

Multiple-Division of Self-Propelled Oil Droplets through Acetal Formation

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Supplementary Information

Materials and Methods

Reagents

Commercially-available reagents and solvents were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) and Kanto Chemical Co. (Tokyo, Japan), respectively, and were used without further purification. Water was distilled and deionized before use with a MilliQ system from Millipore (MA, USA).

Synthesis of 4-(heptyloxy)-1-didecyloxybenzene (diC10A)

To evaluate the effect of the primary product by the reaction of C7BA and C10OH on the dynamics of oil droplets, diC10A was synthesized according to Madsen *et al.*¹ A mixture of C7BA (2.20 g, 10 mmol), C10OH (3.81 g, 24 mmol), *p*-toluenesulfonic acid (381 mg, 2 mmol), and activated 3A molecular sieves (2 g) was stirred in anhydrous hexane (10 mL) for 8 h at 0 °C before quenching with solid NaHCO₃. The mixture was then filtered through celite, and the residue was dissolved in hexane (25 mL). The organic layer was washed with 1 M aqueous NaOH (25 mL), and then dried over anhydrous magnesium sulfate. The unreacted C7BA and C10OH in the solvent were removed by distillation at 200 °C at 0.5 mmHg to obtain diC10A as a colorless viscous liquid at a yield of 21% (1.09 g).

¹H NMR (270 MHz, CDCl₃): δ 7.36 (2H, d, *J* = 8.8 Hz), 6.87 (2H, d, *J* = 8.8 Hz), 5.45 (1H, s), 3.95 (2H, t, *J* = 6.5 Hz), 3.58–3.35 (4H, m), 1.84–1.70 (2H, m), 1.67–1.52 (4H, m), 1.50–1.15 (36H, m), 0.96–0.80 (9H, m). Matrix-

assisted laser desorption/ionization time-of-flight-mass spectrometry (MALDI TOF-MS) using 2,5-dihydroxybenzoic acid as a matrix (m/z): 519.75 $[M + H^+]$; calcd, 519.86 $[M + H^+]$.

Optical microscopic observation of oil droplet dynamics

The observation specimen was prepared as follows. An emulsion of mixed C7BA and CmOH was formed by agitating 200 μL of the surfactant (CnTAB) solution with a mixture of C7BA and C10OH (10 μL). Immediately after mixing C7BA and CmOH in the surfactant solution and encasing the emulsion sample in a thin glass-chamber (15 \times 15 \times 0.28 mm; Frame Seal Chamber, MJ Research Inc., Waltham), real-time observations were conducted at room temperature (23–25 $^{\circ}\text{C}$) using a phase contrast microscope (IX71, Olympus, Japan) equipped with a CCD camera (U-LH100, Olympus, Japan).

Time course measurement of the chemical reactions

A mixture of C7BA and C10OH (10 μL) was added to an aqueous solution in the presence or absence of 50 mM C16TAB solution (200 μL) at room temperature, lyophilized, and dissolved in CDCl_3 . Production of diC10A was analyzed by ^1H NMR spectral measurements of a CDCl_3 solution of C16TAB and products, and the percentage production of diC10A was calculated by integration of the ratio of the signals for acetal methine protons at δ 5.45 ppm to that for the aldehyde methine protons at δ 9.87 ppm using the signal for trimethylammonium from C16TAB protons at δ 3.47 ppm as an internal standard peak (see Fig. S1).

