

Supplementary Information

Preparation and photosensitizing property of novel Cd₁₀S₁₆ molecular cluster dendrimer

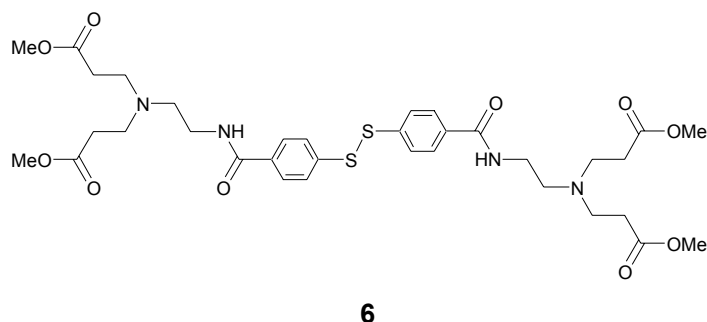
Takaaki Tsuboi, Yutaka Takaguchi,* Sadao Tsuboi

Graduate School of Environmental Science, Okayama University, Tsushima-Naka 3-1-1, Okayama
700-8530, Japan

General method. The NMR spectra were measured using a spectrometer (AL300; JEOL). Elemental analysis was carried out using an elemental analyzer (2400 Series II CHNS/O; PerkinElmer Inc.). ICP-AES performed by VISTA-PRO (Seiko Instruments Inc.) was to characterize the content of Cd. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MASS) and laser desorption ionization time-of-flight mass spectroscopy (LD-TOF-MASS) was performed using a mass spectrometer (Autoflex; Bruker Daltonics Inc.). Gas chromatography (GC) analyses were carried out on a gas chromatograph (GC18A; Shimadzu Corp.) equipped with an FID detector and a fused silica capillary column (30 m × 0.53 mm i.d., coating DB-1; J&W Scientific Inc.). The GC-MS analyses were performed on a GC-MS workstation (QP5000; Shimadzu Corp.) with a fused silica capillary column (30 m × 0.25 mm i.d., coating TC-5;

GL Science Co. Ltd.). Photoirradiation was carried out using a Pyrex reactor. A 500-W high-pressure mercury lamp (EHB-500; Eikosa Corp.) was used as the light source.

Unless otherwise noted, the reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Kogyo Co. Ltd., Kanto Kagaku, and Aldrich Chemical Co. Inc. Solvents and reagents were used as received without further purification. Dendrimer disulfide **6** was synthesized according to the previously reported method.¹



Preparation of dendron thiol 3. Dendrimer disulfide **6** (399 mg, 0.54 mmol) was dissolved in ethanol (5.4 mL) at room temperature under Ar atmosphere. Sodium borohydride (61.6 mg, 1.6 mmol) was added to the mixture. After stirring for 2 h, the mixture was quenched by addition of water, and extracted with chloroform. The organic layer was washed with brine, dried over MgSO₄, and evaporated to afford the dendron thiol **3** (367 mg, 92% yield) as a thick yellow oil: ¹H NMR (300 MHz; CDCl₃) δ 2.44 (4 H, t, *J* = 6.3 Hz, CH₂CH₂N), 2.62 (2 H, t, *J* = 5.6 Hz, NCH₂CH₂NHC=O), 2.75 (4 H, t, *J* = 6.3 Hz, CH₂CH₂N), 3.51-3.57 (9 H, m, OCH₃, NCH₂CH₂NHC=O, and SH), 7.21 (1 H, brs, NH), 7.28 (2 H, d, *J* = 8.1 Hz, Ar-H), 7.77 (2 H, d, *J* = 8.4 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃)

δ 32.3, 37.0, 48.6, 51.2, 52.5, 127.7, 128.0, 131.5, 135.4, 166.3, 172.9; MALDI-TOF-MASS (matrix, α -cyano-4-hydroxy-cinnamic acid): m/z 368.91 ($[M+H]^+$). Calcd. for $C_{17}H_{24}N_2O_5S$: m/z 369.15.

Photooxygenation of di-*n*-butyl sulfide (4a) sensitized by $Cd_{10}S_{16}$ molecular cluster dendrimer 1. A mixture of di-*n*-butyl sulfide **4a** (25.8 mg, 0.177 mmol) and $Cd_{10}S_{16}$ molecular cluster dendrimer **1** (100 mg, 0.0177 mmol) in chloroform-methanol (9:1, 4.3 mL) was irradiated with a high-pressure mercury lamp, while oxygen was passed through the reaction mixture. After 2.5 h irradiation, the resultant mixture was analyzed by GC; *n*-Decane was used as the internal standard.

