Supplementary Material (ESI) for Chemical Communications

Self-lubricating Nanoparticles: Self-Organization into 3D-Superlattices during a Fast Drying Process

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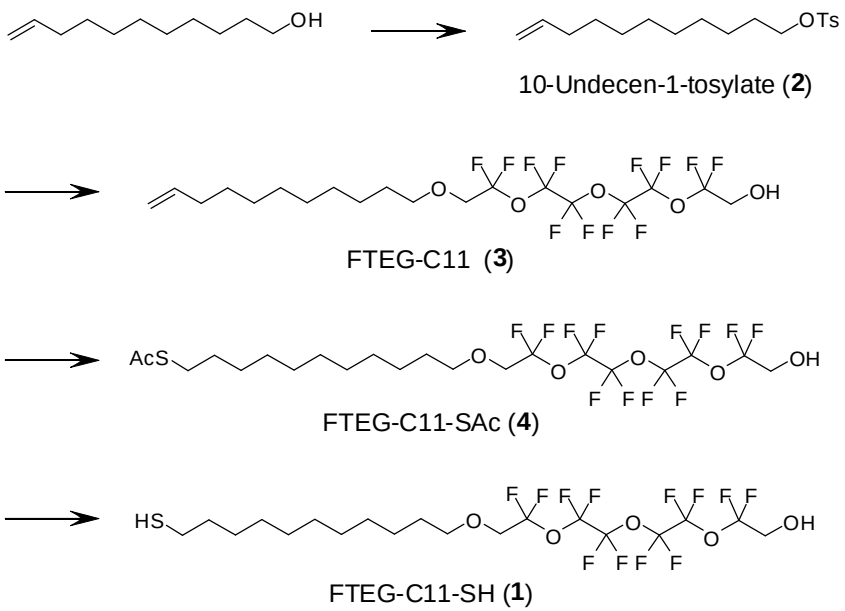
Experimental Section

General

All commercially available reagents were used without further purification. Thin-layer Chromatography (TLC) and Preparative Layer Chromatography (PLC) were performed on glass-backed precoated silica gel plate (60F254, Merck & Co., Inc., USA). Molecules were visualized by Cerium molybdate (10 % Cerium (IV) Sulfate, 15 % aqueous sulfuric acid solution). Products were isolated by column chromatography on silica-gel (Kanto Chemical, 60N, spherical, neutral, 40-50 μm). Hydrophobization of glass substrates performed using commercially available hydrophobizing agent (Siliconize L-25, Fuji-rikagaku Industries, Ltd, Japan). Fluorinated tetraethyleneglycol, 10-undecene-1-ol and *p*-toluenesulfonyl chloride were purchased from Wako Pure Chemical Industries Ltd. (Japan). MALDI-TOF-MS spectra were measured with a Voyger-DE STR-H (Applied Bio Systems). NMR spectra were recorded on a 400 MHz JEOL spectrometer.

1. Synthesis of FTEG-C11-SH (1).



10-Undecen-1-tosylate **(2)**

Triethyl amine (4.05 g, 40 mmol), trimethyl amine (384 mg, 4.0 mmol), and *p*-Tosyl chloride (4.58 g, 24 mmol) in 12 ml anhydrous CH_2Cl_2 were added to 10-undecene-1-ol (3.40 g, 20 mmol) in 10 ml dry CH_2Cl_2 solution at 0 ^oC. The reaction mixture was stirred for 1.5 h at 0 ^oC under N_2 atmosphere. The resulting mixture was washed with 100 ml of water, brine and dried over Na_2SO_4. After concentrated *in vacuo*, the residue was purified by flash SiO_2 column chromatography using Hexane/EtOAc (9:1) as the elutant to give 10-undecene-1-tosylate **2** as a clear syrup (5.82 g, 89.7 % yield). ^1H NMR (400 Mz, $CDCl_3$) δ/ppm: 7.78 (d, 2H, J = 8.4 Hz, C*H* aromat.), 7.34 (d, 2H, J = 8.1 Hz, C*H* aromat.), 5.71-5.90 (br, 1H, -C=C*H*-, olefin), 4.86-5.03 (br, 2H, CH_2=CH-, olefin), 4.01 (t, J = 6.4 Hz, 2H, TsO-CH_2-), 2.44 (s, 3H, -CH_3 OTs), 2.03 (br, 2H, CH_2=CH-CH_2-), 1.58-1.68 (br, 2H, TsO-CH_2-CH_2-), 1.14-1.42 (br, 14H, alkyl chain).

