Formation of Submicron Scale Particles of Narrow Size Distribution from a Water-Soluble Dendrimer with Links to Porphyrins and a Fullerene

Toru Arai,*,† Junya Ogawa,‡ Emiko Mouri,† Mohammed P. I. Bhuiyan,‡ and Norikazu Nishino‡

Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata, Kitakyushu 804-8550, Japan, and Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Wakamatsu, Kitakyushu 808-0196, Japan

Received October 21, 2005; Revised Manuscript Received December 5, 2005

ABSTRACT: A water-soluble L-lysine dendrimer (**6**) with links to porphyrins and a fullerene was synthesized, in which the dendrimer surface was modified with carboxylate groups. The aqueous solution of **6** showed the Soret band characteristic of the aggregated porphyrins in the UV−vis spectra; however, this aggregate was dissociated by the addition of 2-hydroxypropyl-β-cyclodextrin (10 wt % in H_2O). TEM and AFM showed the formation of submicron-scale particles of **6**. TEM showed the spherical particles of **6** with almost uniform size (100−110 nm) in the presence of the cyclodextrin. AFM showed the oval particles of **6** in the absence of the cyclodextrin. DLS measurement indicated that cyclodextrin dissociated the aggregated structure of **6** in H_2O. Thus, a large number of porphyrins and fullerenes were successfully accumulated with a narrow size distribution via the particle formation of the amphiphilic dendrimer.

Introduction

The electron transfer from an excited bacteriochlorophyll dimer to a nearby bacteriopheophytin is an important step in bacterial photosynthesis, which is followed by multistep electron transfers across the biomembrane.[1] Recently, porphyrin (light absorbant and electron donor)−fullerene (C_{60}, electron acceptor) systems have effectively reproduced the long-lived charge-separation state involved in natural photosynthesis.[2−4] The porphyrin−fullerene system is expected not only to be as an artificial photosynthetic system but also to be of use for potential (photoactive) molecular devices such as solar cells and so on.[5,6]

Because of the spherical shape and the large electronic delocalization, fullerene scarcely changes in structure and solvation in the electron-transfer reactions; i.e., fullerene has a small recombination energy.[7] Imahori and co-workers have successfully demonstrated that the photoinduced charge separation is accelerated and that the back electron transfer is retarded in the porphyrin−fullerene systems.[2c] Thus, the prolonged charge-separated states were achieved and characterized with excellent quantum yields for their formation.[4]

By virtue of these pioneering studies on the porphyrin−fullerene systems, one of the recent interests in this field is to integrate multiple porphyrins and fullerenes to enhance the photochemical properties.[8] Imahori and co-workers successfully modified gold, indium−tin oxide, and TiO_2 electrodes with self-assembled monolayers and/or clusters of porphyrin−fullerene systems.[9] Gold nanoparticles were modified by porphyrins as well, to which fullerenes were incorporated to build up large organizations.[10] A dendrimer with many porphyrins formed a supramolecular complex with fullerenes, which was then assembled on a SnO_2 electrode.[11]

Several macromolecules have been synthesized with the porphyrin−fullerene systems, not simply to gather multiple porphyrins and fullerenes but also to suppress the excessive aggregation of dyes that may induce self-quenching. Recent examples are oligothiophene binding porphyrin and fullerene at its termini,[12] dendrimers containing the porphyrin−fullerene systems,[13] polyacetylenes copolymerized from fullerene-linked and porphyrin-linked acetylenes,[14] rotaxanes that mechanically linked the porphyrin and fullerene,[15] and DNA-modified electrodes that fixed the porphyrins and fullerenes.[16]

Here we propose a dendrimer with carboxylate groups ($-COO^-$) at its surface as a promising candidate for accumulation of the porphyrin−fullerene systems. The dendrimer is characterized by a regulated molecular weight, a three-dimensional size, an electronic structure at its surface, and functional chemical units at predetermined sites. A well-packed structure is expected for the dendrimers of more than certain molecular weights (generations).[17] Of particular interest is the spontaneous self-assembling of the amphiphilic dendrimers, which often generates large sizes of hydrophilic and hydrophobic domains.[18−22] Fréchet et al.[19] and Aoi et al.[20] have synthesized amphiphilic dendrimers combining both the hydrophilic and hydrophobic groups on their surfaces. Hirsch and co-workers have synthesized water-soluble dendrimers tethering a fullerene and carboxylate groups.[21] If the dendrimer with the porphyrin−fullerene system were modified by the carboxylate groups, the molecule would be amphiphilic and would generate polymeric clusters. Here we wish to report the synthesis of a water-soluble dendrimer with a porphyrin−fullerene system and the assembling phenomena in an aqueous solution.

Experimental Section

General. Reagents and solvents for the organic syntheses were from Watanabe Chemical (Hiroshima, Japan), Wako Pure Chemical (Osaka, Japan), and Aldrich Japan (Tokyo, Japan), except for 2-hydroxypropyl-β-cyclodextrin (Cavitron 82003, degree of substitution by the hydroxypropyl group is 4.6) from Cargill (Cedar Rapids, IA).[23]

Preparation of Water-Soluble Dendrimer: 1. L-2-*tert*-Butoxycarbonylamino-8-(fulleropyrrolidinyl)octanoic acid (0.10 g, 0.10

† Faculty of Engineering.
‡ Graduate School of Life Science and Systems Engineering.
* Corresponding author. E-mail: arai@che.kyutech.ac.jp.

10.1021/ma0522817 CCC: $33.50
Published on Web 01/24/2006

mmol),[24] 1-*N*-benzyloxycarbonyl-1,6-diaminohexane·HCl (44 mg, 0.15 mmol), and HOBt·H_2O (23 mg, 0.15 mmol)[25] were dissolved in 20 mL of DMF with the aid of sonication. The mixture was ice-chilled, HBTU (56 mg, 0.15 mmol)[26] and DIEA (26 μL, 0.15 mmol) were added, and the mixture stirred overnight at room temperature, when the unreacted fullerene−amino acid disappeared on a silica gel TLC (eluent; $CHCl_3$−5% MeOH, by volume). After evaporation, the residue was washed with H_2O and MeOH to yield 0.11 g (88 μmol, 88%) of **1**. MALDI-TOF-MS for $C_{89}H_{48}N_4O_5$ *m*/*z*; calcd: 1253.4 [M^+]; found (α-cyano-4-hydroxycinnamic acid): 1253.2. ^{1}H NMR (DMF-d_7): δ 7.86 (t, J = 6 Hz, 1H, NH), 7.38 (m, 5H, Ph), 7.15 (t, J = 5 Hz, 1H, NH), 6.69 (d, J = 8 Hz, 1H, NH), 5.08 (s, 2H, CH_2Ph), 4.53 (s, 4H, pyrrolidino-CH_2), 4.10 (m, 1H, amino acid α-CH), 3.13 (m, 6H, CH_2), 1.96−1.33 (m, 27H, CH_2 and Boc).

