Supporting Information

The Dissociation Rate of Acetylacetonate Ligands Governs the Size of Ferrimagnetic Zinc Ferrite Nanocubes

Aidin Lak,[,†] Tamara Kahmann,[‡] Simon Jakob Schaper,[¶] Jaroslava Obel,[§] Frank Ludwig,[‡] Peter Müller-Buschbaum,[¶] Jan Lipfert[*,†]*

† Department of Physics and Center for NanoScience, LMU Munich, Amalienstr. 54, 80799 Munich, Germany

‡Institute for Electrical Measurement Science and Fundamental Electrical Engineering, Technische Universität Braunschweig, Hans-Sommer-Str. 66, 38106 Braunschweig, Germany

¶Lehrstuhl für Funktionelle Materialien, Physik-Department, Technische Universität München, James-Franck-Str. 1, 85748 Garching, Germany

§Department of Chemistry and Pharmacy, Analytical Division, LMU Munich, Butenandtstr. 5-13, 81377 Munich, Germany

E-mail: lak.aidin@physik.uni-muenchen.de; jan.lipfert@lmu.de

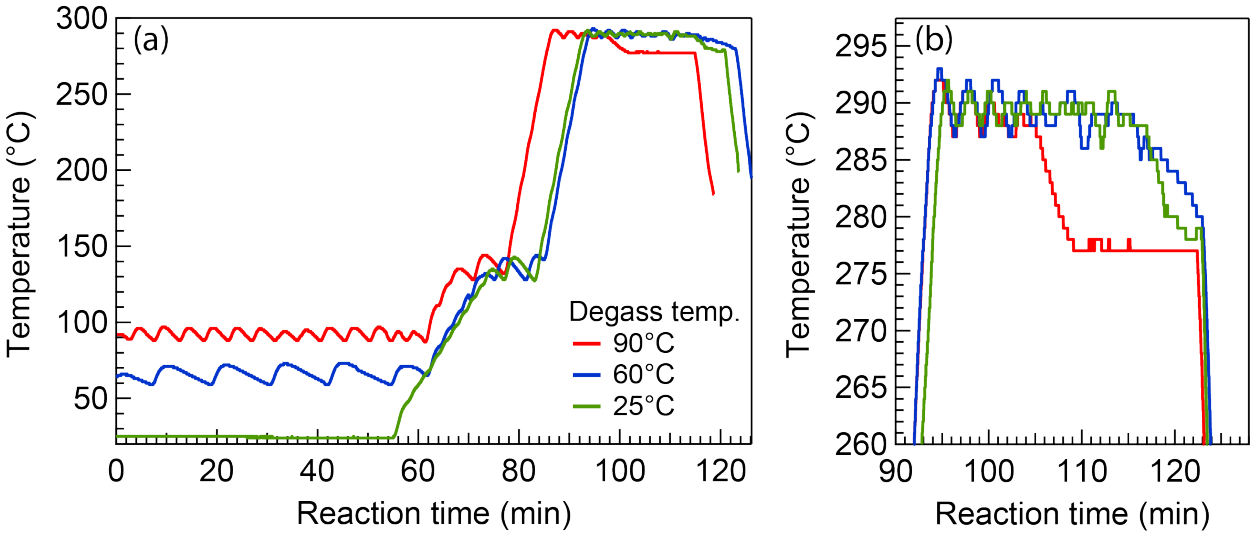

Figure S1. Recorded heating profiles for three particle synthesis reactions at three degassing temperatures. In (a) the profiles of the whole synthesis reaction are plotted and in (b) only a zoom in the reflux step is shown. The fluctuations in temperature are due to on/off temperature controller used. The reason that the synthesis reaction degassed at 90°C reaches 290°C earlier than other two reactions is because this reaction needs less time to reach the homogenizing step at 130°C, and therefore stays for a shorter time in the middle step.

