Electronic Supplementary Information

Size selectable nanoparticle assemblies with magnetic anisotropy tunable across the superparamagnetic to ferromagnetic range

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Materials and Methods

Materials: All reagents and Fe salts were obtained from Sigma-Aldrich and used without further purification. Fatty acids were obtained from Sigma-Aldrich (purity > 99.9%), and again were used without further purification.

Nanoparticle synthesis

8-MNPs were prepared by alkaline co-precipitation, while 15-MNPs were prepared by thermal decomposition.

Preparation of 8-MNPs: The method used was described by Sun and Zeng.[S1] In a typical preparation iron (III) acetylacetonate (2 mmol), 1,2-hexadecanediol (10 mmol), oleic acid (6 mmol), oleyl amine (6 mmol), and diphenyl ether (20 mL) were used. The mixture was gradually heated to 265ºC to reflux for 15 min under a nitrogen atmosphere. The black mixture was removed from the heat source and allowed to cool naturally to room temperature. The solid material was precipitated from solution by addition of ethanol, and isolated by magnetic means. As a washing step, the nanoparticles were dispersed in 15 mL of *n*-heptane, precipitated again by addition 60 mL of ethanol and isolated. They were subsequently redispersed in 15 mL of n-heptane without addition of further surfactant. The nanoparticles were subsequently dispersed in heptane without addition of further surfactant. The resulting suspensions appeared red-brown in color, suggesting the presence of maghemite, γ-Fe_2O_3. The heptane suspension was centrifuged for 35 minutes at 13,000 rpm using a tabletop Eppendorf Centrifuge 5415 D in order to sediment and remove any aggregated particles. The size of the nanoparticles was determined by Dynamic Light Scattering and confirmed by TEM measurements. The calculated size agrees with results published previously. [S2]

Preparation of 15-MNPs: The method used was a modification of the procedure of Shen and Laibinis.[S3] In a typical preparation 0.43 mmol of $FeCl_2 \cdot 4H_2O$, 0.86 mmol of $FeCl_3 \cdot 6H_2O$ and 5.00 mmol of NaCl were dissolved in 20 mL deionised water and heated to 80°C under nitrogen atmosphere while stirring vigorously. Upon reaching this temperature 0.39 mmol of oleic acid was added dropwise, followed by 0.70 mL (also dropwise) of 28% w/w NH_4OH. The solution immediately turned dark brown. The reaction mixture was kept at 80°C for the next 15 minutes and then allowed to cool to room temperature. 35 mL of methanol and 35 mL of acetone were added to the flask and the nanoparticles were separated by magnetic means. They were then washed sequentially with 20 mL acetone, methanol, again acetone and finally ethanol. Then the nanoparticles were dispersed in 15 mL of n-heptane, precipitated again with an addition of 70mL of ethanol and then finally redispersed with 20 mL of n-heptane. The resulting heptane suspension was centrifuged for 40 minutes at 13,000 rpm using a tabletop Eppendorf Centrifuge 5415 D in order to sediment and remove any aggregated particles. The supernatant was retained for characterisation and cluster growth experiments. The size of the nanoparticles was determined by Dynamic Light Scattering and confirmed by TEM measurements. The calculated size agrees with results published previously.[S4]

Assembly of 8-MNPCs: Clusters were formed using a 8-MNP heptane suspension, prepared as above, at a typical Fe concentration of 1 - 4 mM. In a typical experiment 1.2 mLs of the suspension was placed over *c.*50.0 mg of cyanopropyl-modified silica particles [50±20 μm, Alltech Associates] that formed a thin layer at the bottom of the cuvette and monitored continuously by DLS. Stable suspensions of a given MNPC size were prepared by removing the sample from contact with silica.

Assembly of 15-MNPCs: Clusters were formed using a 15-MNP heptane suspension, prepared as above, at a typical Fe concentration of 5 – 10 mM. In a typical experiment 1.2 mLs of the suspension was placed over *c.*50.0 mg of cyanopropyl-modified silica particles [50±20 μm, Alltech Associates] that formed a thin layer at the bottom of the cuvette and monitored continuously by DLS. Stable suspensions of a given MNPC size were prepared by removing the sample from contact with silica, or by addition of one drop of a pure OA.