Photooxygenation of thioanisole (4b) sensitized by $Cd_{10}S_{16}$ molecular cluster dendrimer 1. A mixture of thioanisole **4b** (21.5 mg, 0.173 mmol) and $Cd_{10}S_{16}$ molecular cluster dendrimer **1** (98.0 mg, 0.0173 mmol) in chloroform-methanol (9:1, 4.2 mL) was irradiated with a high-pressure mercury lamp, while oxygen was passed through the reaction mixture. After 4 h irradiation, the resultant mixture was analyzed by GC; *n*-Decane was used as the internal standard.

Photooxygenation of diphenyl sulfide (4c) sensitized by $Cd_{10}S_{16}$ molecular cluster dendrimer 1. A mixture of diphenyl sulfide **4c** (22.0 mg, 0.118 mmol) and $Cd_{10}S_{16}$ molecular cluster dendrimer **1** (100 mg, 0.0177 mmol) in chloroform-methanol (9:1, 4.3 mL) was irradiated with a high-pressure mercury lamp, while oxygen was passed through the reaction mixture. After 4 h irradiation, the resultant mixture was analyzed by GC; *n*-Decane was used as the internal standard.

Photooxygenation of benzyl methyl sulfide (4d) sensitized by $Cd_{10}S_{16}$ molecular cluster dendrimer 1. A mixture of benzyl methyl sulfide **4d** (19.5 mg, 0.141 mmol) and $Cd_{10}S_{16}$ molecular cluster dendrimer **1** (80.0 mg, 0.0141 mmol) in $CDCl_3$ - CD_3OD (9:1, 3.4 mL) was irradiated with a

high-pressure mercury lamp, while oxygen was passed through the reaction mixture. After 3 h irradiation, the resultant mixture was analyzed by NMR; 3-methyl-2-butene was used as the internal standard.

Photooxygenation of the benzyl sulfide (4e) sensitized by Cd₁₀S₁₆ molecular cluster dendrimer 1. A mixture of benzyl sulfide **4e** (26.3 mg, 0.123 mmol) and Cd₁₀S₁₆ molecular cluster dendrimer **1** (69.6 mg, 0.0123 mmol) in CDCl₃-CD₃OD (1:5, 3 mL) was irradiated with a high-pressure mercury lamp, while oxygen was passed through the reaction mixture. After 2 h irradiation, the resultant mixture was analyzed by NMR; 3-methyl-2-butene was used as the internal standard.

Confirmation of the structure of Cd₁₀S₁₆ molecular cluster dendrimer 1 by ¹H NMR. Figure S1 shows the ¹H NMR spectrum (CDCl₃, 300 MHz) of Cd₁₀S₁₆ molecular cluster dendrimer **1** in the presence of 20 equivalents of cetyltrimethylammonium bromide. The peak integration ratio of δ 7.00–7.95 (aromatic and amide protons) and δ 2.28–2.90 (methylene protons of dendritic wedge) is 5:10, which consist with the structure of **1**. Magnified ¹H NMR charts of the aromatic region (7.00–7.95 ppm; aromatic and amide protons) and the aliphatic region (2.28–2.90 ppm; methylene protons of dendritic wedge) are shown in Figures S2 and S3, respectively.