2. Compound **1** (0.11 g, 84 μmol) was treated with TFA−CH_2Cl_2 (1:1, by volume, 10 mL) at 0 °C for 1 h. After evaporation, ether was added to solidify the Boc-removed derivative of **1** (TFA salt). This sample and Boc-Lys(Boc)-OH (42 mg, 0.12 mmol)[27,28] were dissolved in 10 mL of DMF with the aid of sonication. The mixture was ice-chilled, HOBt·H_2O (18 mg, 0.12 mmol), HBTU (45 mg, 0.12 mmol), and DIEA (21 μL, 0.12 mmol) were added, and the mixture was stirred overnight at room temperature, when the unreacted Boc-removed derivative of **1** disappeared on a silica gel TLC ($CHCl_3$−5% MeOH). After evaporation, the residue was washed with H_2O and MeOH with the aid of sonication to yield 92 mg (62 μmol, 74%) of **2**. MALDI-TOF-MS for $C_{100}H_{67}N_6O_8Na_1$ *m*/*z*; calcd: 1503.7 [M−H + Na]$^+$; found (sinapic acid): 1503.8. ^{1}H NMR (DMSO-d_6, 313 K): δ 7.82 (br, 1H, NH), 7.63 (d, J = 8 Hz, 1H, NH), 7.33 (m, 5H, Ph), 7.14 (d, J = 7 Hz, 1H, NH), 6.88 (br, 1H, NH), 6.65 (br, 1H, NH), 5.00 (s, 2H, CH_2Ph), 4.45 (s, 4H, pyrrolidino-CH_2), 4.26 (m, 1H, amino acid α-CH), 3.87 (m, 1H, amino acid α-CH), 3.26−2.88 (m, 8H, CH_2), 1.87−1.25 (m, 42H, CH_2 and Boc).

3. Boc groups of **2** (82 mg, 55 μmol) were removed with TFA−CH_2Cl_2 (1:1, 10 mL, 0 °C, 2 h) in a manner similar to the Boc removal of **1**. This sample of the Boc-removed derivative of **2** (TFA salt) and Boc-Lys(Por)-OH (0.15 g, 0.17 mmol) were dissolved in 40 mL of DMF with the aid of sonication. The mixture was ice-chilled, HOBt·H_2O (30 mg, 0.20 mmol), HBTU (64 mg, 0.17 mmol), and DIEA (35 μL, 0.20 mmol) were added, and the mixture was stirred overnight at room temperature, when H_2O was added and the precipitates were washed with ether. This crude material was again dissolved in DMF and divided into three portions, and then each was subjected to size-exclusion chromatography (SEC, Sephadex LH-20, DMF, 22 mm × 88 cm). Two bands were visible on the column: the desired porphyrin−fullerene conjugate and the excess Boc-Lys(Por)-OH. The appropriate fractions were collected, and the solvent was evaporated to yield 115 mg (37 μmol, 67%) of **3**. MALDI-TOF-MS for $C_{208}H_{160}N_{18}O_{12}$ *m*/*z*; calcd: 3103.6 [M^-]; found (2-(4-hydroxyphenylazo)benzoic acid, negative mode): 3102.3. ^{1}H NMR (DMSO-d_6, 313 K): δ 8.84 (m, 16H, pyrrole-β), 8.28−6.70 (m, 46H, NH, aromatic-CH), 4.94 (s, 2H, CH_2Ph), 4.32−3.96 (m, 8H, pyrrolidino-CH_2, amino acid α-CH), 3.42−2.62 (m, 30H, CH_2, tolyl-CH_3), 1.66−1.38 (m, 54H, CH_2 and Boc), −3.14 (m, 4H, pyrrole-NH).

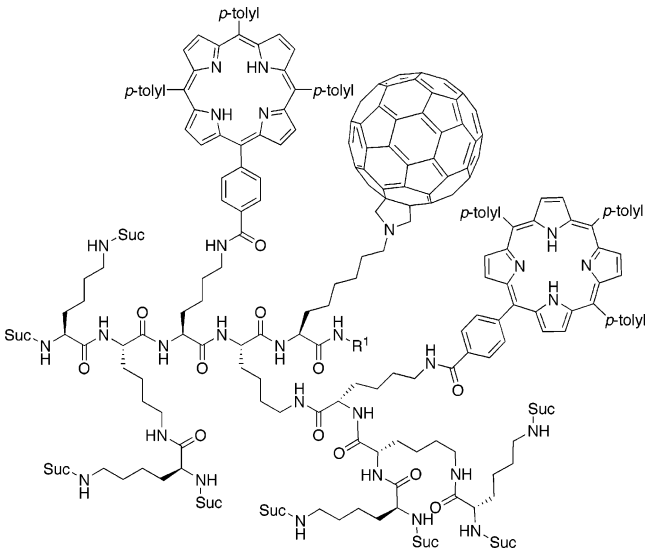
4. Boc groups of **3** (95 mg, 31 μmol) were removed with TFA−CH_2Cl_2 (1:1, 10 mL, 0 °C, 4 h) in a manner similar to **1**. This sample of the Boc-removed derivative of **3** (TFA salt) and Boc-Lys(Boc)-OH (36 mg, 0.10 mmol) were dissolved in 10 mL of DMF with the aid of sonication. The mixture was ice-chilled, HOBt·H_2O (18 mg, 0.12 mmol), HBTU (42 mg, 0.11 mmol), and DIEA (21 μL, 0.12 mmol) were added, and the mixture was stirred 12 h at room temperature. Then, Boc-Lys(Boc)-OH, (26 mg, 75 μmol), HOBt·H_2O (14 mg, 86 μmol), HBTU (28 mg, 75 μmol), and DIEA (21 μL, 0.12 mmol) were further added, and the resultant mixture was stirred 24 h at room temperature. This reaction mixture was subjected to SEC (LH-20, DMF), in which the appropriate fractions were collected and the solvent evaporated to yield 84 mg (24 μmol, 77%) of **4**. MALDI-TOF-MS for $C_{230}H_{200}N_{22}O_{18}Na_1$ *m*/*z*; calcd: 3583.3 [M + Na]$^+$; found (2-(4-hydroxyphenylazo)benzoic acid): 3584.2. ^{1}H NMR (DMSO-d_6, 313 K): δ 8.69 (m, 16H, pyrrole-β), 8.28−6.57 (m, 50H, NH, aromatic-CH), 4.92 (s, 2H, CH_2Ph), 4.32−3.91 (m, 10H, pyrrolidino-CH_2, amino acid α-CH), 3.34−2.62 (m, 34H, CH_2, tolyl-CH_3), 1.75−1.29 (m, 84H, CH_2 and Boc), −3.15 (m, 4H, pyrrole-NH).