NMR Methods

The ^{1}H NMRD data was recorded using a Spinmaster FFC-2000 Fast Field Cycling NMR Relaxometer, (http://www.stelar.it/ Stelar SRL; Mede, Italy). The system operated at a measurement frequency of 9.25 MHz for ^{1}H, with a 90° pulse of 6 μs. T1 measurements were performed as a function of external field, B0, with standard pulse sequences incorporating B0 field excursions, a field switching rate of 20 MHz/ms was used. The field range covered on the Stelar Spinmaster was from 10 kHz to 20 MHz The low frequency ^{1}H relaxation is determined by the Néel process (correlation time τ_N), *i.e.* reorientation of the moments of the MNPs in the effective magneto-crystalline field. At high frequency (high external field), ^{1}H relaxation is outer sphere in nature. Simulations using the SPM model[S5] confirm ΔE values below 1.5 GHz.

Iron Determination

Total iron content was determined by atomic absorption spectroscopy. Samples were prepared for analysis as follows. Concentrated HCl solution (0.5 mL) and 1 mL deionized H_2O was added to a small aliquot (typically 0.3 - 0.5 mL) of the nanoparticle suspension. The mixture was heated until only 1 drop of liquid remained, at which time 25 mL deionized water was added. The solution was heated to boiling, then immediately removed from heat and allowed to cool to room temperature. The volume was adjusted to 100 mL. Spectra were recorded on a Varian SpectrAA Spectrometer with a single slit burner. The light source was a Fe-cathode lamp with a wavelength of 248.3 nm. Previous experiments have shown that oleic acid and its conjugate base do not interfere with the iron determination.

Dynamic light scattering

DLS experiments were performed at 25 °C on a Malvern NanoZS (Malvern Instruments, Malvern UK) which uses a detection angle of 173°, and a 3 mW He-Ne laser operating at a wavelength of 633 nm. The hydrodynamic diameter and the polydispersity index (PDI) values were obtained using cumulants analysis.

Electron Microscopy Methods

The preparation of samples for EM analysis involved depositing a drop (15 μL) of the diluted relevant dispersion in heptane onto carbon-coated (400 mesh) copper grids and allowing the solvent to evaporate, prior to imaging. STEM images were obtained using a Hitachi S5500 Field-Emission SEM (at an accelerating voltage of 20 kV). TEM images were obtained using JEOL 2000 FX TEMscan (at an accelerating voltage of 80 kV).

NP-NP interaction modelling.

The interaction potential between two iron oxide nanoparticles coated with oleic acid ligands was calculated as a sum of contributions from attractive van der Waals and magnetic and repulsive steric interactions. The latter interactions arise due to exclusion of the solvent (heptane) molecules from the space between the particles (osmotic interaction) and from contraction of ligand chains at very close particle separations (elastic interaction): [S6]

$$\Phi(d) = \Phi_{vdW}(d) + \Phi_{magnetic}(d) + \Phi_{osmotic}(d) + \Phi_{elastic}(d)$$

Where d is the particle separation (surface to surface distance). The non-retarded van der Waals interaction was calculated using the formula:

$$\Phi_{\mathrm{vdW}}(d) = -\frac{A}{6}\left[\frac{2r^2}{d^2-4r^2} + \frac{2r^2}{d^2} + \frac{1}{2}\ln\left(1 - \frac{d^2-4r^2}{d^2}\right)\right]$$

where r is the particle radius. The Hamaker constant for magnetite across the solvent was calculated as $7.5\cdot10^{-20}$J, on the basis of the values of dielectric constants, ε_i, and refractive indices, n_i, of magnetite and heptane, respectively:

$$A = \frac{3}{4}kT\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}}\frac{(n_1^2-n_3^2)^2}{(n_1^2+n_3^2)^{3/2}}$$

where h is the Planck constant and ν_e is the main electronic UV absorption frequency, taken as $1.88\cdot10^{16}\mathrm{s}^{-1}$.