Quantitative Rietveld crystal structure analysis. The Rietveld pattern refinement method has been applied to simulate XRD patterns. The tetrahedral and octahedral Wyckoff sites were assumed 8a (1/8,1/8,1/8) and 16d (1/2, 1/2, 1/2), respectively (ref. to table S1). The refinements were carried out using the FullProf Suite program. The Thompson-Cox-Hastings Pseudo-Voigt with an axial divergence asymmetry was selected as the peak shape. The background was set to a linear interpolation of background points which were obtained using the WinPLOTR software (FullProf package). The refined parameters were limited to the scale factor, the zero of detector, the crystal lattice constant *a*, the Wyckoff atomic position of oxygen u(O32e), the atom occupancy of Fe^{3+} and Zn^{2+} in tetrahedral sites, spherical harmonic parameters up to 8^{th} order parameters of the anisotropic Lorentzian size broadening assuming K62=0. The overall Debye-Waller factor *B* was set to 0.5 in all the refinements.

Table S1. Atom types, Wyckoff atomic positions and sites, and occupancies used in the Rietveld pattern refinement analysis. The refined atomic positons of oxygen are given in Table 1 in the main text. The values given here are nominal.

$Zn_{0.35}Fe_{2.65}O_4$						
atom	valence	x	y	z	site	occupancy
Fe(T_d)	3+	0.125	0.125	0.125	8a	0.65
Zn(T_d)	2+	0.125	0.125	0.125	8a	0.35
Fe(O_h)	2.5+	0.5	0.5	0.5	16d	1
O	2-	0.25	0.25	0.25	32e	1

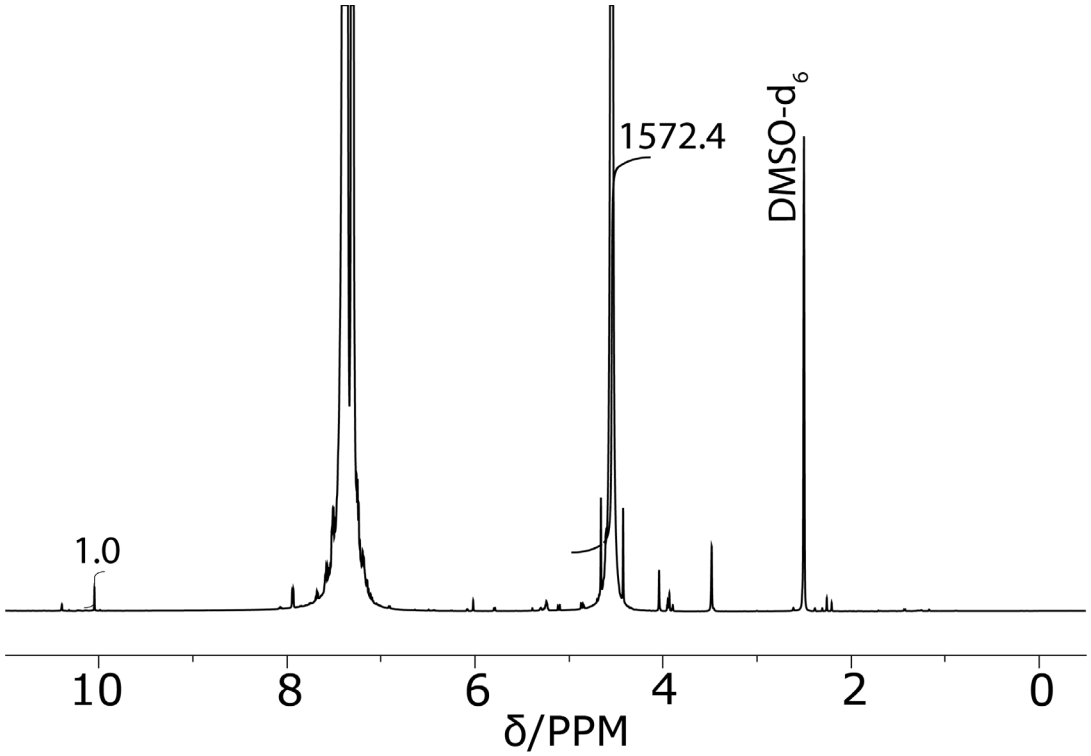

Figure S2. ^{1}H NMR spectrum of DBE stored for six months at ambient conditions. The spectrum was recorded in DMSO-d_6 at 600 MHz.

