Electronic Supplementary Information

Molecular Mechanisms for Delicately Tuning the Morphology and Property of Fe_3O_4 Nanoparticle Clusters

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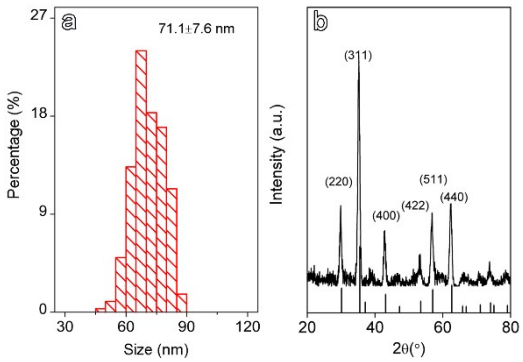

Fig. S1. Histogram of particle size (a) and powder X-ray diffraction pattern (b) of Fe_3O_4 particle clusters formed in DEG, together with the JCPDS card (88-0866) data for Fe_3O_4 shown at the bottom of frame b.

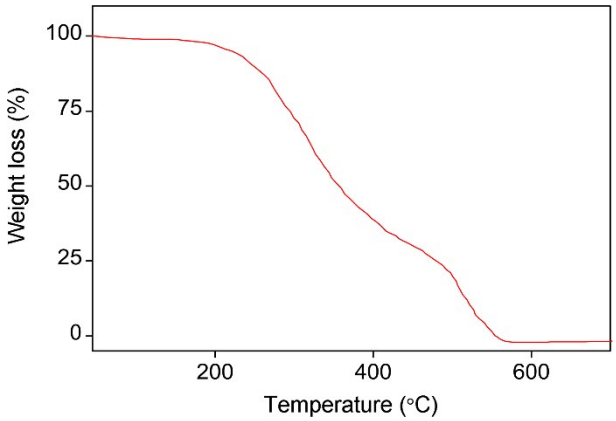

Fig. S2. The thermal gravity curves of the PAA.

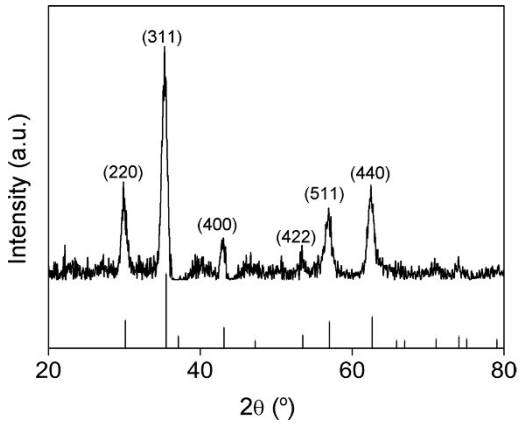

Fig. S3. Powder X-ray diffraction patterns of Fe_3O_4 nanoparticles achieved in DEGME, together with the JCPDS card (88-0866) data for Fe_3O_4 shown at the bottom.

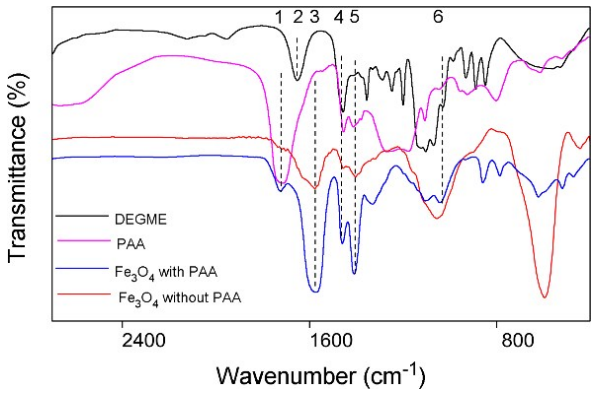

Fig. S4. FTIR spectra of DEGME, PAA, and Fe_3O_4 clusters obtained in DEGME with or without PAA, with 6 vertical dashed lines showing different characteristic peaks of organic residues (1: 1724 cm^{-1}, 2: 1649 cm^{-1}, 3: 1576 cm^{-1}, 4: 1458 cm^{-1}, 5: 1407 cm^{-1}, and 6: 1058 cm^{-1}).

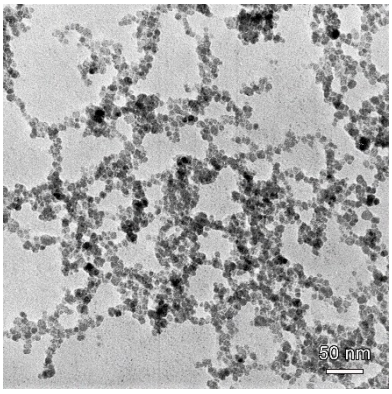

Fig. S5. A representative TEM image of Fe_3O_4 nanoparticles formed in DEGME in the absence of PAA.