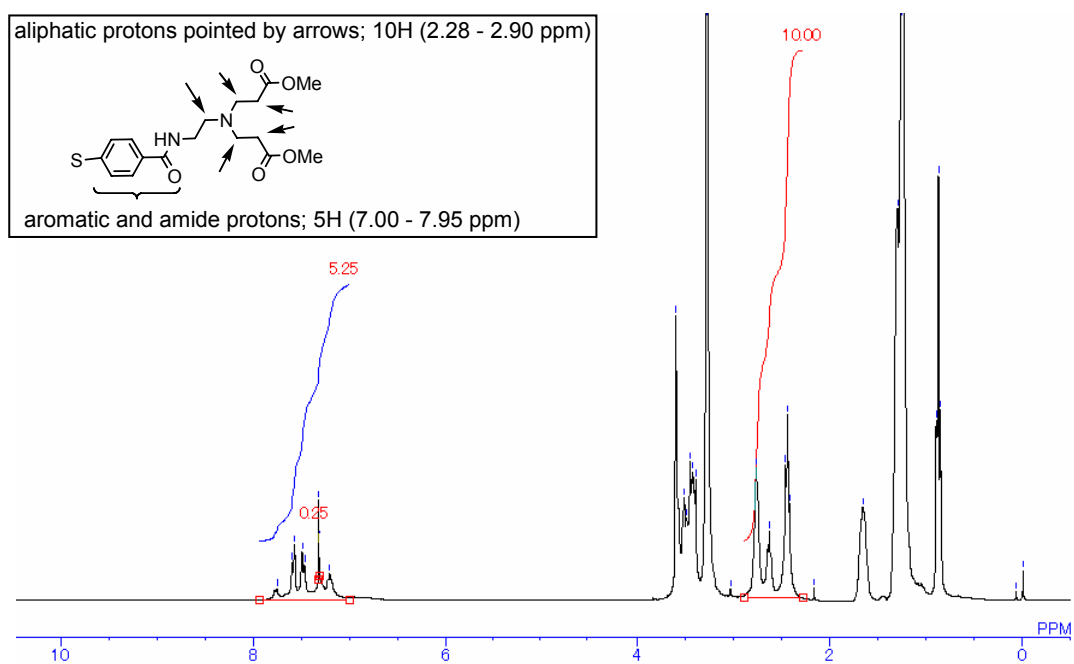


Figure S1. ^1H NMR spectra of $\text{C}_{10}\text{S}_{16}$ molecular cluster dendrimer **1** (0.91 mM) in the presence of CTAB (18.2 mM) in CDCl_3 .

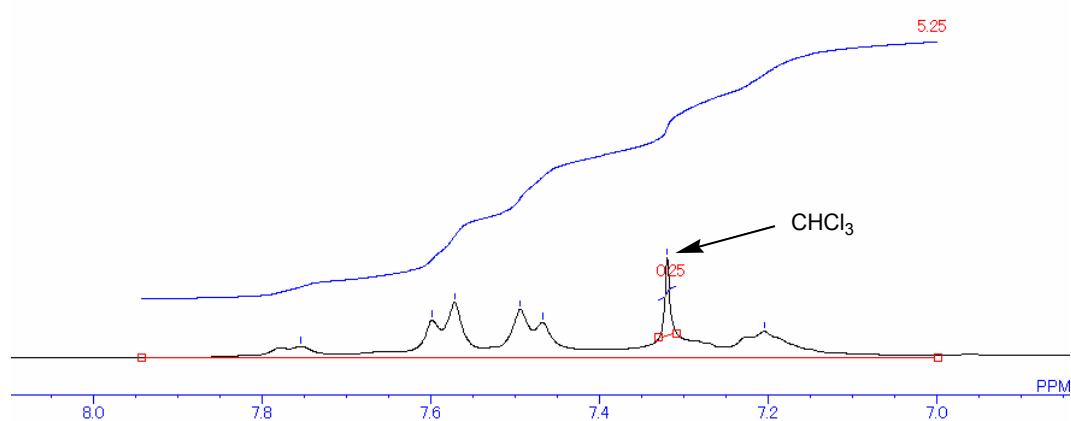


Figure S2. Magnified ^1H NMR chart of the aromatic region (7.00–7.95 ppm; aromatic and amide protons) of $\text{C}_{10}\text{S}_{16}$ molecular cluster dendrimer **1** (0.91 mM) in the presence of CTAB (18.2 mM) in CDCl_3 .

