

Electronic Supplementary Information

Ionic Liquids as Recycling Solvents for The Synthesis of Magnetic Nanoparticles

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1. Experimental details

Synthesis of ionic liquids

The synthesis of BMI.NTf₂ and BMI.PF₆ were done by modification of the process developed by Cassol et al.(C. C. Cassol, G. Ebeling, B. Ferrera, J. Dupont, Adv. Synth. Catal. 348 (2006) 243) and involves the following steps:

Synthesis of Butyl Methanesulfonate: Methanesulfonyl chloride (1.60 mol) was added under vigorous stirring to a solution of n-butanol (1.60 mol) and triethylamine (1.60 mol) in dichloromethane. The reaction temperature was kept between 10-20°C. Then, the organic layer was washed with water. The combined organic extracts were dried over MgSO₄ and the solvent was removed under reduced pressure to give a colorless liquid.

Synthesis of 1-Butyl-3-methylimidazolium Methanesulfonate: equimolar amounts of butyl methanesulfonate and 1-methylimidazole (1.59 mol) were mixed and the reaction mixture was kept at room temperature. One crystal of 1-butyl-3-methyl imidazolium methanesulfonate was added and the resulting crystalline reaction mass was kept at room temperature for 24 h. Recrystallization was performed using acetone as solvent.

Synthesis of 1-n-butyl-3-methylimidazolium trifluoromethanesulfonimide (BMI.NTf₂): A mixture of 1-butyl-3-methylimidazolium methanesulfonate (165 mmol), LiNTf₂ (174 mmol) and distilled water (65 mL) were vigorously stirred for 30 min and dichloromethane (200mL) was added. The organic phase was separated, washed with water and dried with MgSO₄ and filtered through a basic alumina column. Solvent evaporation system was used to dichloromethane evaporation. The final product was a viscous and colorless liquid, the BMI.Tf₂N ionic liquid. The purity (> 97%) of the ionic liquid was determined by ¹HNMR using the intensity of the ¹³C satellites of the imidazolium N-methyl group as internal standard. The ¹HNMR spectrum was recorded on a Varian Mercury Plus spectrometer (300 MHz) at room temperature.

Synthesis of 1-n-butyl-3-methylimidazolium hexafluorophosphate (BMI.PF₆): A mixture of 1-butyl-3-methylimidazolium methanesulfonate (470 mmol), KPF₆ (493 mmol) and distilled water (250 mL) were vigorously stirred for 30 min. The upper aqueous phase was separated and discarded. Then, KPF₆ (23 mmol) and distilled water (40 mL) were added to the remaining layer. The mixture was stirred for 15 min followed by the addition of 200 mL of dichloromethane. The organic phase was separated, dried with MgSO₄ and filtered through a basic alumina column. Solvent evaporation system was used to dichloromethane evaporation. The purity (> 94%) of the product was verified as described above for the BMI.NTf₂.

2. Characterization techniques

NIR spectra of Fe_3O_4 NPs obtained at 150 °C (a) and 250 °C (b)

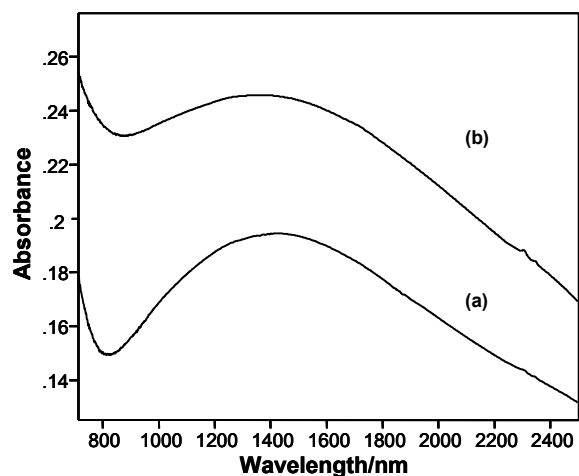


Figure S-1. NIR spectra of Fe_3O_4 NPs obtained at 150 °C (a) and 250 °C (b). The spectra were recorded from a thin film of the sample dispersed in hexane in a NaCl window.