Figures

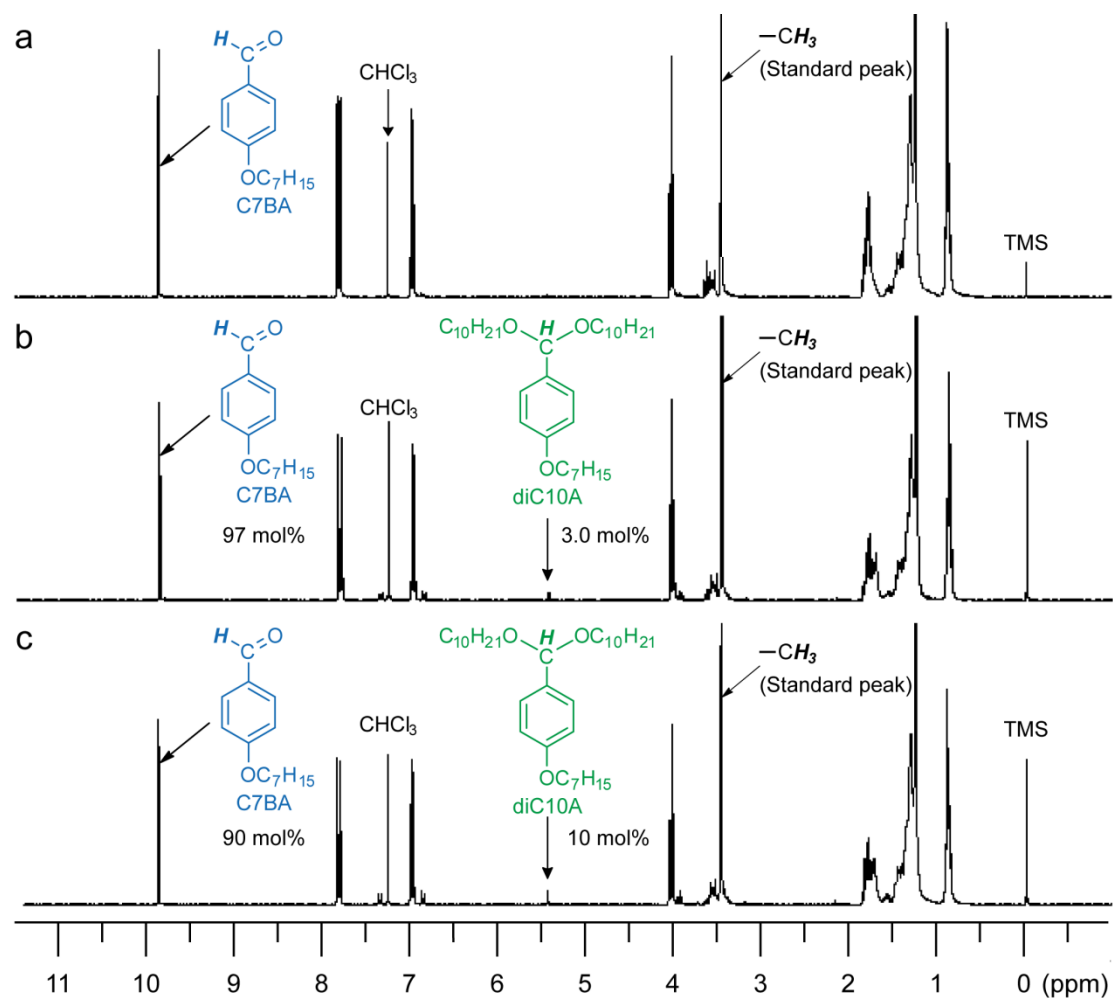


Fig. S1 ^1H NMR spectra (CDCl_3 solution) of the product from the reaction of C7BA and C10OH (7:3, the molar ratio) in C16TAB solution (50 mM) with HCl (0.01 M) at room temperature. The sample of the reaction mixture was examined at (a) 0, (b) 30, and (c) 60 min after the dispersion was prepared. The molar composition of diC10A and C7BA was calculated by integration of the ratio of the signals for acetal methine protons at δ 5.45 ppm to that for the aldehyde methine protons at δ 9.87 ppm, using the trimethylammonium from C16TAB protons at δ 3.47 ppm as an internal standard peak.