FTEG-C11 **(3)**

10-undecene-1-tosylate (792 mg, 2.44 mmol) in 2 ml dry DMF was added to a solution of fluorinated tetraethyleneglycol (2.0 g, 4.88 mmol), and K_2CO_3 (506 mg, 3,66 mmol) in dry DMF (3 ml). The mixture was stirred for 14 hours at 80 °C. The reaction mixture was diluted with EtOAc (5 ml) and neutralized with 15 w% NH_4Cl aq. (20 ml), and washed with 100 ml of water and brine. After dried over anhydrous Na_2SO_4 and concentrated in *vacuo*, the residue was purified by flash SiO_2 column chromatography using Hexane/EtOAc (9:1) as the elutant to give a product **(3)** as a clear syrup (866 mg, 63.2 % yield). 1H NMR (400 MHz, $CDCl_3$) δ/ppm: 5.71-5.90 (br, 1H, -C=C*H*-, olefin), 4.85-5.05 (br, 2H, C*H*$_2$=CH-, olefin), 3.91 (m, 2H, HO-C*H*$_2$-CF_2-), 3.80 (t, 2H, *J* = 9.6 Hz, -CF_2-C*H*$_2$-O-), 3.60 (t, 2H, *J* = 6.7 Hz, -O-C*H*$_2$-CH_2-), 2.65 (t, 1H, *J* = 8.4 Hz, -OH), 2.03 (br, 2H, CH_2=CH-C*H*$_2$-), 1.52-1.63 (br, 2H), 1.20-1.44 (br, 12H, alkyl chain). MALDI-TOF MS (m/z): $[M+Na]^+$ calcd for $C_{19}H_{26}F_{12}O_5Na$, 585.15; found, 584.96.

FTEG-C11-SAc **(4)**

FTEG-C11 **3** (360 mg, 0.64 mmol), AcSH (247 mg, 3.24 mmol), AIBN (53 mg, 0.32 mmol) were dissolved in toluene anhydrous (3 ml). The reaction mixture was stirring for 45 min at 100 °C under N_2 atmosphere. After diluted with MeOH, the solution was concentrated in vacuo. The residue was purified by flash SiO_2 column chromatography and PLC using Hexane/$CHCl_3$ (2:8) as the elutant to give a product **(3)** as a clear syrup (324 mg, 79.0 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 3.93 (m, 2H, HO-C*H*$_2$-CF_2-), 3.81 (t, 2H, *J* = 9.6 Hz, -CF_2-C*H*$_2$-O-), 3.60 (t, 2H, *J* = 6.5 Hz, -O-C*H*$_2$-CH_2-), 2.86 (t, 2H, *J* = 7.4 Hz, -C*H*$_2$-SAc), 2.63 (t, 1H, *J* = 7.4 Hz, -OH), 2.32 (s, 3H, Ac), 1.50-1.62 (br, 4H), 1.20-1.44 (br, 14H, alkyl chain).

FTEG-C11-SH (1)

Compound **4** (93.6 mg, 1.52×10^{-4} mol) and CH_3ONa (2.93 μl, 28 % MeOH solution, 1.52×10^{-5} mol) were dissolved and stirring for 4 hours in MeOH anhydrous (3 ml) at room temperature. The mixture was neutralized with Dowex (50WX8-200) and concentrated in vacuo. The residue was purified by PLC using $CHCl_3$ as the developing solvent to give a product **1** as a white crystal (45.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 3.94 (m, 2H, HO-C*H*$_2$-CF_2-), 3.81 (t, 2H, *J* = 9.6 Hz, -CF_2-C*H*$_2$-O-), 3.60 (t, 2H, *J* = 6.5 Hz, -O-C*H*$_2$-CH_2-), 2.68 (t, 2H, *J* = 7.3 Hz, -C*H*$_2$-SH), 1.47-1.74 (br, 4H), 1.14-1.42 (br, 14H, alkyl chain). MALDI-TOF MS (m/z): $[M+Na]^+$ calcd for $C_{19}H_{28}F_{12}O_5SNa$, 619.14; found, 619.13.

Preparation of FTEG-AuNPs

Citrate-stabilized AuNPs (5 or 20 nm in a diameter) were purchased from Funakoshi (Japan). The aqueous dispersions of citrate-stabilized AuNPs (1 ml) were concentrated by centrifugal evaporation at 5,500 g and then added into a THF solution (1 ml) of the FTEG-C11-SH (typically 10 mM), followed by vigorous stirring for 2 days. We note that the concentration of thiols in this solution is 20-50 times of the molecules of Au atoms on the nanoparticle surface. The resulting solutions were centrifuged 3 times to remove citrate and excess thiols. The hydrodynamic diameter of nanoparticles was determined using dynamic light scattering (DLS, DelsaNANO HC, Beckman Coulter Inc., USA).