FTIR spectra of Fe_3O_4 NPs obtained at 250 °C

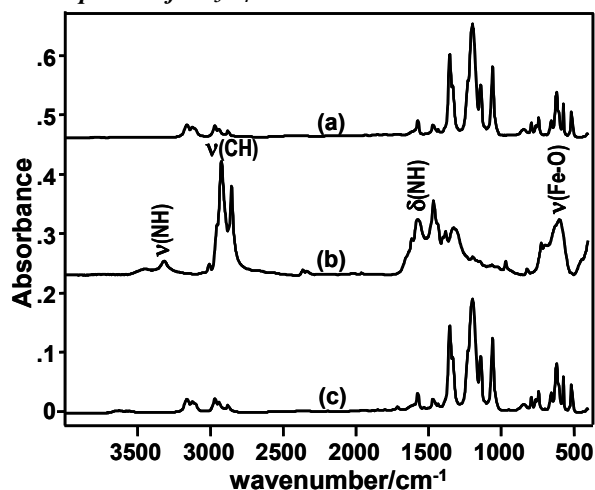


Figure S-2. Infrared spectra of: (a) BMI.NTf₂ ionic liquid before the reaction; (b) a thin film of the magnetite NPs covered by oleylamine as obtained in the synthesis; (c) BMI.NTf₂ ionic liquid after the 20th reaction is completed at 250 °C in 1.5 h of reaction.

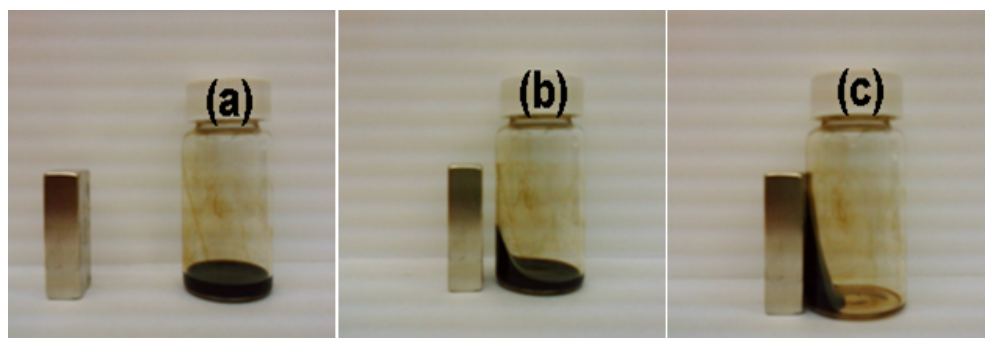


Figure S-3. Photographs of a magnetic fluid (Fe_3O_4 NPs dispersed in cyclohexane) exposed to a permanent magnet (Nd): far from the sample (a), closer (b) and touching the glass wall (c)

CHN Analysis

Table S-1. Results of CHN analysis for samples prepared at 150 °C

IL	%C (m/m)	%H (m/m)	%N (m/m)	%oleylamine (m/m)	%oleylamine (m/m) calc. ¹
BMI.NTf ₂	11.42	2.17	0.62	14.13	12.7

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm².

TGA results

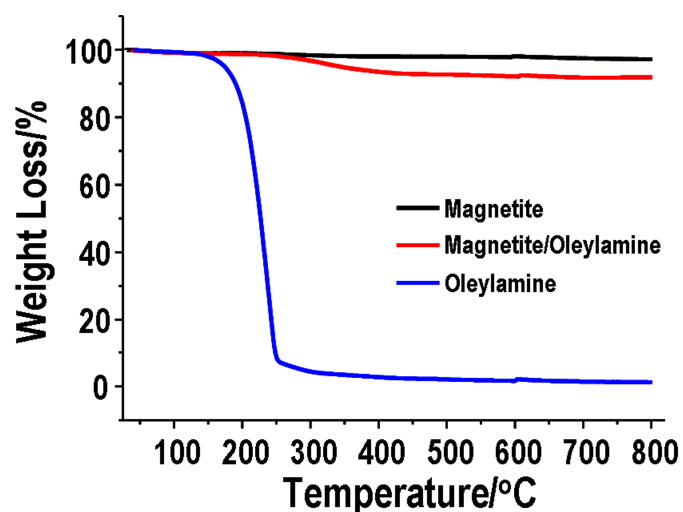


Figure S-4. TGA curves for the indicated samples (magnetite/OA obtained at 150 °C in BMI.NTf₂). Note the weight loss of 13.5% begins near 250 °C and ends near 400 °C (red curve). This is due to the release of OA from the magnetite surface. This weight % corresponds to nearly one monolayer of OA.

