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Magnetic and Thermal Responses of a Nonvolatile Shape Memory Fluid

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Supplemental Information

Experimental Section

Materials: Ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) was purchased from Kanto Chemical. All other chemicals were reagent grade and obtained from Aldrich or Kanto Chemical. Commercially available reagents and solvents were used without further purification, except methyl acrylate (Kanto Chemical), which was purified by distillation under reduced pressure in a nitrogen atmosphere, and octadecylamine, which was recrystallized twice from hexane.

Synthesis of C18AA: 10.1 g (119 mmol) of distilled methl acrylate was added to 2.0 g (7.4 mmol) of octadecylamine in 15 mL of methanol. The solution was stirred at room temperature for 3 days, and then the solvent and excess methyl acrylate were removed from the solution by evaporation. The obtained intermediate and ethylenediamine anhydrous (17.8 g, 297 mmol) were dissolved in 20 mL of distilled methanol, and the mixture was stirred for a week at room temperature. After removing the solvent and ethylenediamine by evaporation and freeze-drying, C18AA was obtained as a light yellow solid. The crude solid was recrystallized from a mixed solvent of toluene and methanol.

Preparation of Fe_3O_4 NPs: A 1 M aqueous solution of $FeCl_2$ (100 μL) was mixed with given concentrations (50–500 mM) of C18AA aqueous solution (1 mL). The mixture became black within a few hours and was stood at room temperature for 24 h without stirring.

Preparation of oil-type magnetic fluids: Oil-type magnetic fluids were prepared by the addition of each organic solvent (1 mL) to the dried Fe_3O_4 NPs, followed by vigorous agitation of the mixture and subsequent sonication. The dried Fe_3O_4 NPs were obtained by evaporation of water from the as-prepared aqueous dispersion of Fe_3O_4 NPs (1 mL), so that the oil-type magnetic fluid (1 mL) contained 0.1 g of C18AA and 7.7 mg of Fe.

Preparation of O/W emulsion-type magnetic fluids: A 0.8 M aqueous solution of HCl (40 μL) was added to various concentrations of C18AA in toluene (480 μL), and the mixture was stirred vigorously for three days. After the mixture was homogeneous, the aqueous magnetic fluid (280 μL) prepared with [C18AA]=200 mM was added to form the O/W emulsion. The volume fraction of oil to water in the emulsion eventually became 6:4, and the concentration of HCl was diluted to 0.1 M in the water phase. In the present system, the concentration of C18AA was defined as

$$[\mathrm{C18AA}]_{\mathrm{w}} = \frac{\mathrm{C18AA}(g)}{320\times 10^{-3} + \mathrm{C18AA}(g)}, \qquad (1)$$

which is the weight percent concentration of C18AA when it is assumed that all C18AA molecules are present in the water phase.

Characterization: The morphology of the Fe_3O_4 NPs was observed using transmission electron microscopy (TEM; Jeol JEM-1011 with 100 kV accelerating voltage). XRD measurements were performed on a diffractometer (Rigaku Ultima IV) with Cu Kα radiation operated at 40 kV and 40 mA with a step of 0.02° (2θ). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Jeol JPS-9010MC spectrometer. The samples for TEM, XPS, and XRD measurements were prepared by casting Fe_3O_4 NPs dispersions onto carbon-coated copper grids, glass substrates, and silicon substrates, respectively.

Zeta potential measurements of the Fe_3O_4 NPs were performed on an Otsuka Electronics ELS-Z1 TR instrument using aqueous dispersions of the as-prepared Fe_3O_4 NPs diluted 25 times, with the pH adjusted by the addition of NaOH or HCl.

Magnetic susceptibility and hysteresis loop measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS XL). Magnetization curves were obtained at 300 K in fields up to 20 kOe. Dried Fe_3O_4 NPs were prepared for measurements by the evaporation of water from the as-prepared aqueous dispersions.

Dynamic rheological measurements were performed on a rheometer (Thermo Scientific MARS) equipped with parallel-plate geometry at a diameter of 35 mm. Measurements of the storage (G') and loss (G") moduli to determine the complex viscosity η*, were performed as a function of temperature from 20 to 70 °C at a constant frequency of 1 Hz and a sheer stress τ, of 1 Pa. The rate of temperature increase was controlled at 0.05 °C/min. The complex viscosity η* was obtained from the following equation:

$$\eta^* = [(G'^2+G''^2)/(2\pi f)^2]^{1/2}, \qquad (2)$$

where *f* is the frequency of the oscillation.

