Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Photochemistry and aggregation behavior of triethylene glycol (TEG) terminated stilbene dendrimer

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Supporting Information

Synthesis of G0, G1, G2 and G3 are depicted in Scheme S1.

G1-Br, G2-Br and G3-Br were prepared according to the literature.

Matthew Brewis, Madeleine Helliwell and Neil B. McKeown, Tetrahedron **2003**, *59*, 3863.

G0 : 10-Tosyloxy-2,5,8-trioxadecane (594 mg, 1.87 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene (87.4 mg, 0.358 mmol), 18-crown-6-ether (142 mg, 0.537 mmol) and K_2CO_3 (435 mg, 3.15 mmol) were reacted in THF (3 ml) / DMF (10 ml) under N_2 and the mixture was refluxed for 4 days. After the reaction was completed, the mixed solution was filtered and evaporated. The residue was purified by silica gel columnchromatography using ethyl acetate/MeOH (19:1→9:1) as an eluent to give **G0** as colorless oil (175 mg, 59%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 6.97 (s, 2H), 6.68 (d, *J* = 2.2 Hz, 4H), 6.44 (t, *J* = 2.2 Hz, 2H), 4.16 (t, *J* = 4.8 Hz, 8H), 3.88 (t, *J* = 4.8 Hz, 8H), 3.78-3.66 (m, 24H), 3.58-3.56 (m, 8H), 3.35 (s, 12H); MALDI-TOF MS (*m/z*) M^+ calcd for $C_{42}H_{68}O_{16}$ 828.45; found, 829.68.

G1 : G1-Br (1.15 g, 2.32 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene(70.0 mg, 0.287 mmol), 18-crown-6-ether (204 mg, 0.772 mmol) and K_2CO_3 (536 mg, 3.88 mmol) were reacted in THF (20 ml) under N_2 and the mixture was refluxed for 4 days. The solution was poured into water (100 ml) and extracted with dichloromethane (50 ml×3). The organic layer was washed with brine (100 ml) and dried over Mg_2SO_4. The solvent was removed by evaporation under reduced pressure. The residue was purified by silica gel columnchromatography using ethyl acetate/MeOH (4:1) as an eluent to give **G1** as colorless oil (131 mg, 24%).

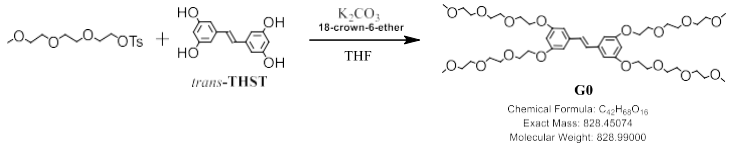
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.01 (s, 2H), 6.77 (d, *J* = 2.1 Hz, 4H), 6.63 (d, *J* = 2.1 Hz, 8H), 6.54 (t, *J* = 2.1 Hz, 2H), 6.47 (t, *J* = 2.1 Hz, 4H), 5.00 (s, 8H), 4.14 (t, *J* = 4.8 Hz, 16H), 3.86 (t, *J* = 4.8Hz, 16H), 3.77-3.65 (m, 48H), 3.57-3.55 (m, 16H), 3.39 (s, 24H); MALDI-TOF MS (*m/z*) $[M+Na]^+$ calcd for $C_{98}H_{148}O_{36}Na$ 1923.97; found, 1926.60.

G2 : G2-Br (628 mg, 0.608 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene(33.1 mg, 0.136 mmol), 18-crown-6-ether (43.9 mg, 0.166 mmol) and K_2CO_3 (138 mg, 1.00 mmol) were reacted in THF (20 ml) / DMF (10 ml) under N_2 and the mixture was refluxed for 4 days. After the reaction was completed, the mixed solution was filtered and evaporated. The residue was purified by silica gel columnchromatography using ethyl acetate/MeOH (3:1) as an eluent to give **G2** as colorless oil (280 mg, 51%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.07 (s, 2H), 6.81 (d, *J* = 2.0 Hz, 4H), 6.71 (d, *J* = 2.0 Hz, 8H), 6.59 (d, *J* = 2.0 Hz, 16H), 6.61-6.56 (m, 6H), 6.46 (t, *J* = 2.0 Hz, 8H), 6.53 (t, *J* = 2.0 Hz, 8H), 5.01 (s, 8H), 4.97 (s, 16H), 4.11 (t, *J* = 4.8 Hz, 64H), 3.84 (t, *J* = 4.8Hz, 32H), 3.75-3.63 (m, 96H), 3.55-3.53 (m, 32H), 3.37 (s, 48H); MALDI-TOF MS (*m/z*) $[M+Na]^+$ calcd for $C_{238}H_{308}O_{76}Na$ 4069.01; found, 4071.00.