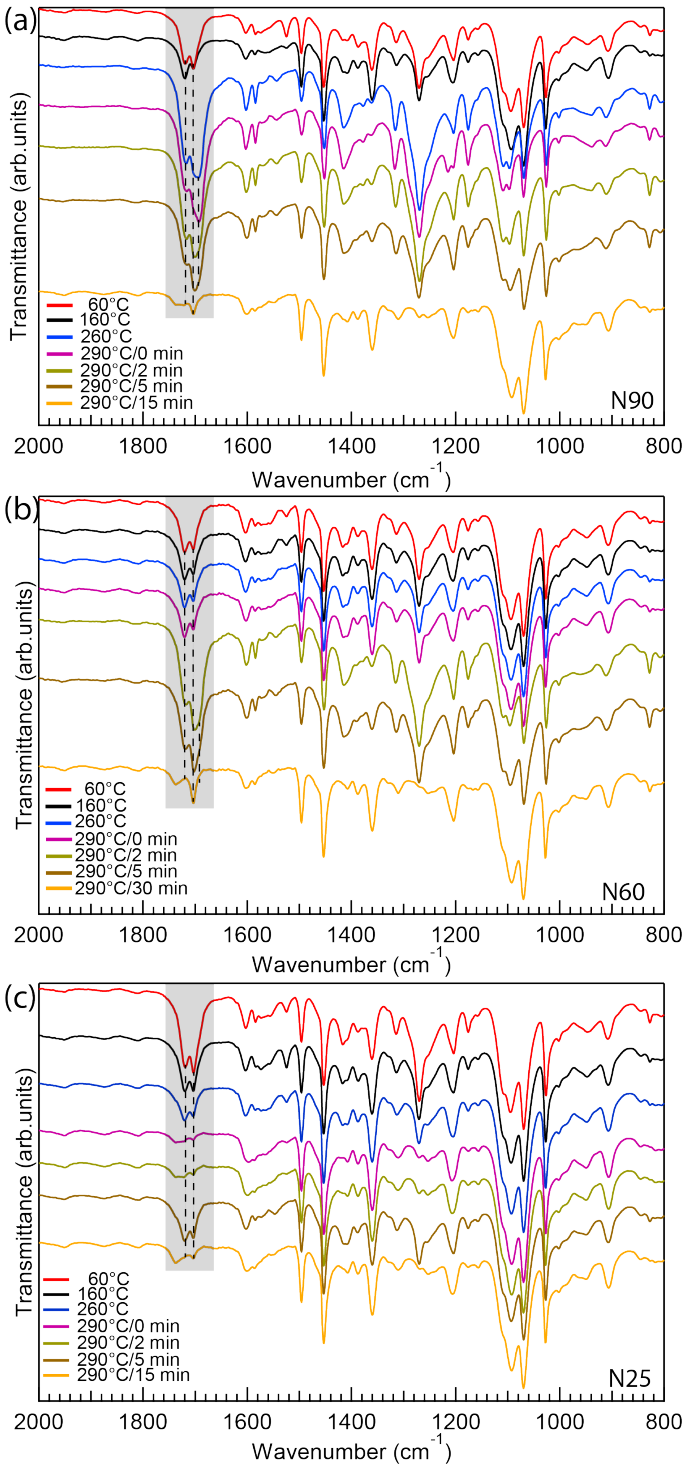

Figure S3. Attenuated total reflection Fourier transform infrared spectroscopy. The FTIR spectra of all three samples from 800 to 2000 cm^{-1} are shown. The regions of the spectra which are marked with a grey rectangular are presented in Fig. 3 of the main text.