¹H-NMR analysis

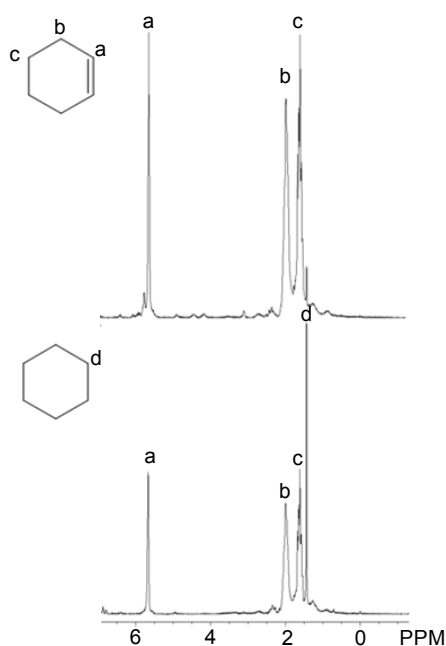


Figure S-5. ¹H-NMR spectra of pure cyclohexene (upper curve) and of the cyclohexene solution containing Pd(OAc)₂ as catalyst after ten minutes of purging with the gas liberated in the synthesis of Fe₃O₄ nanoparticles (lower curve). The Pd(OAc)₂ catalyst promotes the hydrogenation of cyclohexene leading to the formation of cyclohexane.

Results for the BMI.PF₆

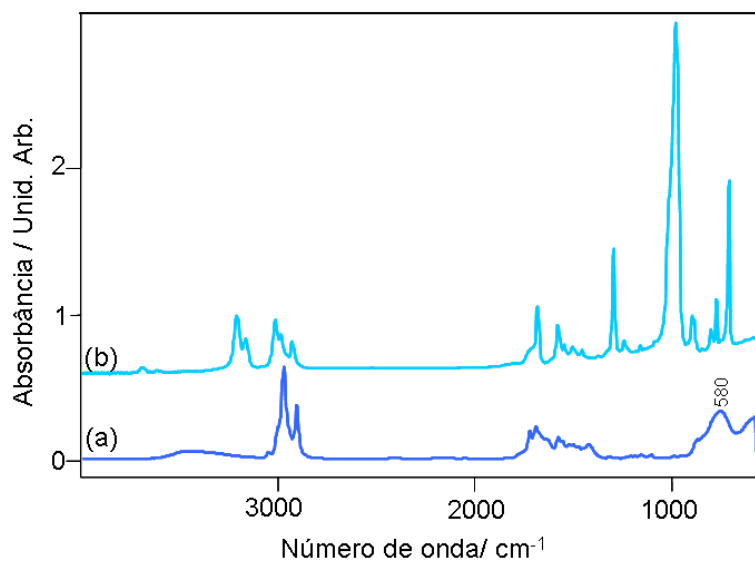


Figure S-6. FTIR spectra of (a) BMI.PF₆ and (b) Fe₃O₄ NPs obtained in BMI.PF₆ at 250 °C after 1.5 h of reaction.

TEM and HRTEM (BMI.PF₆)

