Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for:

A study of the role of the solvent during magnetite nanoparticle synthesis: tuning size, shape and self-assembly

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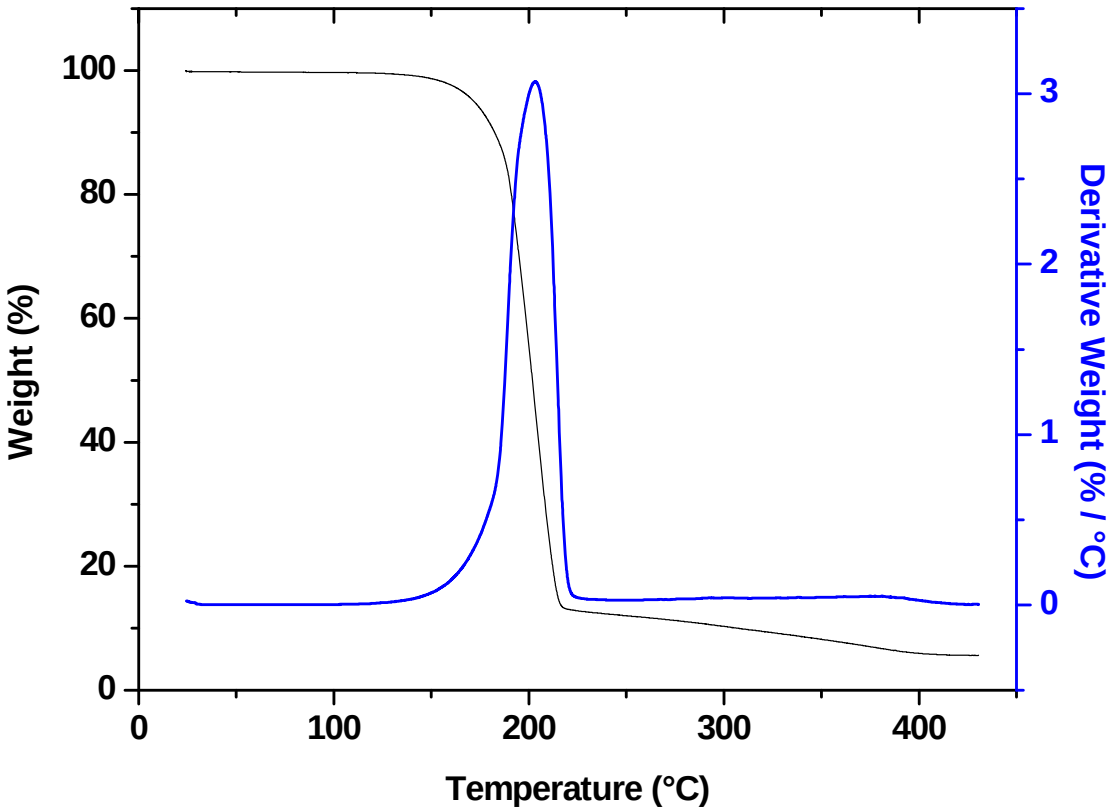

Figure S1. TGA decomposition curve for $Fe(acac)_3$. TGA can be used to determine the temperature at which a metal containing precursor decomposes, allowing for logical placements of heating steps in an experiment. The measurements were performed on a TGA Q500, with a 10 °C / min ramp rate under a N_2 atmosphere.