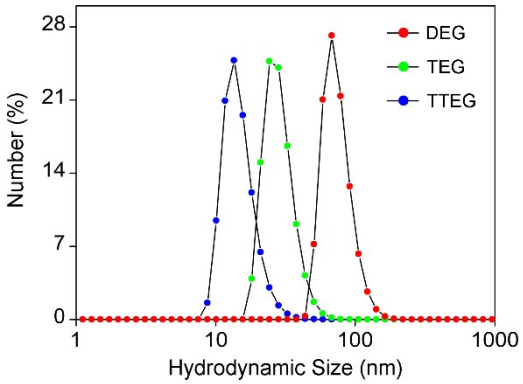

Fig. S6. Hydrodynamic size distribution profiles of Fe_3O_4 particle clusters prepared in different dihydric alcohols.

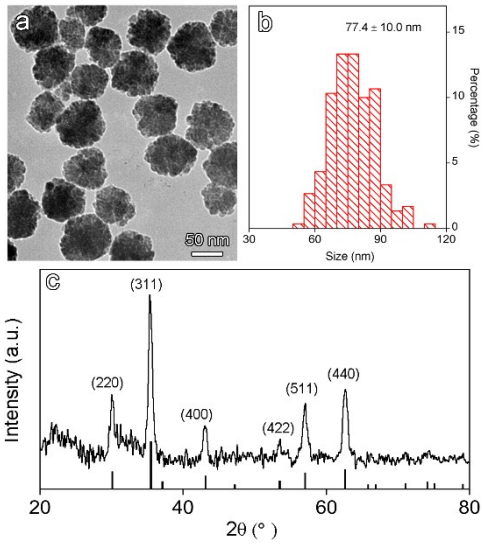

Fig. S7. A TEM image (a), histogram of particle size (b), and powder X-ray diffraction patterns (c) of Fe_3O_4 particle clusters obtained in TEG for comparing with those obtained in DEG (Fig. 1d) (pair 1 clusters).

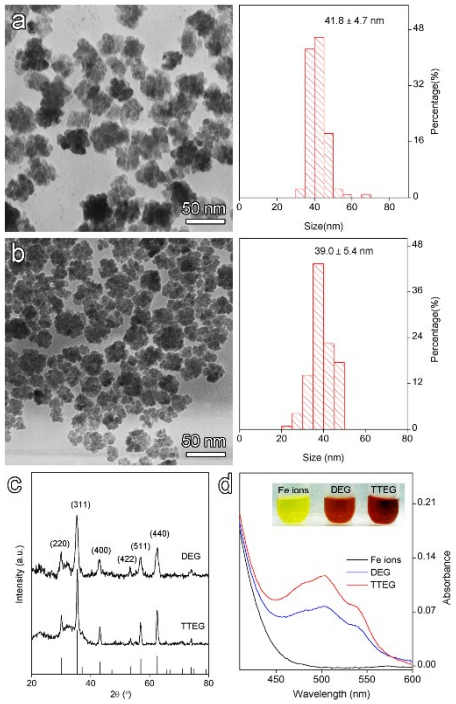

Fig. S8. TEM image and the corresponding histogram of particle size of two comparable Fe_3O_4 clusters obtained in DEG (a) and TTEG (b), respectively, and their X-ray diffraction patterns for determining Scherrer size of the primary particles (c). Frame d shows UV-Vis absorption spectra of the solutions of DOX-loaded particle clusters after being digested with concentrated HCl in comparison with that of a DMSO solution containing equal amount of Fe^{3+} (inset: photographs of the solutions obtained).

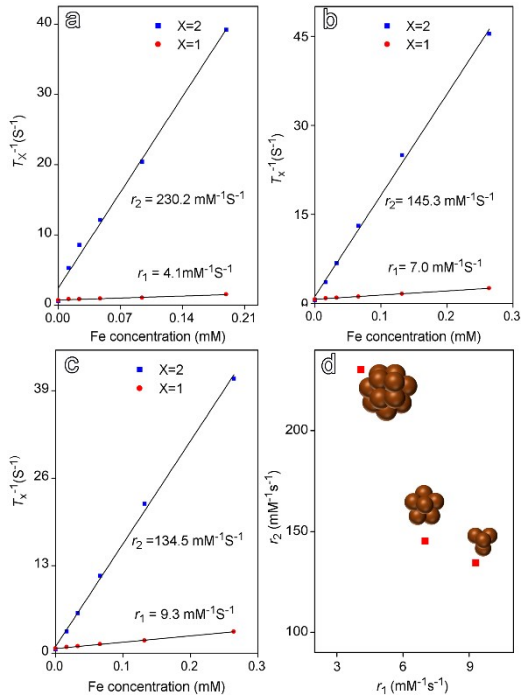

Fig. S9. Fe concentration dependent T_x relaxation rate (x = 1, 2) together with linear fits for aqueous suspension of samples prepared in DEG (a), TEG (b), and TTEG (c), respectively, together with r_2/r_1 relationship at 3 T (d).

