Electronic Supplementary Information

Novel thermo-responsive coloring phenomena in water/surfactant/oil emulsions

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Preparation of iridescent colored materials with Au NPs *via* the Brust method[1]

A 6.77 mM tetraoctylammonium bromide (TOAB) toluene solution (27 mL) was added to 1 mM $HAuCl_4$ aqueous solution (15 mL) and vigorously stirred for several hours. $AuCl_4^-$ transferred from the aqueous phase to the toluene solution of 33 mM C18AA using TOAB as the phase transfer reagent. After removal of the water phase, a 0.75 M $NaBH_4$ aqueous solution (3.6 mL) was added to the toluene solution. The addition of $NaBH_4$ brought about an immediate color change in the toluene phase from orange to a turbid reddish color (Fig. S1 inset left), which was considered to originate from the plasmon resonance band of the Au NPs.

This color changed to an iridescent bluish color with increasing temperature above ~38 °C (Fig. S1 inset). The reflection spectra of the iridescent colored material taken at an incident angle θ of 45° showed a sharp peak at ~480 nm (Fig. S1). Further, increasing the temperature above ~47 °C resulted in the disappearance of the iridescent color and the formation of an opaque emulsion again. (Fig. S1 inset). The peak in the reflection spectra also disappeared at above ~47 °C (Fig. S1). This coloring transition was found to be completely reversible over many cycles.

It is significant that materials having optical functions, such as noble metal NPs could be incorporated into the present iridescent emulsion system without affecting the interference color or the coloring temperature of the emulsions. In fact, the iridescent color and the coloring temperature range of the present emulsions were affected only by the C18AA and TOAB compositions, regardless of the Au NPs.

1) M. Brust, M. Walker, D. Bathell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* 1994, 801.
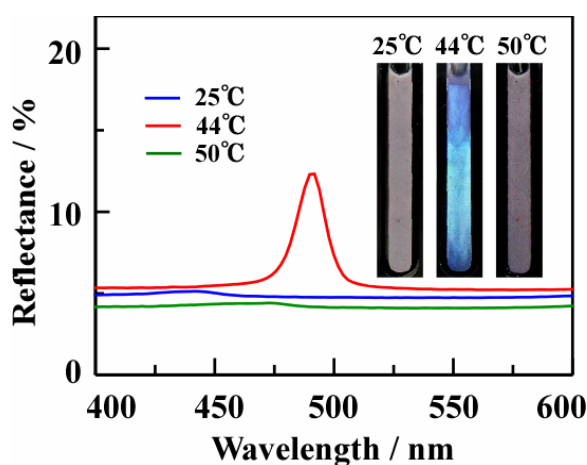

Fig. S1. The direct UV-vis reflection spectra of iridescent emulsions in the presence of Au NPs at [C18AA]=30 mM, [TOAB]=6 mM and ϕ_O=0.88. The incident angle was 45 °. Inset shows photographs of the iridescent emulsions.

Optical properties of the iridescent emulsion

Direct reflection spectra of the colored samples were measured by the UV-vis spectrometer (JASCO, V570) and the absolute reflectivity measurement accessory (JASCO, ARN-475) at the interface of a glass cell with a thickness of 10 mm. The temperature of the samples was controlled with a water jacket thermostated by a refrigerated bath circulator. Fig. S2a shows peaks appearing at 460-550 nm for a water/C18AA+TOAB/toluene solution at [C18AA] = 30 mM, [TOAB] = 6 mM and a certain volume fraction of toluene, ϕ_O=0.88, at 44 °C. The peaks shifted to shorter wavelengths with increasing incident angle. Because this shift is a characteristic feature of the interference color, we calculated the lattice spacing for the periodic structure of the iridescent emulsion using the Bragg equation (1) [2].

$$\lambda = 2d \, (\, n^2_{eff} - \sin^2\theta \,)^{1/2} \quad (1)$$
$$\sin^2\theta = -\lambda^2 / (4d^2) + n^2_{eff} \quad (2)$$

Here, λ is the wavelength of the peak, d is the lattice spacing, θ is the incident and reflection angle, and n_{eff} is the average refractive index. The plot of λ^2 against $\sin^2\theta$ was linear, as shown in Fig. S2b, indicating that the iridescent color of the water/C18AA+TOAB/toluene system is definitely derived from interference color [3]. The lattice spacing, d, was estimated to be 180 nm for the 30 mM-C18AA/6 mM-TOAB/toluene/water sample at 44 °C.

2) (a) H. Fudouzi, *J. Colloid Interface Sci.* 2004, **275**, 277; (b) A. Richel, N. P. Johnson, *Appl. Phys. Lett.* 2000, **76**, 1816.