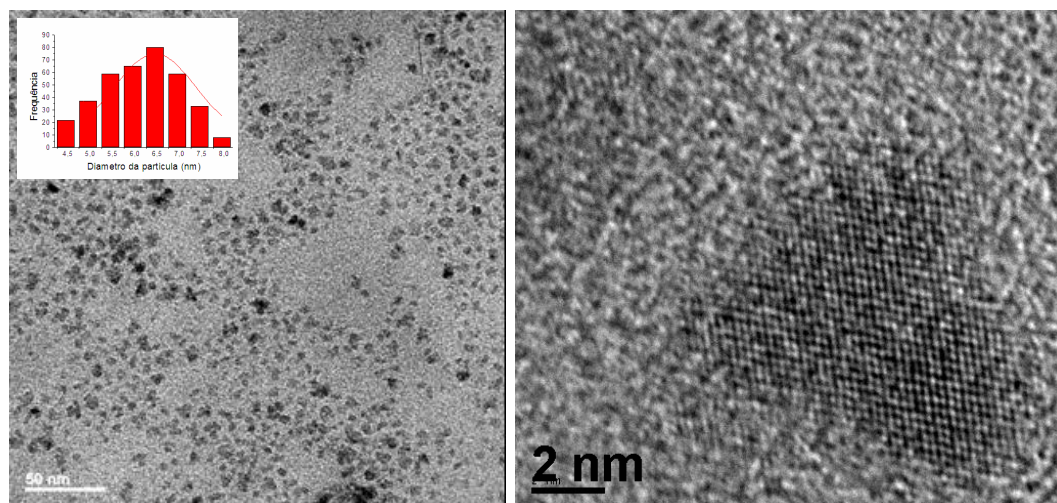


Figure S-7 (left) TEM image and histogram (inset, mean diameter 6.2 ± 0.9 nm) of Fe₃O₄ NPs obtained in BMI.PF₆ at 150 °C and 1.5 h of reaction in the presence of OA. (right) a HRTEM image of a Fe₃O₄ nanocrystal.

Table S-2 CHN Analysis for the Fe₃O₄ obtained in BMI.PF₆ at 150 °C in 1.5 h of reaction

IL	%C (m/m)	%H (m/m)	%N (m/m)	%oleylamine (m/m)	%oleylamine (m/m) calc. ¹
BMI.PF ₆	12.28	2.29	0.55	15.12	16.7

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm²

Magnetization measurements

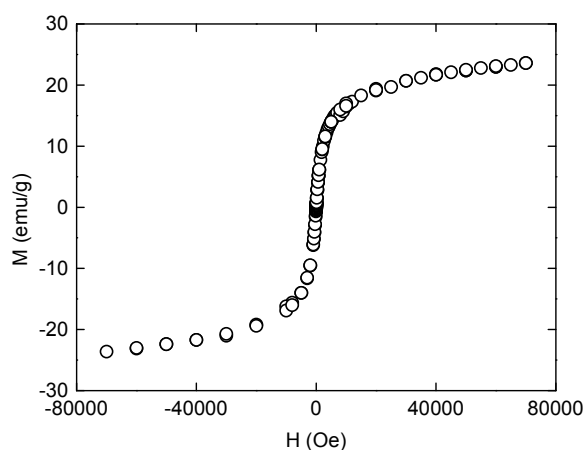


Figure S-8. Hysteresis loop at 300 K for the Fe_3O_4 NPs obtained at 150 °C in BMI.PF_6 .

