

Photoisomerization and energy transfer in naphthalene terminated stilbene dendrimers

Satoshi Nakazato, Tsutomu Takizawa, and Tatsuo Arai*

Supporting Information

Table S1. Molar extinction coefficients of *trans*-TMST, *trans*-G3, and *trans*-NpG4.

	<i>trans</i> -TMST ^{S1}	<i>trans</i> -G3 ^{S2}	<i>trans</i> -NpG4
$\epsilon_{(285 \text{ nm})} / 10^4 \text{ mol}^{-1} \text{ cm}^{-1} \text{ dm}^3$	1.86	4.63	19.4

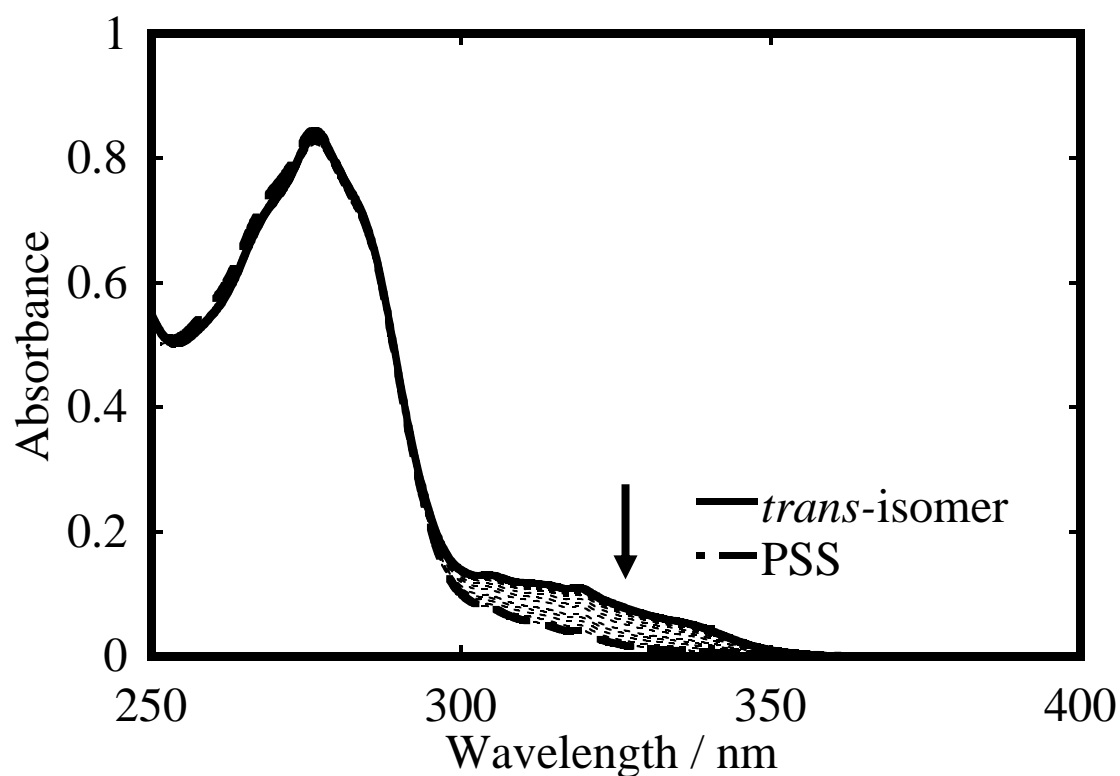


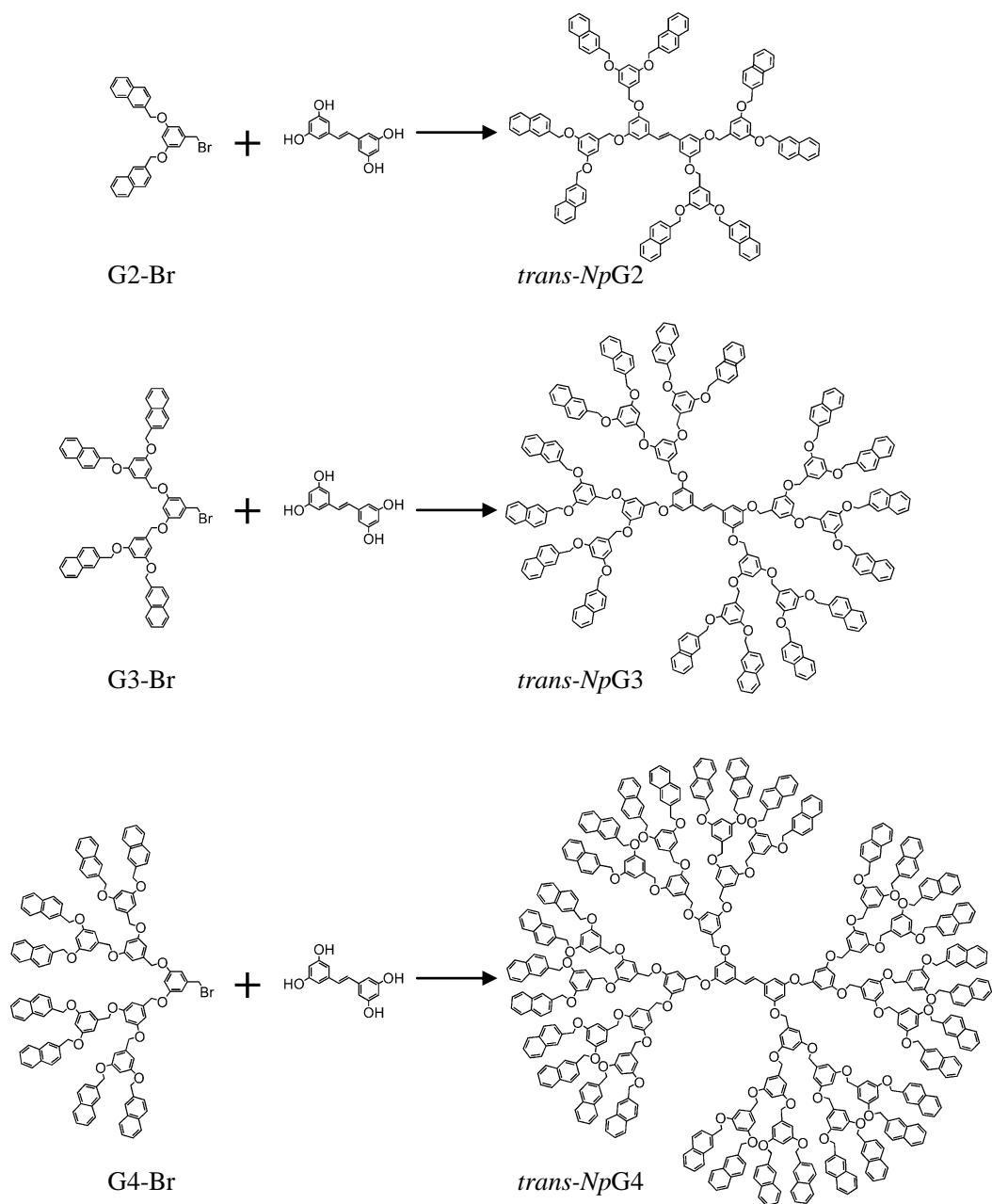
Figure S1. Change of absorption spectra of *trans*-NpG4 in deaerated THF solution on irradiation at 330 nm.

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 absorbance at the excitation wavelength was lower than 0.1 for each sample. The fluorescence quantum yields were determined by using anthracene ($\Phi_{\text{Fl}} = 0.27$ in ethanol) as a standard. The *trans*-to-*cis* photoisomerization quantum yields were determined by using *trans*-TMST ($\Phi_{\text{t} \rightarrow \text{c}} = 0.38$ in THF) as a standard. Isomer composition at the photostationary state was estimated by determining the percentage of *trans*-isomer from the relative intensities of the fluorescence spectra of the *trans*-isomer taken at the initial state and the photostationary state.

Synthesis

Synthesis of *trans-NpG2*, *trans-NpG3*, and *trans-NpG4* are depicted in Scheme S1.



Scheme S1. Synthesis of *trans-NpGn* dendrimers.