Since the separation of the particles in a cluster is very small, the dipolar magnetic interaction was calculated according to a simplified formula: [S7]

$$\Phi_{\mathrm{magn}}(\mathrm{d}) = \frac{-1}{3\mathrm{k_B T}}\left(\frac{\mathrm{m_1.m_2}}{4\pi\mu_0\mathrm{d}^3}\right)^2$$

where the saturation magnetization was determined using the SPM model[S5] to be 43 emu/g for both 8-MNPs and 15-MNPs.

The osmotic and elastic interactions were calculated according to formulas recently reviewed elsewhere. [S6] Briefly, the former one was calculated using the equation:

$$\Phi_{\mathrm{osm}} = \frac{4\pi rkT}{\upsilon_{\mathrm{solv}}} \cdot \phi^2 \left(\frac{1}{2} - \chi\right) L^2 \left(\frac{d - 2r}{2L} - \frac{1}{4} - \ln\left(\frac{d - 2r}{L}\right)\right)$$

where χ is the Flory-Huggins interaction parameter between the ligand and the solvent. It was taken as 0 here because of the similar cohesion energies of the long hydrophobic chains of oleic acid and of heptane), and φ is the surface coverage fraction by the stabilizing ligand. L is the length of the ligand (1.8nm for oleic acid), v_{solv} is the molecular volume of heptane.

The elastic interaction is only important at very small separations (less than one ligand length) which are not attained by the oleic-acid stabilized particles due to the osmotic repulsion constituting a sufficient barrier at larger separations. It was calculated, according to [S6] as:

$$\Phi_{\mathrm{elas}} = \frac{2\pi rkTL^2\varrho}{MW_2} \cdot \phi \cdot f(d - 2r, L)$$

where ρ and MW_2 represent the ligand density and molecular weight.

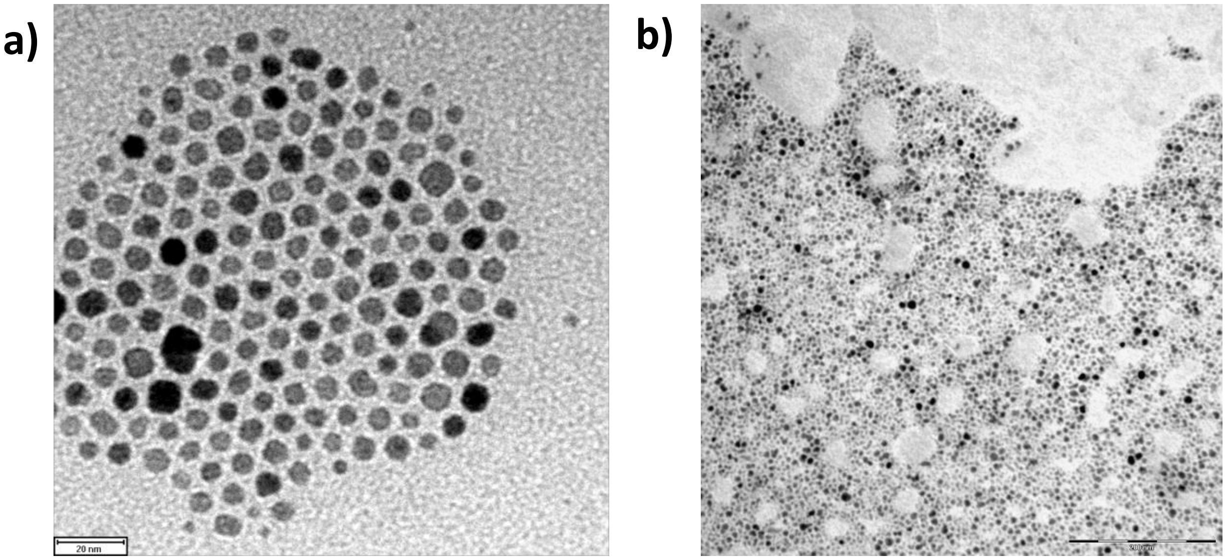

Figure S1: (a) TEM image of 8-MNPs. The scale bar is 20 nm (b) TEM image of 15-MNPs, scale bar is 200nm.