5. Boc groups of **4** (74 mg, 21 μmol) were removed with TFA−CH_2Cl_2 (3:2, 10 mL, 0 °C, 1 h) in a manner similar to **1**. This sample of the Boc-removed derivative of **4** (TFA salt) and Boc-Lys(Boc)-OH (43 mg, 0.12 mmol) were dissolved in 5.0 mL of DMF, ice-chilled, HOBt·H_2O (21 mg, 0.14 mmol), HBTU (49 mg, 0.13 mmol), and DIEA (24 μL, 0.14 mmol) were added, and the mixture was stirred overnight at room temperature. The mixture was subjected to SEC (LH-20, DMF), in which the appropriate fractions were collected and the solvent evaporated to yield 66 mg (24 μmol, 71%) of **5**. MALDI-TOF-MS for $C_{274}H_{280}N_{30}O_{30}Na_1$ *m*/*z*; calcd: 4496.5 [M + Na]$^-$; found (2-(4-hydroxyphenylazo)benzoic acid): 4496.2. ^{1}H NMR (DMSO-d_6, 313 K): δ 8.69 (m, 16H, pyrrole-β), 8.28−6.63 (m, 58H, NH, aromatic-CH), 4.92 (br, 2H, CH_2Ph), 4.30−3.88 (m, 14H, pyrrolidino-CH_2, amino acid α-CH), 3.34−2.62 (m, 42H, CH_2, tolyl-CH_3), 1.64−1.35 (m, 144H, CH_2 and Boc), −3.16 (m, 4H, pyrrole-NH).

6. Boc groups of **5** (20 mg, 4.5 μmol) were removed with TFA−CH_2Cl_2 (1:1, 10 mL, 0 °C, 1 h) in a manner similar to **1**. This sample of the Boc-removed derivative of **5** (TFA salt) was dissolved in 2.0 mL of pyridine, succinic anhydride (19 mg, 0.19 mmol) was added, and the mixture was stirred overnight at room temperature. The mixture was subjected to SEC (LH-20, DMF), in which the appropriate fractions were collected and the solvent evaporated to yield 17 mg (3.7 μmol, 83%) of **6**. ^{1}H NMR (DMSO-d_6, 313 K): δ 8.73 (m, 16H, pyrrole-β), 8.29−6.72 (m, 58H, NH, aromatic-CH), 4.95 (br, 2H, CH_2Ph), 4.05−2.04 (m, overlapped with H_2O, pyrrolidino-CH_2, amino acid α-CH, CH_2, tolyl-CH_3), 1.63−1.29 (m, 72H, CH_2), −2.90 (m, 4H, pyrrole-NH).

Measurement. The molecular model was illustrated with an energy optimization program with the MM2 parameters on CAChe (v.4.9 for PowerMac) software. ^{1}H NMR spectra were measured on a JEOL JNM α-500 (500 MHz) in DMSO-d_6 at 313 K, unless otherwise noted. The spin−lattice relaxation time (T_1) and the spin−spin relaxation time (T_2) were measured by the inversion−recovery method and the Carr−Purcell−Meiboom−Gill method,[29] respectively. Ten valuable parameters were employed for the measurements of the relaxation times, 64−256 scans were collected for each parameter, and the relaxation times were obtained from nonlinear least-squares fittings. MALDI-TOF-MS was performed on an Applied Biosystems Voyager Linear DE mass spectrometer operating with a delayed extraction mode, in which 100−200 spectra were collected for each measurement. UV−vis and the fluorescence spectra were recorded on Hitachi U-2010 and Hitachi F-2500 (equipped with a Hamamatsu R928F photomultiplier), respectively. The relative intensities of the emissions were calculated from (peak area of the emissions)/(absorptivity at the excitation wavelength), and the fluorescence quantum yield Φ_f was obtained relative to the known value for tetraphenylporphyrin.[30] The transmission electron microscope (TEM) was operated at a nominal electron beam voltage of 250 or 300 kV on a Hitachi H-9000NAR. The atomic force microscope (AFM) was operated on a Digital Instruments Nanoscope III by the tapping mode. One drop of the aqueous sample solution was placed on a collodion film attached to a copper supporting grid for TEM or a slide glass (prewashed with H_2SO_4/H_2O_2 and rinsed with H_2O/EtOH) for AFM and then dried in a vacuum desiccator. The dynamic light scattering (DLS) was measured on an Otsuka Electronics DLS-7000 spectrophotometer equipped with a He−Ne laser (10 mW, 633 nm) using a 12 mm cylindrical cell at 298 K. The scattering angle was fixed at 90°, and the absorption of the incident light by the sample was not correlated.[31] The time correlation function $G_1(\tau)$ was obtained and then analyzed by the histogram method to evaluate the distribution of the particle sizes.

Scheme 1. Water-Soluble Dendrimer 6 ($-R^1$ = $-(CH_2)_6NHCO_2CH_2Ph$, $-$Suc = $-CO(CH_2)_2COO^-$, *p*-Tolyl = $-C_6H_4$-*p*-CH_3)



Results and Discussion

Synthesis of a Water-Soluble Dendrimer with a Porphyrin−Fullerene System. An L-lysine dendrimer was chosen to attach to the porphyrin−fullerene system in this study because it is a typical and well-characterized dendrimer and can easily be incorporated with various functional groups.[27,32] We have synthesized both the porphyrin-linked L-amino acid, (*N*-α-(*tert*-butoxycarbonyl)-*N*′-ϵ-(4-(tritolylporphyrin-5-yl)benzoyl)-L-lysine),[27a,28] and the fullerene-linked L-amino acid, (L-2-(*tert*-butoxycarbonylamino)-8-(fulleropyrrolidinyl)octanoic acid),[24] in enantiomeric pure forms to be used as monomers for the L-amino acid dendrimers. Mimicking the recent report on the porphyrin−fullerene system,[13c] we adopted a system with a pair of porphyrins and a fullerene (Scheme 1). Figure 1 illustrates a molecular model of **6** generated by CAChe-MM2. In this modeling, the side chains of the porphyrin-linked amino acids and the fullerene-linked amino acid were of the extended structure. Therefore, the porphyrins and fullerene stuck out of the surface-modified poly(L-lysine) dendrimer. It should be noted here that the MM2 modeling of such a large molecule might scarcely reproduce the molecular structure in the solution phase. In an aqueous solution, **6** may assume a globular-like structure via the hydrophobic interaction and the $\pi-\pi$ interaction between the porphyrin(s) and fullerene unlike the illustration in Figure 1.