ZFC/FC curves

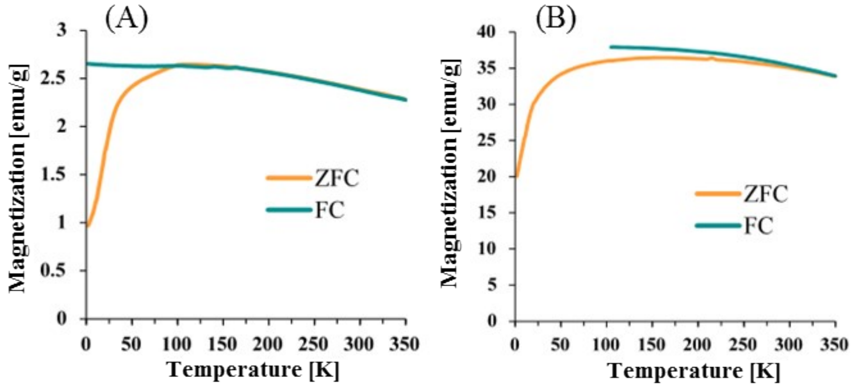


Figure S1. ZFC/FC curves for Fe_3O_4 NPs prepared at [C18AA]=200 mM (A) before (B) after washing with ethanol.

For Fe_3O_4 NPs covered with C18AA before washing (Figure S1A), the ZFC magnetization curve had a peak at 96 K, the blocking temperature, and coincided with the FC magnetization curve at high temperatures. This blocking behavior suggests that the NPs obtained here exhibit superparamagnetism. However, for Fe_3O_4 NPs without C18AA after washing, the ZFC curve did not coincide with the FC curve, even at 300 K (Figure S1B). The removal of C18AA from the surface of the NPs probably leads to flocculation of the NPs, which enables ferromagnetic behavior.

Zeta potential

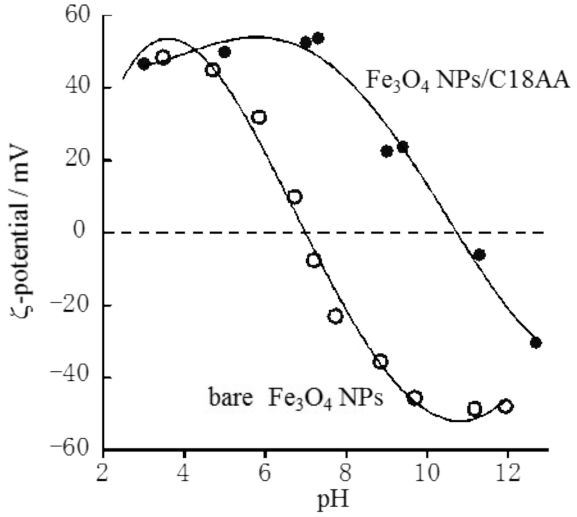


Figure S2. Zeta potentials of Fe_3O_4 NPs as a function of pH. The solid circles are for Fe_3O_4 NPs dispersed by C18AA in water at [C18AA]=200 mM, and the open circles are for bare NPs dispersed in water.

XPS spectra

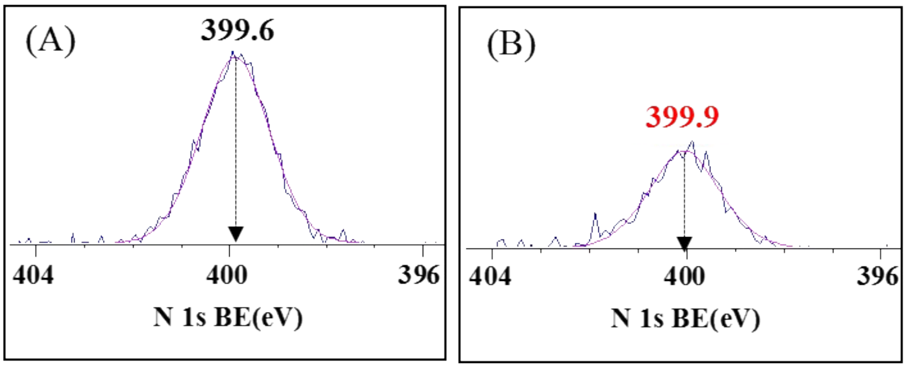


Figure S3. XPS spectra in the N1s region for (A) C18AA and (B) C18AA adsorbed on the surface of Fe_3O_4 NPs obtained at [C18AA]=200 mM. NPs were washed with chloroform.