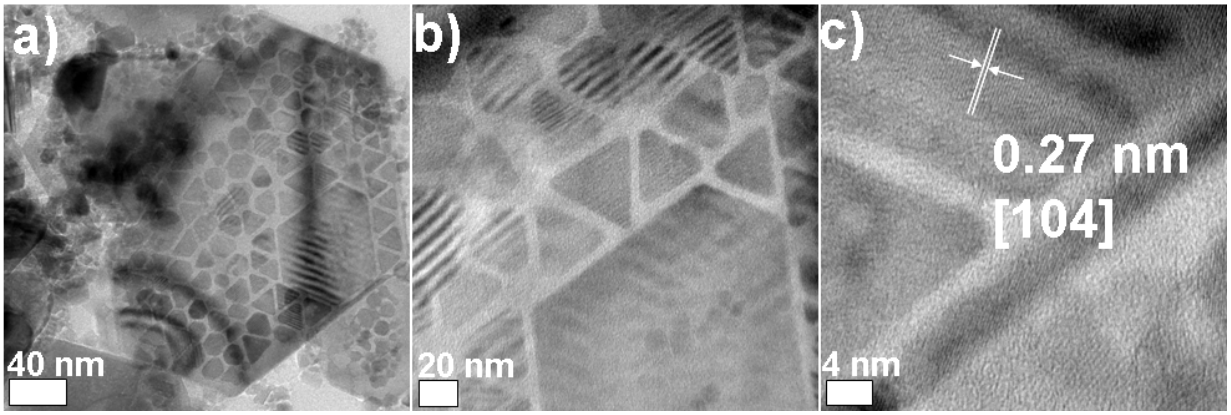

Figure S2. Additional TEM images from nanoparticle formation using benzyl ether, showing (a) a large hexagonal platelet, (b) alignment of smaller triangular particles underneath the platelet and (c) the fringe spacing at the particle edge, the distance 0.27 nm corresponding to α-Fe_2O_3 [104] reflections.

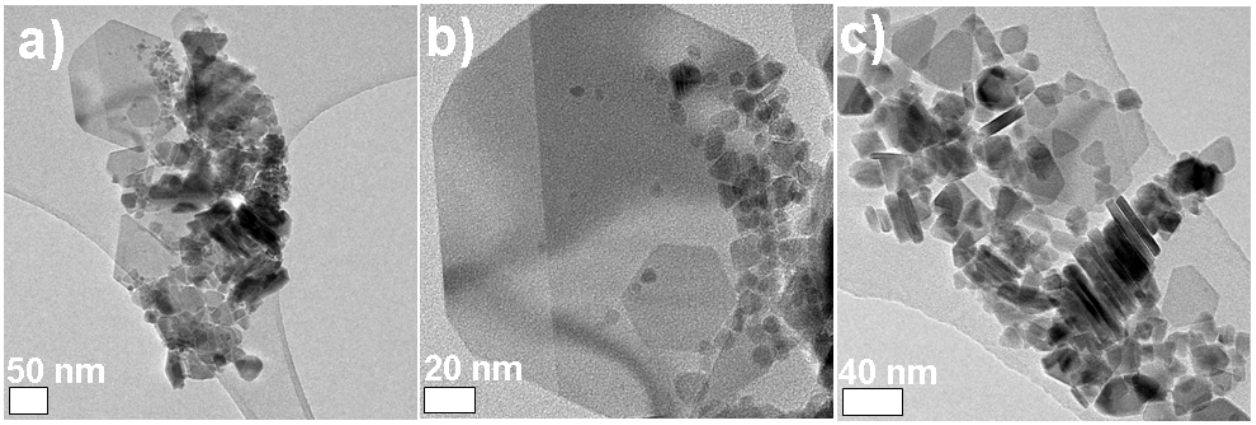

Figure S3. Non chelating solvents tend to yielded platelets, such as those derived using (a,b) dioctyl ether and (c) squalene.