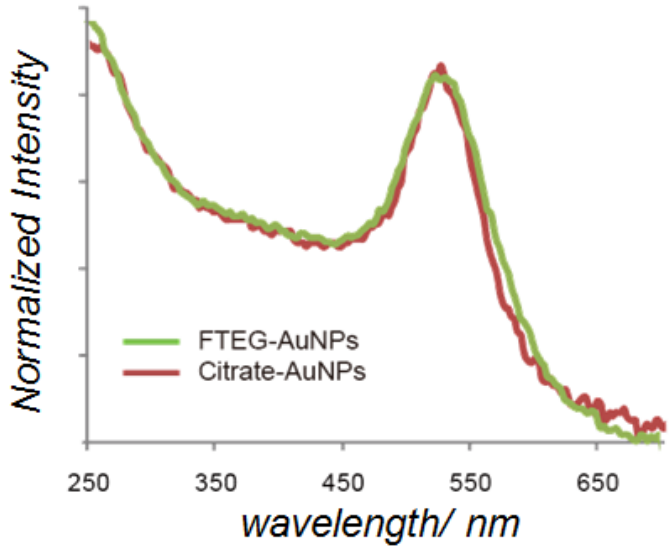
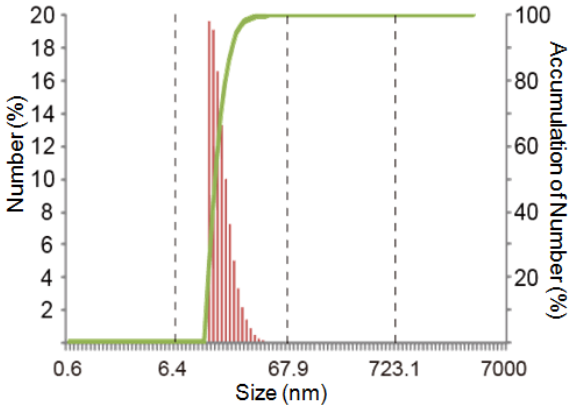


Figure S1. Absorption spectra of Citrate-AuNPs (20 nm) in water and FTEG-AuNPs (core diameter: 20 nm) in EtOH.



Results (Contin)

	Diameter (nm)	st. deviation (nm)
Peak 1:	20.1	5.9
Peak 2:	0	0
Peak 3:	0	0
Peak 4:	0	0
Peak 5:	0	0
Average	20.1	5.9

Figure S2. DLS analysis of FTEG-AuNPs (core diameter: 20 nm) dispersion in EtOH at 25 °C. A particle concentration was 1.0×10^{-13} /ml.

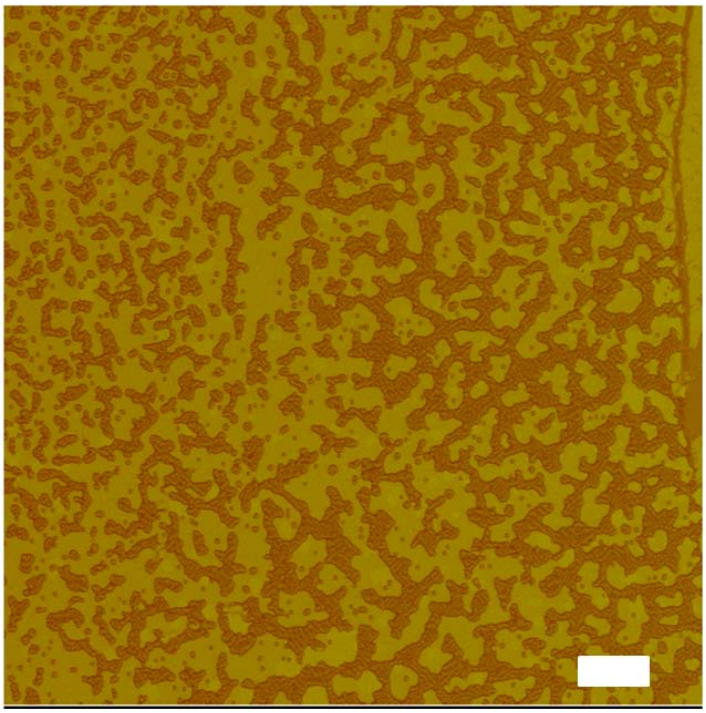


Figure S3. AFM image of a 20 nm FTEG-AuNPs cast film deposited on hydrophilic glass substrate from MeOH solutions. Brown regions show monolayered nanoparticle islands. White bar indicate 1 μm.

Table S1. Solubility of FTEG-AuNPs (5, 20 nm) in several organic solvents. The figures in parentheses shows their permittivity.

Poor solvent				Good solvent			
1,4-Dioxane	(2.22)	DMSO	(48.9)	Diethylether	(4.27)	MeOH	(33.0)
$CHCl_3$	(4.81)	H_2O	(80.1)	THF	(7.52)	CH_3CN	(36.6)
Toluene	(2.38)			BuOH	(18.0)	DMF	(38.3)
CH_2Cl_2	(8.93)			EtOH	(24.0)		