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. $\Phi_f$ values were determined using anthracene ($\Phi_f = 0.27$ in EtOH) as a standard.$^{S_1}$ 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.$^{S_2}$ 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 $\chi^2$ and the Durbin–Watson parameters were used to determine the quality of the fit obtained by nonlinear regression. The quantum yield of photoisomerization was determined by irradiation at 325 nm from a 150 W xenon lamp shone through a monochromator using diphenylbutadiene ($\Phi_{\text{tt} \rightarrow \text{ct}} = 0.11$ in cyclohexane) 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$E,3E$)-1,4-Bis(3,5-dihydroxyphenyl)buta-1,3-diene, a core of dendrimer, has been reported elsewhere.$^{18}$ To prepare dendron ($\text{G}_2\text{-Br}$) containing polar termini, the convergent synthesis of Hawker and Fréchet was employed.$^{55,56}$

$\text{G}_2$. (1$E,3E$)-1,4-Bis(3,5-dihydroxyphenyl)buta-1,3-diene (35 mg, 0.129 mmol) and $\text{G}_2\text{-Br}$ (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 K₂CO₃ (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 G2500HXL) using chloroform
as an eluent, to give G2 as a pale yellow solid (70 mg, 36 µmol) in 20% yield. ¹H NMR (400 MHz,
CDCl₃): 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) ¹³C NMR (100 MHz, CDCl₃, 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 C₂₄₄H₂₁₄O₆₀Na, 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. ¹H NMR (400 MHz,
DMF-d₇, 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 C₂₂₈H₁₈₂O₆₀Na,
3902.11; found, 3903.25.
References


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.