G2-Br, G3-Br, and G4-Br were prepared according to the literature^{S3}.

trans-NpG2: G2-Br (781 mg, 1.6 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene (53.0 mg, 0.22 mmol), 18-crown-6 ether (50.2 mg, 0.19 mmol) and K₂CO₃ (129 mg, 0.93 mmol) were reacted in acetone (40 ml) under N₂ and the mixture was refluxed for 7 days. The solvent was removed by evaporation under reduced pressure. Then the residue was poured into water (90 ml) and extracted with dichloromethane (200 ml). The solvent was removed by evaporation under reduced pressure and the residue was washed with toluene, dichloromethane, chloroform and acetone. The recrystallization of the residue from chloroform gave *trans-NpG2* as a pale yellow amorphous powder (147 mg, 0.079 mmol, 36 %).

¹H NMR (600 MHz; CDCl₃): δ 4.99 (8H, s), 5.18 (16H, s), 6.51 (2H, t, *J*=2.2 Hz), 6.65 (4H, t, *J*=2.2 Hz), 6.72 (4H, d, *J*=2.2 Hz), 6.73 (8H, d, *J*=2.2 Hz), 6.93 (2H, s), 7.42-7.48 (24H, m), 7.77-7.78 (32H, m).

MALDI-TOF MS, *m/z*: found: 1876.1, calcd for [C₁₃₀H₁₀₀O₁₂Na⁺] 1875.7.

trans-NpG3: G3-Br (408 mg, 0.40 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene (23.4 mg, 0.097 mmol), 18-crown-6 ether (21.4 mg, 0.081 mmol) and K₂CO₃ (37.4 mg, 0.27 mmol) were reacted in acetone (60 ml) under N₂ and the mixture was refluxed for 9 days. The solvent was removed by evaporation under reduced pressure. Then the residue was poured into water (120 ml) and extracted with dichloromethane (140 ml). The solvent was removed by evaporation under reduced pressure and the residue was purified by flash chromatography on silica gel using chloroform-hexane (2 : 1) as an eluent. The obtained compound was further purified by HPLC equipped with GPC column (TOSHO G2500H_{XL}), using chloroform as an eluent, to give *trans-NpG3* as a

pale yellow amorphous powder (35.4 mg, 0.0089 mmol, 9.2 %).

^1H NMR (600 MHz; CDCl_3): δ 4.88 (8H, s), 4.90 (16H, s), 5.08 (32H, s), 6.49 (2H, t, $J=1.8$ Hz), 6.51 (4H, t, $J=2.0$ Hz), 6.59 (8H, t, $J=2.1$ Hz), 6.61 (8H, d, $J=2.0$ Hz), 6.67 (16H, d, $J=2.1$ Hz), 6.69 (4H, d, $J=1.8$ Hz), 6.93 (2H, s), 7.38-7.43 (48H, m), 7.71-7.77 (64H, m).

MALDI-TOF MS, m/z : found: 3972.5, calcd for $[\text{C}_{274}\text{H}_{212}\text{O}_{28}\text{Na}^+]$ 3972.5.

trans-NpG4:G3-Br (544 mg, 0.27 mmol), *trans*-3,3',5,5'-tetrahydroxystilbene (15.5 mg, 0.064 mmol), 18-crown-6 ether (10.1 mg, 0.38 mmol) and K_2CO_3 (26.2 mg, 0.19 mmol), were reacted in a mixed solvent of acetone (20 ml) and DMF (10 ml) under N_2 and the mixture was refluxed for 7 days. Then the solvent was removed by evaporation under reduced pressure. The residue was poured into water (90 ml) and extracted chloroform (100 ml). The solvent was removed by evaporation under reduced pressure and the residue was purified by flash chromatography on silica gel using chloroform as an eluent. The resulting material was further purified by HPLC equipped with GPC column (TOSHO G2500H_{XL}) using chloroform as an eluent. The solvent was removed by evaporation and the residue was purified by recrystallization from mixed solvent of toluene and n-hexane, to give *NpG4* as a pale yellow amorphous powder (288 mg, 0.035 mmol, 55 %).

^1H NMR (600 MHz; CDCl_3): δ 4.74 (24H, s), 4.76 (32H, s), 4.97 (64H, s), 6.43-6.59 (90H, m), 6.81 (2H, s), 7.38-7.43 (96H, m), 7.71-7.77 (128H, m).

MALDI-TOF MS, m/z : found: 8174.1, calcd for $[\text{C}_{562}\text{H}_{436}\text{O}_{60}\text{Na}^+]$ 8172.4.