TEM Results for NiFe_2O_4 and MnFe_2O_4 obtained in BMI.NTf_2

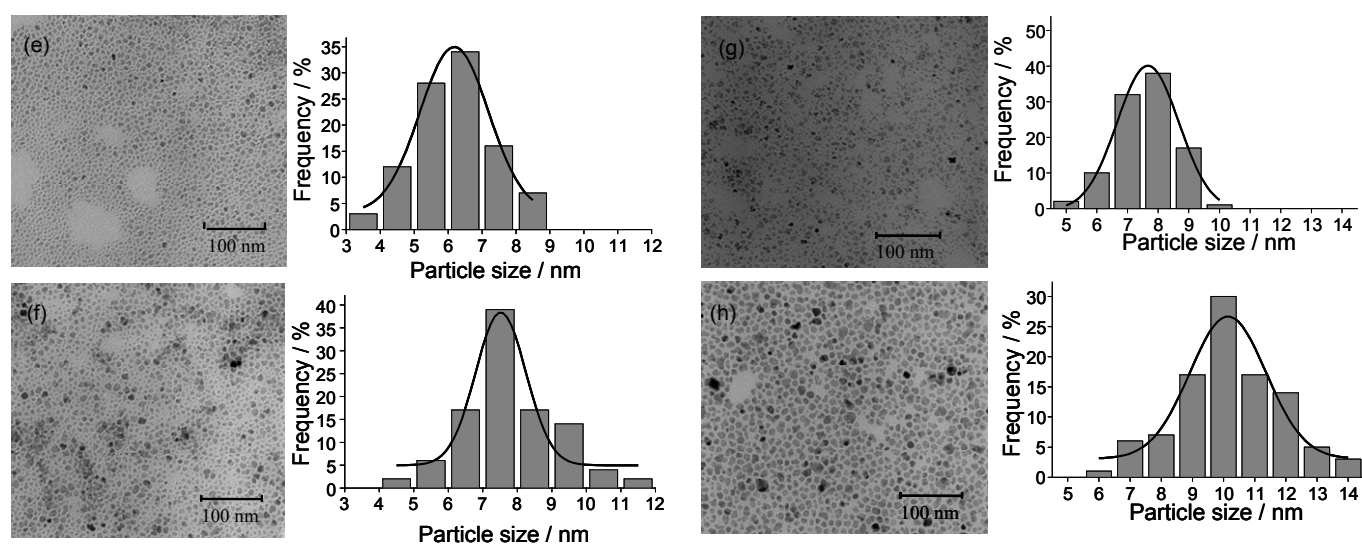


Figure S-9. TEM micrographs and histograms of NiFe_2O_4 (e,f) and MnFe_2O_4 (g,h) NPs. (e,g) were obtained after 1.5 h and (f,h) after 3.0 h of reaction at 200 °C.

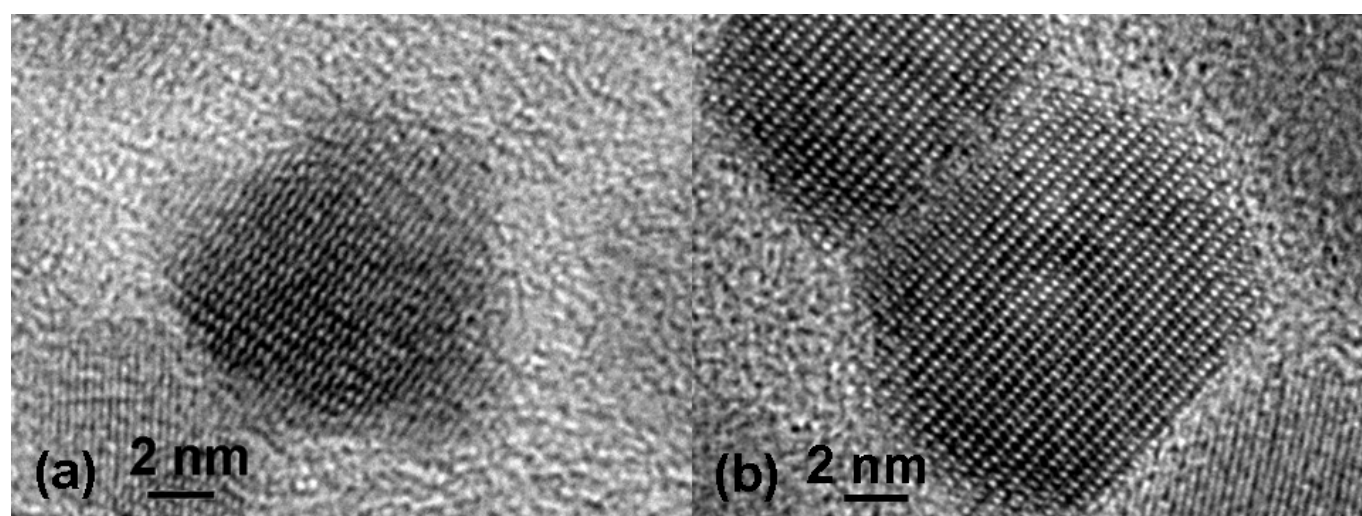


Figure S-10. HRTEM images of Fe_3O_4 NPs obtained after 1.5 h (a) and 3.0 h of reaction at 200 °C.

