Electronic Supplementary Information for:

Photochromism of a water-soluble vesicular [2.2]paracyclophane-bridged imidazole dimer

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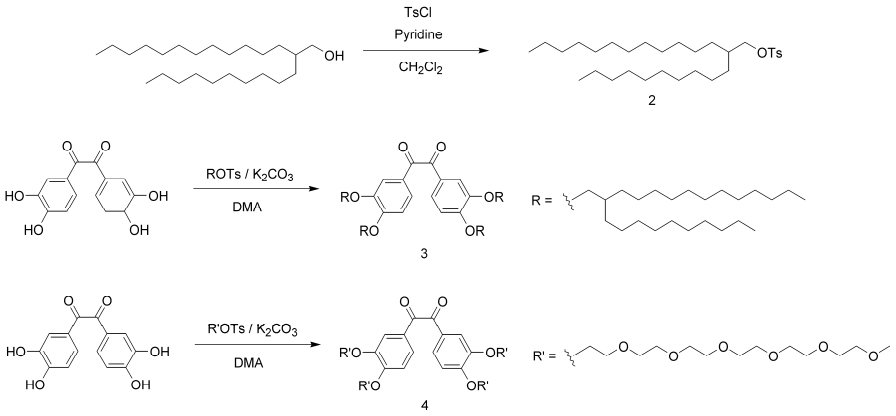
1. Synthesis

Scheme S1



Materials: All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Wakogel® C-300) and alumina gel (about 45 μm, Wako Co. Ltd). All reagents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Company, Inc, and ACROS Oraganics, and were used without further purification. All reaction solvents were distilled on the appropriate drying reagents prior to use.

3,3',4,4'-Tetrahydroxybenzil was prepared according to a literature procedure.[S1]

2-[2-(2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethyl-4-Methylbenzenesulfonate was prepared according to a literature procedure.[S2]

2-Decyl-tetradecyloxy tosylate (2)

To a solution of 2-decyl-1-tetradecanol (4.028 g, 11.357 mmol) and tosyl chloride (2.398 g, 12.578 mmol) were dissolved in CH_2Cl_2 (12 mL) was added pyridine (1.287 g, 16.270 mmol) dropwise at room temperature. After the reaction mixture had been stirred for 3 days at room temperature, the solution was poured into saturated NH_4Cl aq. and washed with water. The organic layer was evaporated. The product was purified with silica gel column chromatography (hexane/CH_2Cl_2 = 3/1), to give white solid (2), 1.2 g (33 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79 (d, J = 7.7 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 3.91 (d, J = 5.8 Hz, 2H), 2.45 (s, 3H), 1.60–1.55 (m, 1H), 1.31–1.12 (m, 40H), 0.87 (t, J = 6.5 Hz, 6H).

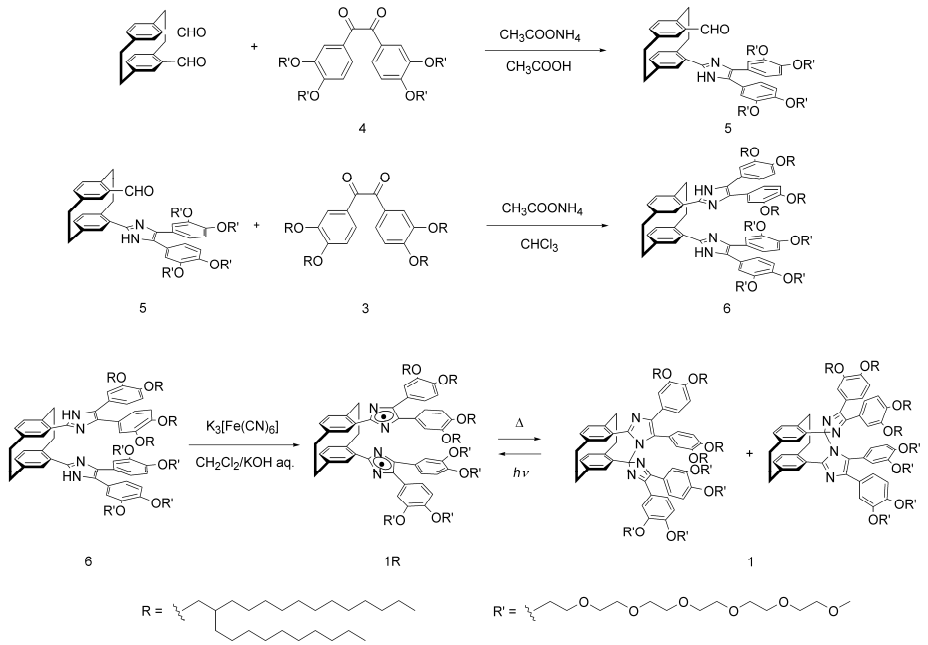
3,3',4,4'-Tetra-2-decyl-tetradecyloxybenzil (3)

3,3',4,4'-tetrahydroxybenzil (51 mg, 0.186 mmol), 2-decyl-tetradecyloxy tosylate (416 mg, 0.817 mmol), potassium carbonate (258 mg, 1.867 mmol) were stirred in DMA (4 mL) for 2 days at 70 °C.

The reaction mixture was cooled to room temperature and dissolved in CH_2Cl_2. The mixture was filtered and the filtrate was washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated. The product was purified with silica gel column chromatography (hexane/ CH_2Cl_2 = 3/1), to give yellow liquid (3), 220 mg (70 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 1.9 Hz, 2H), 7.40 (dd, *J* = 8.3, 1.9 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 3.92–3.90 (m, 8H), 1.84–1.80 (m, 4H), 1.54–1.25 (m, 160H), 0.89–0.86 (m, 24H); FAB–MS: *m/z* 1621$[M+H]^+$.

3,3',4,4'-tetra{2-[2-(2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy}-benzil (4)
3,3',4,4'-tetrahydroxybenzil (155 mg, 0.564 mmol), 2-[2-(2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethyl-4-Methylbenzenesulfonate (1.112 mg, 2.481 mmol), potassium carbonate (823 mg, 5.956 mmol) were stirred in DMA (5 mL) for 42 h at 70 °C. The reaction mixture was cooled to room temperature and extracted with CH_2Cl_2. The combined organic layer was washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated. The product was purified with silica gel column chromatography (CH_2Cl_2/acetone/ethanol = 8/1/1), to give yellow liquid (4), 595 mg (76 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.59 (d, *J* = 1.9 Hz, 2H), 7.44 (dd, *J* = 8.3, 1.9 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.24–4.21 (m, 8H), 3.90 (t, *J* = 5.0 Hz, 8H), 3.75–3.51 (m, 80H), 3.38 (s, 12H); FAB–MS: *m/z* 1388$[M+H]^+$.