3) Y. Imura, H. Nakazawa, E. Matsushita, C. Morita, T. Kondo, T. Kawai, *J. Colloid Interface Sci.* 2009, **336**, 607.
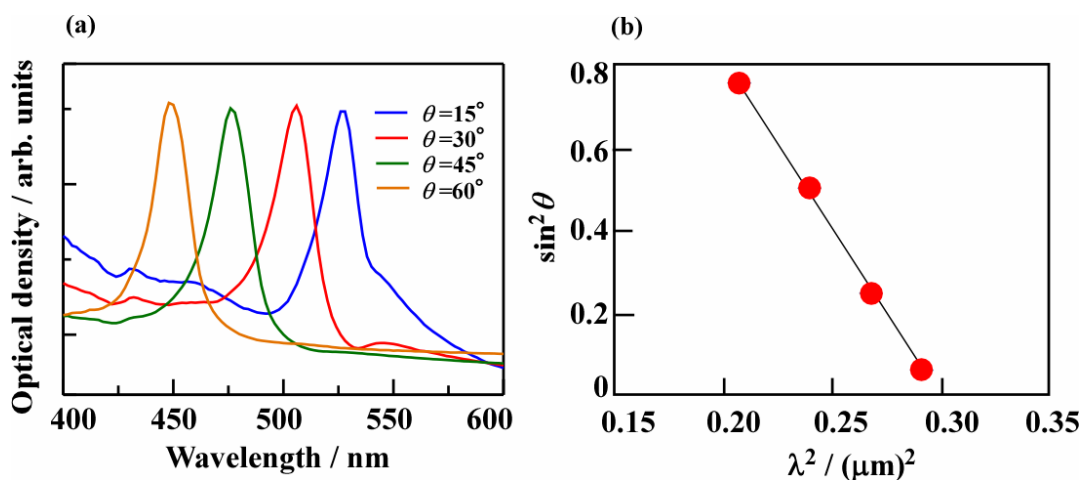

Fig. S2 (a) The direct UV-vis reflection spectra of iridescent emulsions measured by changing the incidence and detection angles from 15 - 60°. (b) Plot of $\sin^2\theta$ as a function of λ^2 based on the Bragg equation.

Characterization of the emulsion

The emulsion phase inversion was confirmed by measurement of the viscosity, the conductivity and the optical microscopic images. All measurements were performed at [C18AA]=30 mM, ϕ_o=88%.

Viscosity measurements were performed on a rheometer (MARS, Thermo-schientific) using parallel plate with a diameter of 35 mm with Peltier based temperature control. The samples were kept for at least 5 min at each temperature prior to the measurements. Zero-shear viscosity η_0 was determined as the plateau value of viscosity in a low shear rate regime at [TOAB]/[C18AA]=0.2 (the coloring temperature was appeared at 38~47 °C)

Conductivities ρ were determined by the resistance value using equatation (3).

$$\kappa \, [1/m] = \rho \, [S/m] \times R \, [\Omega] \qquad (3)$$

Here, κ is the cell constant and R is the resistance. The resistance R was measured by the sourcemeter (Model2400, KEITHLEY) using a Pt-evaporated electrode (BAS Inc.). To determine the cell constant κ, standard KCl solution was used. The sample vial was settled in the thermostatic bath, and the temperature of the sample was monitored by the thermocouple. Prior to each measurements, the sample was kept for at least 10 min. As shown Figure S3, the conductivities showed the two peaks at 37 °C and 48 °C. It is assumed that these discontinuous values of conductivity were due to the transition of the emulsion structure from the droplets to the multi-layers.[4] [TOAB]/[C18AA]=0.2 (the coloring temperature was 38~47 °C)

4) P. Izquierdo, J. Esquena, Th. F. Tadros, C. Dederen, M. J. Garcia, N. Azemar, C. Solans, *Langmuir* 2002, **18**, 26.

The confocal microscopy images of the O/W or W/O emulsions in phase **I** and **III** were taken by a laser-scanning microscope (LSM710, CARL ZEISS). Fluorescence microscopic images were obtained using the water-soluble dye rhodamine 6G as a fluorescent probe. Exicitation laser wavelength was 561 nm. Optical microscopic reflection images of the iridescent emulsions in phase **II** were taken by digital microscope (VHX-200, KEYENCE). Polarlized microscopic images were also taken by a inverted microscope (DMI4000B, Leica) under the crossed polarization. All optical microscopic observation was carried out at 28 ± 2 °C. The temperature of the sample was monitored by a thermocouple placed on the sample cell. The surfactant ratio was adjusted as given below.

Phase **I**: [TOAB]/[C18AA]=0.2 (the coloring temperature was 38~47 °C),
Phase **II**: [TOAB]/[C18AA]=0.5 (the coloring temperature was 25~32 °C),
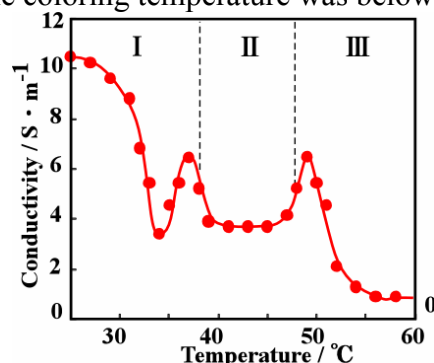Phase **III**: [TOAB]/[C18AA]=0.8 (the coloring temperature was below 25 °C).

Fig. S3 Temperature dependence of the electric conductivity of the iridescent emulsion at [C18AA]=30 mM, [TOAB]=6 mM.