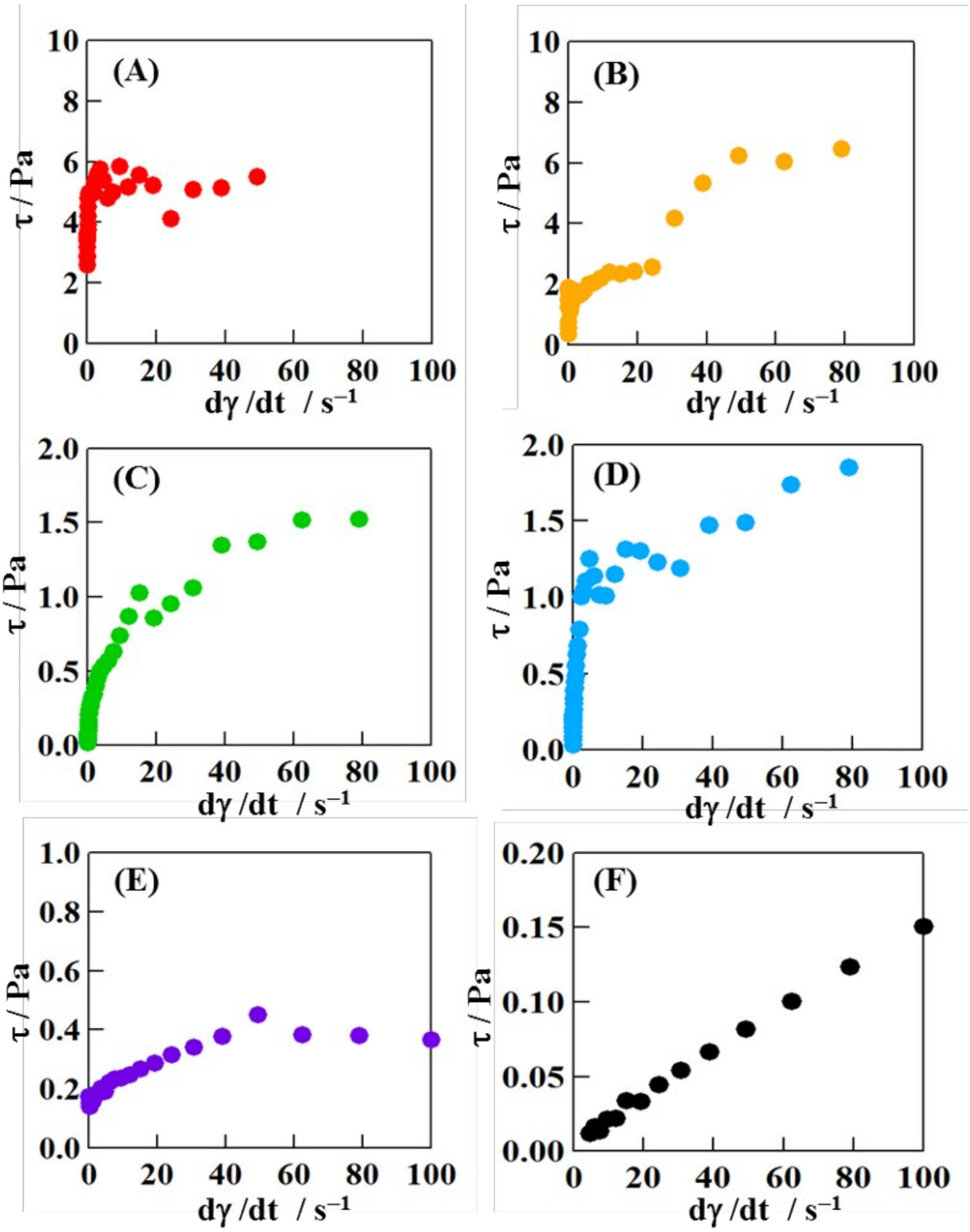


Figure S4 Flow curves for Fe_3O_4/C18AA NPs dispersed in (A) hexane, (B) cyclohexane, (C) toluene, (D) benzene, (E) THF, and (F) water.

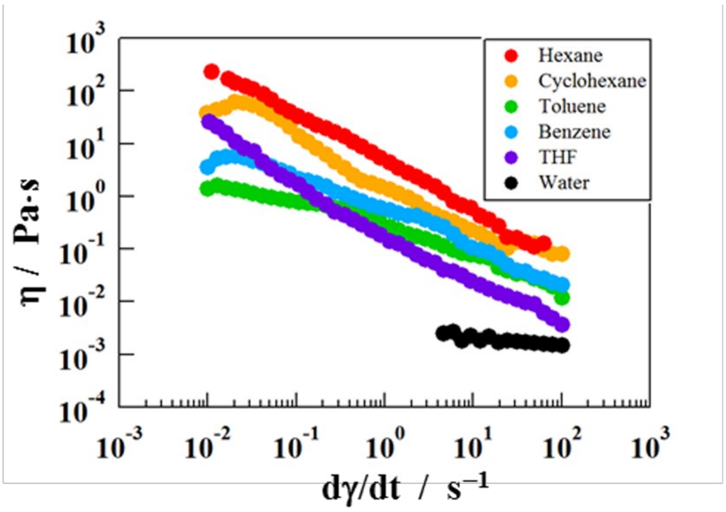


Figure S5 Viscosity curves for Fe_3O_4/C18AA NPs dispersed in various solvents.