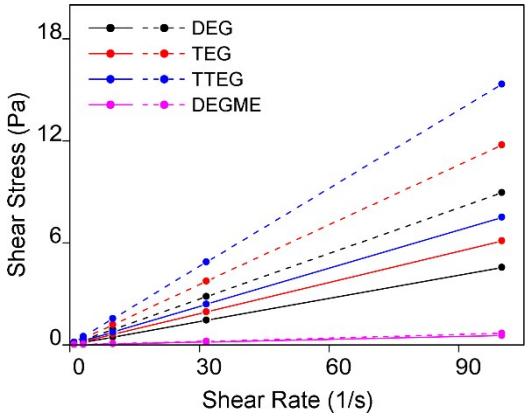

Fig. S10. Plot of shear stress against shear rate overlaid with linear fits for extracting the viscosity of different reaction systems at 20°C before (solid: alcohol+$FeCl_3$) and after (dashed line: alcohol+$FeCl_3$+NaOH) NaOH was introduced into each reaction system.

Table S1 Scherrer sizes of Fe_3O_4 particles calculated according to different diffraction peaks together with overall particle cluster sizes.[⊥]

Alcohol	Cluster size (nm)	XRD pattern	2-theta (°)	(*hkl*)	FWHM (°)	Calculated size (nm)	Average size (nm)
DEGME	N/A	Fig. S2	30.1	(220)	0.54	14.56	10.5
			35.5	(311)	0.80	9.83	
			62.5	(440)	1	7.86	
DEG	71.1	Fig. S1b	30.1	(220)	0.66	11.91	11.5
			35.5	(311)	0.68	11.56	
			62.5	(440)	0.72	10.92	
TEG	29.5	Fig. 5c	30.1	(220)	2.32	3.38	5.2
			35.5	(311)	0.86	9.14	
			62.5	(440)	2.58	3.04	
TTEG	15.3	Fig. 5c	30.1	(220)	2.56	3.07	3.0
			35.5	(311)	2.32	3.39	
			62.5	(440)	2.98	2.64	
TEG	77.4	Fig. S6c	30.1	(220)	0.74	10.62	10.9
			35.5	(311)	0.62	12.68	
			62.5	(440)	0.84	9.36	
DEG	41.8	Fig. S7c	30.1	(220)	0.98	8.02	7.9
			35.5	(311)	0.98	8.02	
			62.5	(440)	1.02	7.71	
TTEG	39.0	Fig. S7c	30.1	(220)	2.5	3.14	6.7
			35.5	(311)	0.84	9.36	
			62.5	(440)	1.02	7.71	

[⊥]Scherrer size was calculated with Scherrer Formula, $d=k\lambda/B\cos\theta$, where k is Scherrer constant (0.89), λ is the wavelength of X ray (0.154 nm), B is the full width at half maximum (FWHM) of the diffraction peak, and θ is diffraction angle.

Table S2 Calculated cell parameters of Fe_3O_4 particle clusters according to the corresponding powder X-ray diffraction patterns of samples.

	Average lattice Constants	α	β	γ
Fe_3O_4 (JCPDS88-0866)	8.385	90.0°	90.0°	90.0°
Samples achieved in TEG	8.529	90.0°	90.0°	90.0°
Samples achieved in TTEG	8.433	90.0°	90.0°	90.0°

Calculation of the viscosity

According to equation S(1) given below, the viscosity (η) of different reaction systems at 20°C was extracted (Fig. S10).

$$\eta = \frac{\tau}{D} \qquad \text{S(1)}$$

As the temperature dependent viscosity can be expressed by

$$ln\frac{\eta}{\eta_0} = -1.94 - 4.80 \times \frac{T_0}{T} + 6.74 \times (\frac{T_0}{T})^2 \quad \text{S(2)}$$

the viscosities of different reaction systems 200°C were calculated and given in Table I.

The diffusion coefficient *D*

D can be obtained from Einstein's formula

$$D = \frac{k_B T}{6\pi\eta r_p} \quad \text{S(3)}$$

Where k_B is Boltzmann constant, T is reaction temperature, η is the viscosity of solvent, and r_p is the average radius of the nanoparticle. It can be seen from equation S(3) that D is inversely correlated with μ.