Supplementary Information

Mimicking Multipass Transmembrane Proteins: Synthesis, Assembly and Folding of Alternating Amphiphilic Multiblock Molecules in Liposomal Membranes

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1. Methods

^{1}H and ^{13}C NMR spectra were recorded on 400 MHz FT NMR JEOL JNM-LA400 spectrometer, where the chemical shifts were determined with respect to tetramethylsilane (TMS, δ 0.00) or a residual non-deuterated solvent as an internal standard. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) spectrometry was performed in reflector mode with α-cyano-4-hydroxycinnamic acid (CHCA) as a matrix on Bruker Daltonics REFLEX III spectrometer. UV-Vis spectra were recorded on JASCO V-530 UV-Vis spectrophotometer. Fluorescence spectra were recorded on JASCO FP-6500 spectrophotometer. Centrifugation was performed using TOMY MX-301 High Speed Micro Centrifuge. Dynamic light scattering was performed with Otsuka Electronics FDLS-3000 and analyzed with CONTIN algorithm. Fluorescent and phase contrast microscopy were performed with Olympus BX-51 microscope, where U-MWU2 mirror unit (Excitation Filter: 330–385 nm, Emission Filter: 420 nm, Dichroic Mirror: 400 nm) was used for fluorescence observation. Analytical TLC was performed on precoated, glass-backed silica gel (Merck 60 F_{254}). Visualization of the developed chromatogram was performed by UV absorbance, Hanessian's stain and iodine.

2. Reagents

$CuSO_4 \cdot 5H_2O$, K_2CO_3, NaN_3, Na_2SO_4, 2-propyn-1-ol and sodium ascorbate were purchased from Nacalai Tesque. KOH (powder) was purchased from Merck. CHCA was purchased from Tokyo Chemical Industry (TCI). Anhydrous acetone and dimethyl sulfoxide (DMSO) were purchased from Kanto Chemical. 1,2-Dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) was purchased from Avanti Polar Lipids. Deuterated solvents were purchased from Acros Organics. These commercial reagents were used without purification. Anhydrous CH_2Cl_2 and tetrahydrofuran (THF) were purchased from Kanto Chemical and passed through sequential two drying columns on a Glass-Contour system just prior to use. Deionized water

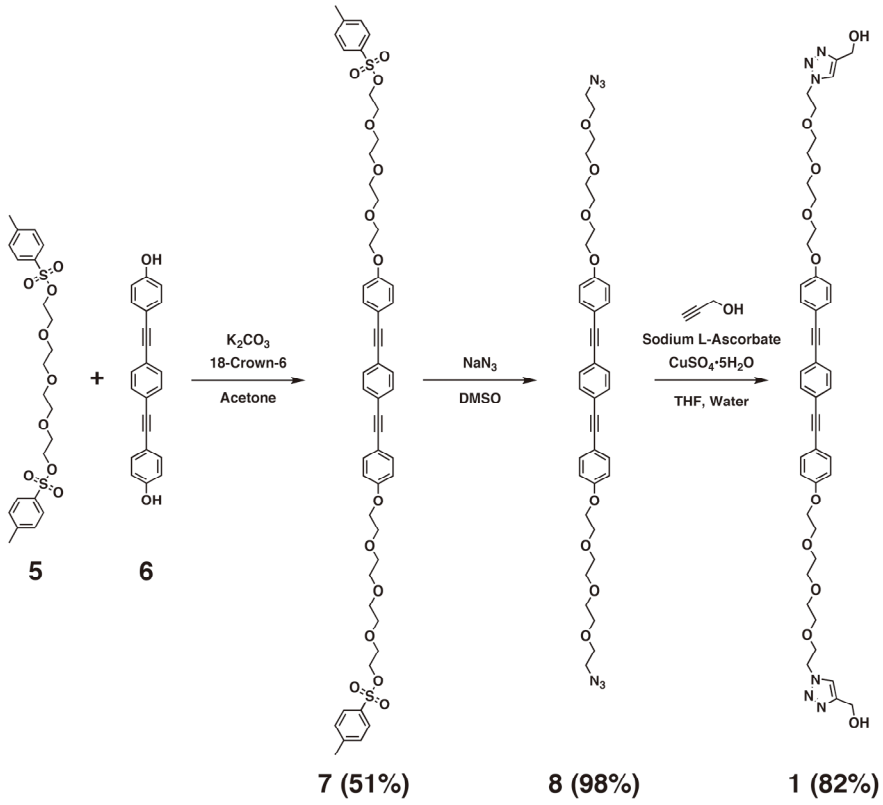
(filtered through a 0.22 μm membrane filter, >18.2 MΩ cm) was purified in a Milli-Q system of Millipore Corp.

3. Preparation of Giant Unilamellar Liposomes

DOPC was dissolved in a mixture of $CHCl_3$ and MeOH (2:1), which was transferred into a glass tube and gently dried under N_2 flow to produce thin lipid film. The film was subsequently dried under vacuum and hydrated with ultrapure Milli Q for 3 h at 37 ºC. The final lipid concentration was 0.20 mM.

4. Synthesis

Scheme S1.