Scheme 2 outlines the synthesis of a water-soluble dendrimer **6**.[27] The core is the fullerene-containing L-amino acid **1**, which connected NH$-(CH_2)_6-$NHCO_2CH_2Ph at the C-terminal as a potential linker to a certain functional group in the future. After removing the Boc protection of **1** with TFA, *N*-α-*N*′-ϵ-bis(*tert*-butoxycarbonyl)-L-lysine (Boc-Lys(Boc)-OH) was coupled using HBTU[26]/HOBt·H_2O in DMF/*N*,*N*-diisopropylethylamine (DIEA) to yield **2**. After removing the Boc groups of **2**, a pair of *N*-α-(*tert*-butoxycarbonyl)-*N*′-ϵ-(4-(tritolylporphyrin-5-yl)benzoyl)-L-lysine (Boc-Lys(Por)-OH) were attached to yield **3**, which linked a pair of porphyrins and a fullerene. Boc removal and the coupling of Boc-Lys(Boc)-OH were then repeated twice to yield **5** with eight Boc groups. Finally, these Boc groups of **5** were removed, and the amino groups generated were reacted with succinic anhydride in pyridine, to yield a water-soluble dendrimer **6** in 83% yield (based on **5**). Compounds **3**−**6** were purified with size exclusion chromatography (SEC) using Sephadex LH-20 gel (DMF), in which the appropriate fractions containing only the desired products were collected. These dendrimers (**3**−**6**) eluted as a single peak in the SEC. The intermediate compounds **1**−**5** were characterized by ^{1}H NMR and MALDI-TOF-MS, whereas **6** was characterized by ^{1}H NMR. It may be noted here that the porphyrin−fullerene system without the L-lysine covering (**3**) was soluble in *o*-dichlorobenzene, a typical solvent for fullerene. In contrast, the porphyrin−fullerene system with two generations of modification by L-lysines (**5**) was practically insoluble in *o*-dichlorobenzene and was quite soluble in DMF.

^{1}H NMR spectra further showed the well-packed structure of **5** with two generations of L-lysines (Table 1). The monomeric porphyrin-linked amino acid, (Boc)-Lys(Por)-OH, and the intermediate dendrimers, **3**−**5**, showed a similar chemical shift for the pyrrole-β protons, although the signal widths were significantly broadened for the higher-generation dendrimers (**3** < **4** < **5**, data not shown). The ^{1}H NMR relaxation times have been utilized to analyze the molecular motions of the amphiphilic polymers by Yusa et al. and other groups.[33] In the present system, the spin−lattice relaxation times (T_1) of these pyrrole-β protons were similar, and in contrast, the spin−spin relaxation time (T_2) significantly decreased (**3** > **4** > **5**) with the increasing dendrimer generations. These facts indicate the decreased molecular mobility of the porphyrins in the higher generation dendrimers, such as **5**, due to the covering by L-lysines. As for the Boc protons, (Boc)-Lys(Por)-OH, **3**−**5** showed similar chemical shifts and similar T_1 values. The T_2 values of the Boc protons did not significantly differ with the increasing dendrimer generations. This is probably because Boc groups were located near the molecular surface, and therefore, the molecular packing did not notably influence the mobility of the Boc groups.

UV−vis spectra of **3**−**5** in DMF showed little difference regarding the λ_{max} values (419, 516, 551, 592, and 648 nm, Figure 2). These spectra closely resembled the monomeric porphyrin, (Boc)-Lys(Por)-OH, because fullerene had little absorbance in this region.[34] The intensities of the Soret band absorptions is in the order of **3** > **4** > **5**, with molar absorptivities of 981 000, 844 000, and 771 000 M^{-1} cm^{-1}, respectively, which are smaller than twice that of ϵ_{419} of (Boc)-Lys(Por)-OH (620 000). The fluorescence spectra (data not shown) also showed that the emission intensities at 654 nm were in the order of **3** > **4** > **5** (100:60:46). In the higher-generation dendrimers with the well-packed structure, the porphyrins may be located near and may interact with each other in their ground state. The interaction between porphyrins in DMF should be weak than in the aqueous system. The orientation between the aggregated porphyrins in DMF is possibly random and not fixed, which may account for the weakened and broadened Soret absorptions. A similar phenomenon (weakened and broadened Soret absorptions without detectable shifts) has been reported

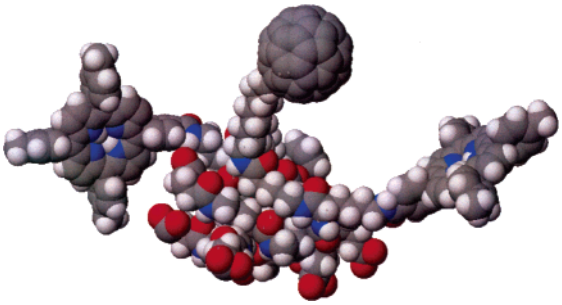
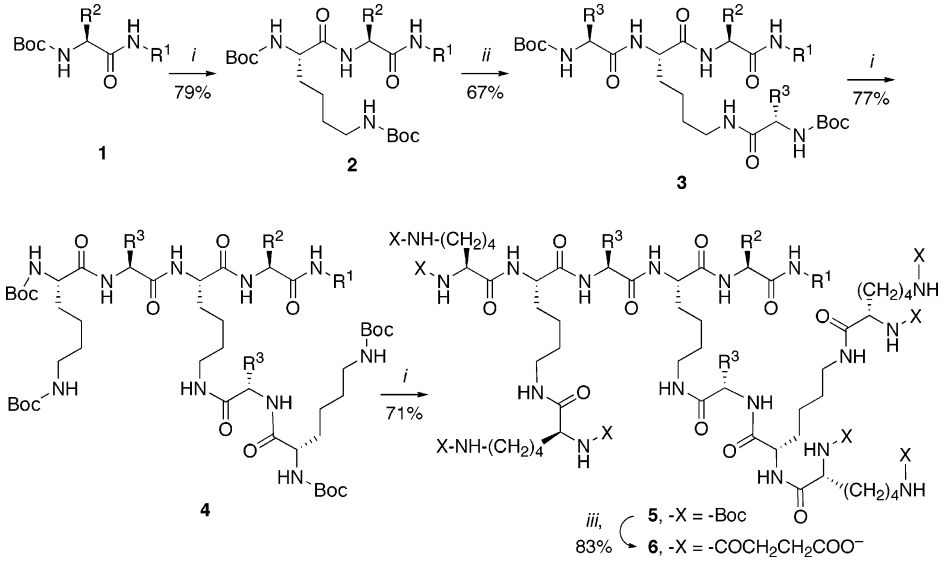


Figure 1. MM2-optimized structure of **6**.