Scheme S2



[2.2]Paracyclophane-4,13-dicarbaldehyde was prepared according to a literature procedure.[S3-S5]

***pseudogem*-{4-formyl-13-[4,5-(3,4-di{2-[2-(2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenyl)-1*H*-imidazol-2-yl]}[2.2]paracyclophane (5)**

[2.2]Paracyclophane-4,13-dicarbaldehyde (222 mg, 0.840 mmol), compound **4** (764 mg, 0.550 mmol) and ammonium acetate (660 mg, 8.562 mmol) were refluxed in acetic acid (22.5 mL) for 1 day. The reaction mixture was cooled with ice bath, and neutralized with aqueous NH_3, to form a yellow precipitate. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and evaporated. The product was purified with silica gel column chromatography (CH_2Cl_2/acetone/ethanol = 8/1/1), to give yellow liquid (5), 640 mg (71 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.98 (s, 1H), 9.61 (s, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.15–7.05 (m, 6H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.90 (s, 1H), 6.85 (dd, *J* = 7.7, 1.3 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 4.45–4.34 (m, 1H), 4.15 (t, *J* = 5.0 Hz, 2H), 4.10 (t, *J* = 5.0 Hz, 4H), 4.01 (t, *J* = 5.0 Hz, 2H), 3.95–3.91 (m, 1H), 3.79–3.70 (m, 8H), 3.65–3.34 (m, 80H), 3.30 (s, 1H), 3.22 (d, 5.0 Hz, 12H), 3.17–2.95 (m, 5H); *m/z* (HR–ESI–TOF–MS): calcd. 1631.8832 ($C_{84}H_{131}N_2O_{29}$); found 1631.8836 $[M+H]^+$.

***pseudogem*-[4,5-(3,4-di{2-[2-(2-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}ethoxy)ethoxy]ethoxy}phenyl)-1*H*-imidazol-2-yl_4,5-(3,4-di{2-decyl-tetradecyloxy}phenyl)][2.2]paracyclophane (6)**

The reaction mixture of compound 5 (975 mg, 0.598 mmol),

3,3',4,4'-tetra-2-decyl-tetradecyloxybenzil (1.191 g, 0.735 mmol) and ammonium acetate (796 mg, 10.326 mmol) in $CHCl_3$ was degassed with two freeze-pump-thaw cycles and stirred for 3days at 110 °C in the sealed tube. The reaction mixture was added water and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and evaporated. The product was purified with silica gel column chromatography (CH_2Cl_2/acetone/ethanol = 8/1/1), and then alumina gel column chromatography (AcOEt) to give yellow liquid (6), 944 mg (49 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.19 (d, J = 1.9 Hz, 1H), 7.13–7.11 (m, 3H), 6.94–6.90 (m, 3H), 6.74–6.72 (m, 3H), 6.63–6.54 (m, 7H), 6.50 (d, J = 8.3 Hz, 1H), 4.26 (d, J = 10.3 Hz, 2H), 4.10–4.06 (m, 2H), 3.22–3.14 (m, 6H), 1.82–1.64 (m, 4H), 1.53–1.18 (m, 160H), 0.90–0.85 (m, 24H); *m/z* (HR–ESI–TOF–MS): calcd. 3231.4548 ($C_{194}H_{333}N_4O_{32}$); found 3231.4573 $[M+H]^+$.

***pseudogem*-TDDPI-TPDPI[2.2]PC and *pseudogem*-TPDPI-TDDPI[2.2]PC (1)**

All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of **6** (150 mg, 0.046 mmol) in CH_2Cl_2 (3 mL) was added the solution of potassium ferricyanide (0.767 mg, 2.330 mmol) and KOH (260 mg, 4.634 mmol) in water (5 mL), and the reaction mixture was vigorously stirred for 1 h. The organic layer was separated, exhaustively washed with water, and concentrated in *vacuo*. The product was purified with silica gel column chromatography (CH_2Cl_2/acetone/ethanol = 9/1/1), to give yellow liquid (1), 68 mg (45 %). Compound **1** has two structural isomers, isomer A and isomer B (*pseudogem*-TDDPI-TPDPI[2.2]PC and *pseudogem*-TPDPI-TDDPI[2.2]PC). These isomers are separated with silica gel column chromatography (CH_2Cl_2/acetone/ethanol = 10/1/1). Moreover, each isomer could have diastereomers due to hindered rotation about C–C bond between the imidazole ring and the phenyl ring. The existence of two diastereomers is confirmed by the NMR spectra. Isomer A: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73–7.68 (m, 1H, one diastereomer), 7.55–7.50 (m, 1H, one diastereomer), 7.21 (s, 1H, one diastereomer), 7.16 (s, 1H, one diastereomer), 7.06 (s, 1H, one diastereomer), 7.01–7.00 (m, 2H, two diastereomers), 6.93–6.90 (m, 2H, two diastereomers), 6.80–6.42 (m, 27H, two diastereomers), 4.60–4.40 (m, 1H, one diastereomer), 4.32–4.27 (m, 1H, one diastereomer), 4.15–4.04 (m, 8H, two diastereomers), 4.01–3.38 (m, 206H, two diastereomers), 3.37 (s, 24H, two diastereomers), 3.35–2.92 (m, 8H, two diastereomers), 2.37–2.28 (m, 1H, one diastereomer), 2.09–1.94 (m, 1H, one diastereomer), 1.47–1.02 (m, 320H, two diastereomers), 0.89–0.87 (m, 48H, two diastereomers); *m/z* (HR–ESI–TOF–MS): calcd. 3229.4391 ($C_{194}H_{331}N_4O_{32}$); found 3229.4345 $[M+H]^+$. Isomer B: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (s, 1H, one diastereomer), 7.24 (s, 2H, one diastereomer), 7.17 (d, J = 2.5 Hz, 2H, one diastereomer), 7.06 (d, J = 2.5 Hz, 1H, one diastereomer), 6.96 (s, 1H, one diastereomer), 6.91–6.88 (m, 4H, two diastereomers), 6.82–6.41 (m, 25H, two diastereomers), 4.61–4.48 (m, 2H, two diastereomers), 4.03–3.39 (m, 212H, two diastereomers),

3.38–3.37 (m, 24H, two diastereomers), 3.36–2.90 (m, 10H, two diastereomers), 1.84–1.69 (m, 4H, two diastereomers), 1.48–1.20 (m, 320H, two diastereomers), 0.89–0.87 (m, 48H, two diastereomers); *m/z* (HR–ESI–TOF–MS): calcd. 3229.4391 ($C_{194}H_{331}N_4O_{32}$); found 3229.4345 $[M+H]^+$.

2. ^{1}H NMR Spectra

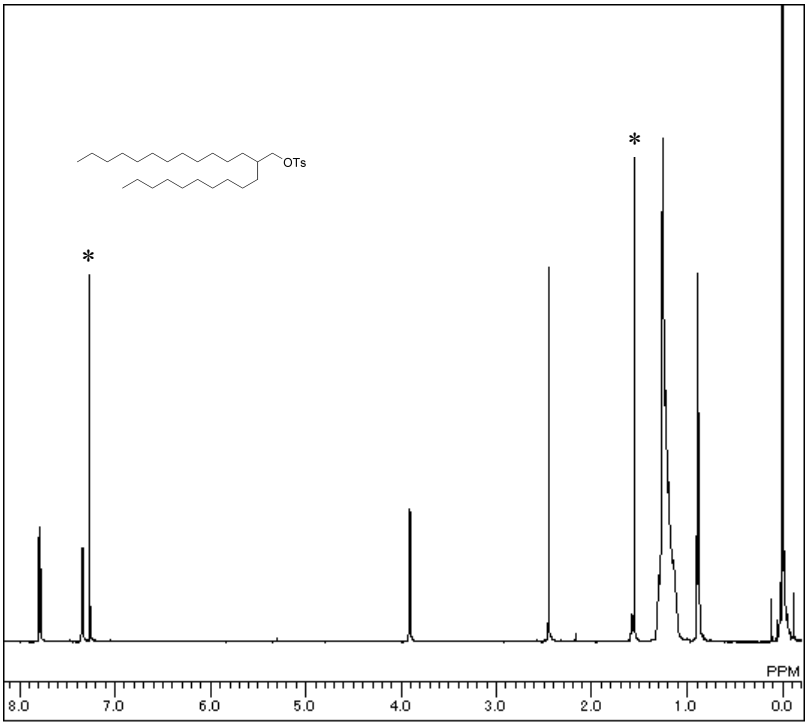


Fig. S1 ^{1}H-NMR spectrum of 2-decyl-tetradecyloxy tosylate in $CDCl_3$ (* solvent peak).