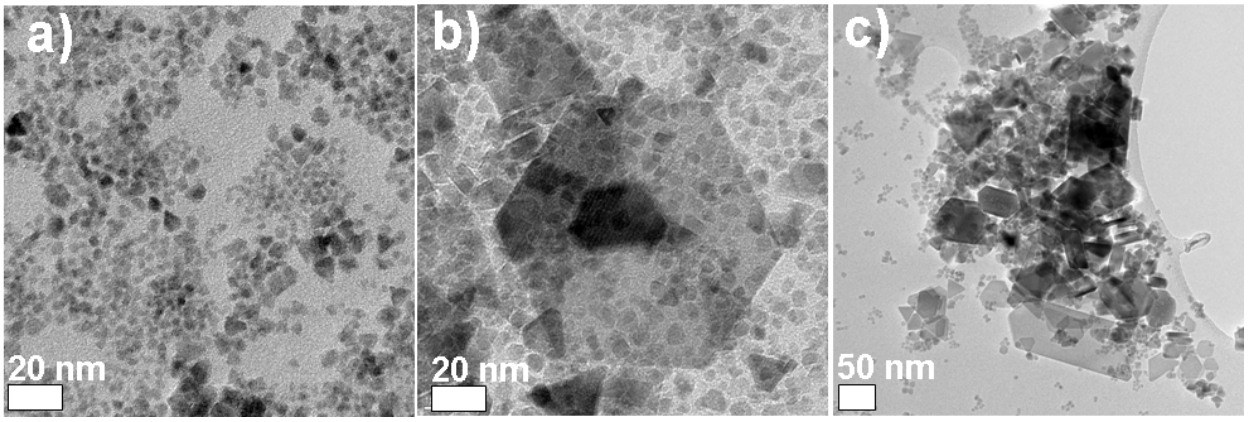

Figure S4. TEM images showing the evolution of platelets throughout a reaction that used benzyl ether as a solvent. Reaction times are (a) 30 minutes (b) 2 hours and (c) 6 hours.