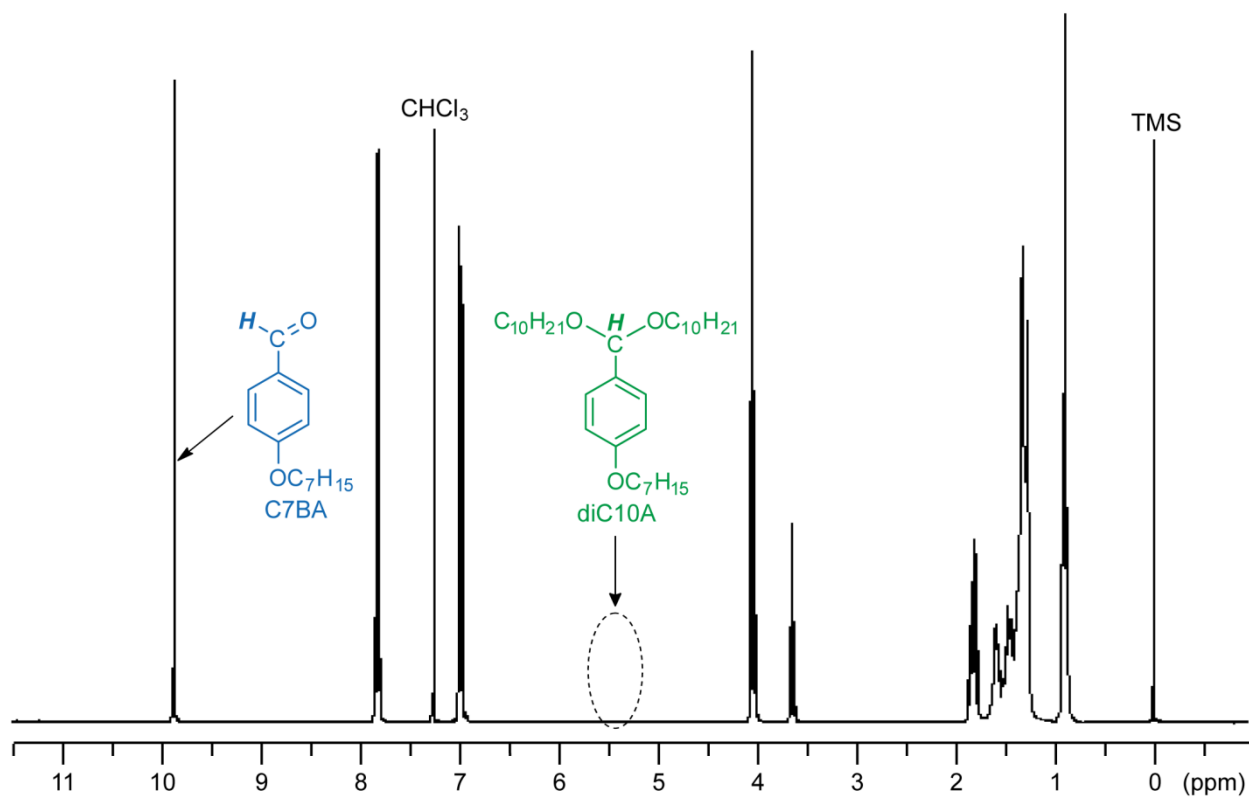


Fig. S2 $^1\text{H NMR}$ spectrum (CDCl_3 solution) of the product from the reaction of C7BA and C10OH (7:3, the molar ratio) in 0.01 M HCl solution at room temperature for 6 days.