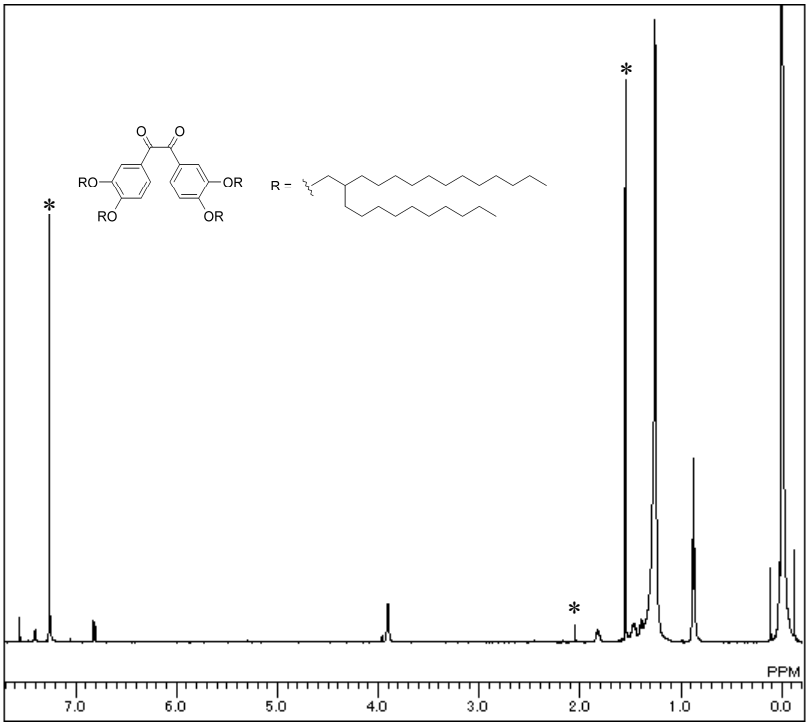


Fig.S2 ^{1}H-NMR spectrum of 3,3',4,4'-tetra-2-decyl-tetradecyloxybenzil in $CDCl_3$ (* solvent peaks).

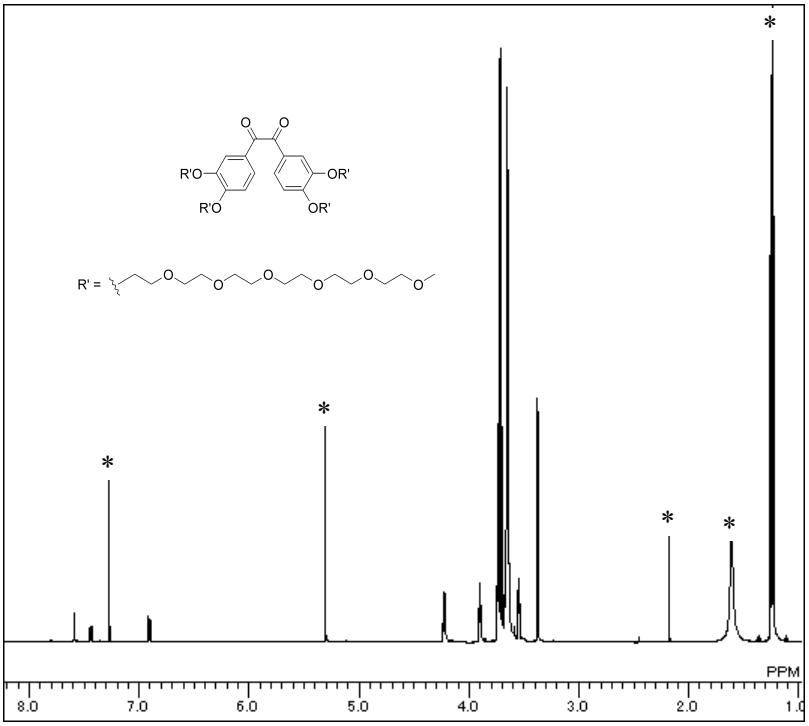


Fig. S3 ^{1}H-NMR spectrum of compound **4** in $CDCl_3$ (* solvent peak).

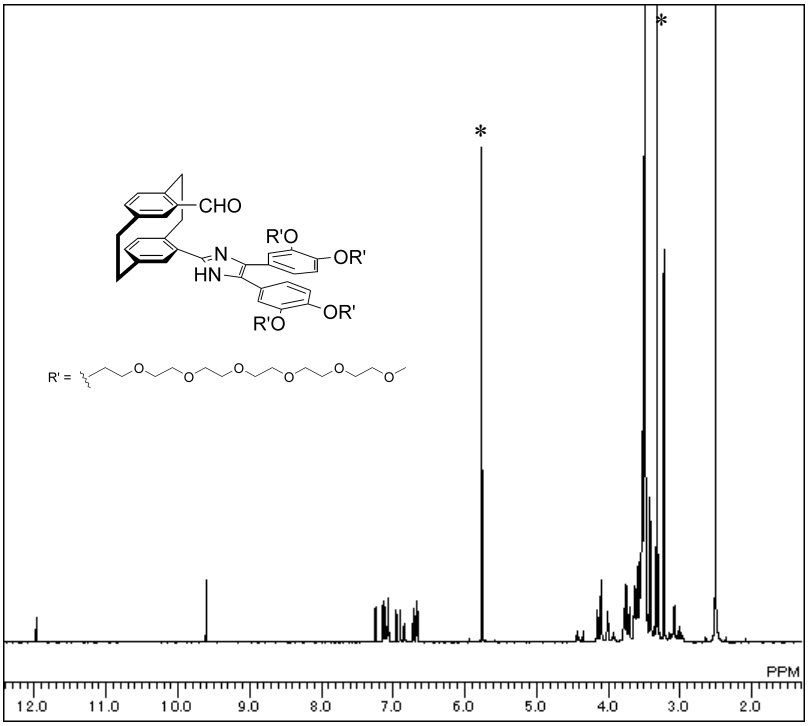


Fig. S4 ^{1}H-NMR spectrum of compound **5** in DMSO-d_6 (* solvent peaks).

