Photochemical & Photobiological Sciences (Communications)

Extremely Efficient and Long Lifetime Fluorescence of *cis*-Stilbene Containing a Rigid Dendrimer

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Supporting Information

Experimental

Materials and General Instrumentation. All reagents and solvents of the highest commercial quality were purchased from Tokyo Chemical Industry Co. Ltd., Wako Pure Chemical Industries, Ltd. (Osaka, Japan), or Aldrich Chemical Co., Inc. (Milwaukee, WI) and were used without further purification. NMR spectra were recorded on a JNM-EX270 (JEOL Ltd., Tokyo, Japan) instrument at 270 MHz for ^{1}H NMR and at 67.8 MHz for ^{13}C NMR. δ values are given in parts per million relative to tetramethylsilane. Silica gel column chromatography was performed using silica gel 60N (Kanto Chemical Co. Inc., Tokyo, Japan).

Measurements. Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The concentration for steady state fluorescence measurements was adjusted so that the

absorption maximum of the excitation wavelength was 0.1 for each sample. Fluorescence decay measurements were performed by using a time-correlated single-photon counting method.[S1] Laser excitation at 375 nm was achieved by 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 fluorescence decay were detected by using a microchannel plate photomultiplier (Hamamatsu, R3809U) equipped with a TCSPC computer board module (Becker and Hickl, SPC630). 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.[S2] The time resolution was 20 ps.

(*Z*)-1,2-Di[(1,1'-biphenyl)-4-yl]ethene (*cis*-**G0**) was prepared according to a previous report.[S3]

Synthesis of *cis*-**G1**, *cis*-**G2**, *trans*-**G1**, and *trans*-**G2** are depicted in Scheme S1.

cis-**G1**: A mixture of tetraphenylcyclopentadienone (**1**)[S4] (310 mg, 0.81 mmol) and (*Z*)-1,2-bis(4-ethynylphenyl)ethene (**3**)[S5] (45 mg, 0.20 mmol) in diphenylether (15 mL) was stirred at 180 °C for 20 h under nitrogen. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure. The crude product was

purified by flash chromatography on silica gel with hexane–CH_2Cl_2 (2 : 1) as eluent and by using an HPLC equipped with a GPC column (TOSOH G2500HXL) with $CHCl_3$ as eluent, to give 120 mg (0.12 mmol, 60%) of *cis*-**G1**. ^{1}H NMR (270 MHz; $CDCl_3$): δ 7.57 (2H, s), 7.20–7.10 (12H, m), 6.97–6.77 (36H, m), 6.45 (2H, s, C*H*=C*H*); MALDI-TOF MS, *m*/*z*: found: 940.50, calcd for [$C_{74}H_{52}$+Na] 940.41.

cis-**G2**: A mixture of G2-dendron (**2**)[S4] (900 mg, 0.78 mmol) and **3** (62 mg, 0.27 mmol) in diphenylether (16 mL) was stirred at 140 °C for 3 days under nitrogen. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexane–CH_2Cl_2 (2 : 1) as eluent and by using an HPLC equipped with a GPC column (TOSOH G2500HXL) with $CHCl_3$ as eluent, to give 10 mg (0.004 mmol, 1.5%) of *cis*-**G2**. ^{1}H NMR (270 MHz; $CDCl_3$): δ 7.51-7.44 (6H, s), 7.17–7.07 (32H, m), 6.97–6.63 (86H, m), 6.55-6.43 (8H, m, ArH and C*H*=C*H*); MALDI-ToF MS, *m*/*z*: found: 2486.50, calcd for [$C_{194}H_{132}$+Na] 2484.02.

trans-**G1**: A mixture of **1** (960 mg, 2.5 mmol) and (*E*)-1,2-bis(4-ethynylphenyl)ethene (**4**)[S6] (140 mg, 0.62 mmol) in diphenylether (30 mL) was stirred at 180 °C for 17 h under nitrogen. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure. The crude product was purified by flash

chromatography on silica gel with hexane–CH_3Cl (1:1) as eluent and by using an HPLC equipped with a GPC column (TOSOH G2500HXL) with $CHCl_3$ as eluent, to give 210 mg (0.22 mmol, 36%) of *cis*-**G1**. ^{1}H NMR (270 MHz; $CDCl_3$): δ 7.57 (2H, s), 7.27 (4H, d, *J* = 7.3 Hz), 7.15-7.10 (14H, m), 6.96 (2H, s, C*H*=C*H*), 6.95-6.91 (12H, m), 6.84-6.85 (14H, m), 6.79-6.75 (4H, m); MALDI-ToF MS, *m*/*z*: found: 940.37, calcd for [$C_{74}H_{52}$+Na] 940.41.

trans-**G2**: A mixture of **2** (900 mg, 0.78 mmol) and **4** (62 mg, 0.27 mmol) in diphenylether (16 mL) was stirred at 140 °C for 3 days under nitrogen. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexane–CH_3Cl (2 : 1) as eluent and by using an HPLC equipped with a GPC column (TOSOH G2500HXL) with $CHCl_3$ as eluent, to give 51 mg (0.02 mmol, 7%) of *cis*-**G2**. ^{1}H NMR (270 MHz; $CDCl_3$): δ 7.51 (2H, s), 7.48 (2H, s), 7.44 (2H, s), 7.23 (4H, d, *J* = 8.1 Hz), 7.15–7.13 (26H, m), 7.05 (4H, m), 6.93-6.80 (54H, m), 6.77-6.68 (26H, m), 6.65 (4H, d, *J* = 8.1 Hz), 6.54 (4H, d, *J* = 8.1 Hz), 6.47 (4H, d, *J* = 8.1 Hz); MALDI-ToF MS, *m*/*z*: found: 2482.47, calcd for [$C_{194}H_{132}$+Na] 2484.02.