Magnetic measurements

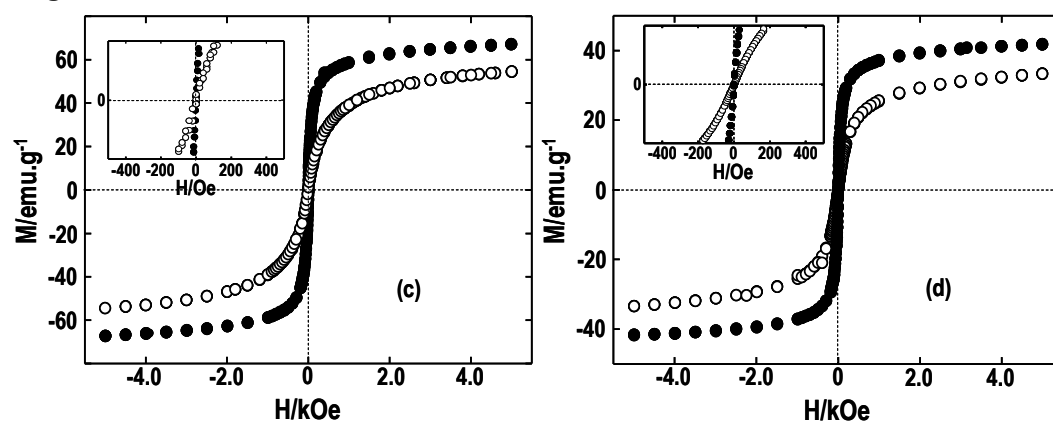


Figure S-11. Hysteresis loops at 300 K for (c) Fe_3O_4 and (d) MnFe_2O_4 obtained at 200 °C for (○) 1.5 h and (●) 3 h reaction times. The insets show the hysteresis loops at lower magnetic fields.

FTNIR and FTIR spectra

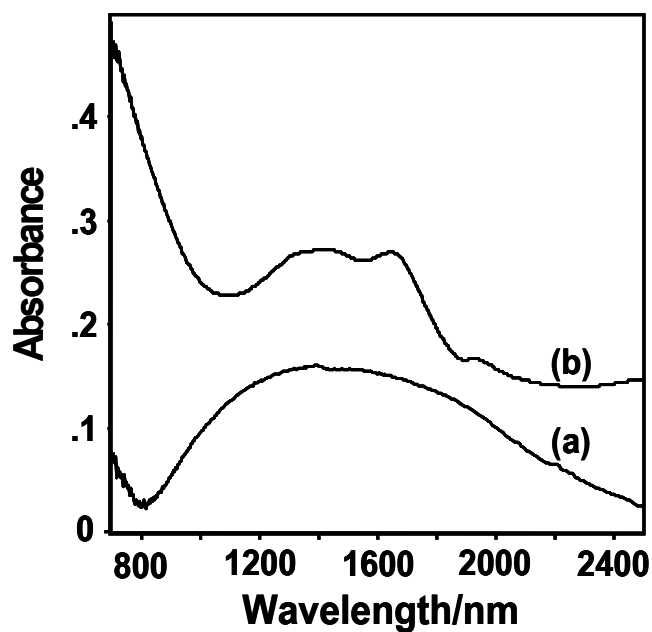


Figure S-12. NIR spectra of Fe_3O_4 (a) and CoFe_2O_4 (b) NPs obtained at 200 °C in 1.5 h reaction. The spectra were recorded from a thin film of the sample dispersed in hexane in a NaCl window. The NIR spectrum of CoFe_2O_4 NPs shows two main absorptions near 1640 and 1350 nm, as observed before for CoFe_2O_4 NPs obtained by the co-precipitation method.

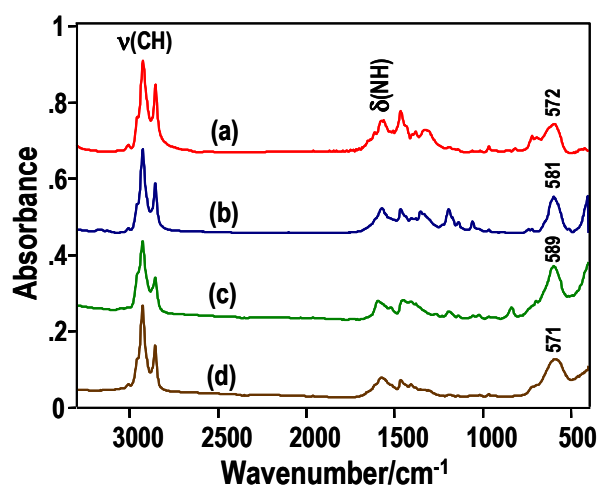


Figure S-13. FTIR spectra of Fe_3O_4 (a), CoFe_2O_4 (b), NiFe_2O_4 (c), and MnFe_2O_4 (d) NPs obtained in BMLNTf_2 after 1.5 h of reaction at 200 °C.