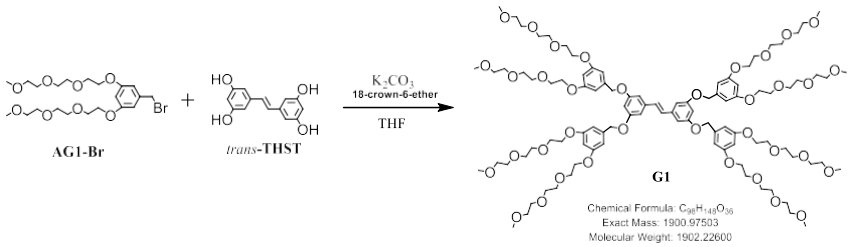
G3 : G3-Br (563 mg, 0.267 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene(14.4 mg, 0.059 mmol), 18-crown-6-ether (36.6 mg, 0.138 mmol) and K_2CO_3 (104 mg, 0.753 mmol) were reacted in THF (20 ml) / DMF (10 ml) under N_2 and the mixture was refluxed for 3 days. After the reaction was completed, the mixed solution was filtered and evaporated. The residue was purified by silica gel columnchromatography using ethyl acetate/MeOH (9:1→5:2→4:3) as an eluent to give **G3** as colorless oil (117 mg, 24%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.10 (s, 2H), 6.84 (d, *J* = 2.0 Hz, 4H), 6.76 (d, *J* = 2.0 Hz, 8H), 6.69 (d, *J* = 2.0 Hz, 16H), 6.62-6.60 (m, 6H), 6.58 (d, *J* = 2.0 Hz, 16H), 6.53 (t, *J* = 2.0 Hz, 8H), 6.43 (t, *J* = 2.0 Hz, 16H), 5.01 (s, 8H), 4.98 (s, 16H), 4.94 (s, 32H), 4.08 (t, *J* = 4.7 Hz, 64H), 3.81 (t, *J* = 4.7 Hz, 64H), 3.75-3.60 (m, 192H), 3.56-3.49 (m, 64H), 3.35 (s, 96H); MALDI-TOF MS (*m/z*) $[M+Na]^+$ calcd for $C_{434}H_{628}O_{156}Na$ 8359.11; found, 8364.06.



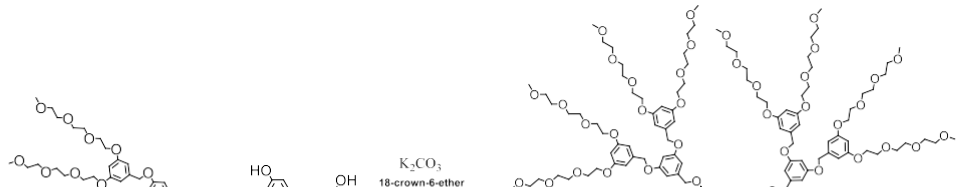
G0

Chemical Formula: $C_{42}H_{68}O_{16}$
Exact Mass: 828.45074
Molecular Weight: 828.99000



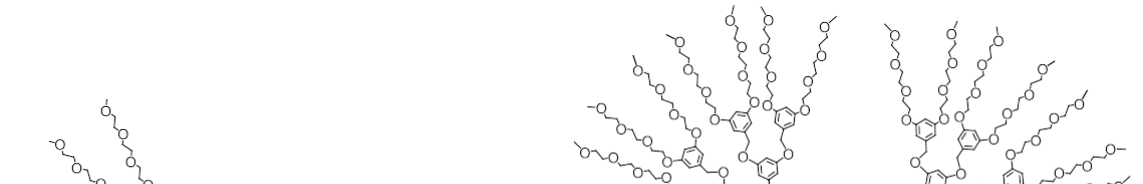
G1

Chemical Formula: $C_{98}H_{148}O_{36}$
Exact Mass: 1900.97503
Molecular Weight: 1902.22600



G2

Chemical Formula: $C_{210}H_{308}O_{76}$
Exact Mass: 4046.02362
Molecular Weight: 4048.69800



G3

Chemical Formula: $C_{434}H_{628}O_{156}$
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Molecular Weight: 8341.64200