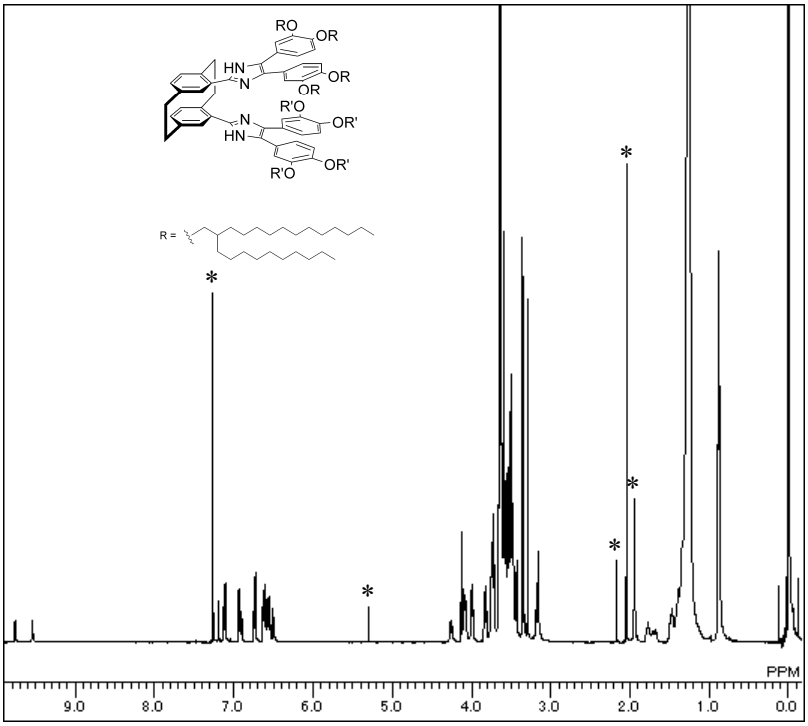


Fig. S5 ^{1}H-NMR spectrum of compound **6** in $CDCl_3$ (* solvent peak).

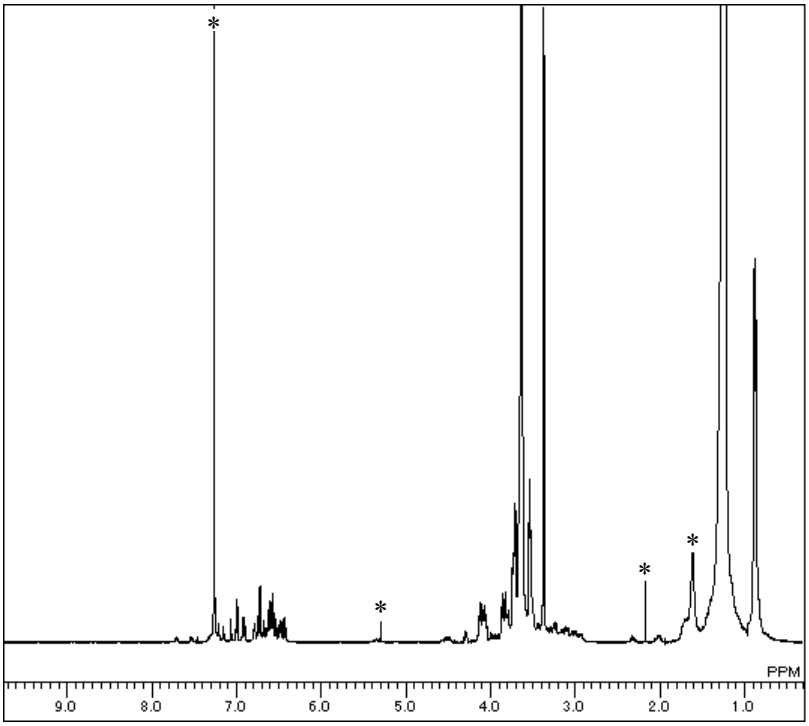


Fig. S6 ^{1}H-NMR spectrum of compound **1** (isomer A) in $CDCl_3$ (* solvent peaks).

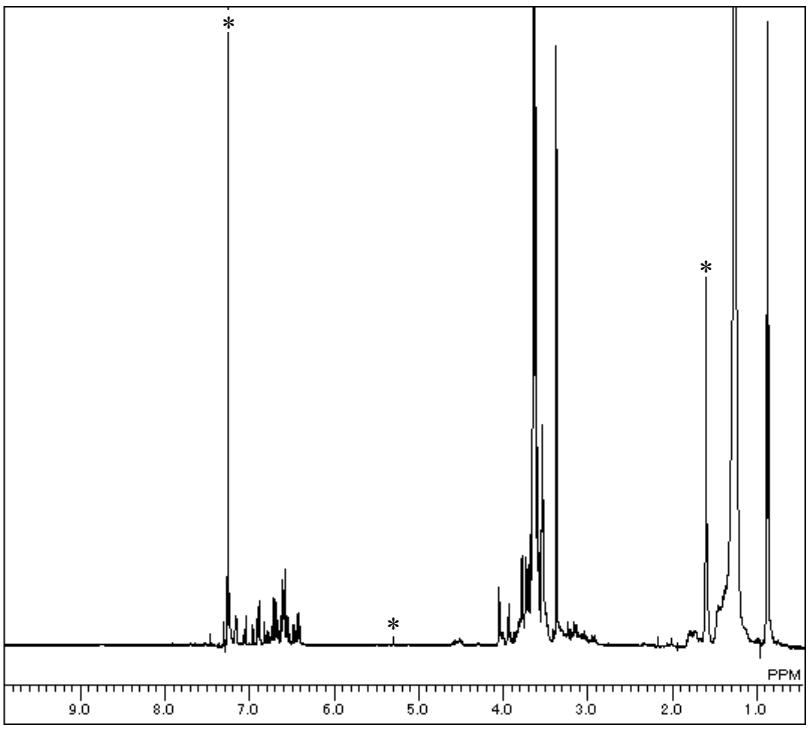


Fig. S7 ^{1}H-NMR spectrum of compound **1** (isomer B) in $CDCl_3$ (* solvent peak).

3. HR−ESI−TOF−MS spectra

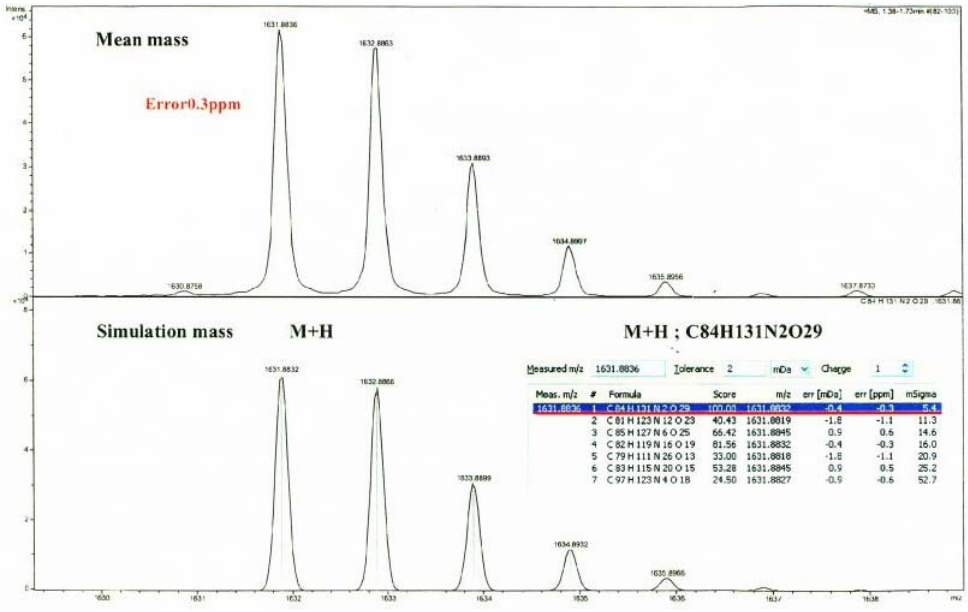


Fig. S8 HR−ESI−TOF−MS of compound **5**.