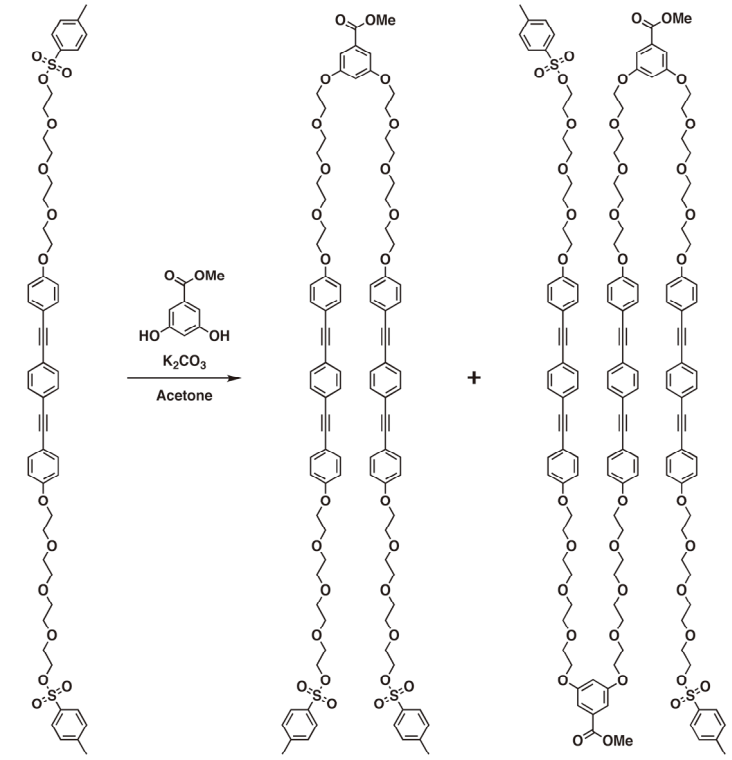
(1) Synthesis of 7. To a dry acetone (30 mL) solution of **5**[1] (20.0 g, 39.8 mmol) and **6**[2] (1.20 g, 3.87 mmol) were added K_2CO_3 (1.70 g, 12.3 mmol) and 18-crown-6 (5 mol%) at room temperature under Ar, and the resulting mixture was refluxed overnight in the dark. Then, the reaction mixture was evaporated to dryness under reduced pressure. Brine (30 mL) was added to the residue, which was then extracted with $CHCl_3$ (30 mL). The organic extract was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The crude product was purified by gradient flash chromatography on a Biotage Isolera One system with High-Performance Silica cartridge with hexane and AcOEt (82/18 to 0/100) as eluents to allow isolation of **7** in 51% yield (1.90 g, 1.96 mmol) as off-white solids. ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.79 (d, J = 7.8 Hz, 4H), 7.47 (s, 4H), 7.44 (d, J = 8.8 Hz, 4H), 7.33 (d, J = 7.8 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 4.16–4.13 (m, 8H), 3.87–3.59 (m, 24H), 2.43 (s, 6H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z:

calculated for $C_{52}H_{58}O_{14}S_2$: 970.33; found: 970.91 $[M]^+$, 993.89 $[M + Na]^+$.

(2) Synthesis of 8. To a dry DMSO (90 mL) solution of **7** (2.5 g, 2.57 mmol) was added NaN_3 (418 mg, 6.44 mmol) at room temperature under Ar, and the resulting mixture was heated to 90 ºC. After being stirred for 6 h in the dark, the mixture was poured into ice water (150 mL) to precipitate pale orange solids, which were then collected by filtration and washed with water to allow isolation of **8** in 98% yield (1.8 g, 2.52 mmol) as off-white solids. ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.46 (s, 4H), 7.45 (d, J = 8.8 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 4.14 (t, J = 5.8 Hz, 4H), 3.87 (d, J = 5.8 Hz, 4H), 3.85–3.64 (m, 20H), 3.37 (t, J = 4.9 Hz, 4H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{38}H_{44}N_6O_8$: 712.32; found: 713.86 $[M + H]^+$, 685.84 $[M – N_2 + H]^+$, 657.84 $[M – 2N_2 + H]^+$.

(3) Synthesis of 1. To a suspension of **8** (954 mg, 1.34 mmol) in a mixture of THF (8 mL), $CHCl_3$ (8 mL) and water (2 mL) were added 2-propyn-1-ol (187 mg, 3.35 mmol), sodium ascorbate (53 mg, 0.27 mmol) and $CuSO_4$•$5H_2O$ (36 mg, 0.14 mmol) at room temperature, and the resulting mixture was refluxed for 12 h in the dark. The resulting orange solution was vacuumed to dryness at 30 ºC. Water (10 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (7500 rpm) at 20 ºC for 30 min and washed twice with water and once with EtOH to allow isolation of **1** in 82% yield (907 mg, 1.10 mmol) as off-white solids. ^{1}H NMR (400 MHz, $CDCl_3$ containing 20% CD_3OD and 0.03% TMS, 22 ºC): δ 7.80 (s, 2H), 7.47 (s, 4H), 7.45 (d, J = 5.9 Hz, 4H), 6.89 (d, J = 5.9 Hz, 4H), 4.71 (s, 4H), 4.53 (t, J = 3.4 Hz, 4H), 4.15 (t, J = 2.9 Hz, 4H), 3.88–3.60 (m, 24H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{44}H_{52}N_6O_{10}$: 824.37; found: 825.92 $[M + H]^+$, 847.96 $[M + Na]^+$.

Scheme S2.