Table S-3 CHN Analysis for the ferrite NPs obtained in BMI.NTf₂ at 150 °C after 1.5 h of reaction

Sample	%C (m/m)	%H (m/m)	%N (m/m)	%oleylamine (m/m) exp.	%oleylamine (m/m) calc. ¹	Wheightloss% ²
Fe ₃ O ₄	14.13	2.71	0.77	13.30	14.6	12.3
CoFe ₂ O ₄	13.53	2.25	0.30	16.08	19.7	13.8
NiFe ₂ O ₄	11.83	1.98	0.72	14.51	14.6	12.2
MnFe ₂ O ₄	11.77	1.53	0.42	13.72	13.8	12.8

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm²

² Mass percent of OA as obtained by TGA (see Fig.S-14)

TGA results

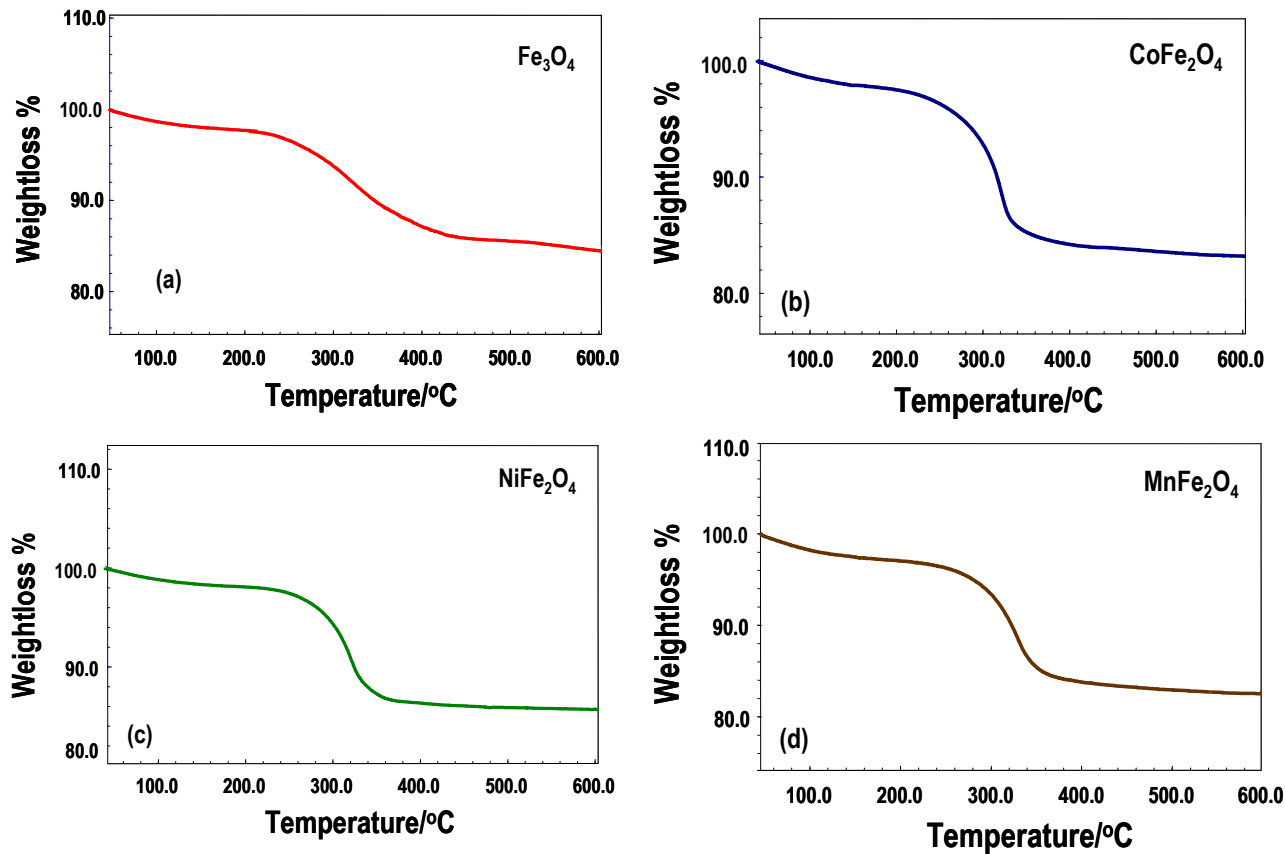


Figure S-14. TGA measurements for Fe₃O₄ (a), CoFe₂O₄ (b), NiFe₂O₄ (c), and MnFe₂O₄ (d) samples obtained after 1.5 h of reaction in BMI.NTf₂ at 200 °C. (See Table S-3 for the weightlosses corresponding to the OA decomposition).