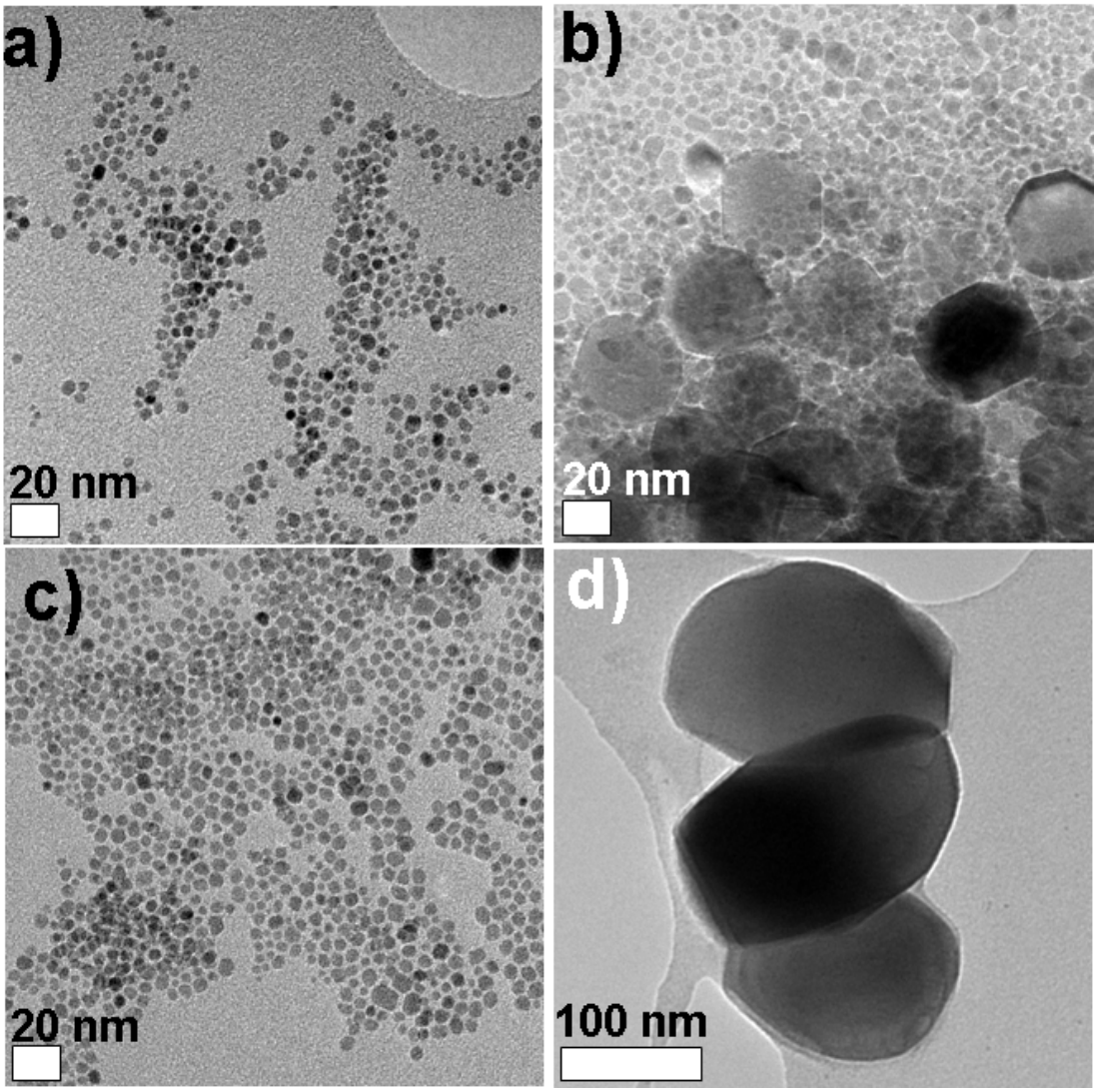

Figure S5. Additional TEM images from DEG reactions: (a,b) from the reaction without a heating step when the heating rate was slowed to 5 °C/minute. (c) Particles obtained using a 180 °C hold step, in comparison with (d) species obtained under reflux.