References

S1 Nishimura, Y.; Kamada, M.; Ikegami, M.; Nagahata, R.; Arai, T., *J. Photochem. Photobiol. A: Chem.*, 2006, **178**, 150.

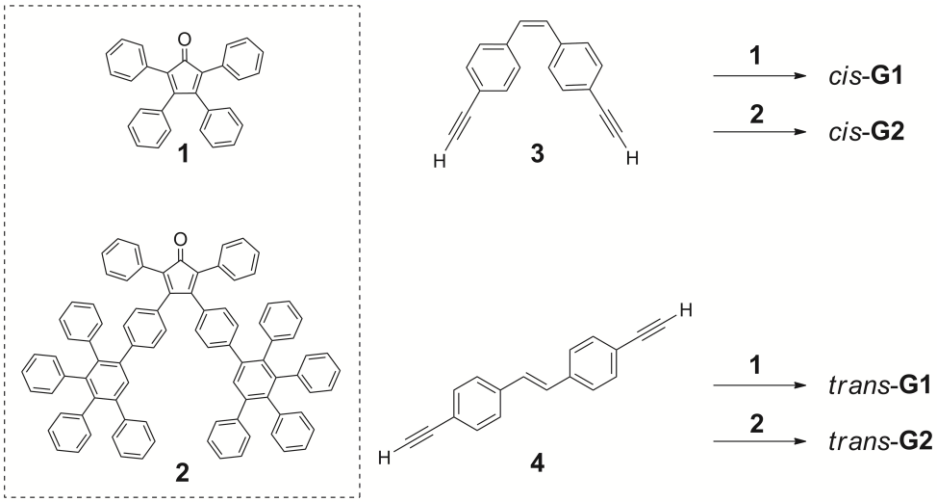
S2 Boens, N.; Tamai, N.; Yamazaki, I.; Yamazaki, T., *Photochem. Photobiol.* 1990, **52,** 911.

S3 Z. Fengqiang, J. Motoyoshiya, Y. Nishii, H. Aoyama, A. Kakehi, M. Shiro, *J. Photochem. Photobiol. A: Chem.*, 2006, **184**, 44.

S4 M. Imai, M. Ikegami, A. Momotake, R. Nagahata, T. Arai, *Photochem. Photobiol. Sci.*, 2003, **2**, 1181.

S5 R. Winter, M. Linseis, *Ger. Offen.*, 2009, 45pp. CODEN:GWXXBX; DE102008030926.

S6 N. T. Lucas, E. G. A. Notaras, M. P. Cifuentes, M. G. Humphrey, *Organometallics*, 2003**, 22**, 284.



Scheme S1.

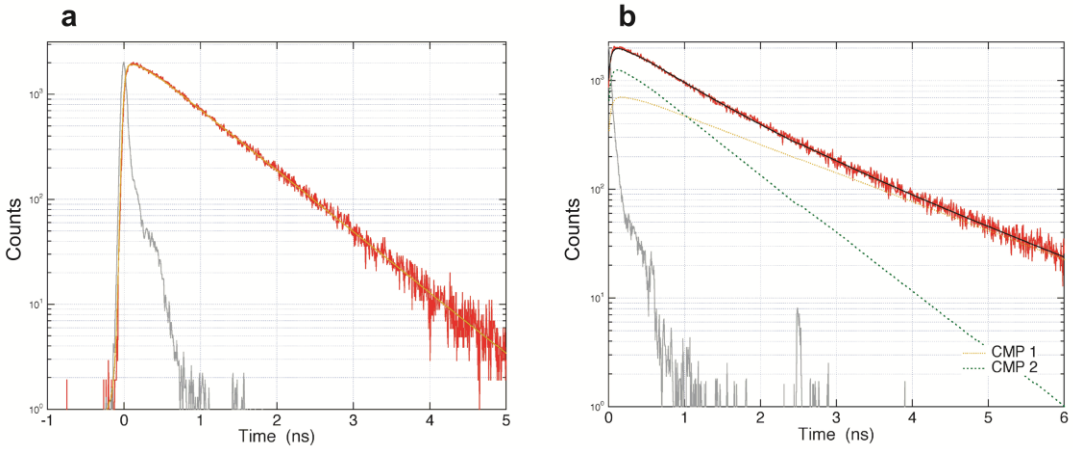


Figure S1. Fluorescence decay plots of *trans*-**G2** (a) and *cis*-**G2** (b) in benzene under argon at room temperature. The excitation and monitoring wavelengths are 375 nm and 450 nm, respectively.