7 (51%) **9 (42%)** **10 (27%)**

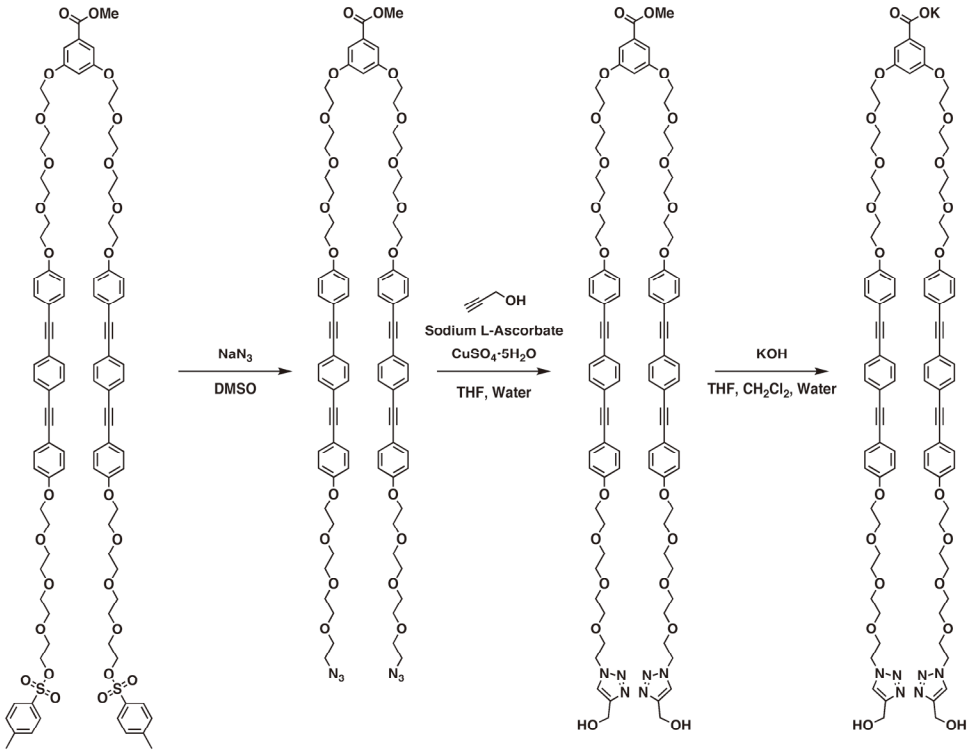
(4) Oligomerization of 7 with methyl 3,5-dihydroxybenzoate to obtain 9 and 10. To a dry acetone solution (2 mL) of **7** (480 mg, 0.495 mmol) and methyl 3,5-dihydroxybenzoate (21 mg, 0.125 mmol) was added K_2CO_3 (51 mg, 0.370 mmol) at room temperature under Ar, and the resulting mixture was refluxed overnight in the dark. The reaction mixture was evaporated to dryness under reduced pressure, and brine (30 mL) was added to the residue, which was then extracted with $CHCl_3$ (30 mL). The organic extract was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude product was purified by size exclusion chromatography on a Japan Analytical Industry LC-9201 Recycling Preparative HPLC system with JAIGEL-1H and 2H columns with $CHCl_3$ as an eluent running at 3.5 mL min^{-1} to allow isolation of **9** and **10** as pale orange solids in 42% (92 mg, 52 μmol) and 27% (11 mg, 4.3 μmol) yields, respectively.

9: ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.79 (d, J = 7.8 Hz, 4H), 7.46 (s, 8H), 7.43 (d, J = 8.8 Hz, 8H), 7.33 (d, J = 7.8 Hz, 4H), 7.19 (s, 2H), 6.88 (d, J = 8.8

Hz, 8H), 6.69 (s, 1H), 4.16–4.13 (m, 16H), 3.88–3.59 (m, 48H), 2.43 (s, 6H) ppm; MALDI-TOF MS (CHCA, positive mode): *m*/*z*: calculated for $C_{98}H_{108}O_{26}S_2$: 1766.02; found: 1767.03 $[M + H]^+$, 1806.88 $[M + K]^+$.

10: ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.79 (d, J = 7.8 Hz, 4H), 7.46 (s, 12H), 7.43 (d, J = 8.8 Hz, 12H), 7.33 (d, J = 7.8 Hz, 4H), 7.19 (s, 4H), 6.88 (d, J = 8.8 Hz, 12H), 6.69 (s, 2H), 4.16–4.12 (m, 24H), 3.88–3.59 (m, 72H), 2.43 (s, 6H) ppm; MALDI-TOF MS (CHCA, positive mode): *m*/*z*: calculated for $C_{144}H_{158}O_{38}S_2$: 2560.90; found: 2561.20 $[M + H]^+$.

Scheme S3.



