Ultra-efficient trans-to-cis photoisomerization of diphenylbutadiene dendrimers in water

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Supporting Information

Measurement

^{1}H and ^{13}C NMR spectra were measured with a Bruker ARX-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectrometer in solutions of $CDCl_3$ or DMSO-d_6 with tetramethylsilane as an internal standard. Absorption spectra were recorded using a Shimadzu UV-1600 spectrophotometer. Fluorescence and excitation spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer. Φ_f values were determined using anthracene ($\Phi_f = 0.27$ in EtOH) as a standard.[S1] A correction was made for each sample to take into account the difference in refractive indices among the solvents. Fluorescence lifetimes of lipophilic dendrimers **G1** and **G2** were determined with a Horiba NAES-1100 time-resolved spectrofluorometer. Fluorescence decay measurements of water-soluble dendrimers **wG1** and **wG2** were performed using a time-correlated single-photon counting method.[S2] Laser excitation at 375 nm was achieved using a diode laser (PicoQuant, LDH-P-C-375) with a power control unit (PicoQuant, PDL 800-B) at a repetition rate of 2.5 MHz. Temporal profiles of the fluorescence decay were detected using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630). The full-width at half-maximum (FWHM) of the instrument response function was 51 ps. The values of χ^2 and the Durbin–Watson parameters were used to determine the quality of the fit obtained by nonlinear regression.[S3] The quantum yield of photoisomerization was determined by irradiation at 325 nm from a 150 W xenon lamp shone through a monochromator using diphenylbutadiene ($\Phi_{tt\rightarrow tc}$= 0.11 in cyclohexane)[S4] as a standard.

Solvents

THF (spectroscopic grade, Nacalai Tesque, Inc.) was used as received. Distilled water (fractionation chromatography grade) and 1 N potassium hydroxide solution (volumetric analysis grade) were obtained from Wako Pure Chemical Industries Ltd. and used as received. Sample solutions were deoxygenated by bubbling with highly purified argon via a needle.

Materials

The synthesis of (1*E*,3*E*)-1,4-Bis(3,5-dihydroxyphenyl)buta-1,3-diene, a core of dendrimer, has been reported elsewhere.[18] To prepare dendron (**G2-Br**) containing polar termini, the convergent synthesis of Hawker and Fréchet was employed.[S5, S6]

G2. (1*E*,3*E*)-1,4-Bis(3,5-dihydroxyphenyl)buta-1,3-diene (35 mg, 0.129 mmol) and **G2-Br** (606 mg, 0.58 mmol) in a mixed solvent of THF (6 mL) and DMF (2 mL) was added to a mixture of 18-crown-6-ether (24 mg, 0.09 mmol) and K_2CO_3 (124 mg, 0.9 mmol) under a nitrogen atmosphere, and the mixture was stirred at 60 °C for 96 h. After filtration of the resulting precipitate the solvent was evaporated and the residue purified via silica gel column chromatography (dichloromethane/ether = 20/1) followed by a GPC column (TOSOH G2500H_{XL}) using chloroform as an eluent, to give **G2** as a pale yellow solid (70 mg, 36 μmol) in 20% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.6 Hz, 32H), 7.43 (d, *J* = 8.6 Hz, 32H), 6.83 (bs, 2H), 6.64 (d, *J* = 2.2 Hz, 24H), 6.63 (d, *J* = 2.0 Hz, 4H), 6.51 (bs, 2H), 6.50 (t, *J* = 2.2 Hz, 12H), 6.47 (t, *J* = 2.0 Hz, 2H), 5.04 (s, 32H), 4.95 (s, 24H), 3.88(s, 48H) ^{13}C NMR (100 MHz, $CDCl_3$, δ): 52.1, 69.4, 69.8, 69.9, 101.5, 101.6, 105.7, 106.4, 127.0, 129.7, 129.8, 133.1, 139.25, 139.3, 139.4, 141.8, 159.8, 160.0, 166.8 MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calcd for $C_{244}H_{214}O_{60}Na$, 4126.36; found, 4129.33.