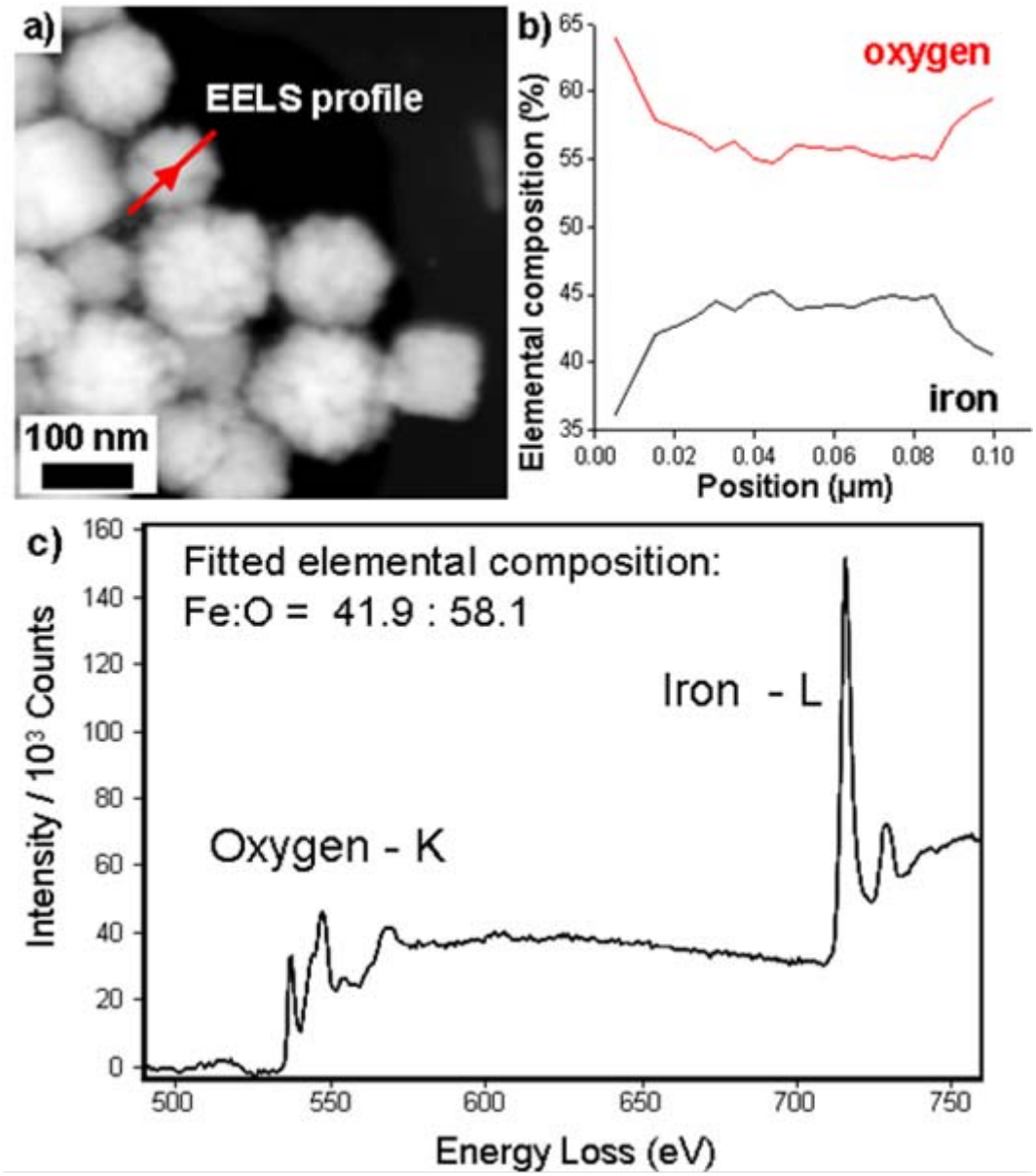

Figure S6.(a) Dark field STEM image showing line trace used for collection of EELS data. (b) Variation in elemental composition of particle indicated in (a) for different points across the particle. (c) The averaged EELS spectra from several points across the particle.

To perform the EELS analysis, measurements were taken at various points across a typical particle by scanning the electron beam across the NP.

The scan area comprised a line of 22 pixels with a 5 nm separation, giving a total scan length of 110 nm, chosen to encompass an entire particle. EELS spectra were collected at each pixel with a dwell time of 10 seconds. Automatic drift correction was performed automatically by the Digital Micrograph software after every 3rd pixel.

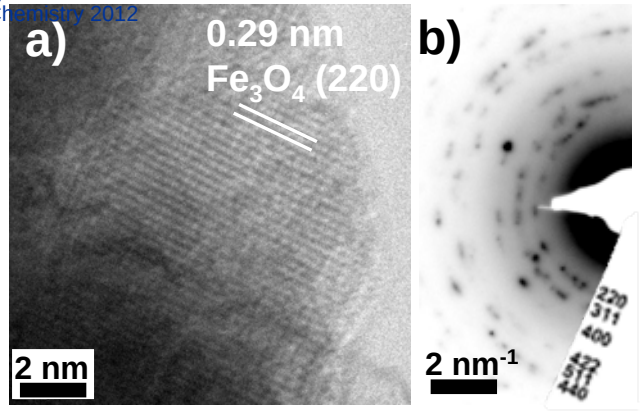

Figure S7. Additional a) TEM image and b) SAED diffraction pattern from the chain agglomerates shown in Fig. 2d) in the main text. The magnetite phase of the un-agglomerated cubes was retained upon assembly.