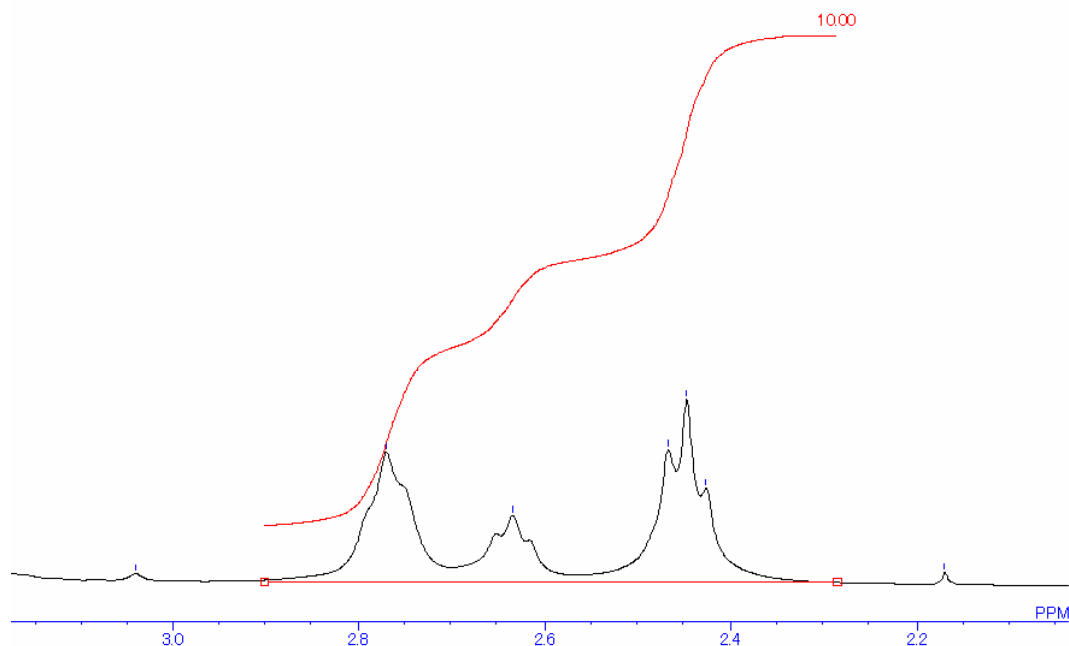


Figure S3. Magnified ^1H NMR chart of the aliphatic region (2.28–2.90 ppm; methylene protons of dendritic wedge) of $\text{C}_{10}\text{S}_{16}$ molecular cluster dendrimer **1** (0.91 mM) in the presence of CTAB (18.2 mM) in CDCl_3 .

Characterization of dendrimer 1 by ICP-AES. Dendrimer **1** (2.90 mg, 5.12×10^{-4} mmol) was dissolved in 1.91 mL of concentrated HNO_3 (analytical grade, 60%), and diluted to 25 ml with ion-exchanged water. This solution was diluted 10000-fold with 1M HNO_3 , and analyzed by ICP-AES. Raw data of ICP-AES are shown in Table S1, and calculated concentrations and contents of Cd atom are shown in Table S2. Calibration curves were initially based on four standards, including the blank (Figure S4).

Table S1. Raw data of ICP-AES analysis

Sample	Intensity	
	Cd (214.439 nm)	Cd (226.502 nm)
Blank	17.975	8.9657
Standard (9.81ppb)	74.86	117.18
Standard (22.16ppb)	165.77	250.83
Standard (31.8ppb)	250.54	367.49
run 1	155.21	235.31
run 2	155.82	236.09
run 3	157.77	237.58
run 4	159.27	248.72
run 5	162.51	240.97

Table S2. Concentrations and contents of Cd atoms.

Run	Cd (214.439 nm)		Cd (226.502 nm)	
	<i>c</i> (ppb)	<i>R</i> (%)	<i>c</i> (ppb)	<i>R</i> (%)
1	19.76	19.15	20.34	19.71
2	19.84	19.23	20.41	19.77
3	20.11	19.49	20.54	19.90
4	20.32	19.69	21.53	20.87
5	20.76	20.11	20.84	20.20
average	20.16	19.53	20.73	20.09