Scheme 2. Synthesis of a Water-Soluble Dendrimer 6 ($-R^1 = -(CH_2)_6NHCO_2CH_2Ph$, $-R^2 =$ -$(CH_2)_6$-fulleropyrrilidine, $-R^3 =$ -$(CH_2)_4NHCOC_6H_4$-*p*-(tritolylporphyrin-5-yl), $-$Suc $= -CO(CH_2)_2COO^-$, *p*-Tolyl $= -C_6H_4$-*p*-CH_3)[a]



[a] Reagents and conditions: (i) TFA, then Boc-Lys(Boc)-OH, HBTU-HOBt, DMF-DIEA; (ii) TFA, then Boc-Lys(Por)-OH, HBTU-HOBt, DMF-DIEA; (iii) TFA, then succinic anhydride, pyridine.

Table 1. ^{1}H NMR Parameters of the Intermediate Dendrimers[a]

	pyrrole-β			Boc		
compounds	δ/ppm	T_1/s	T_2/ms	δ/ppm	T_1/s	T_2/ms
Boc-Lys(Por)-OH	8.83	3.64	184	1.40	615	540
3	8.70	3.31	34.3	1.40	550	203
4	8.69	3.23	18.6	1.36	512	376
5	8.69	3.67	10.3	1.35	559	306

[a] Measured in DMSO-d_6 at 313 K (500 MHz).

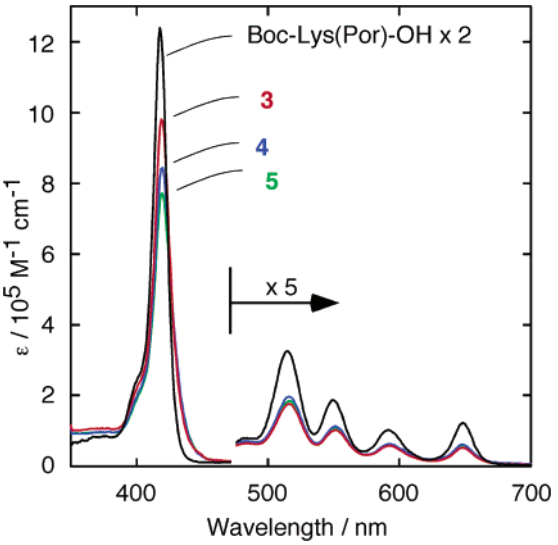


Figure 2. UV−vis spectra of Boc-Lys(Por)-OH (increased twice in intensity for comparison), **3**, **4**, and **5** in DMF.

for the dendrimers linking the zinc porphyrins at the near-surfaces.[35] A ground-state interaction between the porphyrin and fullerene was unlikely because the charge-transfer absorption at around 700−800 nm[13d,36] was not detected in **3**−**6**. The UV−vis spectra of **3**−**5** followed the Lambert−Beer law in the 0.2−1.0 μM range, which indicated the absence of intermolecular interaction.

Thus, two generations of the dendritic modification by L-lysines seemingly formed a well-packed dendrimer, **5**. After the Boc removal of **5**, the amino groups at the dendrimer surface were reacted with succinic anhydride to form a polyanionic dendrimer **6** with eight carboxylate groups ($-COO^-$ in H_2O). When 1.0 mg of this polyanionic dendrimer, **6**, was warmed in 1.0 mL of H_2O at 50 °C for 2 h, a clear and reddish solution (0.22 mM) was obtained. Several days were required for the dissolution of **6** in H_2O (1.0 mg/1.0 mL) at room temperature (25 °C). The aqueous solutions of **6** thus prepared were stable without any precipitations for months at room temperature.

Self-Assembling of the Water-Soluble Dendrimer with the Porphyrin−Fullerene System. An unusually broadened Soret band (λ_{max} at 419 nm, ϵ 174 000, with a shoulder peak at ~407 nm) and typical Q-bands (519, 555, 594, and 651 nm) characterized the UV−vis spectrum of **6** in H_2O (Figure 3a, line (i), 1.4 μM). Such a broadened Soret band in the UV−vis spectra with a blue-shifted shoulder peak (407 nm) suggested an intermolecular aggregation of **6** in H_2O, as has been described for the water-soluble porphyrins. Tetrakis(4-carboxyphenyl)-porphyrin (H_6TCPP, tetraphenylporphyrin with four $-$COOH groups) reportedly showed its absorptions at 408 nm in the dilute surfactant solution and 417 nm in the surfactant micelle, in which the blue-shifted absorption (408 nm) arose from the aggregated porphyrin in the face-to-face orientation and the typical absorption (417 nm) arose from the monomeric porphyrin.[37] In this context, the blue-shifted absorption of **6** in H_2O (Figure 3a, 407 nm) implied a porphyrin aggregation in the face-to-face orientation, although the detail of the structure of **6** is not yet clear. The UV−vis spectra of **6** in H_2O scarcely depended on the concentration in the 0.5−10 μM range, which suggested the stable aggregation of **6** in H_2O.

Cyclodextrins have been known to efficiently dissociate the aggregated porphyrins and to dissolve the water-insoluble porphyrin via supramolecular formation.[38,39] Recently, cyclodextrins have also been utilized to dissolve fullerenes.[16b,40] In the present system, the addition of 10 wt % 2-hydroxypropyl-β-cyclodextrin (degree of substitution by the hydroxypropyl group is 4.6, see Experimental Section) in H_2O changed the assembling of **6** (Figure 3a, line (ii), [**6**] = 1.4 μM). The sharp Soret band appeared at 421 nm (ϵ 293 000), and no shoulder peak appeared at 408 nm. These UV−vis spectra suggested that the porphyrins were not highly aggregated in the H_2O/2-hydroxypropyl-β-cyclodextrin system. The fluorescent emission

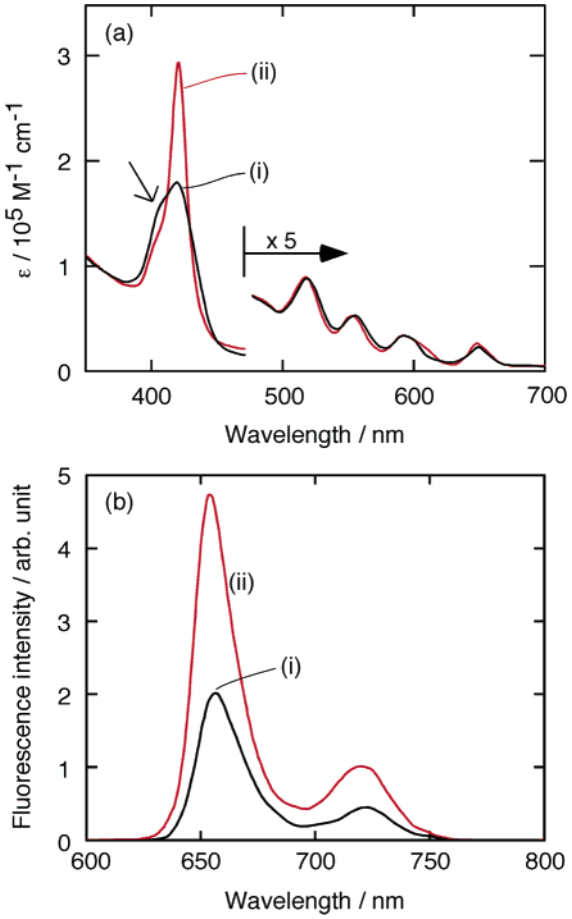


Figure 3. (a) UV−vis and (b) fluorescence spectra of **6** (0.14 μM) in (i) H_2O (arrow in (a) indicates the shoulder peak) and (ii) 10 wt % 2-hydroxypropyl-β-cyclodextrin in H_2O.