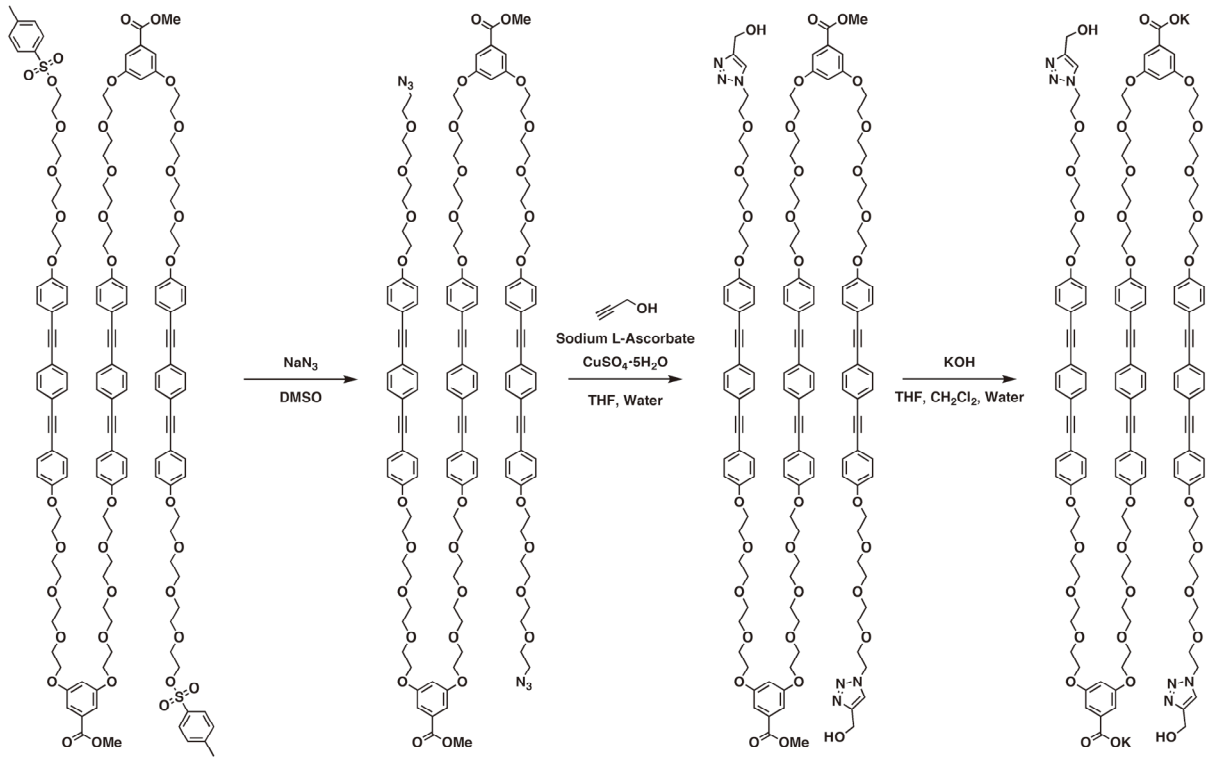
(5) Synthesis of 11. To a dry DMSO (40 mL) suspension of **9** (1.64 g, 0.926 mmol) was added NaN_3 (150 mg, 2.31 mmol) at room temperature under Ar, and the mixture was heated to 90 ºC. The resulting orange solution was stirred for 6 h in the dark. The reaction mixture was poured into ice water (100 mL) to precipitate off-white solids, which were collected by filtration and washed with water to allow isolation of **11** in 77% yield (1.07 g, 0.71 mmol) as off-white solids. ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.46 (s, 8H), 7.43 (d, J = 8.8 Hz, 8H), 7.18 (s, 2H), 6.90–6.84 (m, 8H), 6.69 (s, 1H), 4.16–4.11 (m, 12H), 3.88–3.84 (m, 16H), 3.72–3.67 (m, 36H) ppm; MALDI-TOF MS (CHCA, positive mode): *m*/*z*: calculated for $C_{84}H_{94}N_6O_{20}$: 1507.67; found: 1531.16 $[M + Na]^+$.

(6) Synthesis of 12. To a THF (10 mL), $CHCl_3$ (20 mL) and water (5 mL) suspension of **11** (900 mg, 0.597 mmol) were added 2-propyn-1-ol (84 mg, 1.50 mmol), sodium ascorbate (30

mg, 0.15 mmol) and $CuSO_4 \bullet 5H_2O$ (20 mg, 0.078 mmol) at room temperature, and the mixture was refluxed for 11 h in the dark. The resulting yellow solution was vacuumed to dryness at 30 ºC. Water (10 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (8000 rpm) at 20 ºC for 30 min and washed twice with water and once with MeOH to allow isolation of **12** in 71% yield (690 mg, 0.426 mmol) as off-white solids. ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.78 (s, 2H), 7.46–7.43 (m, 16H), 7.18 (s, 2H), 6.88 (d, J = 8.8 Hz, 8H), 6.69 (s, 1H), 4.78 (d, J = 5.9 Hz, 4H), 4.53 (t, J = 4.9 Hz, 4H), 4.15–4.12 (m, 12H), 3.88–3.83 (m, 19H) 3.73–3.61 (m, 30H), 3.49 (d, J = 5.9 Hz, 4H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{90}H_{102}N_6O_{22}$: 1619.80; found: 1643.01 $[M + Na]^+$.

(7) Synthesis of 2. To a suspension of **12** (153 mg, 94.4 μmol) in a mixture of CH_2Cl_2 (40 mL), THF (5 mL) and water (2 mL) was added KOH (500 mg, 8.93 mmol) at room temperature, and the mixture was refluxed overnight. The resulting brown suspension was vacuumed to dryness at 30 ºC. Water (10 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (8000 rpm) at 20 ºC for 30 min and washed four times with water and twice with EtOH to allow isolation of **2** in 79% yield (120 mg, 74.7 μmol) as off-white solids. ^{1}H NMR (400 MHz, $CDCl_3$ containing 20% CD_3OD and 0.03% TMS, 22 ºC): δ 7.77 (s, 2H), 7.46–7.42 (m, 16H), 7.18 (s, 2H), 6.88 (d, J = 8.8 Hz, 8H), 6.69 (s, 1H), 4.78 (s, 4H), 4.53 (t, J = 4.9 Hz, 4H), 4.15–4.12 (m, 12H), 3.88–3.83 (m, 16H), 3.73–3.61 (m, 30H), 3.49 (s, 4H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{89}H_{99}KN_6O_{22}$: 1642.64; found: 1642.12 $[M]^+$.