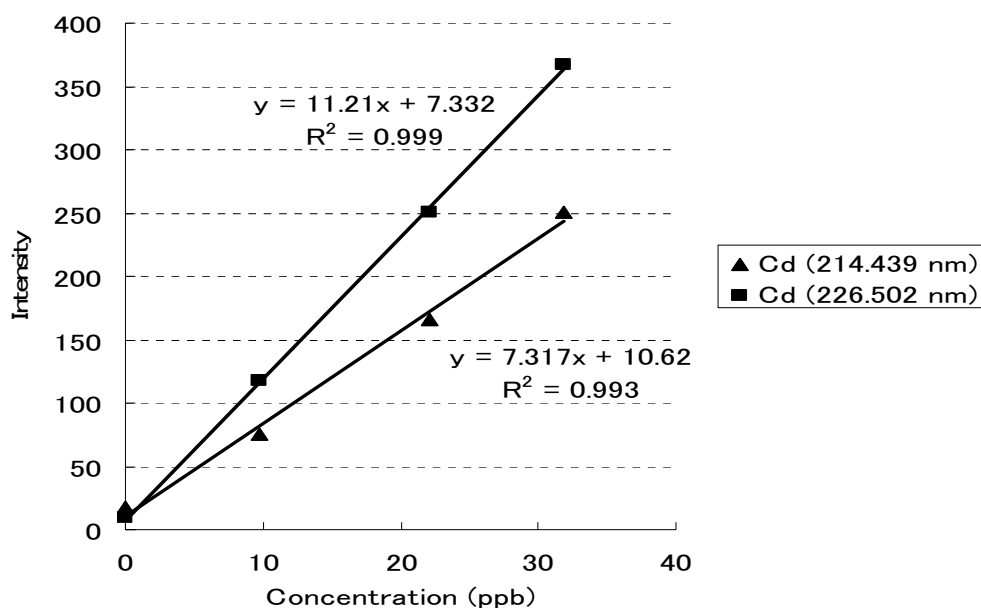


Figure S4. Calibration plots of Cd concentration.

LD-TOF-MASS spectrum of Cd₁₀S₁₆ molecular cluster dendrimer **1**.

LD-TOF-Mass spectrum of molecular cluster dendrimer **1** showed a broad peak centered at *ca.* 5200 as shown in Figure S5. Under laser irradiation conditions of LD-TOF experiment, Cd₁₀S₁₆ molecular cluster was decomposed and aggregate, which was observed in high molecular weight region. When we used an appropriate laser power, we could observe molecular ion as a broad peak around 5200. The difference between this value and the molecular weight of **1** (C₂₀₄H₂₇₆Cd₁₀N₂₄O₆₀S₁₆, 5661.67) could be attributed to removal of dendritic ligand (C₁₇H₂₃N₂O₅S, 367.24) during LD-TOF process.

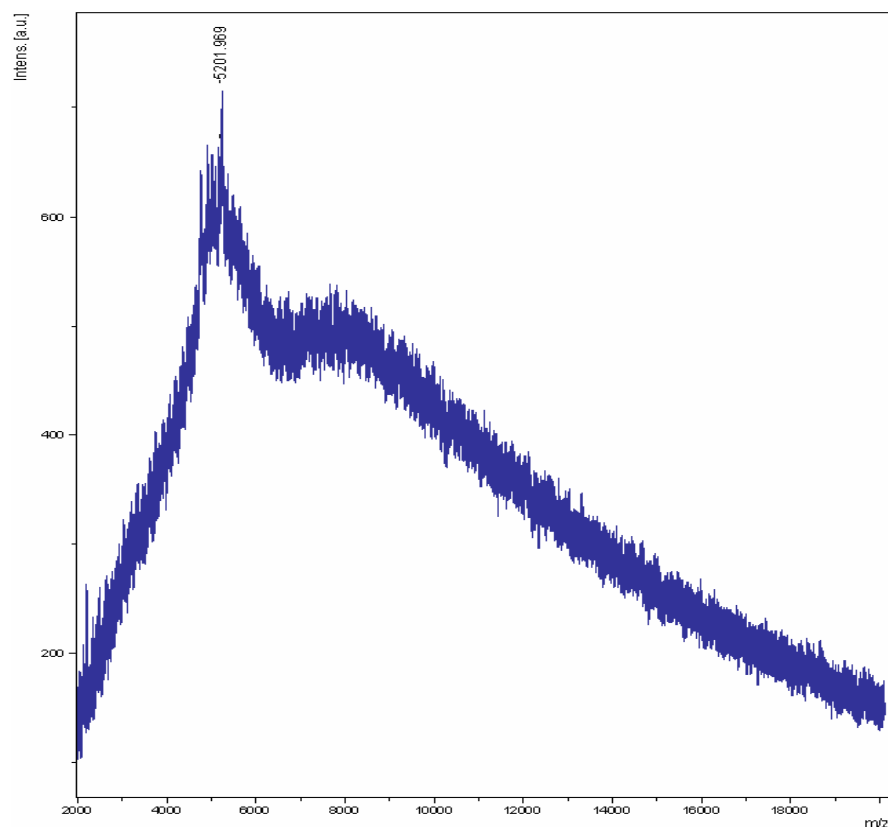


Figure S5. LD-TOF-MASS spectrum of Cd₁₀S₁₆ molecular cluster dendrimer **1**.

References

- 1 Takaguchi, Y.; Saito, K.; Suzuki, S.; Hamada, K.; Ohta, K. Motoyoshiya, J.; Aoyama, H. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1347.