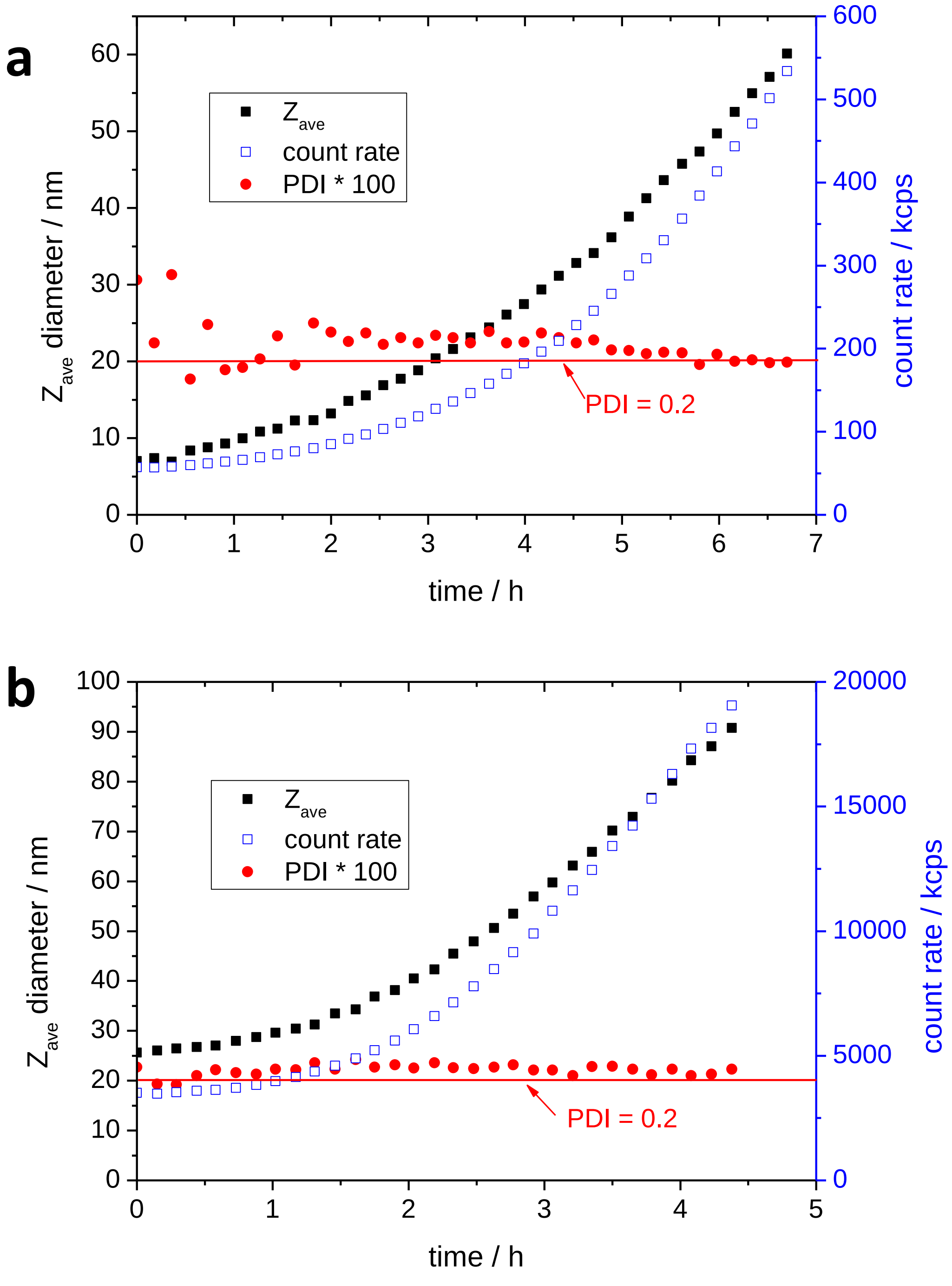

Figure S2: DLS sample growth profiles (black squares) curves for (a) 8-MNPCs and (b) 15-MNPCs which illustrate the polydispersity index (PDI, red dots) which stays constant around 0.2 during the cluster growth. Blue open squares represent the backscattered count rate.