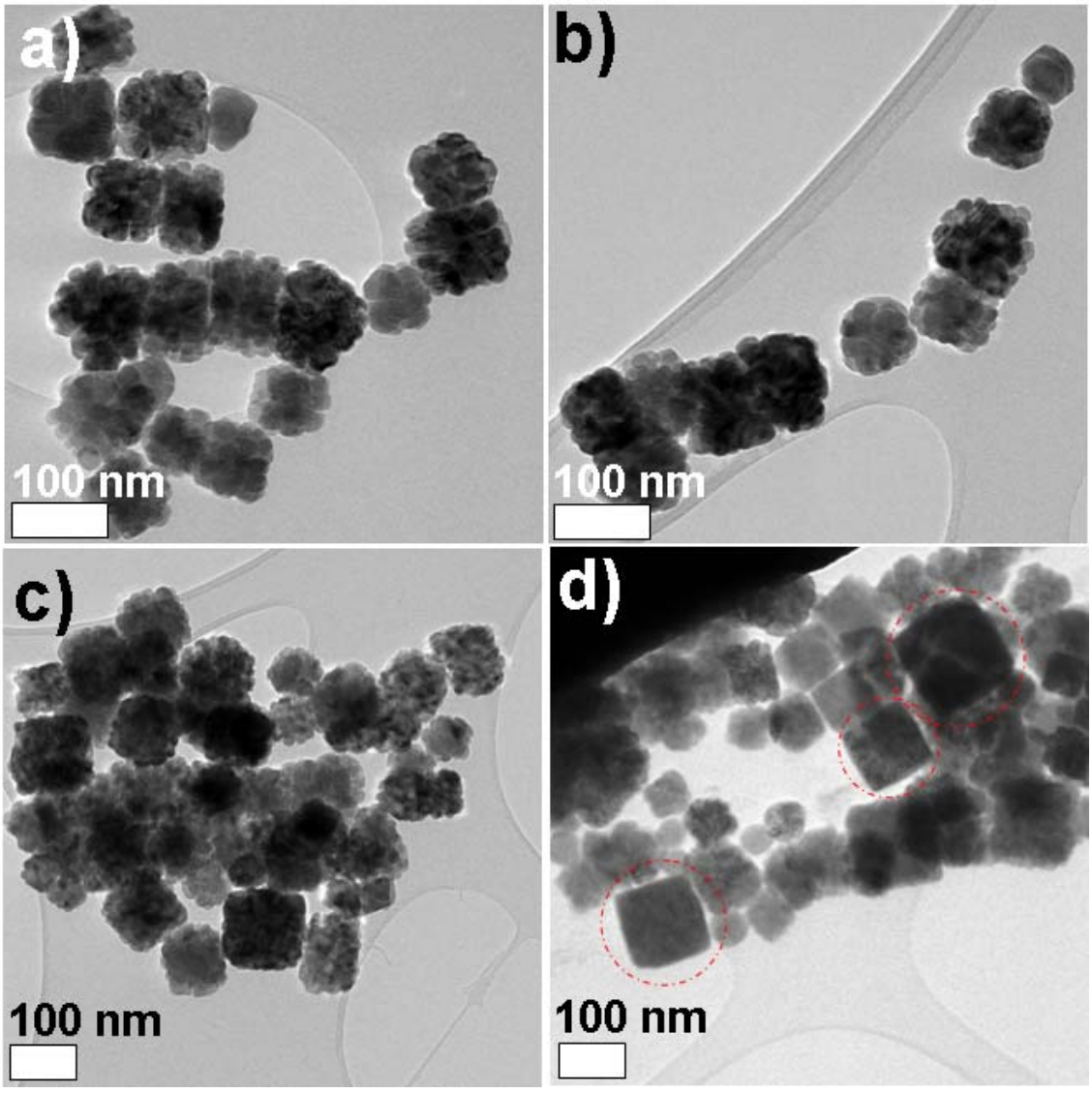

Figure S8. Additional TEM images from M-DEA reactions, showing the compound cubes obtained when the heating step was set to 180 °C. Although the majority of particles exist as compound cubes, some single crystalline cubes could also be seen (highlighted by red circles) (d). Single crystal cubes were present as a minority species, accounting for ~ 1% of the total cube population.

Magnetic data

Magnetic measurements were carried out at room temperature on a Lakeshore VSM magnetometer using the as-obtained powders.

Hysteresis curves and saturation magnetisations were recorded for samples in the case where no heating step was present (Figure S7). The bulk saturation value for magnetite is 96.4 emu/g [i].