Scheme S4.

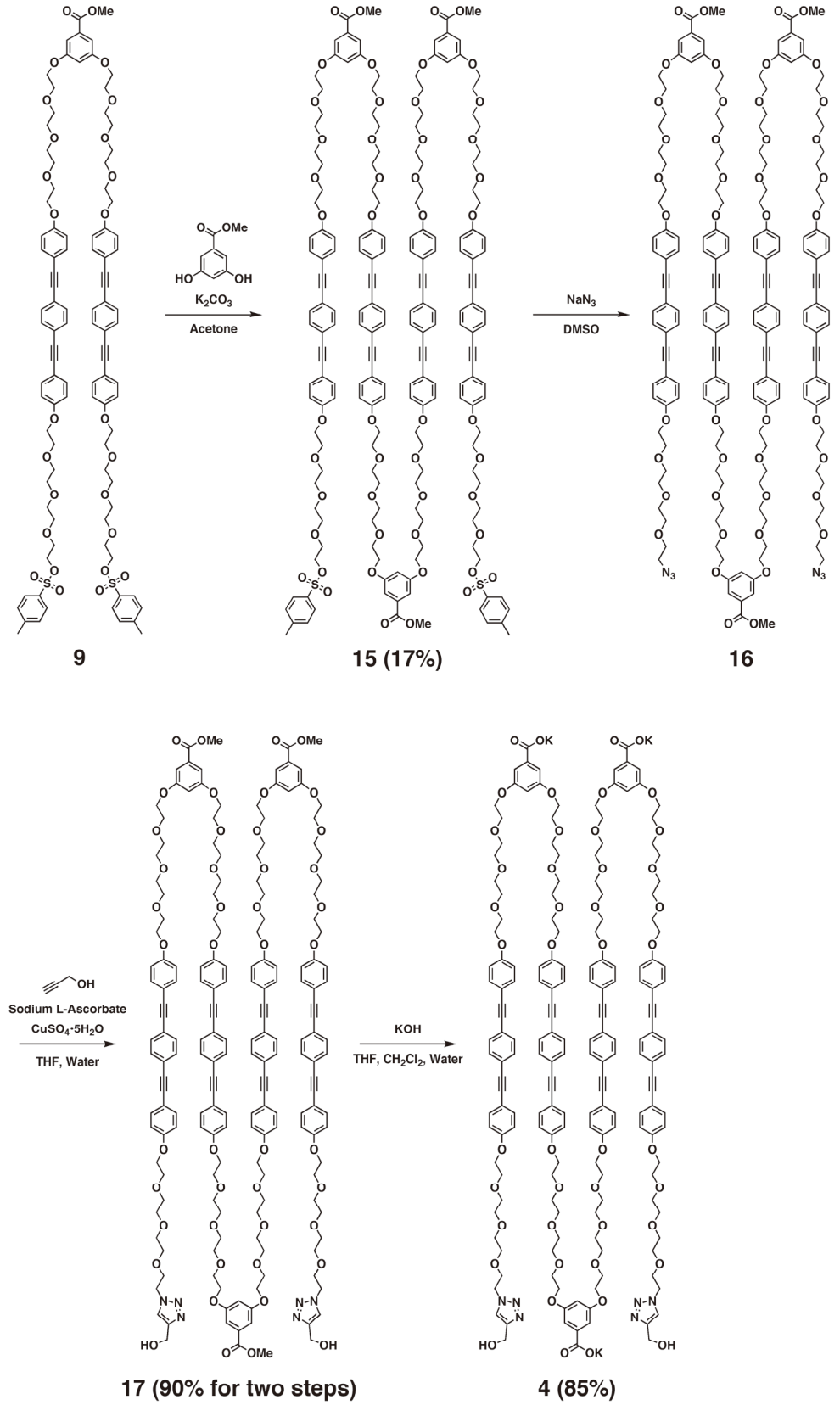


(8) Synthesis of 13. To a dry DMSO (15 mL) suspension of **10** (0.57 g, 0.223 mmol) was added NaN_3 (36 mg, 0.556 mmol) at room temperature under Ar, and the mixture was heated to 90 ºC. The resulting orange solution was stirred for 6 h in the dark. The reaction mixture was poured into ice water (100 mL) and extracted with $CHCl_3$ (100 mL × 2). The organic extract was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure to give **13** (650 mg) as pale yellow solids (contaminated with DMSO). ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.46 (s, 12H), 7.43 (d, J = 8.8 Hz, 12H), 7.18 (s, 4H), 6.89 (d, J = 8.8 Hz, 4H), 6.88 (d, J = 8.8 Hz, 8H), 6.68 (s, 2H), 4.16–4.11 (m, 20H), 3.88–3.83 (m, 26H), 3.75–3.66 (m, 52H), 3.38 (t, J = 4.9 Hz, 4H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{130}H_{144}N_6O_{32}$: 2300.98; found: 2272.32 $[M - N_2]^+$.