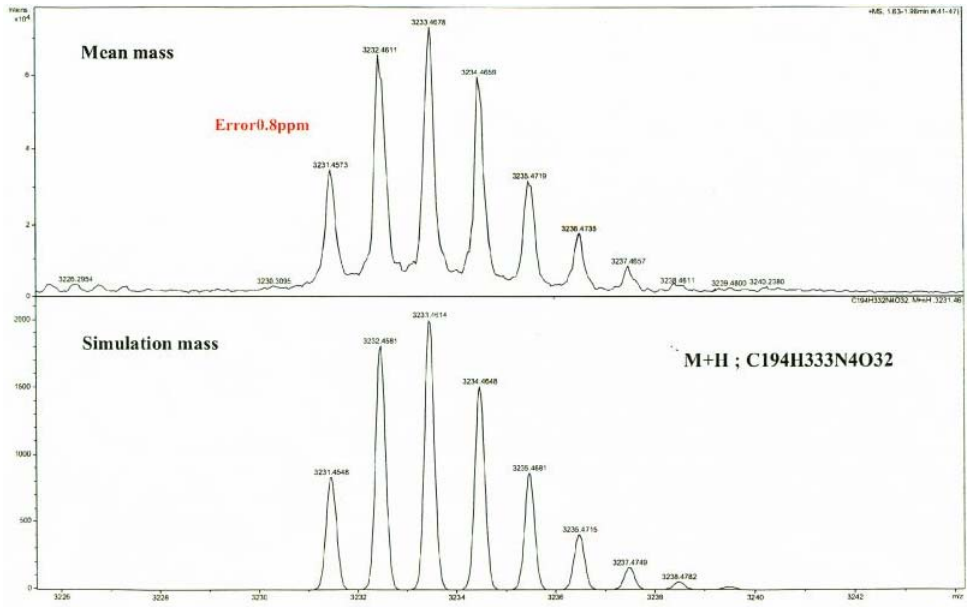


Fig. S9 HR−ESI−TOF−MS of compound **6**.

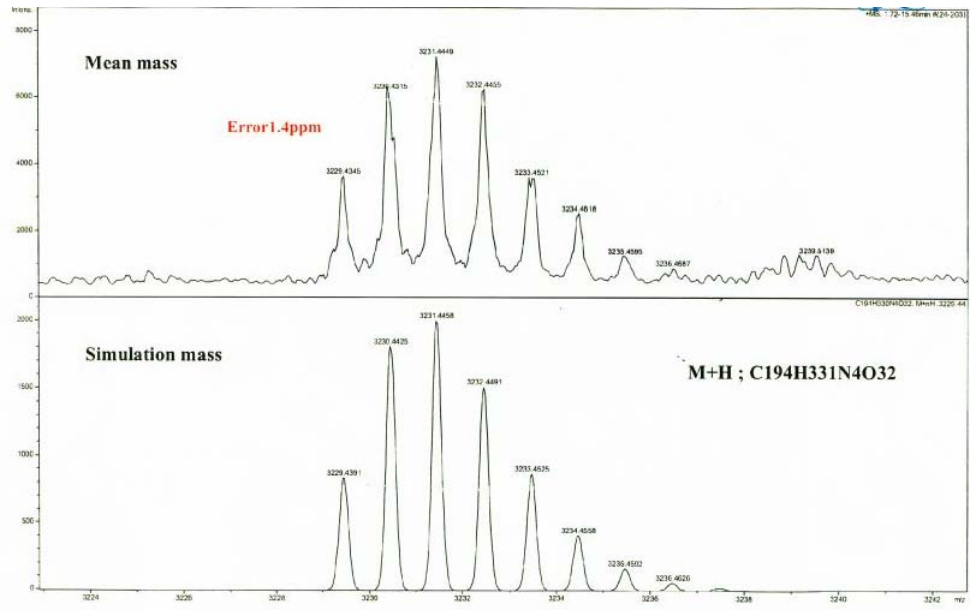


Fig. S10 HR−ESI−TOF−MS of compound **1**.

4. HPLC Chromatogram

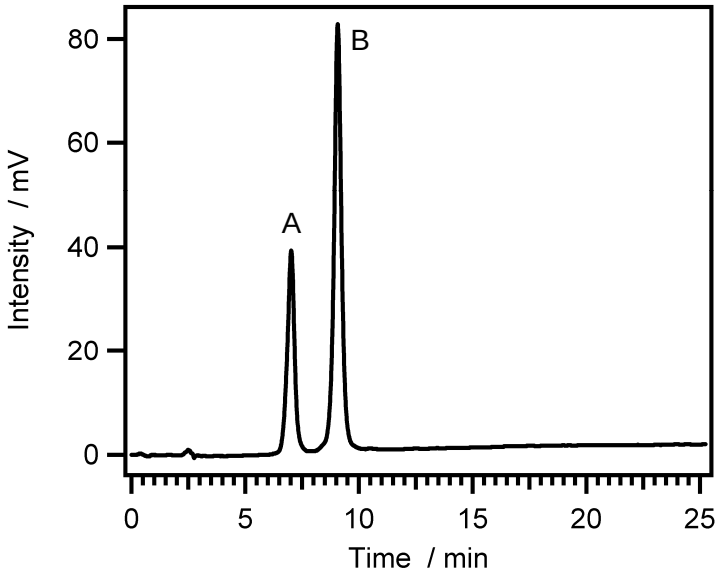


Fig. S11 HPLC chromatogram of the mixture solution of *pseudogem*-TDDPI-TPDPI[2.2]PC and *pseudogem*-TPDPI-TDDPI[2.2]PC; 99% purity. Laser flash photolysis measurements and cryogenic transmission electron microscopy were performed using this mixture solution. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25 cm×4.6 mm, 5 μm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was THF/CH_3CN = 5.5:4.5 with a flow rate of 1.0 mL/min, range; 0.04, inject volume; 2 μL, detection wavelength; 254 nm. The unity of the peaks is confirmed by PDA detector (JASCO, MD-2018).

