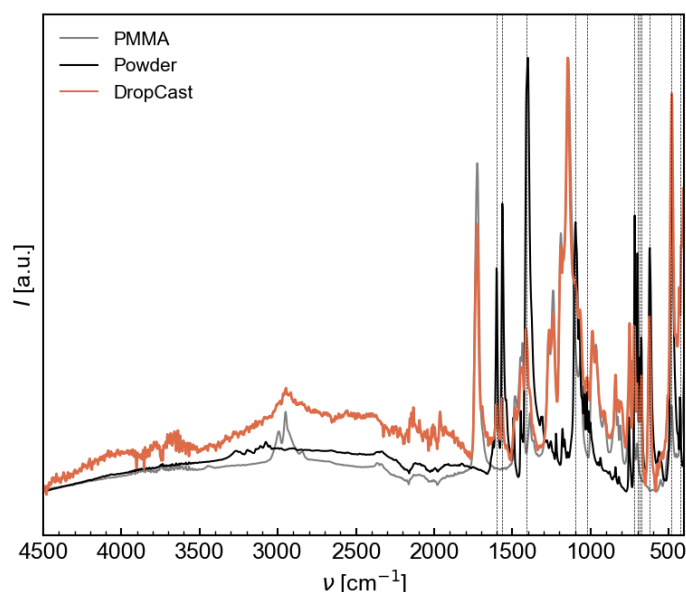


Figure S2. Fourier Transformed Infrared spectra for the pristine PMMA film, Fe_3 powder and drop-casted $\text{Fe}_3(10\%)$ sample in the full experimental spectral range.

Assignment of the $g \sim 1.97$ component

Preliminary attempts to include the $g \sim 1.97$ component in the g_{\perp} distribution intrinsic to Fe_3 were unsuccessful. Considering its g -value, it was then hypothesized to be related to a monomeric Cr^{III} impurity. The possibility for it to be the Cr^{III} analogue of Fe_3 was discarded, first considering the FTIR data, which evidenced the complete absence of absorption peaks at 650 cm^{-1} assigned to the $\nu_{\text{as}}[\text{Cr}_3\text{O}]$ asymmetric stretch,^[1] and second, considering complete absence of magnetic resonances at $g \sim 1.769$, typical of the Cr_3 complex.^[2] To assess the abundance of this component in the sample, it was simulated by a paramagnetic $S = 3/2$ species. Simulations revealed that this component (best-fit parameters: $g_z = 1.980$, $g_y = 1.972$, $g_x = 1.964$, $D = 0$, $\sigma = 9.68 \text{ mT}_{\text{pp}}$) corresponds roughly to 1% of the total spectral intensity, though this cannot be directly correlated to its actual fraction in the sample. Since the absolute value of the spectral intensity also depends on the spin-lattice relaxation rate, T_1^{-1} , which is much faster for exchange-coupled systems than for monomeric species, this value can only be considered as the ceiling of the minor component fraction, which is therefore expected to be significantly lower. If we also take into account the nuclearity of the Fe_3 complex, the minor component should be less than 0.3% of the total metal content. In conclusion, we assign this component to a minor Cr^{III} presence from the starting material.

Estimation of dipolar interactions

The probability $P(r)$ for an interparticle distance r (in \AA) was calculated by the relation $P(r) = 4\pi r^2 N_A c e^{-4\pi r^3 N_A c/3}$ where c is the concentration (in M), and N_A Avogadro's number.^[3,4] For $c = 0.0063 \text{ M}$, the interparticle distance distribution shown in Figure S3, has a mode of $\sim 34.5 \text{ \AA}$.

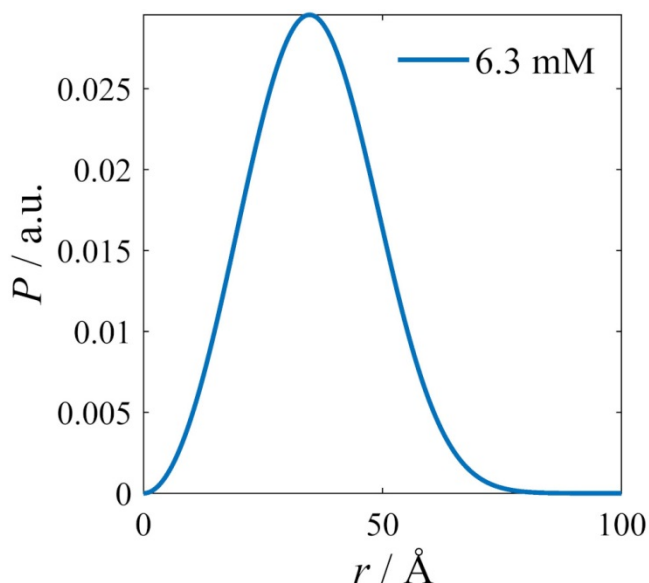


Figure S3. Distribution of interspin distances in the 10% PMMA film, assuming Poisson statistics. The mode of the distribution is 34.5 Å.

At these distances, dipolar couplings are too weak to cause a significant effect in line positions of CW EPR spectra (hence the need of pulse techniques to probe such distances). However, they do decrease the phase memory time, T_M through concentration-dependent mechanisms, leading to line broadening (see: Schweiger, Jeschke, *Principles of pulse electron paramagnetic resonance*, pp. 214-217). Actually, even in the powder sample, the closest intermolecular distances (12.25 Å) are at the limit of what can be detected by CW techniques. Hence, at these concentrations, we assign the spectral changes in the g_{\perp} region to direct interactions with the polymer matrix.

References

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