wG2. A solution of **G2** (80 mg, 19.5 μmol) in 27 mL of mixed solvent (1 M KOH/THF/MeOH = 1/5/1) was stirred at 80 °C for 24 h under a nitrogen atmosphere. The mixture was then acidified by the addition of 1 M HCl. The resulting precipitate was filtered and washed with distilled water and MeOH to give **wG2** as a pale yellow solid (60 mg, 17.5 μmol) in 92% yield. ^{1}H NMR (400 MHz, DMF-d_7, δ): 8.02 (d, *J* = 8.4 Hz, 32H), 7.60 (d, *J* = 8.4 Hz, 32H), 7.18 (bs, 2H), 6.86–6.67 (bs×5, 20H), 5.22 (s, 32H), 5.10 (s, 24H). MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calcd for $C_{228}H_{182}O_{60}Na$, 3902.11; found, 3903.25.

References

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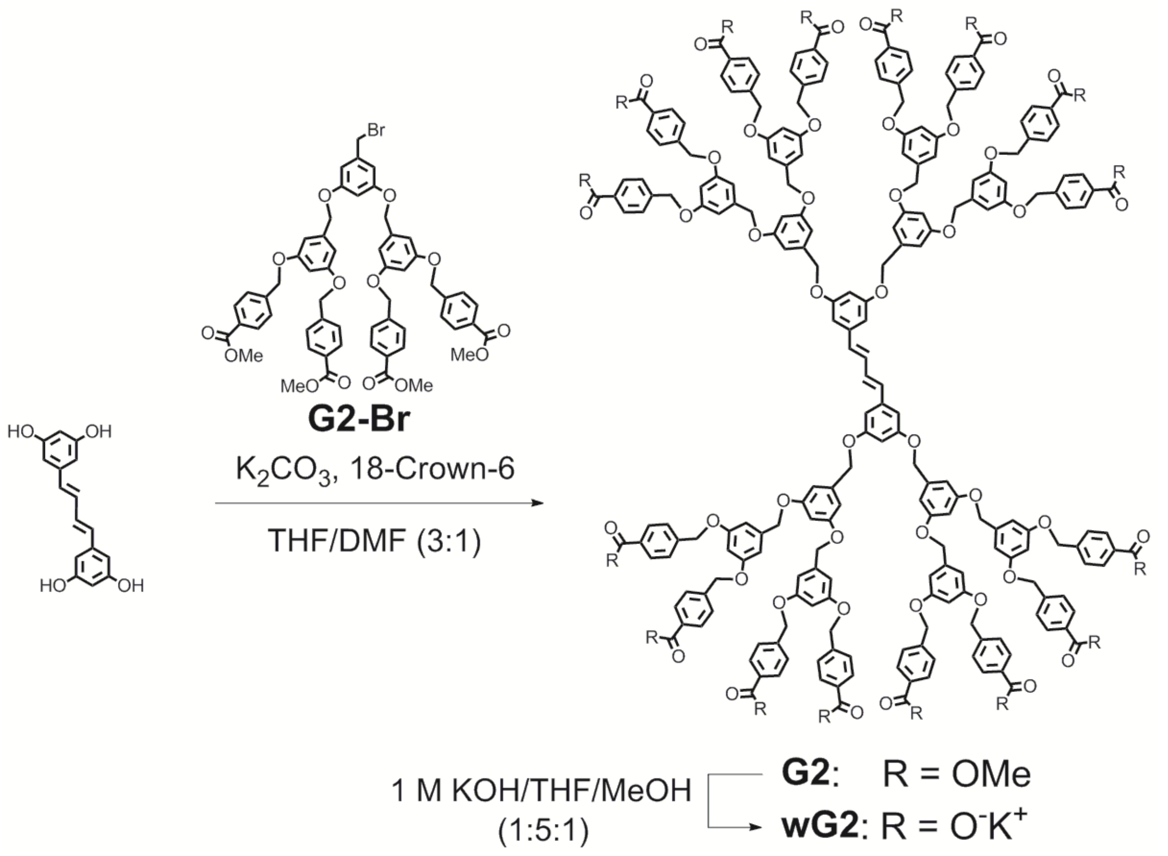
S4. W. A. Yee, S. J. WA, Hug SJ and D. S., Kliger, DS. J. Am. Chem. Soc., 1988, 110, 2164.

S5. S. M. Grayson and, J. M. J. Frechet, Chem. Rev. 2001, 101, 3819.