5. UV–vis absorption spectroscopy

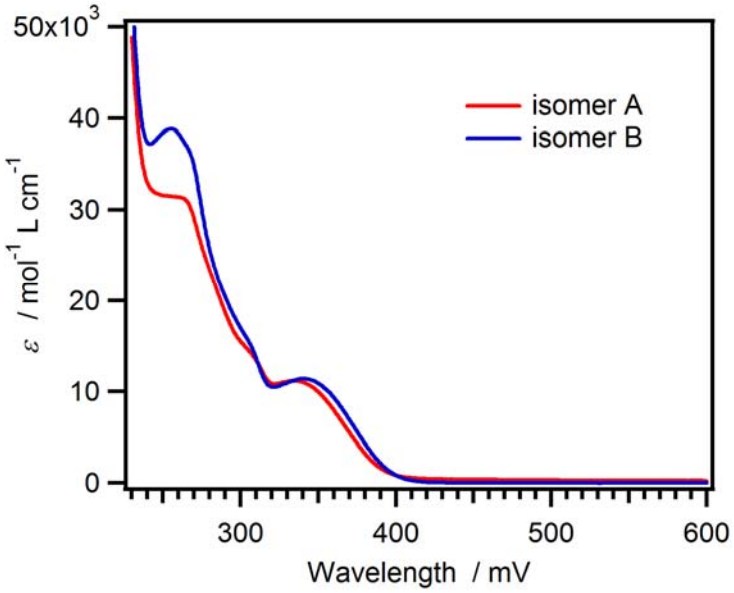


Fig. S12 UV–vis absorption spectra for **1** in acetonitrile; (red) isomer A, (blue) isomer B.

6. Light Microscopy of the photochromism of the aggregates

The light microscopy was carried out with Olympus BX51 microscope. A continuous wave diode laser at 405 nm was employed for the excitation light. The irradiation of the laser pulse (60 ms / pulse) to the aggregates of vesicles is performed with the Mosaic Digital Diaphragm System (Photonic Instruments, Inc.). The photochromism of the aggregates was monitored with a Q IMAGING Scientific Digital CCD Camera (QI Click, exposure time; 15 ms). The vesicle solution (0.5 mM) was prepared by dropwising the acetone solution of **1** (1.5 mg / 0.05 mL) into water (1 mL).

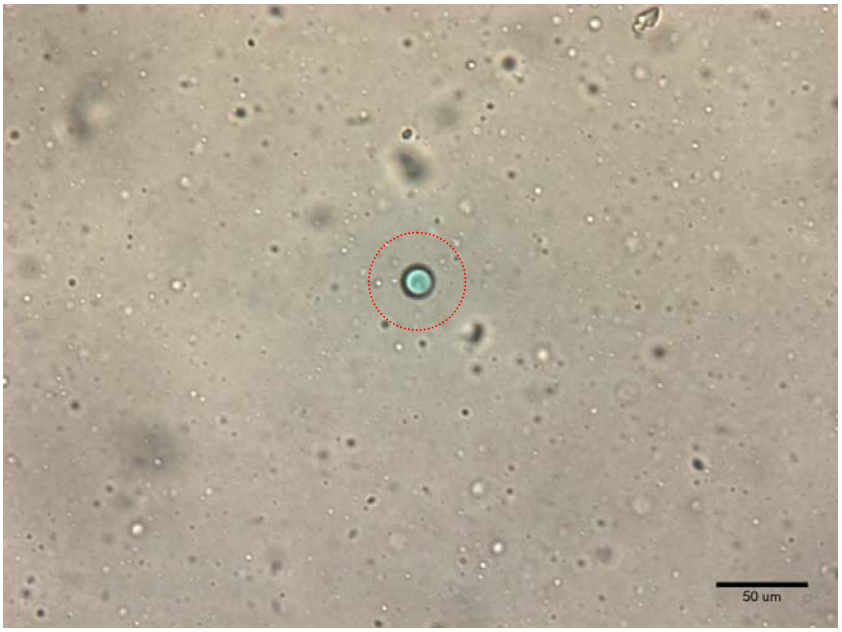


Fig. S13 Photochromism of the aggregate of vesicles in water (0.5 mM solution) at 5 °C. The excitation wavelength is 405 nm. The red circle is the excitation area.

7. Experimental Detail for Laser Flash Photolysis mesurements

The laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrophotometer. A Continuum Minilite II Nd:YAG (Q-switched) laser with the third harmonic at 355 nm (ca. 8 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from an OSRAM HLX64623 halogen lamp was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a spectrometer (Unisoku MD200). Sample solutions were deaerated by argon bubbling prior to the laser flash photolysis experiments.

8. Kinetics for the Thermal Back-Reaction in benzene

From the first-order kinetic plot shown in Fig. S14, the rate constants were obtained at each temperature. The rate constants are summarized in Table S1. The Eyring plots over a temperature ranging from 5 to 40 °C are shown in Fig. S15 and the estimated activation parameters are shown in Table S2.

Table S1. First-order rate constants for the thermal back-reaction of **1** in benzene.

T / °C	k / s^{-1}
5	1.22
10	2.02
15	3.48
20	5.13
25	7.84
30	12.01
35	18.30
40	28.12

Table S2. Activation parameters for the thermal back-reaction of **1** in benzene 25 °C.

$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
61.3	−21.9	67.8

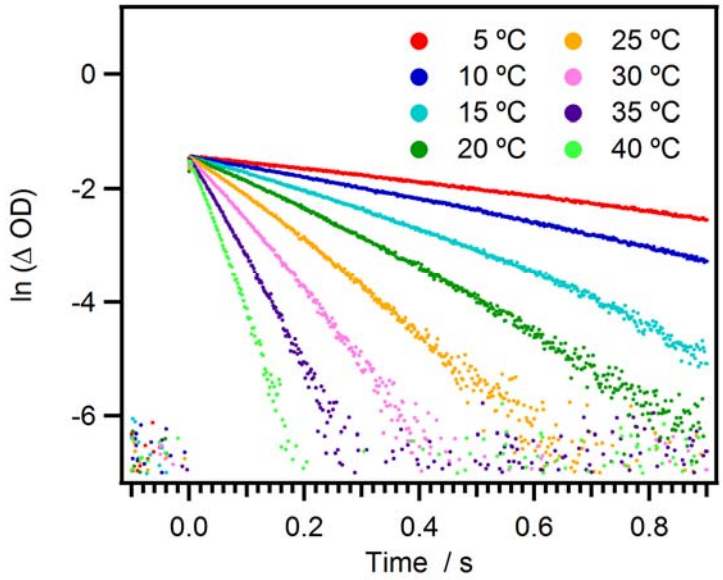


Fig. S14 First-order kinetic profiles of the colored species **1R** monitored at 400 nm in degassed benzene (**1**: 2.1×10^{-4} M, light path length: 10 mm). The measurements were performed in the temperature range from 5 °C to 40 °C.

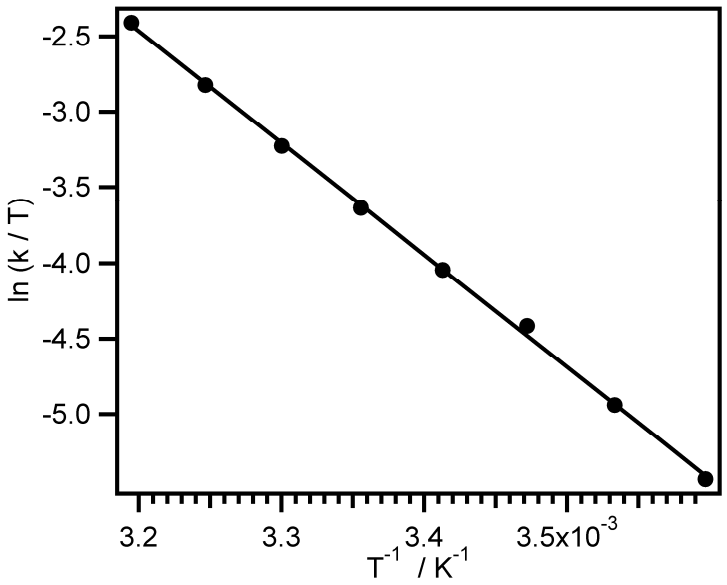


Fig. S15 Eyring plot for the thermal back-reaction of the colored species **1R**.