spectra of **6** (Figure 3b) also changed by the addition of 2-hydroxypropyl-β-cyclodextrin. In H_2O, a small emission appeared for **6** (Figure 3b, line (i), $\lambda_{ex} = 419$ nm, $\lambda_{em} = 655$ and 720 nm, $\Phi_f = 0.040$). In contrast, the emission of **6** was more intense (Figure 3b, line (ii), $\Phi_f = 0.088$) in 10 wt % of 2-hydroxypropyl-β-cyclodextrin in H_2O.

The TEM image of the cast film of an aqueous solution of **6** ([**6**] = 12 μM) showed particles of 90−170 nm in diameter (Figure 4a, ×43 000, 250 kV). Considering the molecular size of **6** of about 3.0−6.0 nm estimated from the model (Figure 1), this TEM image indicated the formation of a large aggregate of **6**. This fact corresponded to the spectroscopic studies of **6** in aqueous solution as described above, which suggested the interaction between the porphyrin−fullerene systems. The observed aggregates in Figure 4a were almost spherical, but some were slightly distorted and the densities of the particles varied, which meant the particle size distribution.

Figures 4b shows the TEM image (×47 000, 250 kV) of the cast film of a solution of **6** ([**6**] = 12 μM) in 10 wt % of 2-hydroxypropyl-β-cyclodextrin in H_2O. Because cyclodextrins often dissociate the aggregates of the hydrophobic molecules, the aqueous cyclodextrin solution of **6** was therefore expected to generate the small aggregates. Contrary to this expectation, Figure 4b showed spherical particles of 100−110 nm in diameter. A striking feature of the particles in Figure 4b is the uniformity of their shape and size. The particles in this TEM image were almost within 100−110 nm and showed little distribution (the amorphous materials in this image were the cyclodextrin). It is not yet clear why the aggregates did not become smaller, but the size distribution became narrow with

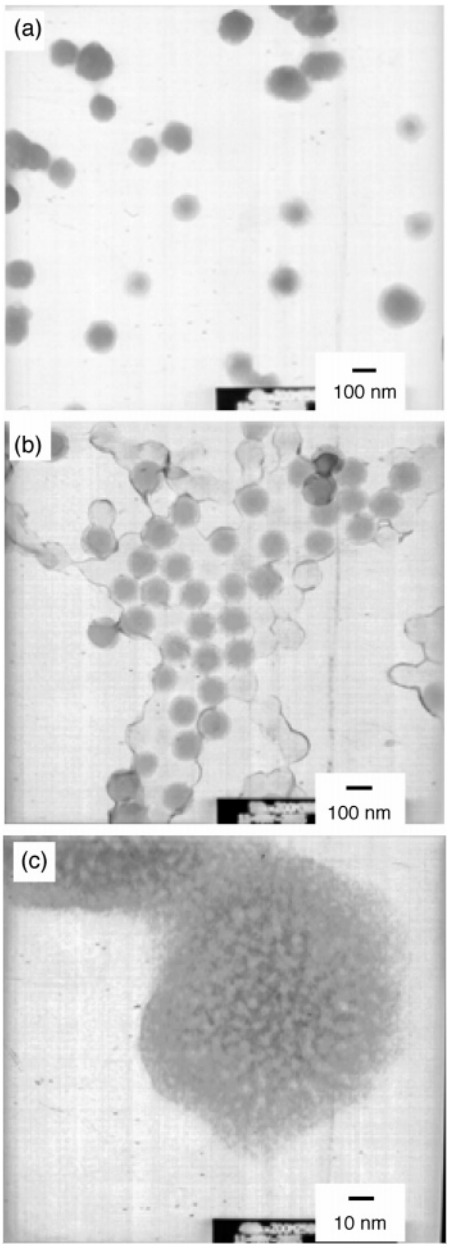


Figure 4. TEM images of the samples cast from the solution **6** (12 μM) in (a) H_2O (×43 000, 250 kV) and (b, c) 10 wt % 2-hydroxypropyl-β-cyclodextrin in H_2O (b, ×47 000, 300 kV; c, ×460 000, 250 kV).

the addition of 2-hydroxypropyl-β-cyclodextrin. Cyclodextrins might decrease the hydrophobic interaction between **6** via complex formation (at least partially) with the hydrophobic moieties (porphyrin or fullerene). Therefore, the homogeneous dispersion of **6** may be achieved in the aqueous cyclodextrin solution, which possibly resulted in the formation of the aggregates with a narrow size distribution. The particles in the cast film of the aqueous cyclodextrin solution of **6** were further analyzed by the TEM with the high magnification conditions (×460 000, 250 kV). On the surface of an about 100 nm particle, small patterns with 3−5 nm diameters were observed (Figure 4c). The size of this pattern was similar to the size of the monomeric **6**; therefore, Figure 4c may be the evidence that a large number of **6** were associated with to form the cluster of about 100 nm size.

The submicron-scale particles were found not only by the TEM but also by the AFM (Figure 5). The egg-shaped particles

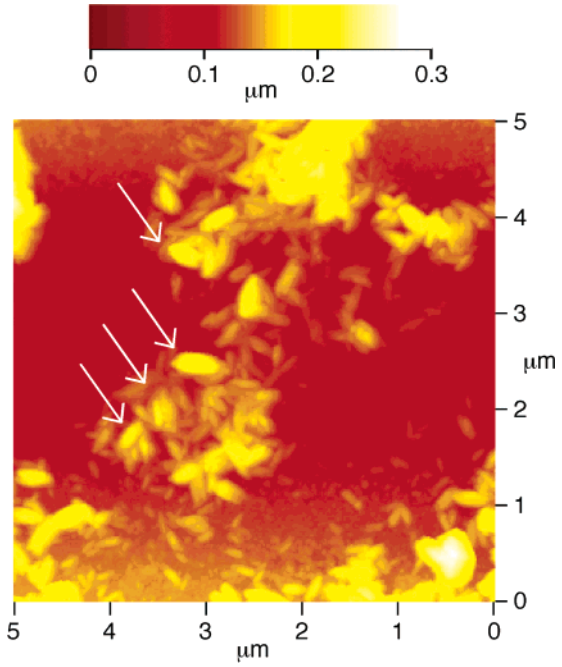


Figure 5. AFM image of a cast film of an aqueous solution of **6** (0.59 μM). The depth scale bar is shown above.