Results for the synthesis in DPE
TEM Results for Fe₃O₄ obtained in DPE and OA

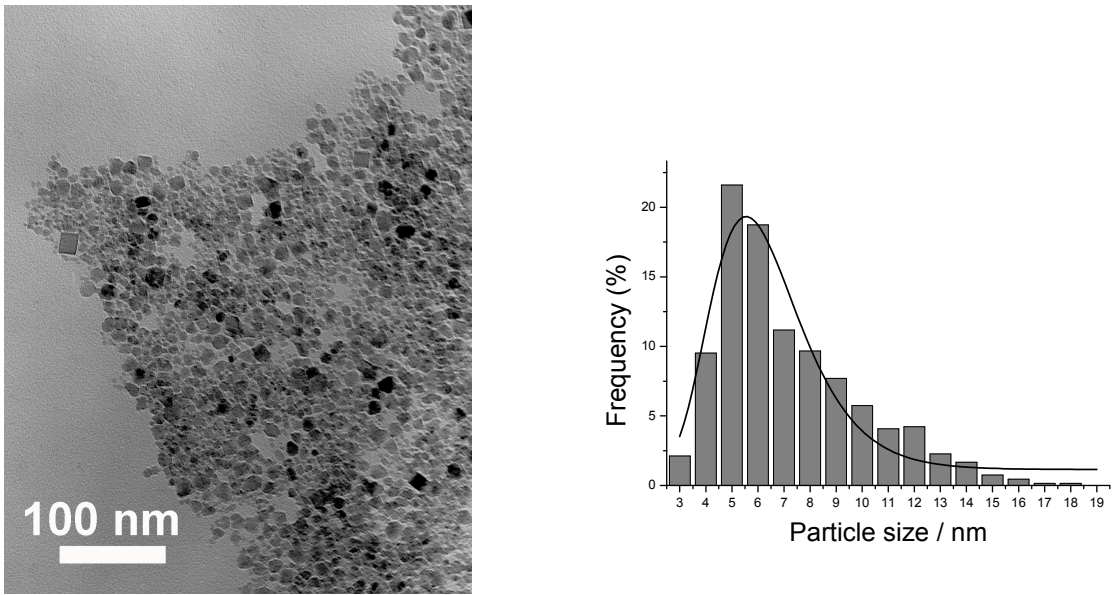


Figure S-15. TEM micrograph and size distribution histogram (lognormal function) of Fe₃O₄ NPs prepared by decomposition of Fe(Acac)₃ in DFE and oleylamine.

CHN Analysis

Table S-4. Results of CHN analysis for samples prepared in DPE

%C (m/m)	%H (m/m)	%N (m/m)	% oleylamine (m/m)	% oleylamine (m/m) calc. ¹	Weightloss% ²
16.07	1.60	0.68	19.9	18.5	9.1

¹ Mass percent of OA calculated for a monolayer of OA and considering that two molecules of OA occupies 1 nm²

² Mass percent of OA as obtained by TGA (see Fig.S-16)

TGA results

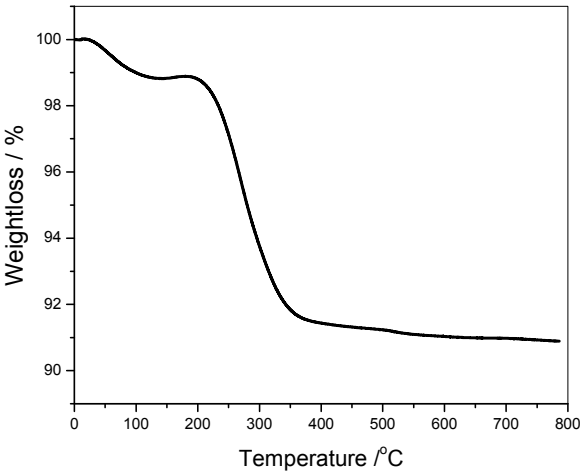


Figure S-16. TGA measurements for Fe₃O₄ obtained in DPE. (See Table S-4 for the weightloss corresponding to the OA decomposition).