9. Kinetics for the Thermal Back-Reaction in water

From the first-order kinetic plot shown in Fig. S16, the rate constants were obtained at each temperature. The rate constants are summarized in Table S3. The Eyring plots over a temperature ranging from 5 to 40 °C are shown in Fig. S17 and the estimated activation parameters are shown in Table S4.

Table S3. First-order rate constants for the thermal back-reaction of **1** in water.

T / °C	k / s^{-1}
5	24.32
10	38.39
15	63.85
20	100.16
25	141.47
30	220.08
35	312.68
40	435.78

Table S4. Activation parameters for the thermal back-reaction of **1** in water at 25 °C.

$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ / kJ mol^{-1}
57.5	−10.6	60.7

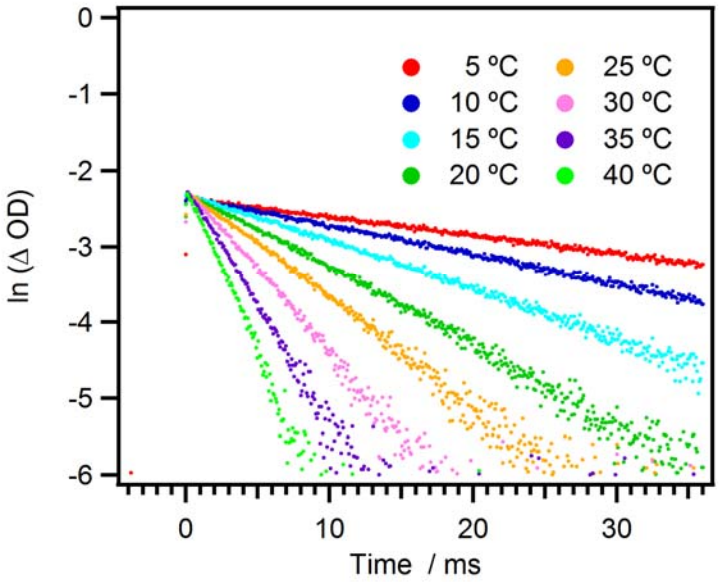


Fig. S16 First-order kinetic profiles of the colored species **1R** monitored at 700 nm in water (**1**: 1.9×10^{-4} M, light path length: 10 mm). The measurements were performed in the temperature range from 5 °C to 40 °C.

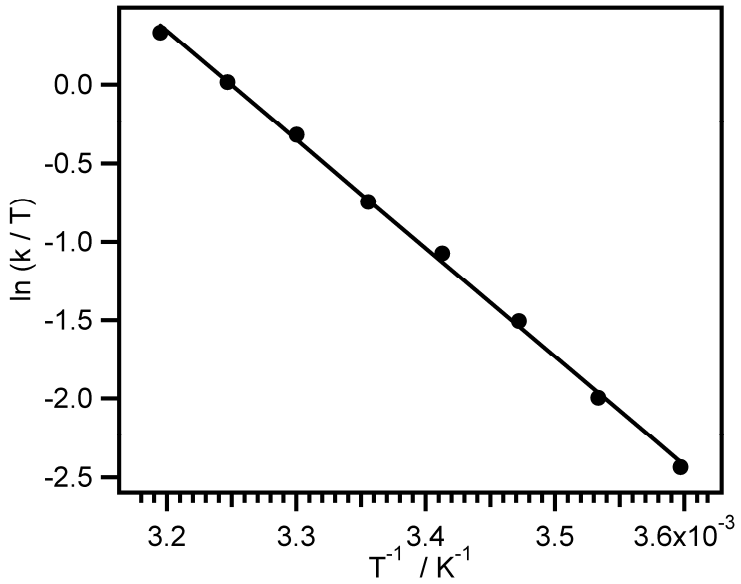


Fig. S17 Eyring plot for the thermal back-reaction of the colored species **1R** in water.

10. Decay profile for the Thermal Back-Reaction of amorphous film of 1

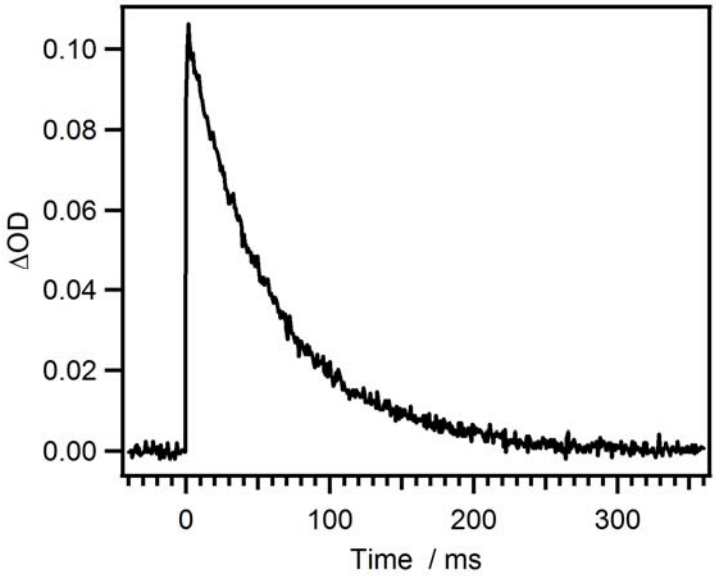


Fig. S18 Decay profile for the amorphous film of the colored species **1R** monitored at 400 nm.

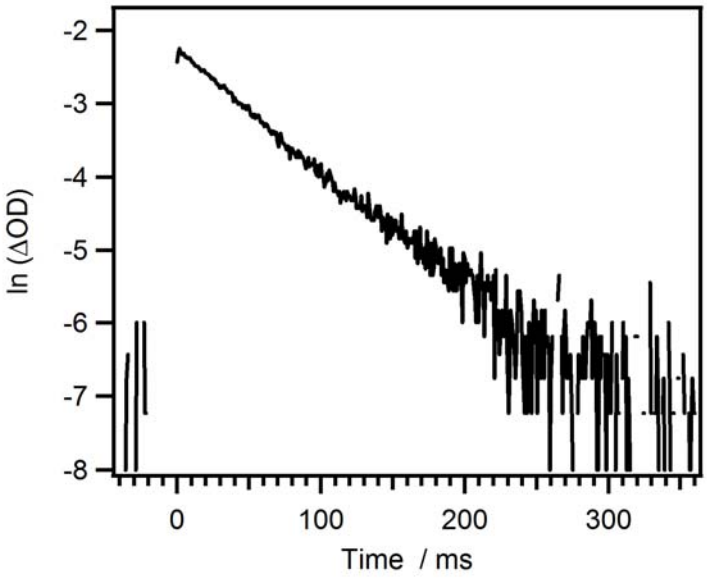


Fig. S19 First-order kinetic profile for the amorphous film of the colored species **1R** monitored at 400 nm.