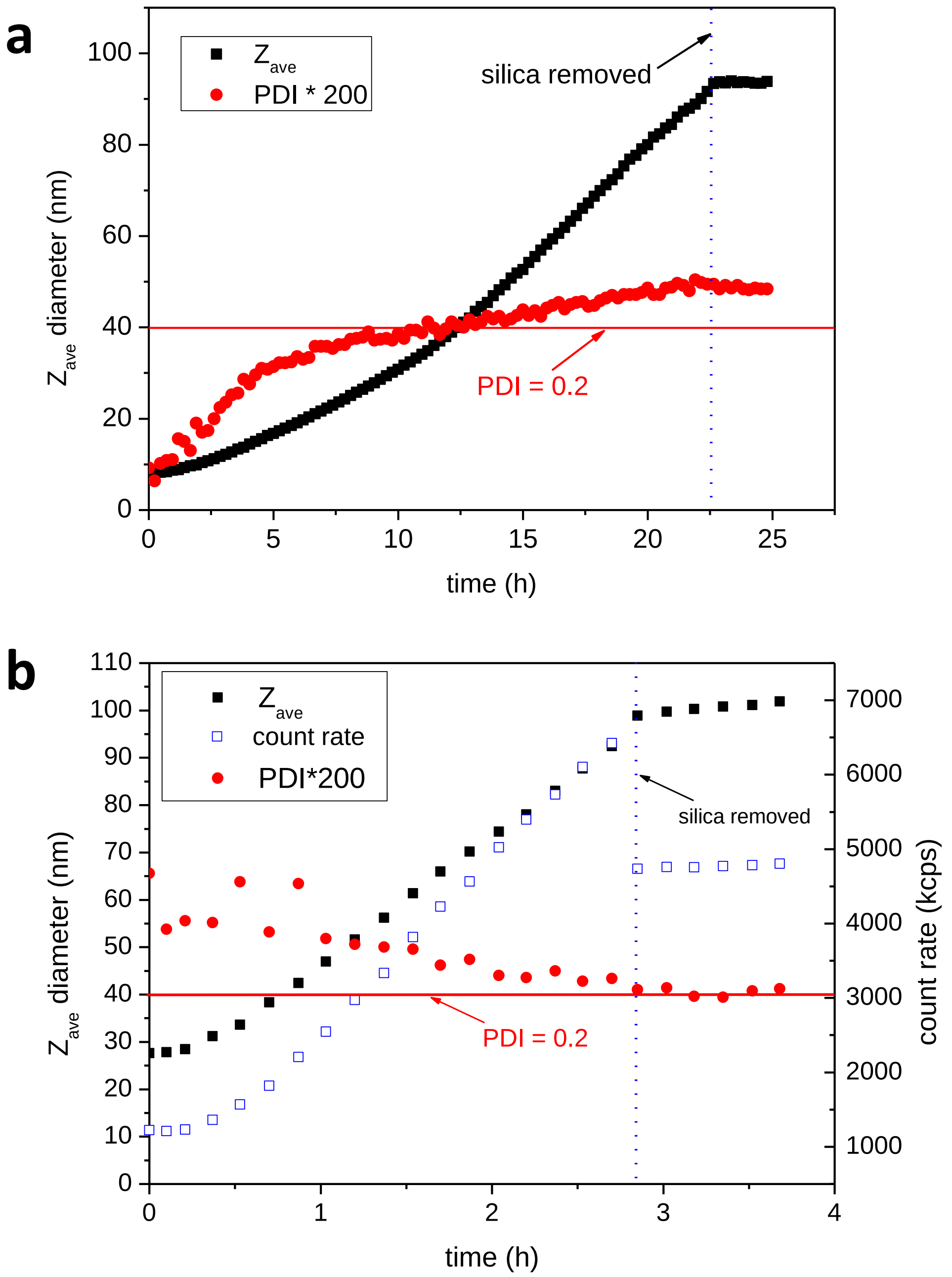

Figure S3: DLS measurement of arresting the growth of (a) 8-MNPCs and (b) 15-MNPCs by removing the silica phase at 22.65 h and 2.85 h, respectively. The time of removing the silica phase is indicated by the blue dotted lines.