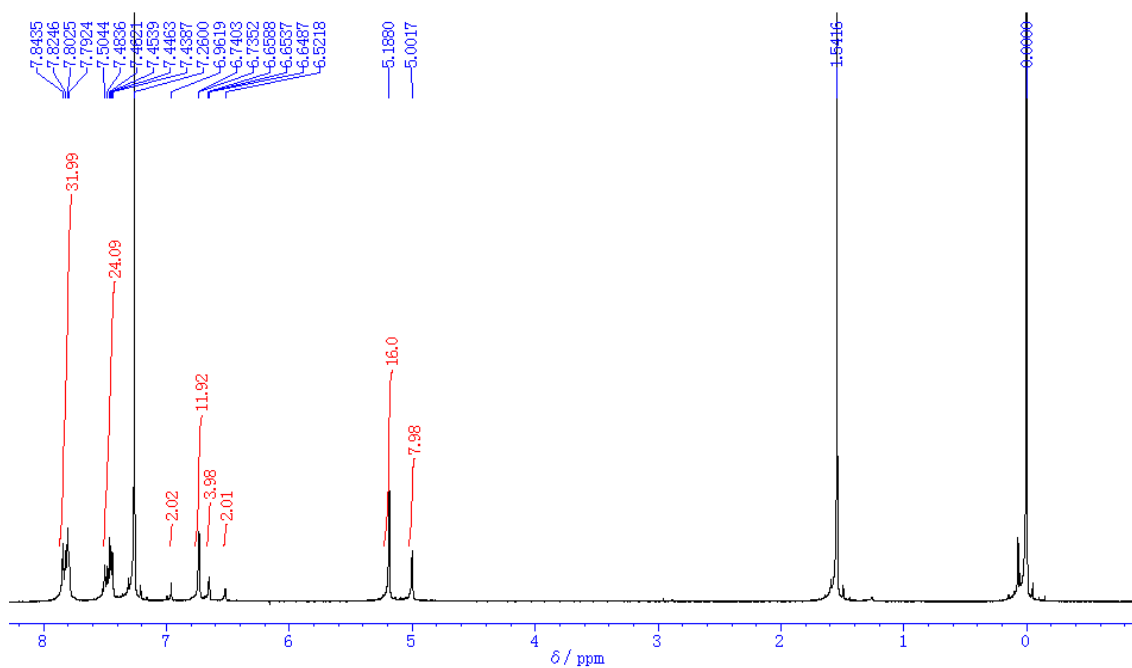


Figure S2. ^1H NMR spectrum of *trans-NpG2* (CDCl_3 , 400 MHz).