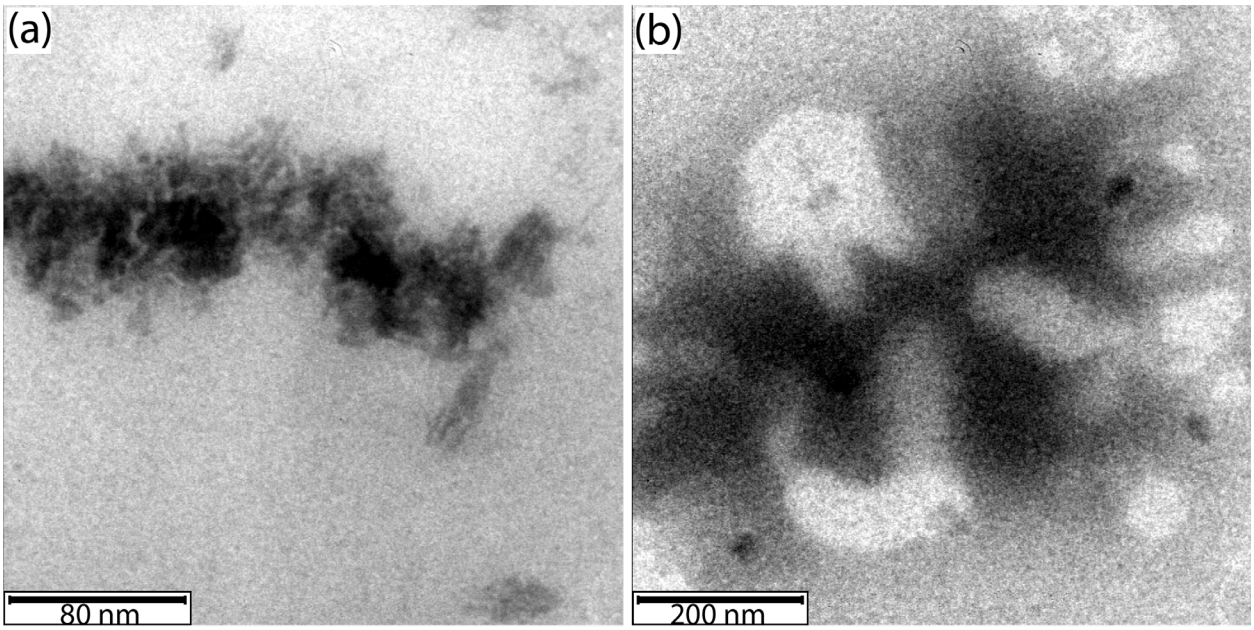

Figure S4. Transmission electron microscopy images of aliquots taken from (a) the synthesis reaction degassed at 90°C after 0 min reflux time at 290°C and (b) the synthesis reaction degassed at 60°C after 2 min reflux time at 290°C.