Thixotropic behavior for oil-type magnetic fluids

Table S1 shows thixotropy index (TI) values calculated from the viscosity curves. All TI values for the organic solvent-type magnetic fluids were greater than 1, which suggests that these dispersions are thixotropic.

Table S1. Thixotropy index (TI) values for Fe_3O_4/C18AA magnetic fluids.

Solvent	TI
Hexane	7.3
Cyclohexane	2.7
Toluene	3.5
Benzene	6.4
THF	3.4
Water	1.1

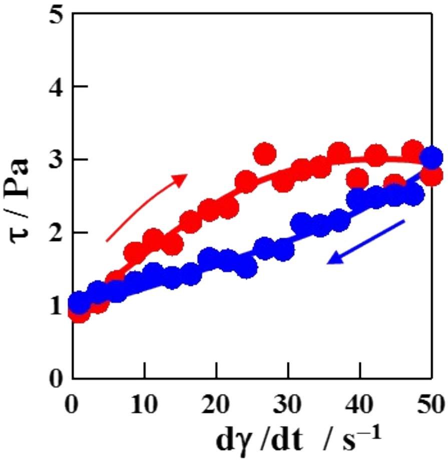
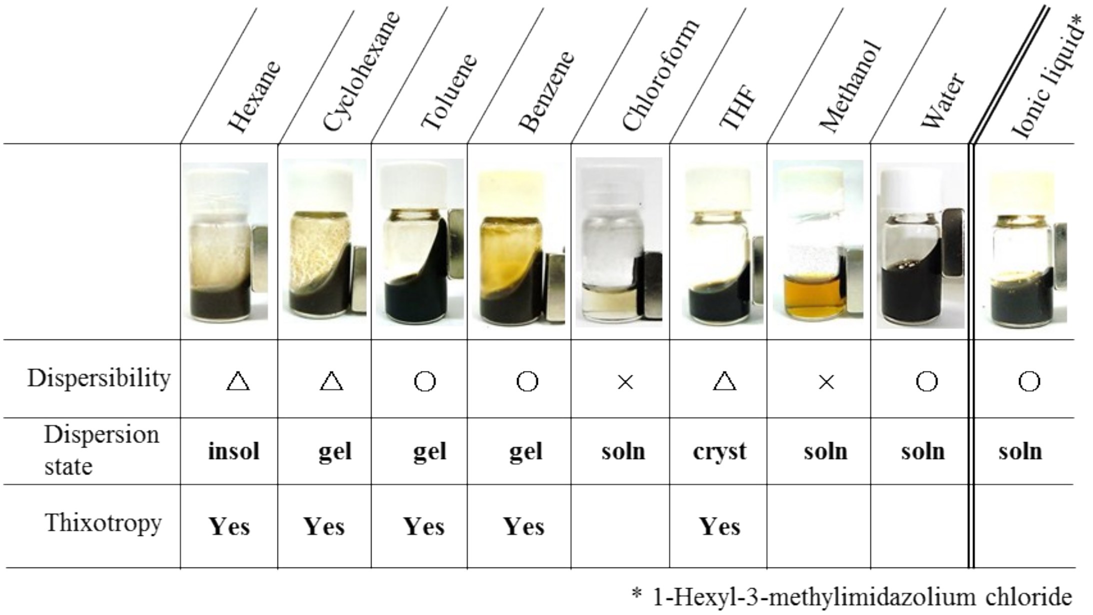


Figure S6. Flow curves for Fe_3O_4/C18AA NPs dispersed in toluene when the shear rate is increased and then decreased.

The flow curve for the oil-type magnetic fluid exhibited a hysteresis loop, strongly supports the thixotropy of the magnetic fluid.

Summary for oil-based magnetic fluids



	Hexane	Cyclohexane	Toluene	Benzene	Chloroform	THF	Methanol	Water	Ionic liquid*
Dispersibility	△	△	○	○	×	△	×	○	○
Dispersion state	**insol**	**gel**	**gel**	**gel**	**soln**	**cryst**	**soln**	**soln**	**soln**
Thixotropy	**Yes**	**Yes**	**Yes**	**Yes**		**Yes**			

* 1-Hexyl-3-methylimidazolium chloride

Figure S7. Appearance of oil-based magnetic fluids when applied with an external magnetic field, the dispersibility, the dispersion state, and the thixotropy. The open circles and open triangles represent stable and temporally stable (for a few hours) dispersibility, respectivey. The X marks mean that precipitation occur within an hour.