11. Experimental Detail for cryo-TEM

The vesicle solution (0.5 mM) was prepared by dropwising the acetone solution of **1** (1.5 mg / 1 mL, 0.05 mL) into water (1 mL). The vesicles were confirmed by cryo-TEM with a JEOL transmission electron microscope (JEM-3100FEF) at Nara Institute of Science and Technology (NAIST).

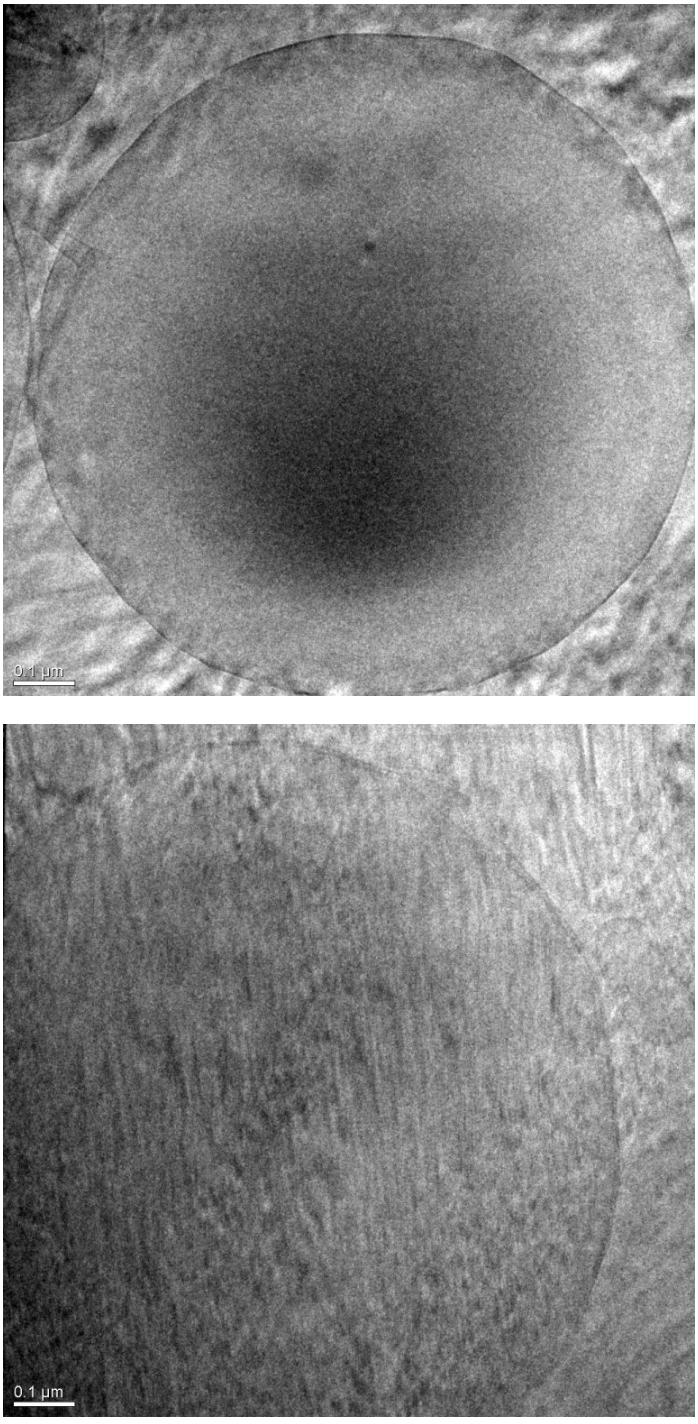


Fig. S20 Cryo-TEM images of the spherical vesicles in water.

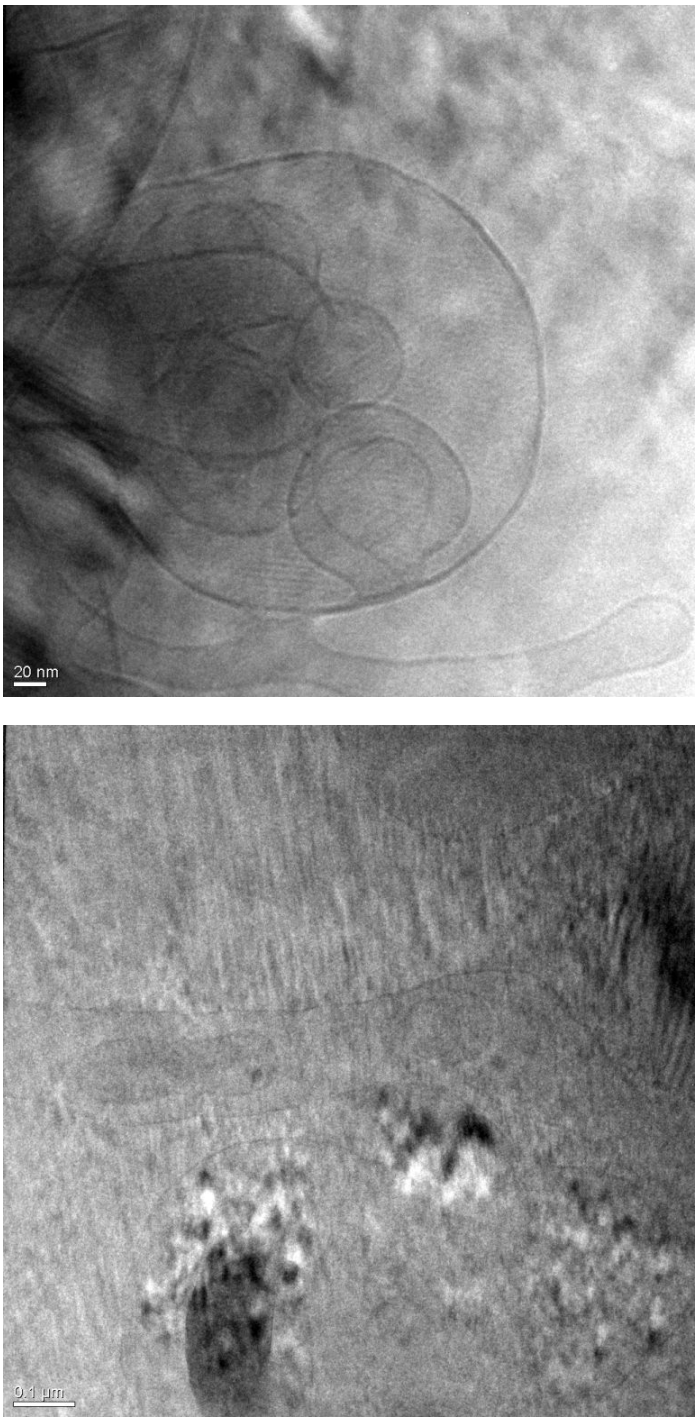


Fig. S21 Cryo-TEM images of the oligo-lamellar vesicles in water.

7. References

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