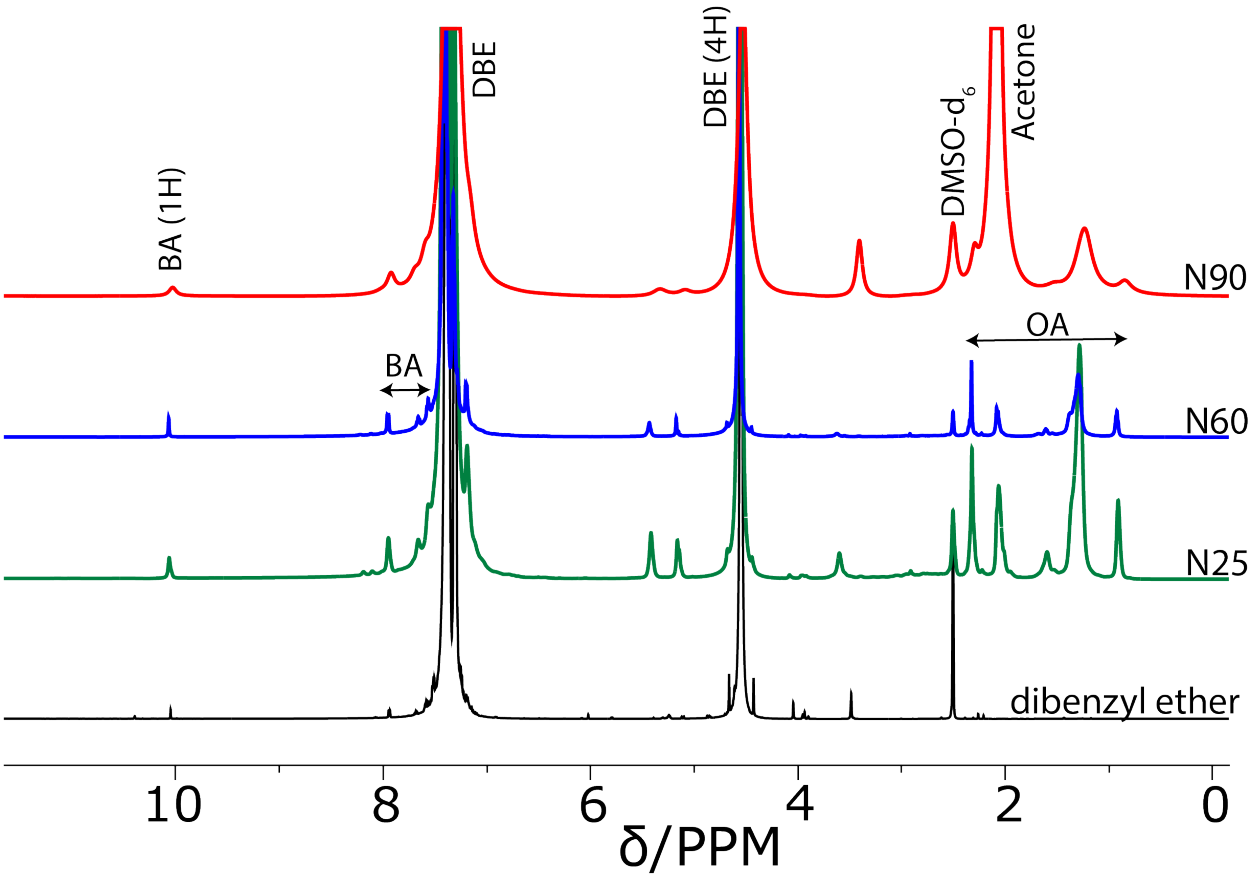

Figure S5. ^{1}H NMR spectra of final synthesis mixtures after extracting particles by centrifuging. For the N90, acetone was added as anti-solvent to facilitate the removal of extremely tiny crystallites, which their presence would otherwise broaden the spectrum. The spectrum of six months stored DBE at ambient conditions is co-plotted for comparison. The spectra were recorded in DMSO-d_6 at 600 MHz.

Further discussion on ^{1}H NMR spectra recorded on the reaction mixtures at the end of synthesis

The ^{1}H NMR spectrum recorded on DBE, which was stored for six months at ambient conditions, shows characteristic peaks of both DBE (peaks between 4 and 7.4 ppm) and BA (peaks between 7.4 and 10 ppm). We found that the amount of BA in 10 mL of DBE after six months storage is around 25 μL, as obtained by multiplying 1/4 of the integral of the peak at 4.56 ppm (DBE, 4H) with 10 (total volume of DBE). Our finding is lower than 2% BA in DBE, which was previously reported based on gas chromatography-mass spectroscopy measurement.[1] The difference could originate from different storage conditions for DBE. In summary, we deduce that between a 40% and 90% of BA remains in the reaction mixture after degassing at 90 and 25°C, sequentially (Fig. 2 of the main text).

The analysis of ^{1}H NMR spectra recorded on the final reaction mixtures after removing the particles showed presence of three major compounds (Fig. S4). The peaks located at 4.56 and 7.19-7.41 ppm, between 7.4 and 10 ppm, and from 0.9 to 2.3 ppm relate to DBE, BA, and oleic acid (OA), respectively. We found that a noticeable amount of BA is produced in all the samples during the reaction, despite its negligible residual amount ~ 23-11 μL at the end of degassing process (Fig. 2, main text). The total volume of BA, deduced from multiplying 1/4 of the integral of the peak at 4.3 ppm (DBE, 4H) with 10, increased from 353 to 615 and 898 μL with degassing temperature. We realized that the maximum reflux temperature dropped by the formation of BA owing to its lower boiling temperature than DBE, occurring earlier during the reflux as the degassing temperature increases (Fig. S1(b)). We hypothesize that the harsh dissociation of acetylacetonate through a high temperature and pressure degassing exposes iron cations for oxidative transformations of DBE to BA and toluene.[2]