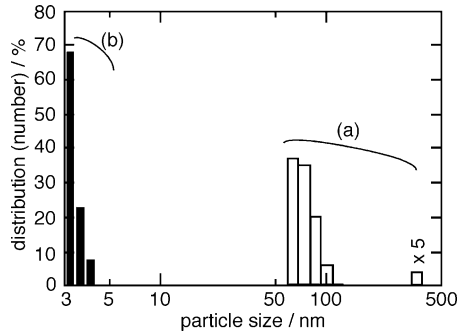


Figure 6. Histogram analyses of the particle size distributions obtained from the DLS measurements of the solution of **6** (12 μM) in (a) H_2O and (b) 10 wt % 2-hydroxypropyl-β-cyclodextrin in H_2O at 298 K.

(100−300 nm) were observed in a cast film of an aqueous solution of **6** ([**6**] = 0.59 μM). The reason is yet not clear why the oval particles were found by AFM and the spherical ones by TEM. The sample with a flat surface suitable for AFM was prepared from a dilute solution, which potentially resulted in the formation of the imperfect particles. Unfortunately, no sample could be prepared from the aqueous cyclodextrin solution that was flat enough for AFM.

DLS (dynamic light scattering) measurements gave further information on the particle sizes of **6** in aqueous solution (Figure 6).[31] The histograms of (a) in Figure 6 show the number-averaged particle size distribution of **6** in H_2O ([**6**] = 12 μM, 298 K), in which the particles of 60−120 nm (and small peak at around 400 nm) were shown. The histograms (a) in Figure 6 indicate the existence of several sizes of aggregates of **6** in H_2O. Although TEM (Figure 4a, 90−170 nm), AFM (Figure 5, 100−300 nm), and DLS differ in the sample preparation (cast film/aqueous solution) and the principle for the observation, submicron particles were found in each method. It may be noted here that the histogram analysis is a little ambiguous with the polydispersion samples because the number-averaged histograms tend to overestimate the small diameter particles. Sonication of the aqueous sample of **6** for 120 min did not change the DLS profile (data not shown). When 10 wt % 2-hydroxypropyl-β-cyclodextrin was added to the aqueous solution of **6** ([**6**] = 12 μM, the histograms of (b) in Figure 6), the particle size became drastically small (3−4 nm), which supported the spectroscopic results (Figure 3) that the cyclodextrins dissociated the aggregated structure. Cyclodextrins might cause the homogeneous dispersion of **6**, which may result in the narrow size distribution of the particles observed in the TEM analysis (Figure 4b).

Conclusions

By using a fullerene-linked amino acid and porphyrin-linked amino acids, a series of L-lysine dendrimers were synthesized embedding a fullerene and a pair of porphyrins. The eight amino groups at the dendrimer surface were modified with the carboxylate groups to obtain the amphiphilic dendrimer **6**. The dendrimer **6** was water-soluble up to 1.0 mg/1.0 mL concentration. UV−vis spectra of the aqueous solution of **6** showed a blue-shifted Soret band, a characteristic of the aggregated porphyrin probably due to the intermolecular assembling of the dendrimer. TEM and AFM observations showed the formation of submicron-scale particles of **6**. Thus, the accumulation of a large amount of porphyrins and fullerenes was achieved via the cluster formation of the amphiphilic dendrimer. The addition of 2-hydroxypropyl-β-cyclodextrin at 10 wt % in H_2O served to weaken the aggregation of **6**. UV−vis spectra of **6** showed that the cyclodextrin dissociated the aggregated porphyrins. TEM observation of the film cast from the solution of **6** in aqueous 2-hydroxypropyl-β-cyclodextrin showed spherical particles with an almost uniform size (100−110 nm). Cyclodextrins might cause the homogeneous dispersion of **6**, which may be responsible for the narrow size distribution. DLS measurement of the aqueous solutions of **6** indicated that the particle size became small upon the addition of the cyclodextrin. The regulation of the size and shape of the assembled dendrimer will be practically meaningful. We will apply the clusters of the amphiphilic dendrimers to photo- and electroactive materials, in which the size of the particle may be important for its function.

Acknowledgment. We thank Prof. Kohji Yoshinaga and Dr. Tamaki Kato (Kyushu Institute of Technology) for valuable discussions, Mr. Noboru Wakayama (Kyushu Institute of Technology, Center for Instrumental Analysis) for the TEM measurements, and Mr. Motokazu Terada (Kyushu Institute of Technology) for helping us in the measurements of AFM and DLS.

References and Notes

(1) (a) Leibl, W.; Mathis, P. In *Molecular to Global Photosynthesis, Series on Photoconversion of Solar Energy*; Archer, M. D., Barber, J., Eds.; Imperial College Press: London, 2004; Vol. 2, pp 117−188. (b) Voet, D.; Voet, J. G. *Biochemistry*, 3rd ed.; John Wiley & Sons: New York, 2004; Chapter 24.

(2) For reviews, see: (a) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 8, pp 153−190. (b) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48. (c) Imahori, H. *Org. Biomol. Chem.* **2004**, *2*, 1425−1433.

(3) Kodis, K.; Liddell, P. A.; de la Garza, L.; Clausen, P. C.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. A* **2002**, *106*, 2036−2048.

(4) (a) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607−2617. (b) Imahori, H.; Guldi, D. M.; Tamaki, K.; Yoshida, Y.; Luo, C.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 6617−6628. (c) Imahori, H.; Sekiguchi, Y.; Kashiwagi, Y.; Sato, T.; Araki, Y.; Ito, O.; Yamada, H.; Fukuzumi, S. *Chem.—Eur. J.* **2004**, *10*, 3184−3196.

(5) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines*; Wiley-VCH: Weinheim, 2003.