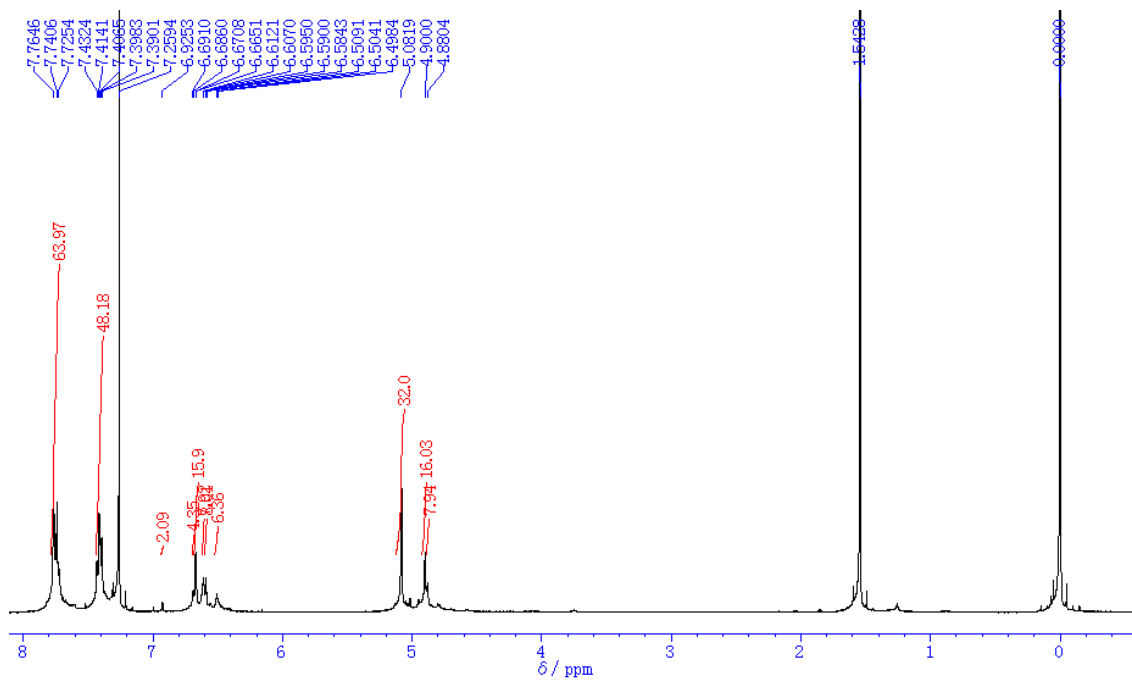


Figure S3. ^1H NMR spectrum of *trans-NpG3* (CDCl_3 , 400 MHz).

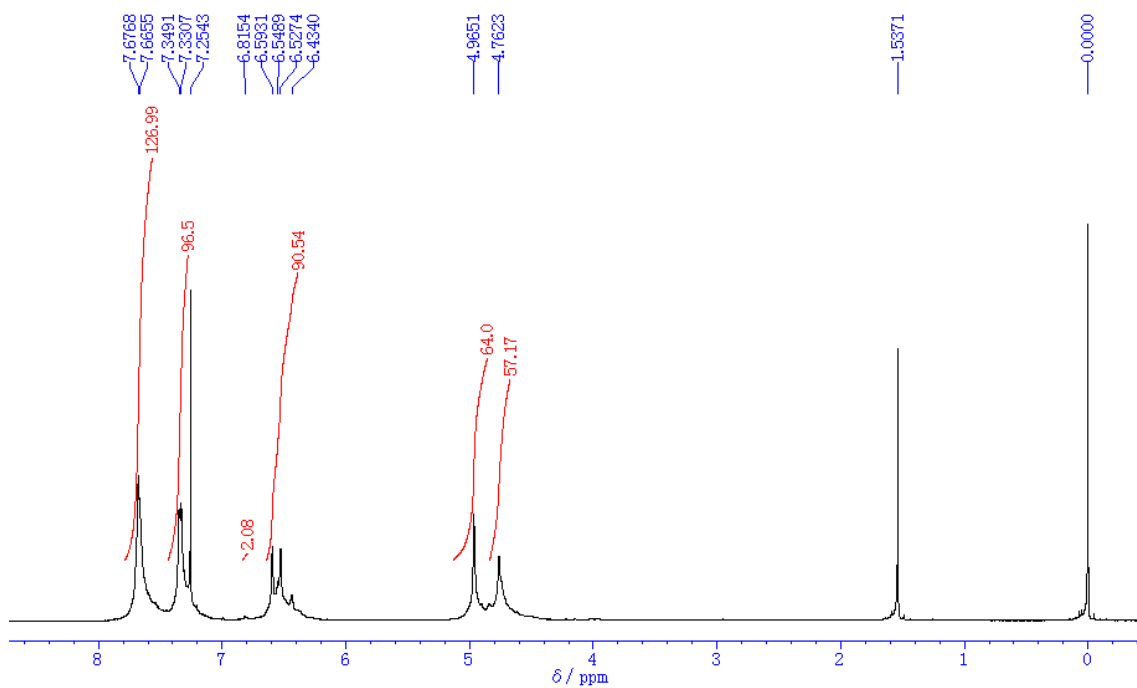


Figure S4. ^1H NMR spectrum of *trans*-NpG4 (CDCl_3 , 400 MHz).