S6. C. J. Hawker, K. L. Wooley and J. M. Fréchet, J. Chem. Soc., Perkin Trans. 1, 1993, 1287–1297.


Br
O
O
OMe
MeO
MeO
O
OMe
G2-Br
HO
OH
HO
OH
K_2CO_3, 18-Crown-6
THF/DMF (3:1)
R
O
1 M KOH/THF/MeOH
(1:5:1)
G2: R = OMe
wG2: R = O^-K^+

Scheme S1.

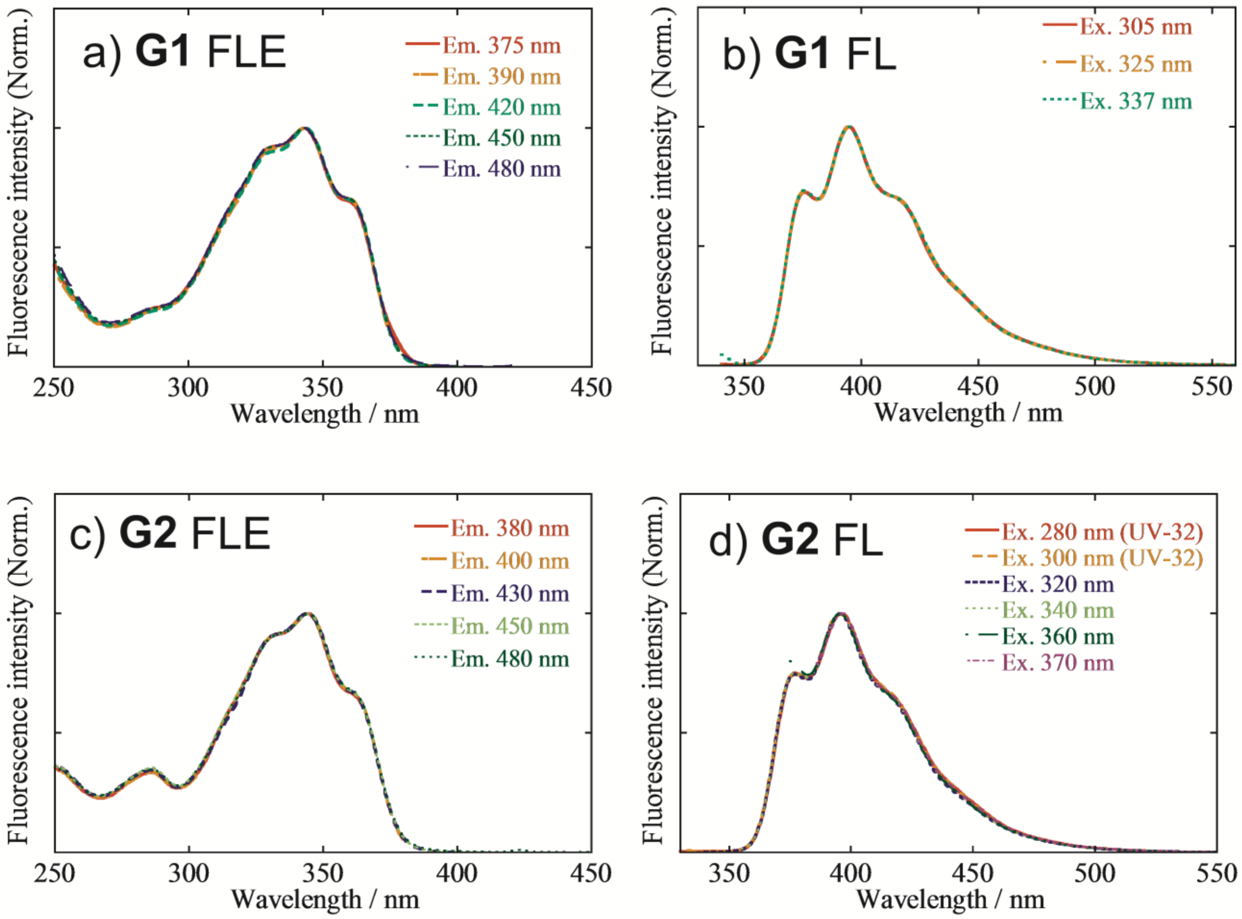


Figure S1. Fluorescence excitation spectra and fluorescence spectra of **G1** (a and b) and **G2** (c and d) in THF. No wavelength dependence was observed for the fluorescence or fluorescence excitation spectra of **G1** and **G2**.