Size dependence of the magnetisation in iron oxide nanoparticles has been observed before [ii] with smaller particles showing decreased saturation magnetisation values and small (or no) coercivity. The decrease in saturation magnetisation is believed to be due to the canting of surface spins, with the effect being more pronounced in smaller particles [iii]. The fact that our samples show saturation magnetisation close to the bulk value indicates that the size of our particles is approaching the limit expected for superparamagnetism, which can be explained by the presence of larger particles and compound particles seen for some of the solvents chosen.

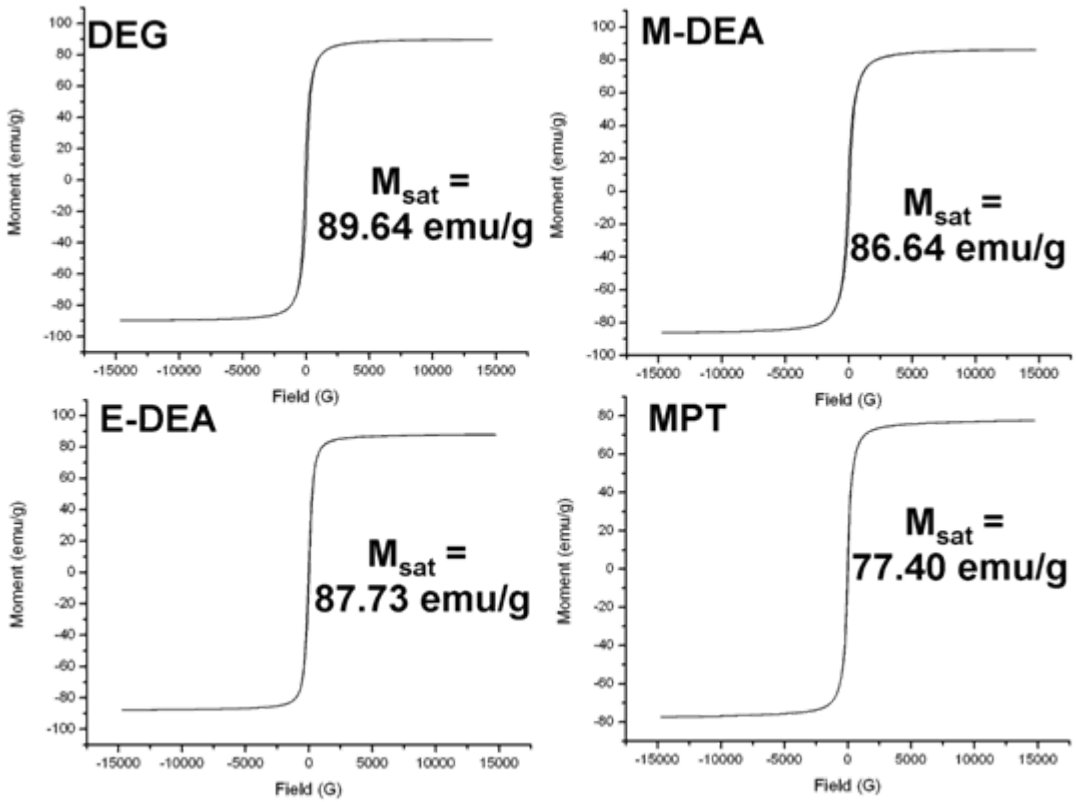

Figure S9. Hysteresis loops collected from nanoparticles synthesised using different solvents and without a heating hold-step.

[i] A. Angermann and J. Töpfer, *J. Mater. Sci.,* 2008, **43**, 5123.
[ii] Y. Jun, Y. Huh, J. Choi, J. Lee, H. Song, S. Kim, S. Yoon, K. Kim, J. Shin, J. Suh and J. Cheon, *J. Am. Chem. Soc.,* 2005, **127**, 5732.
[iii] M. P. Morales, S. Veintemillas-Verdaguer, M. I. Montero, C. J. Serna, A. Roig, L. Casas, B. Martínez and F. Sandiumenge, *Chem. Mater.,* 1999, **11**, 3058.