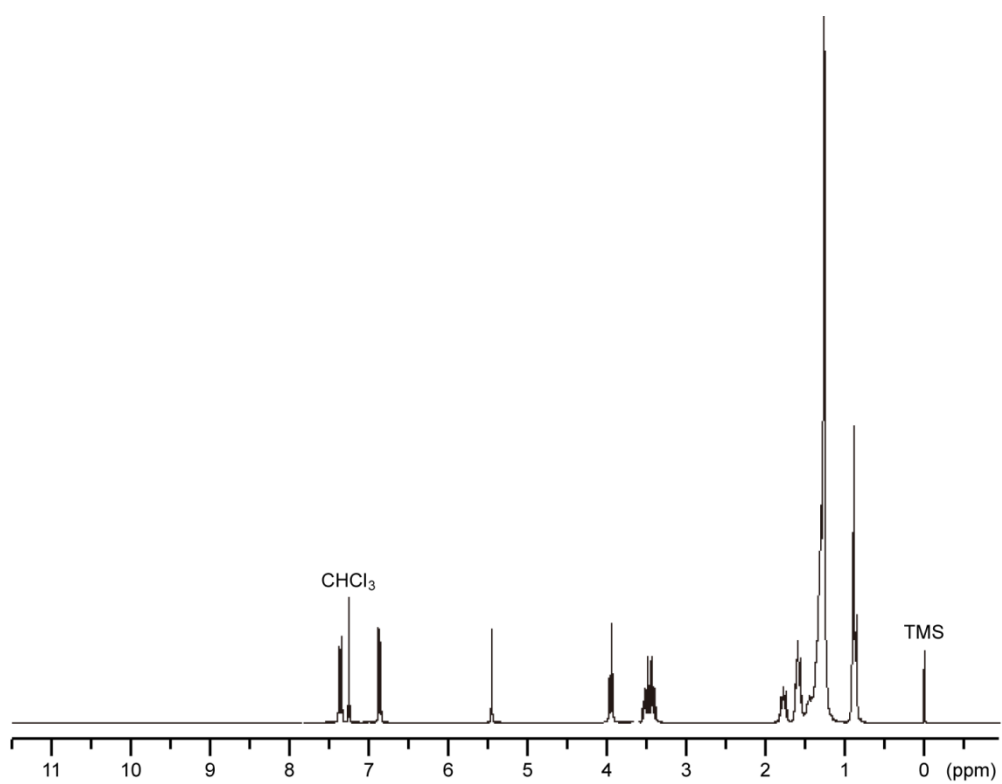


Fig. S3 ^1H NMR spectrum (CDCl_3 solution) of 4-(heptyloxy)-1-dialkyloxybenzene (diC10A).

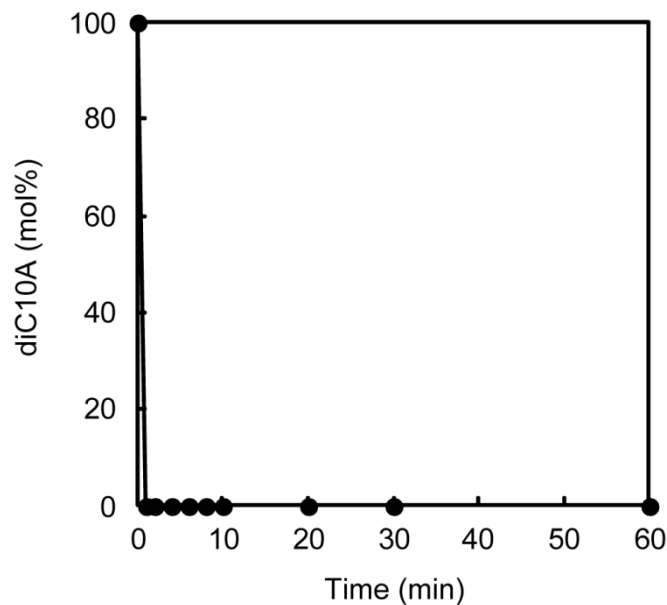


Fig. S4 Time course for the hydrolysis of 4-(heptyloxy)-1-dialkyloxybenzene (diC10A) at room temperature in the presence of C16TAB (50 mM) and HCl (0.01 M), as analyzed by $^1\text{H-NMR}$. DiC10A (10 μL) was added to an aqueous solution of 50 mM C16TAB (200 μL) at room temperature and was lyophilized and dissolved in CDCl_3 . Reduction of acetal was analyzed by $^1\text{H-NMR}$ analysis (CDCl_3 solution) of C16TAB and the hydrolytic product, and the reduction of acetal (mol%) was calculated by integration of the ratio of the signals for acetal methine protons at δ 5.45 ppm and that for the aldehyde methine protons at δ 9.87 ppm, using the methyl proton signal at δ 0.96–0.80 ppm as an internal standard peak (see Fig. S1).

Tables

Table S1 Effect of the C7BA to C10OH molar ratio on the dynamics of oil droplets with diameters in the range of 10–150 μm .

Entry	Molar ratio (mol/mol)		Motion time (min)	P ^[a]	Q ^[b]	R ^[c]
	C7BA	C10OH				
1	10	0	45	n.o.	n.o.	n.o.
2	9	1	–	n.o.	n.o.	n.o.
3	8	2	15	✓	✓	n.o.
4	7	3	>60	✓	✓	✓
5	6	4	>60	✓	✓	✓
6	5	5	>60	✓	✓	n.o.
7 ^[d]	3	7	13	n.o.	n.o.	n.o.
8	0	10	–	n.o.	n.o.	n.o.
9	7	3	>60	✓	✓	n.o.
10	7	3	>60	✓	✓	n.o.