(9) Synthesis of 14. To a suspension of **13** (650 mg contaminated with DMSO) in a mixture of THF (4 mL), $CHCl_3$ (7 mL) and water (1 mL) were added 2-propyn-1-ol (40 mg, 0.71 mmol), sodium ascorbate (11 mg, 0.057 mmol) and $CuSO_4 \bullet 5H_2O$ (7.4 mg, 0.030 mmol) at room temperature, and the mixture was refluxed for 8 h in the dark. The resulting yellow suspension was vacuumed to dryness at 40 ºC. Water (10 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (8000 rpm) at 20 ºC for 30 min and washed twice with water to allow isolation of **14** in 69% yield (for two steps) (370 mg, 0.153 mmol). ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.78 (s, 2H), 7.46–7.43 (m, 24H), 7.18 (s, 4H), 6.87 (d, J = 8.8 Hz, 12H), 6.69 (s, 2H), 4.78 (d, J = 4.9 Hz, 4H), 4.53 (t, J = 4.9 Hz, 4H), 4.15–4.12 (m, 20H), 3.88–3.83 (m, 28H) 3.72–3.61 (m, 52H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{136}H_{152}N_6O_{34}$: 2413.03; found: 2436.50 $[M + Na]^+$.

(10) Synthesis of 3. To a suspension of **14** (375 mg, 0.155 mmol) in a mixture of CH_2Cl_2 (100 mL), THF (100 mL) and water (5 mL) was added KOH (1.20 g, 21.0 mmol) at room temperature, and the mixture was refluxed for 13 h. The resulting brown suspension was vacuumed to dryness at 30 ºC. Water (20 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (8000 rpm) at 20 ºC for 30 min and washed four times with water and twice with EtOH to allow isolation of **3** in 97% yield (370 mg, 0.150 mmol). ^{1}H NMR (400 MHz, $CDCl_3$ containing 20% CD_3OD and 0.03% TMS, 22 ºC): δ 7.77 (s, 2H), 7.45–7.42 (m, 24H), 7.18 (s, 2H), 6.87 (d, J = 8.8 Hz, 12H), 6.69 (s, 1H), 4.78 (d, J = 4.9 Hz, 4H), 4.53 (t, J = 4.9 Hz, 4H), 4.15–4.12 (m, 20H), 3.88–3.83 (m, 22H), 3.72–3.61 (m, 52H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{134}H_{146}K_2N_6O_{34}$: 2460.92; found: 2424.47 $[M - K + 2H]^+$.

Scheme S5.


OMe
HO
OH
K_2CO_3
Acetone
NaN_3
DMSO
N_3
9
15 (17%)
16
OH
Sodium L-Ascorbate
$CuSO_4$·$5H_2O$
THF, Water
KOH
THF, CH_2Cl_2, Water
OK
17 (90% for two steps)
4 (85%)

(11) Synthesis of 15. To a refluxed dry acetone (70 mL) solution of **9** (3.43 g, 1.94 mmol) and methyl 3,5-dihydroxybenzoate (109 mg, 0.648 mmol) was added K_2CO_3 (714 mg, 5.17 mmol) under Ar, and the resulting mixture was refluxed for 12 h. Then, the reaction mixture was cooled to room temperature and evaporated to dryness under reduced pressure. Saturated aqueous NH_4Cl (100 mL) was added to the residue, which was then extracted with $CHCl_3$ (100 mL × 2). The organic extract was dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure. The crude product was purified by size exclusion chromatography on a Japan Analytical Industry LC-9201 Recycling Preparative HPLC system with JAIGEL-1H and 2H columns with $CHCl_3$ as an eluent running at 3.5 mL min^{-1} to allow isolation of **15** in 17% yield (379 mg, 0.113 mmol) as pale orange solids. **15**: ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.79 (d, J = 7.8 Hz, 4H), 7.45 (s, 16H), 7.43 (d, J = 8.8 Hz, 16H), 7.32 (d, J = 7.8 Hz, 4H), 7.18 (s, 6H), 6.88 (d, J = 8.8 Hz, 16H), 6.69 (s, 3H), 4.16–4.11 (m, 32H), 3.88–3.58 (m, 96H), 2.43 (s, 6H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{190}H_{208}O_{50}S_2$: 3353.32; found: 3376.83 $[M + Na]^+$.

(12) Synthesis of 16. To a suspension of **15** (0.379 g, 0.113 mmol) in a mixture of dry DMSO (8 mL) and $CHCl_3$ (1.5 mL) was added NaN_3 (18 mg, 0.277 mmol) at room temperature under Ar. The resulting orange suspension was stirred for 3.5 h at 100 ºC in the dark, and the reaction mixture was poured into ice water (100 mL) and extracted with $CHCl_3$ (100 mL). The organic extract was washed with water (100 mL × 5), dried over anhydrous Na_2SO_4, filtered and evaporated to dryness under reduced pressure to afford **16** (385 mg) as pale yellow solids (contaminated with DMSO). ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.46–7.43 (m, 32H), 7.18 (s, 6H), 6.90 (d, J = 8.8 Hz, 4H), 6.87 (d, J = 8.8 Hz, 12H), 6.69 (s, 3H), 4.16–4.11 (m, 28H), 3.88–3.83 (m, 41H), 3.72–3.66 (m, 64H), 3.38 (t, J = 4.9 Hz, 4H) ppm; MALDI-TOF MS (CHCA, positive mode): m/z: calculated for $C_{176}H_{194}N_6O_{44}$: 3095.31; found: 2268.52 $[M - N_2 + H]^+$.