Scheme

S1

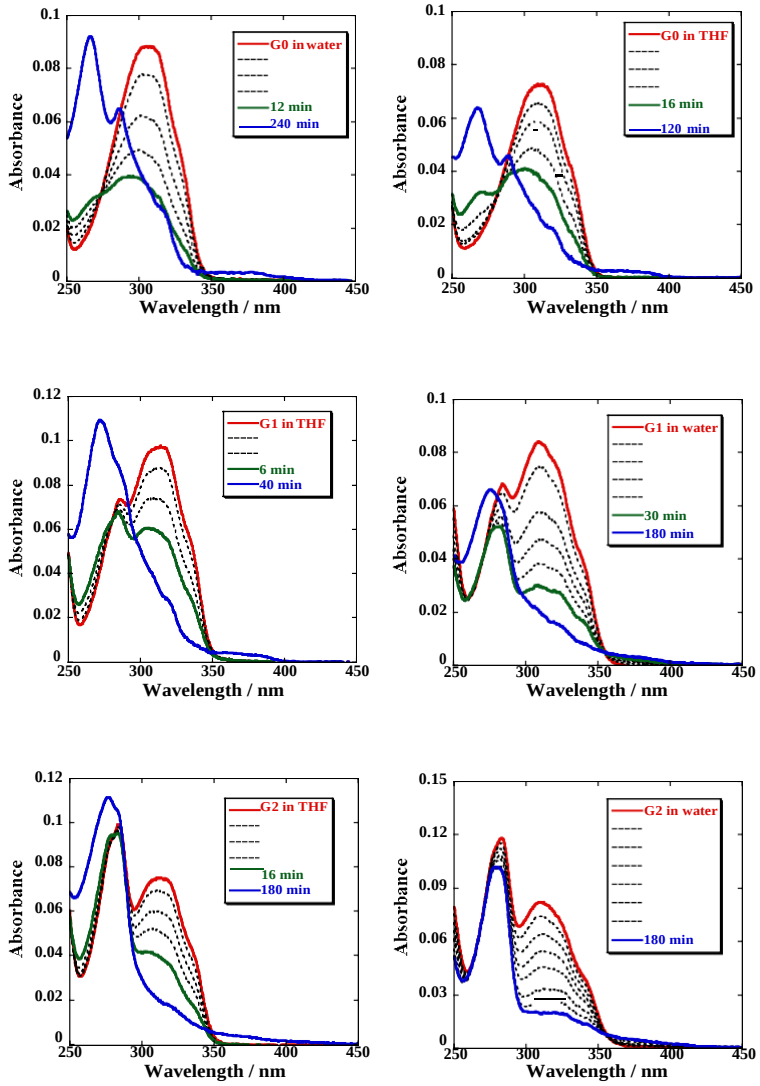
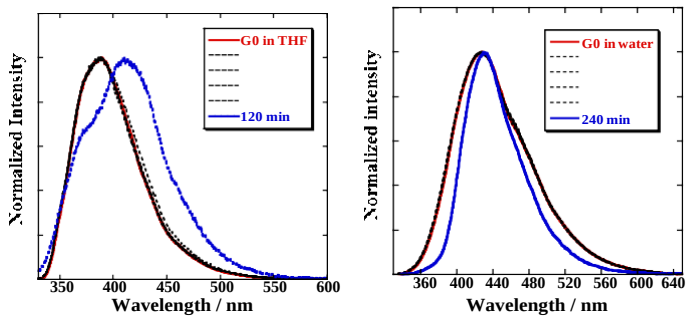


Figure S1. Changes in absorption spectra of G0-G2 in THF or water on irradiation at 310 nm.



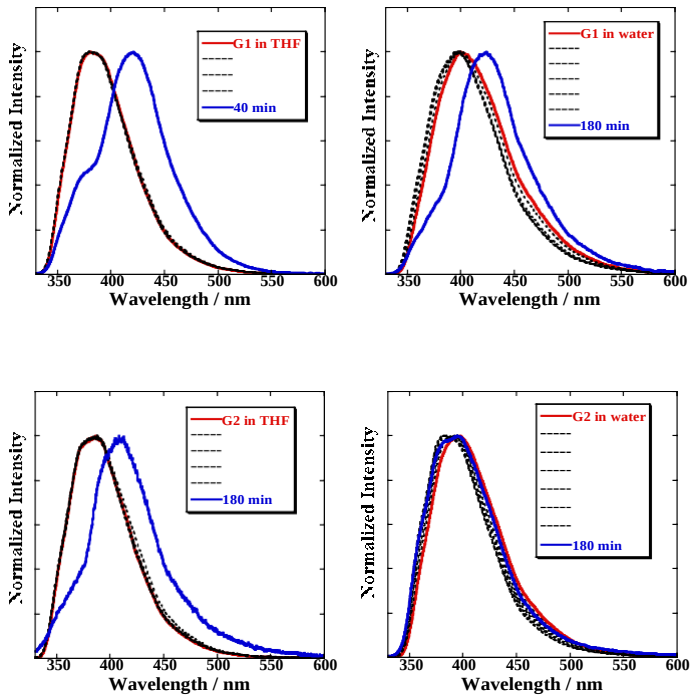


Figure S2. Changes in Fluorescence spectra of G0-G2 in THF or water on irradiation at 310 nm.