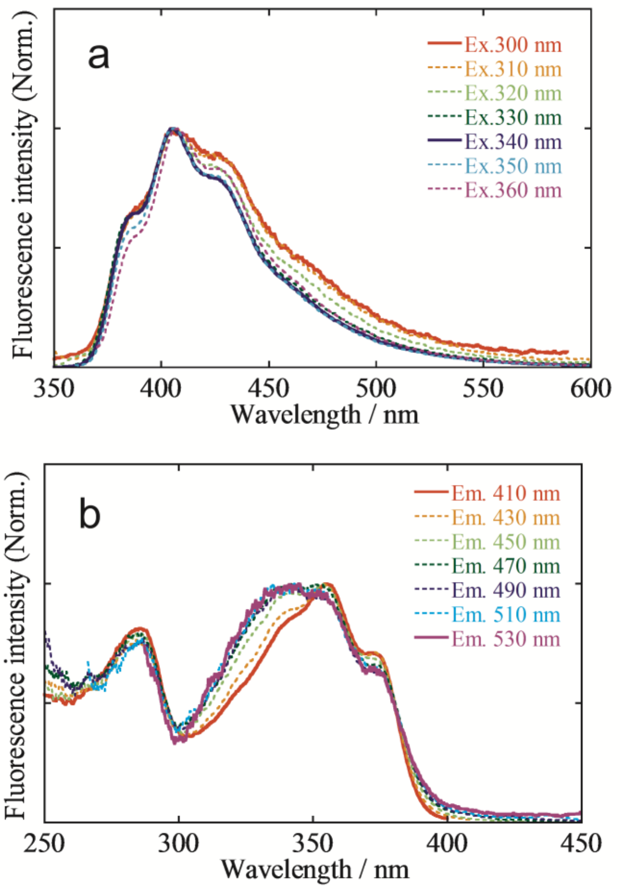


Figure S2. Wavelength dependence of fluorescence spectra (a) and fluorescence excitation spectra (b) of **wG2** in KOHaq.

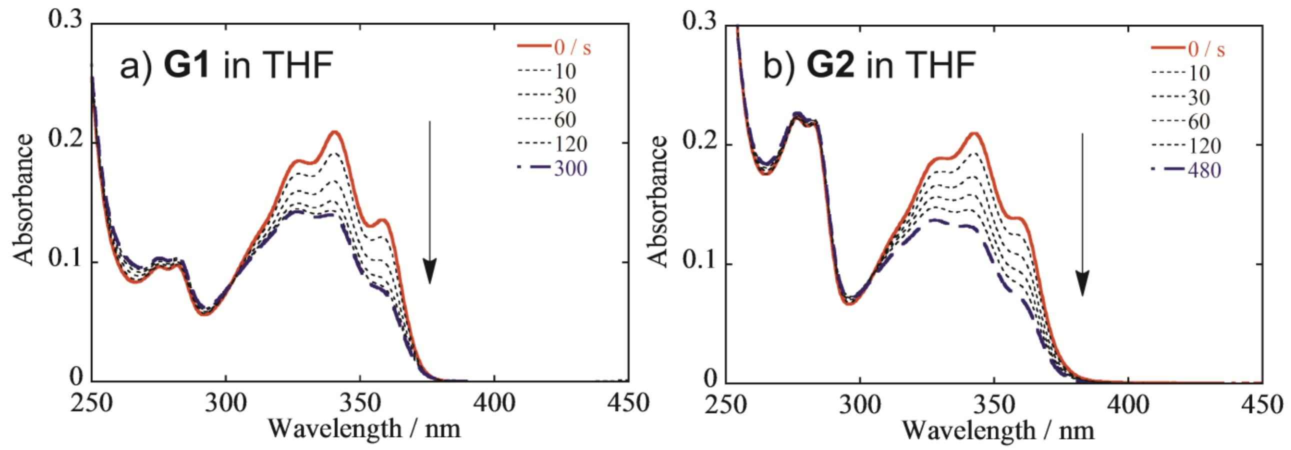


Figure S3. Change in the absorption spectra of **G1** (a) and **G2** (b) upon irradiation at 340 nm in THF.