(13) Synthesis of 17. To a suspension of **16** (355 mg contaminated with DMSO) in a mixture of THF (2 mL), $CHCl_3$ (4 mL) and water (1 mL) were added 2-propyn-1-ol (16 mg, 0.29 mmol), sodium ascorbate (6 mg, 0.031 mmol) and $CuSO_4 \bullet 5H_2O$ (4 mg, 0.016 mmol) at room temperature, and the mixture was refluxed for 9 h in the dark. The resulting yellow suspension was vacuumed to dryness at 40 ºC. Water (10 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (8000 rpm) at 20 ºC for 30 min and washed twice with water to allow isolation of **17** in 90% yield (for two steps) (329 mg, 0.102 mmol). ^{1}H NMR (400 MHz, $CDCl_3$ containing 0.03% TMS, 22 ºC): δ 7.78 (s, 2H), 7.45–7.43 (m, 32H), 7.18 (s, 6H), 6.89–6.87 (m, 16H), 6.69 (s, 3H), 4.78 (s, 4H), 4.52 (s, 4H), 4.14–4.11 (m, 28H), 3.88–3.83 (m, 41H), 3.72–3.66 (m, 66H) ppm; MALDI-TOF MS (CHCA, positive mode): *m*/*z*: calculated for $C_{182}H_{202}N_6O_{46}$: 3207.37; found: 3230.66 $[M + Na]^+$.

(14) Synthesis of 4. To a suspension of **14** (336 mg, 0.105 mmol) in a mixture of CH_2Cl_2 (45 mL), THF (45 mL) and water (2.5 mL) was added KOH (1.2 g, 21.0 mmol) at room temperature, and the mixture was refluxed for 12 h. The resulting brown suspension was vacuumed to dryness at 30 ºC. Water (20 mL) was added to the residue, and the resulting mixture was transferred into a Teflon test tube. Then, the precipitate was collected by centrifugation (10000 rpm) at 20 ºC for 30 min and washed four times with water and twice with EtOH to allow isolation of **4** in 85% yield (283 mg, 0.0894 mmol). ^{1}H NMR (400 MHz, $CDCl_3$ containing 20% CD_3OD and 0.03% TMS, 22 ºC): δ 7.77 (s, 2H), 7.52–7.44 (m, 32H), 7.18 (s, 6H), 6.88 (d, J = 8.8 Hz, 16H), 6.69 (s, 3H), 4.78–4.76 (m, 4H), 4.53–4.51 (m, 4H), 4.13–4.08 (m, 28H), 3.88–3.49 (m, 98H) ppm; MALDI-TOF MS (CHCA, positive mode): *m*/*z*: calculated for $C_{179}H_{193}K_3N_6O_{46}$: 3279.19; found: 3204.64 $[M - 2K + 3H]^+$.