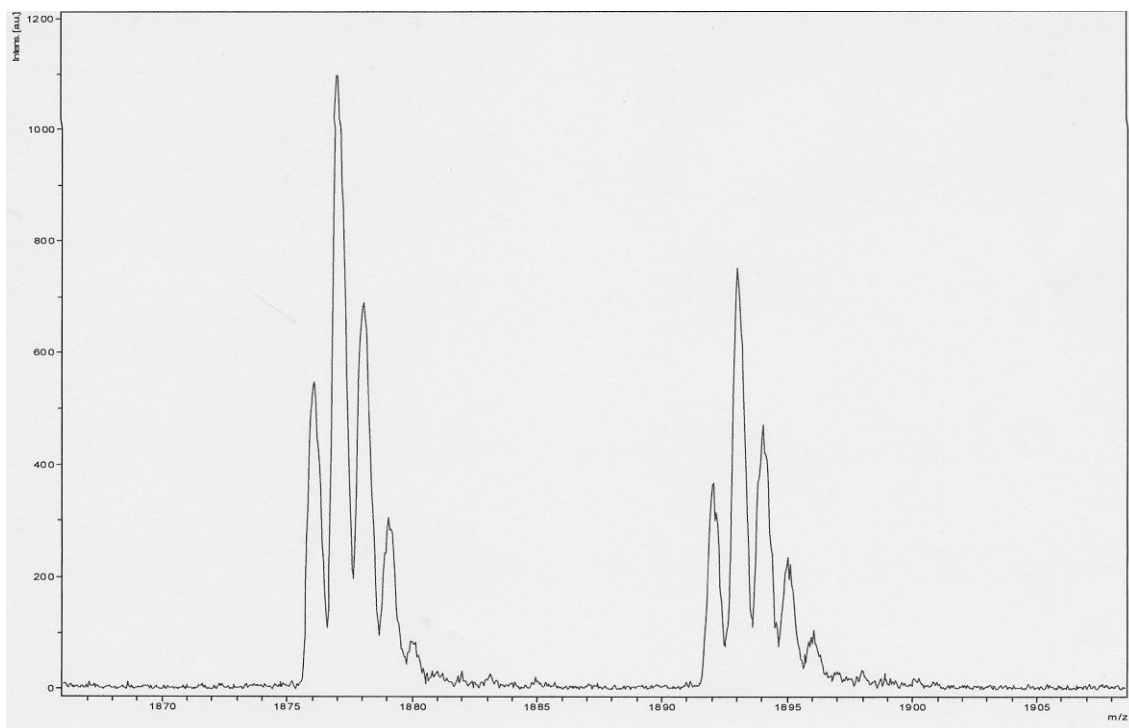


Figure S5. MALDI-TOF mass spectrum of NpG2.