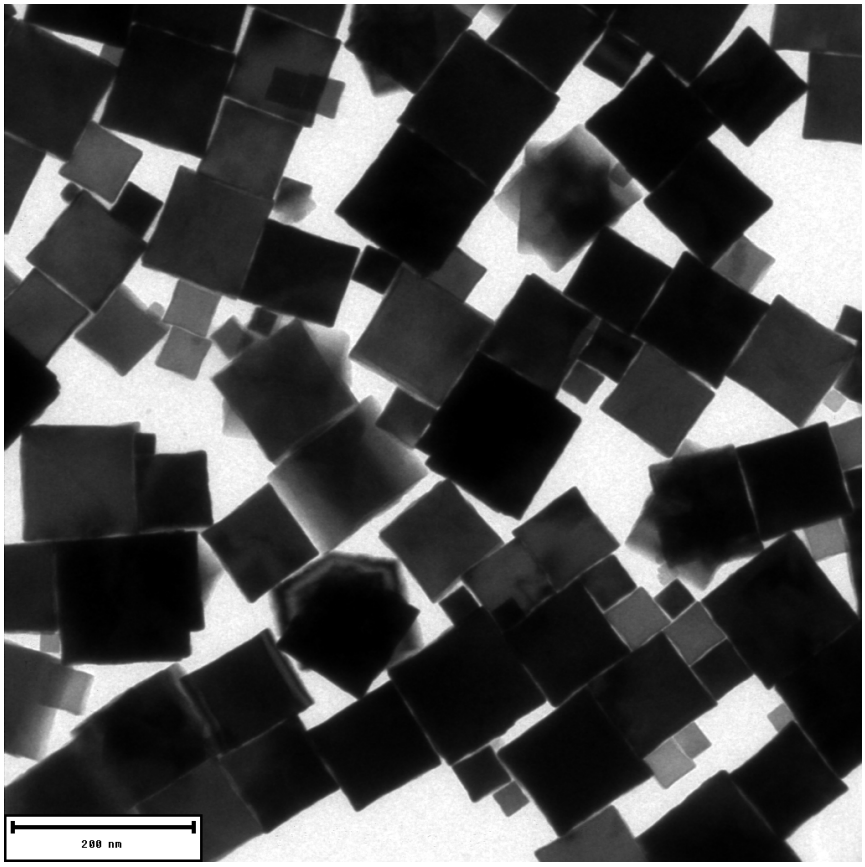

Figure S6. TEM micrograph of zinc ferrite nanocubes synthesized by adding 200 µL benzaldehyde to the synthesis mixture after degassing at 25°C. The other synthesis conditions were similar to the N25 sample. The particle mean size increases from 100 to 115 nm by adding 200µL of BA to the reaction, however, with the cost of broadening the particle size distribution.

References:

(1) Qiao, L.; Fu, Z.; Li, J.; Ghosen, J.; Zeng, M.; Stebbins, J.; Prasad, P. N.; Swihart, M. T. Standardizing Size- and Shape-Controlled Synthesis of Monodisperse Magnetite (Fe3O4) Nanocrystals by Identifying and Exploiting Effects of Organic Impurities. *ACS Nano* **2017**, *11* (6), 6370–6381.

(2) Guardia, P.; Riedinger, A.; Nitti, S.; Pugliese, G.; Marras, S.; Genovese, A.; Materia, M. E.; Lefevre, C.; Manna, L.; Pellegrino, T. One Pot Synthesis of Monodisperse Water Soluble Iron Oxide Nanocrystals with High Values of the Specific Absorption Rate: ESI. *J. Mater. Chem. B* **2014**, *2*, 4426.