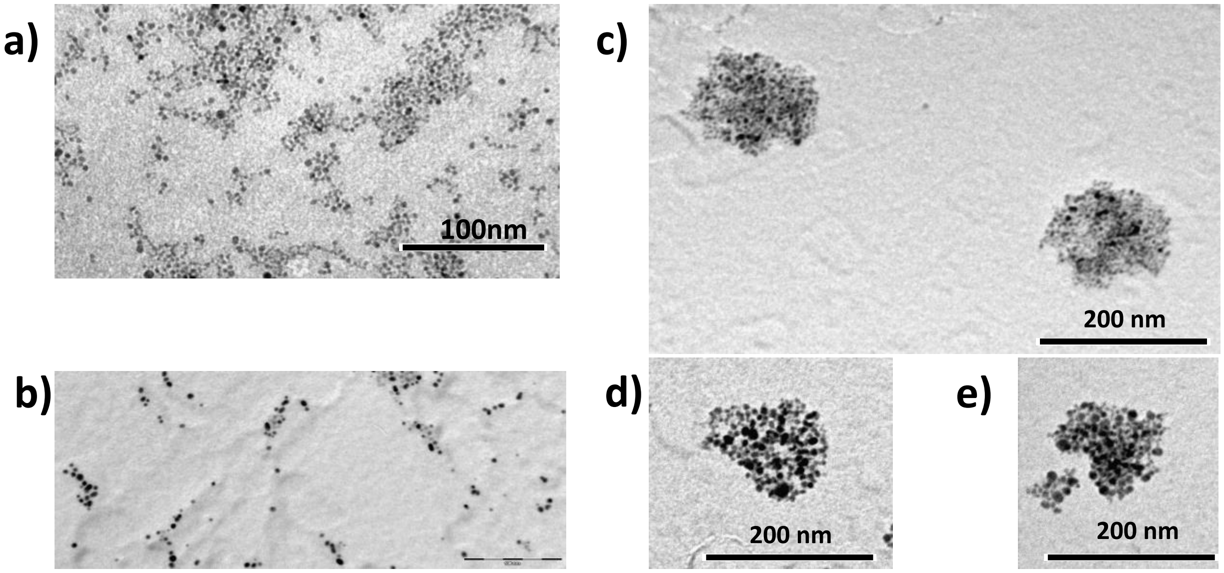

Figure S4: (a) and (b) TEM images of samples prepared by drying dispersions of *8-MNPCs*. No clusters can be discerned in the images, suggesting that the clusters do not survive the drying process on the TEM grid. The scale bar is 100 nm (c), (d) and (e) TEM images of 120 nm *15-MNPCs*, scale bar is 200nm.

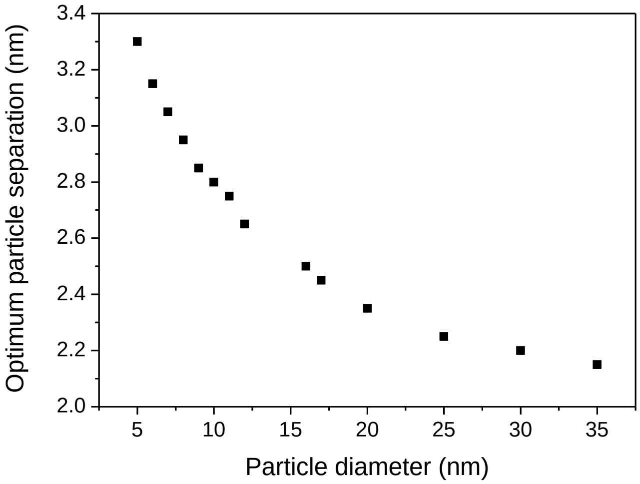

Figure S5: Optimum separation of the oleic acid stabilized MNPs as a function of nanoparticle diameter. Saturation magnetization of the MNPs was taken as 43 emu/g.

References

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