[a] Division of self-propelled mother droplet P. [b] Self-propelled motion of older daughter droplet Q. [c] Self-propelled motion of younger daughter droplets R. [d] Self-propelled oil droplets with diameters less than 10 μm were observed. n. o. = not observed.

Table S2 Effect of C16TAB concentration on the dynamics of oil droplets with diameters in the range of 10–150 μm .

Entry	C16TAB (mM)	Motion time (min)	P ^[a]	Q ^[b]	R ^[c]
1	0	–	n. o.	n. o.	n. o.
2	10	>60	✓	✓	n. o.
3	30	>60	✓	✓	n. o.
4	50	>60	✓	✓	✓
5	75	>60	✓	✓	n. o. ^[d]
6	100	36	✓	✓	n. o. ^[d]

[a] Division of self-propelled mother droplet P. [b] Self-propelled motion of older daughter droplet Q. [c] Self-propelled motion of younger daughter droplets R. [d] Younger daughter oil droplets R that did not exhibit the self-propelled motion were rapidly dissolved in solution. n. o. = not observed.

Table S3 Effect of the surfactant molecule on the dynamics of oil droplets composed of C7BA and C10OH (7:3, molar ratio) in 50 mM cationic surfactant solution containing 0.01 M HCl at room temperature.

Entry	Surfactant	Motion time (min)	P ^[a]	Q ^[b]	R ^[c]
1	C12TAB	>60	✓	✓	n. o.
2	C14TAB	>60	✓	✓	n. o.
3	C16TAB	>60	✓	✓	✓

[a] Division of self-propelled mother droplet P. [b] Self-propelled motion of older daughter droplet Q. [c] Self-propelled motion of younger daughter droplets R. n. o. = not observed.

Table S4 Effect of the alkanol molecule on the dynamics of oil droplets composed of C7BA and C10OH (7:3, molar ratio) in 50 mM cationic surfactant solution containing 0.01 M HCl at room temperature.

Entry	Alkanol	Motion time (min)	P ^[a]	Q ^[b]	R ^[c]
1	C6OH	>60	✓	✓	n. o.
2	C8OH	27	✓	✓	✓
3	C10OH	>60	✓	✓	✓

[a] Division of self-propelled mother droplet P. [b] Self-propelled motion of older daughter droplet Q. [c] Self-propelled motion of younger daughter droplets R. n. o. = not observed.

Table S5 Behavior of self-propelled oil droplets and acetal production in dispersions of C7BA and C10OH under various conditions at room temperature.

Entry	Dispersion	Motion time (min)	P ^[a]	Q ^[b]	R ^[c]	diC10A (%) ^[d]
1	0.001 M HCl	>60	✓	✓	n. o.	6
2	0.01 M HCl	>60	✓	✓	✓	10
3	0.1 M HCl	>60	✓	✓	n. o. ^[e]	n. d.
4	0.001 M NaCl	25	n. o.	n. o.	n. o.	2
5	0.01 M NaCl	57	✓	✓	n. o.	2
6	0.1 M NaCl	>60	✓	✓	n. o.	1

[a] Division of self-propelled mother droplet P. [b] Self-propelled motion of older daughter droplet Q. [c] Self-propelled motion of younger daughter droplets R. [d] The amount of diC10A (mol%) was analyzed using a lyophilized sample 60 min after preparation of the dispersion. [e] Younger daughter oil droplets R that did not exhibit the self-propelled motion were rapidly dissolved in solution. n. o. = not observed. n. d. = not detected.

Video Clips

Two video clips have been attached to show the unique coupled dynamics of oil droplets composed of C7BA and C10OH (7/3, molar ratio) in a 50 mM dispersion of C16TAB containing 0.01 M HCl at room temperature.

Video 1: Self-propelled motion and division of a mother oil droplet (27 μm diameter) and self-propelled motion of a larger daughter droplet (19 μm diameter).

Video 2: Self-propelled motion and dissolution of smaller daughter droplets of 1–5 μm in diameter.

Reference

- 1 R. Madsen, B. Fraser-Reid, *J. Org. Chem.*, 1995, **60**, 772.