5. UV-Vis Absorption Spectroscopy

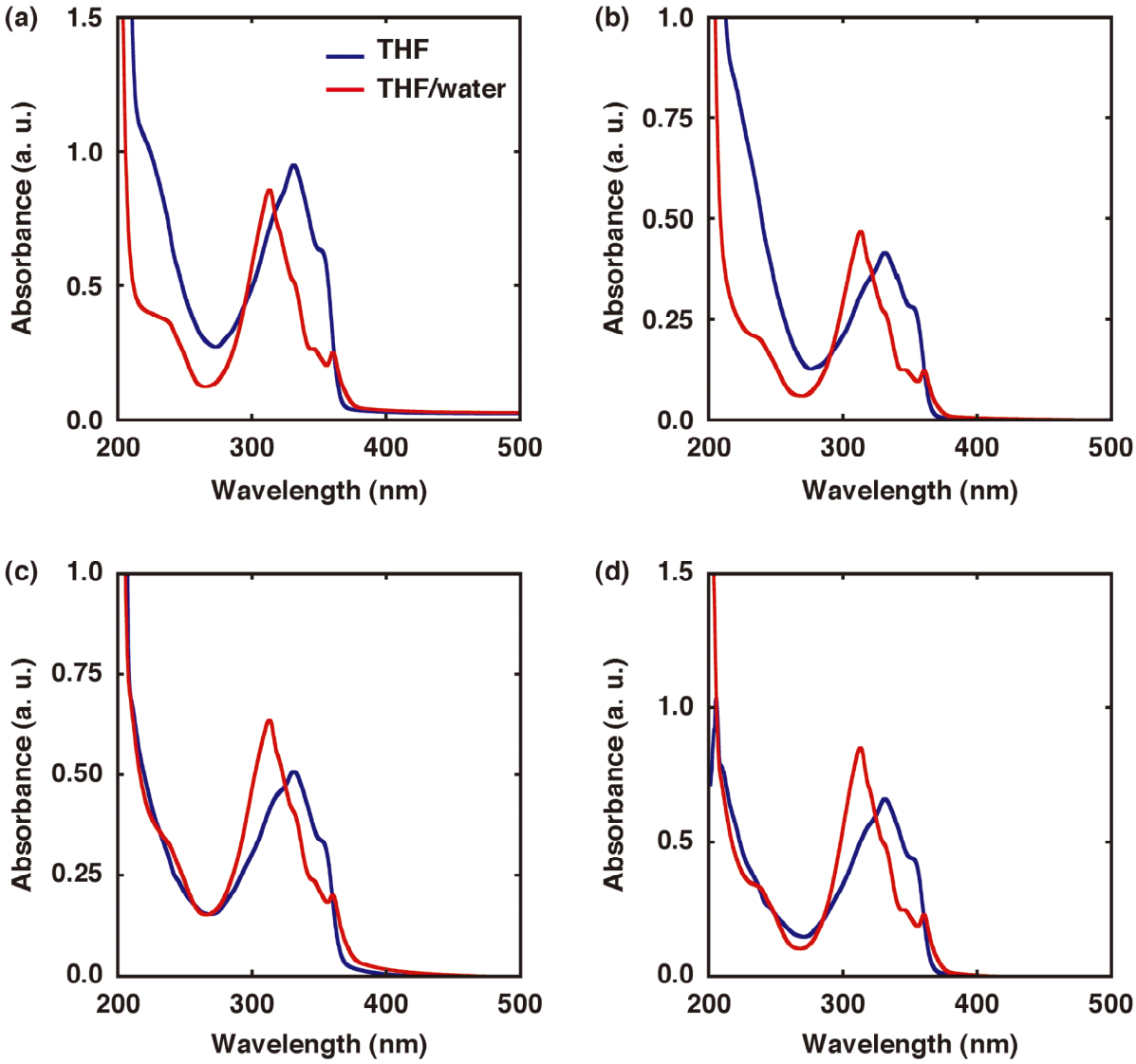


Fig. S1 UV-Vis absorption spectra of (a) **1**, (b) **2**, (c) **3** and (d) **4** in THF (2.0×10^{-5} M, blue lines) and THF/water (1/9) (2.0×10^{-5} M, red lines).

6. Dynamic Light Scattering Analyses

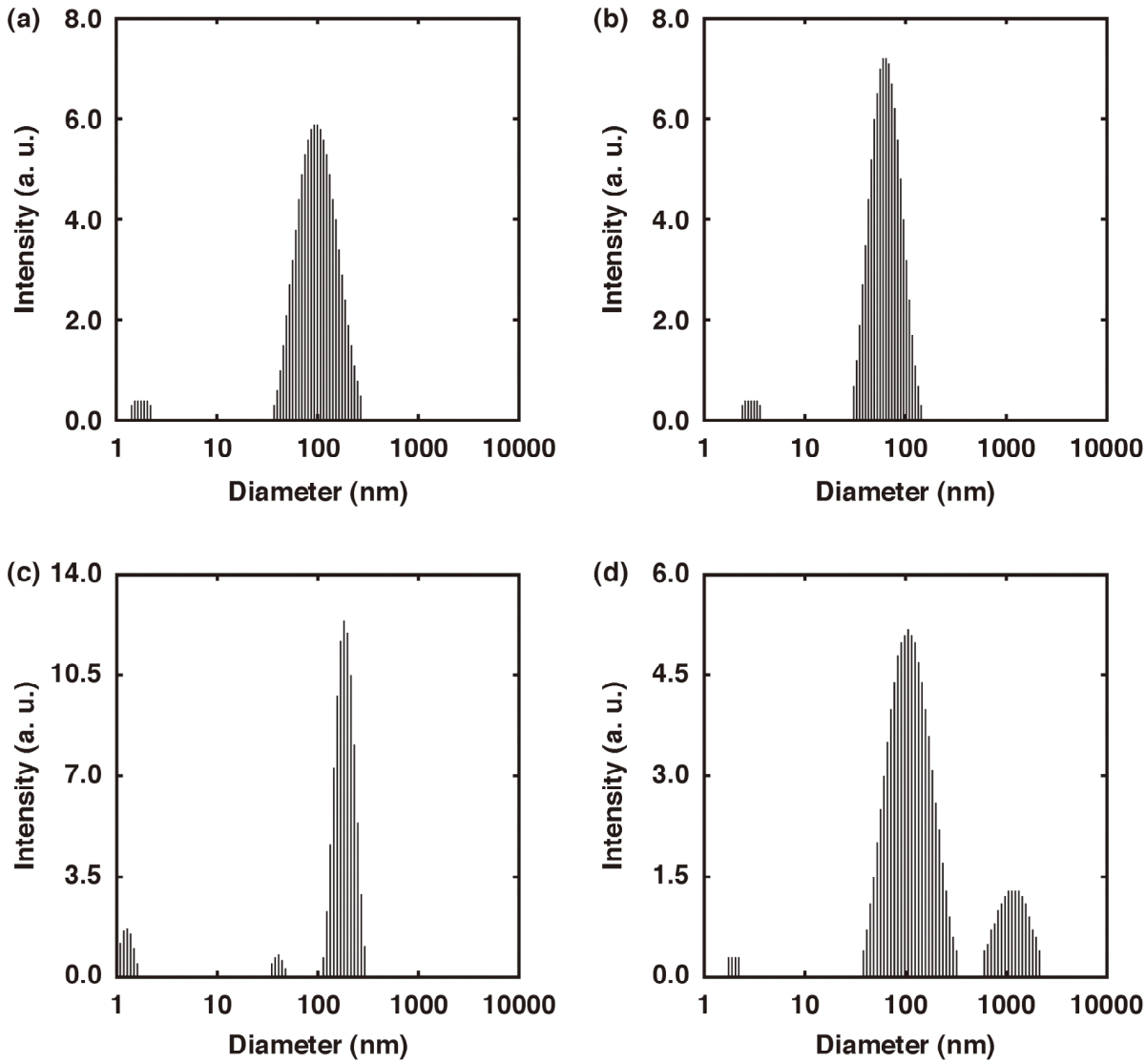


Fig. S2 Dynamic light scattering profiles of 2.0×10^{-5} M THF/water (1/9) solution of (a) **1**, (b) **2**, (c) **3** and (d) **4**. Average hydrodynamic diameters were (a) 90.7, (b) 59.8, (c) 178.0 and (d) 172.7 nm.

7. References

1. C. M. Yam and A. K. Kakkar, *Langmuir*, 1999, **15**, 3807.
2. A. C. French, A. L. Thompson and B. G. Davis, *Angew. Chem. Int. Ed.*, 2009, **48**, 1248.