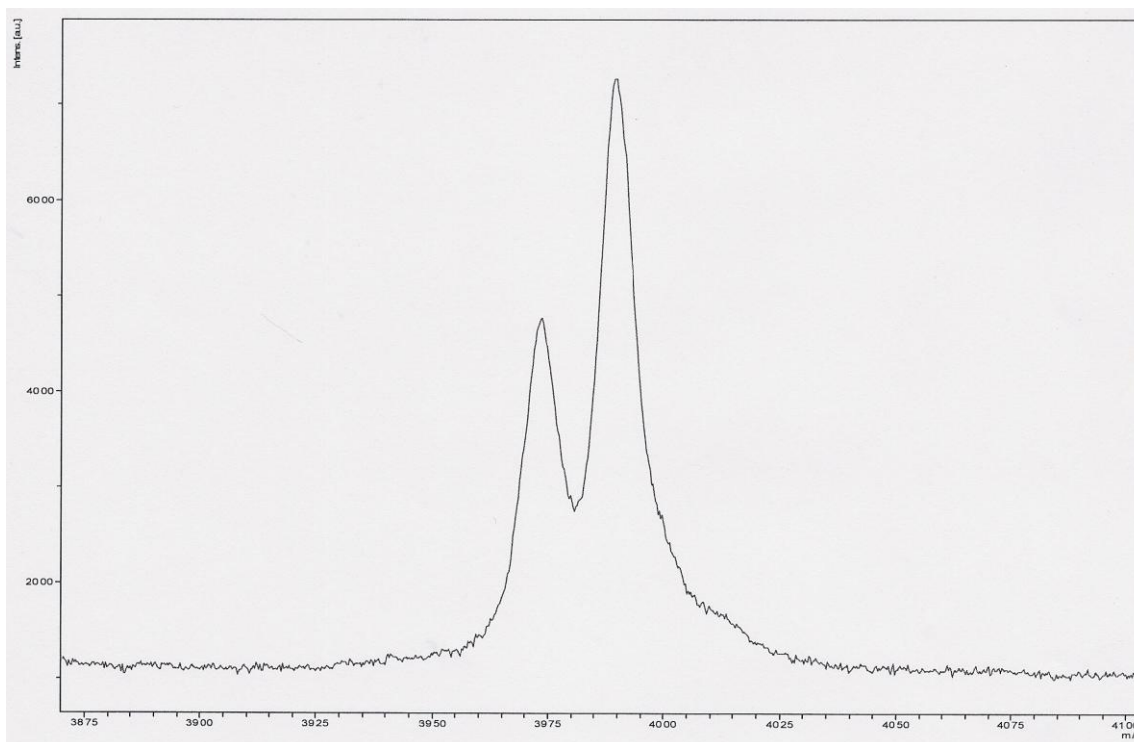


Figure S6. MALDI-TOF mass spectrum of *NpG3*.

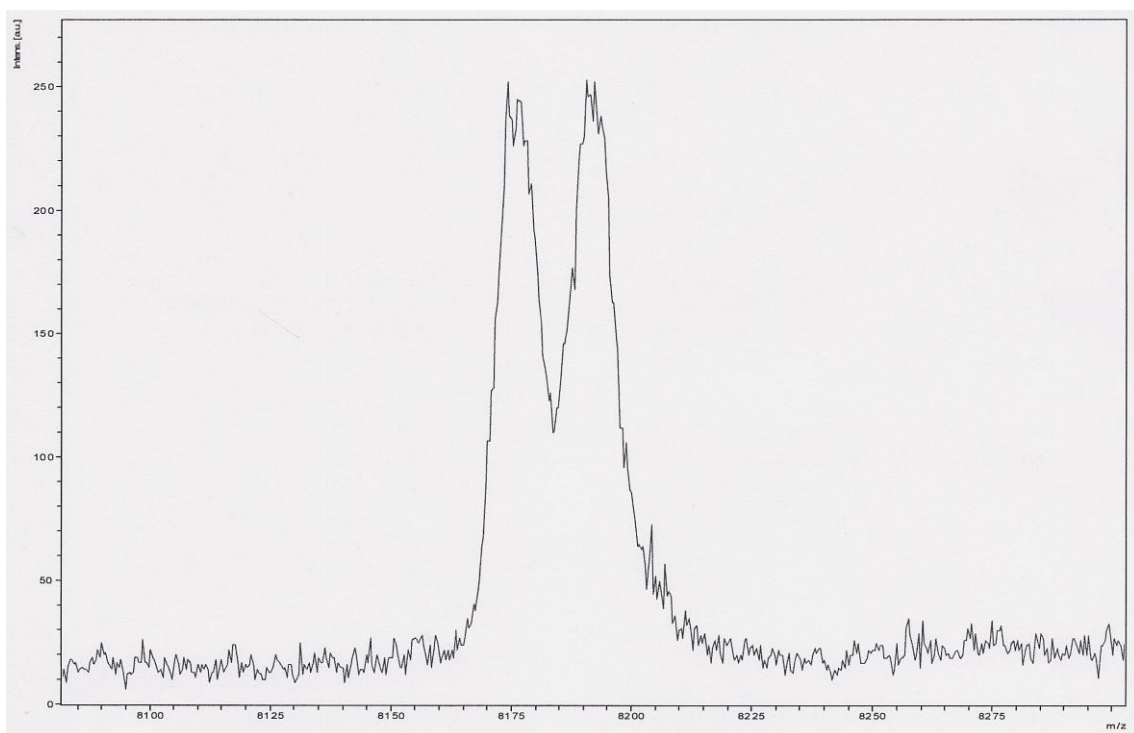


Figure S7. MALDI-TOF mass spectrum of *NpG4*.

References

- S1.** J. Hayakawa, M. Ikegami, T. Mizutani, Md. Wahadoszamen, A. Momotake, Y. Nishimura, T. Arai, *J. Phys. Chem. A*, 2006, **110**, 12566.
- S2.** M. Uda, T. Mizutani, J. Hayakawa, A. Momotake, M. Ikegami, R. Nagahata, T. Arai, *Photochem. Photobiol.*, 2002, **76**, 596.
- S3.** M. Plevoets, F. Vögtle, L. Cola, V. Balzani, *New J. Chem.*, 1999, 63.