(6) For instance, see: (a) Straight, S. D.; Andréasson, J.; Kodis, K.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2005**, *127*, 2717−2724. (b) Nishino, T.; Ito, T.; Umezawa, Y. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 5659−5662.
(7) Fukuzumi, S.; Guldi, D. M. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 2, pp 270−337.
(8) For reviews, see: (a) Imahori, H.; Fukuzumi, S. *Adv. Funct. Mater.* **2004**, *14*, 525−536. (b) Fukuzumi, S.; Hasobe, T.; Ohkubo, K.; Crossley, M. J.; Kamet, P. V.; Imahori, H. *J. Porphyrin Phthalocyanines* **2004**, *8*, 191−200.
(9) (a) Imahori, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *J. Phys. Chem. B* **2000**, *104*, 2099−2108. (b) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100−110. (c) Yamada, H.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Ahn, T. K.; Kim, S. K.; Kim, D.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 9129−9139. (d) Hasobe, T.; Imahori, H.; Fukuzumi, S.; Kamat, P. V. *J. Mater. Chem.* **2003**, *13*, 2515−2520.
(10) (a) Hasobe, T.; Imahori, H.; Kamat, P. V.; Ahn, T. K.; Kim, S. K.; Kim, D.; Fujimoto, A.; Hirakawa, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1216−1228. (b) Imahori, H.; Fujimoto, A.; Kang, S.; Hotta, H.; Yoshida, K.; Umeyama, T.; Matano, Y.; Isoda, S. *Adv. Mater.* **2005**, *17*, 1727−1730.
(11) (a) Hasobe, T.; Kamat, P. V.; Absalom, M. A.; Kashiwagi, Y.; Sly, J.; Crossley, M. J.; Hosomizu, K.; Imahori, H.; Fukuzumi, S. *J. Phys. Chem. B* **2004**, *108*, 12865−12872. (b) Hasobe, T.; Kashiwagi, Y.; Absalom, M. A.; Sly, J.; Hosomizu, K.; Crossley, M. J.; Imahori, H.; Kamat, P. V.; Fukuzumi, S. *Adv. Mater.* **2004**, *16*, 975−979.
(12) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565−2575.
(13) (a) Camps, X.; Dietel, E.; Hirsch, A.; Pyo, S.; Echegoyen, L.; Hackbarth, S.; Röder, B. *Chem.—Eur. J.* **1999**, *5*, 2362−2373. (b) Choi, M.-S.; Aida, T.; Luo, H.; Araki, Y.; Ito, O. *Angew. Chem., Int. Ed.* **2003**, *42*, 4060−4063. (c) Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 13934−13935. (d) Charvet, R.; Jiang, D.-L.; Aida, T. *Chem. Commun.* **2004**, 2664−2665.
(14) Lu, F.; Xiao, S.; Li, Y.; Liu, H.; Li, H.; Zhuang, J.; Liu, Y.; Wang, N.; He, X.; Li, X.; Gan, L.; Zhu, D. *Macromolecules* **2004**, *37*, 7444−7450.
(15) Li, K.; Schuster, D. I.; Guldi, D. N.; Herranz, M. Á.; Echegoyen, L. *J. Am. Chem. Soc.* **2004**, *126*, 3388−3389.
(16) (a) Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. *J. Am. Chem. Soc.* **2001**, *123*, 4855−4856. (b) Ikeda, A.; Hatano, T.; Konishi, T.; Kikuchi, J.-i.; Shinkai, S. *Tetrahedron* **2003**, *59*, 3537−3540. (c) Shinkai, S.; Takeuchi, M.; Bae, A.-H. *Supramol. Chem.* **2005**, *17*, 181−186 and references therein. (d) Bae, A.-H.; Hatano, T.; Sugiyasu, K.; Kishida, T.; Takeuchi, M.; Shinkai, S. *Tetrahedron Lett.* **2005**, *46*, 3169−3173.
(17) For a review, see: Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendron. Concepts, Syntheses, Applications*; Wiley-VCH: Weinheim, 2001.
(18) For the reviews of the self-assembling dendrimers, see: (a) Imae, T. In *Structure-Performance Relationships in Surfactants*, 2nd ed.; Surfactant Science Series 112; Esumi, K., Ueno, M., Eds.; Marcel Dekker: New York, 2003; pp 525−545. (b) Smith, D. K.; Hirst, A. R.; Love, C. S.; Hardy, J. G.; Brignell, S. V.; Huang, B. *Prog. Polym. Sci.* **2005**, *30*, 220−293.
(19) (a) Fréchet, J. M. J. *Science* **1994**, *263*, 1710−1715. (b) Yu, D.; Vladimirov, N.; Fréchet, J. M. J. *Macromolecules* **1999**, *32*, 5186−5192.
(20) (a) Aoi, K.; Itoh, K.; Okada, M. *Macromolecules* **1997**, *30*, 8072−8074. (b) Ito, M.; Imae, T.; Aoi, K.; Tsutsumiuchi, K.; Noda, H.; Okada, M. *Langmuir* **2002**, *18*, 9757−9764 and references therein.
(21) (a) Brettreich, M.; Burghardt, S.; Böttcher, C.; Bayerl, S.; Hirsch, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1845−1848. (b) Maierhofer, A. P.; Brettreich, M.; Burghardt, S.; Vostroesky, O.; Hirsch, A.; Langridge, S.; Bayerl, T. M. *Langmuir* **2000**, *16*, 8884−8891.
(22) For instance, see: (a) Percec, V.; Dulcey, A. E.; Balagurusamy, V. S. K.; Miura, Y.; Smidrkal, J.; Peterca, M.; Nummelin, S.; Edlund, U.; Hudson, S. D.; Heiney, P. A.; Duan, H.; Magonov, S. N.; Vinogradov, S. A. *Nature (London)* **2004**, *430*, 764−768. (b) Jang, C.-J.; Ryu, J.-H.; Lee, J.-D.; Sohn, D.; Lee, M. *Chem. Mater.* **2004**, *16*, 4226−4231. (c) Cho, B.-K.; Jain, A.; Gruner, S. M.; Wiesner, U. *Science* **2004**, *305*, 1598−1601. (d) Ornatska, M.; Bergman, K. N.; Rybak, B.; Peleshanko, S.; Tsukruk, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5246−5249. (e) Ornatska, M.; Peleshanko, S.; Rybak, B.; Holzmueller, J.; Tsukruk, V. V. *Adv. Mater.* **2004**, *16*, 2206−2212. See also refs 13c and 13d.
(23) http://www.cargillfoods.com/pdfs/starch/82003.pdf.
(24) Watanabe, L. A.; Bhuiyan, M. P. I.; Jose, B.; Kato, T.; Nishino, N. *Tetrahedron Lett.* **2004**, *45*, 7137−7140.
(25) Abbreviations: Boc, *tert*-butoxycarbonyl; Boc-Lys(Boc)-OH, *N*-α-*N*′-ϵ-bis(*tert*-butoxycarbonyl)-L-lysine; Boc-Lys(Por)-OH, *N*-α-(*tert*-butoxycarbonyl)-*N*′-ϵ-(4-(tritolylporphyrin-5-yl)benzoyl)-L-lysine; DIEA, *N*,*N*-diisopropylethylamine; HBTU, *O*-(benzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate; HOBt·H_2O, 1-hydroxybenzotriazole hydrate; TFA, trifluoroacetic acid.
(26) Knorr, R.; Trzeciak, A.; Bannwarth, W.; Gillessen, D. *Tetrahedron Lett.* **1989**, *30*, 1927−1930.
(27) (a) Maruo, N.; Uchiyama, M.; Kato, T.; Arai, T.; Nishino, N.; Akisada, H. *Chem. Commun.* **1999**, 2057−2058. (b) Kato, T.; Uchiyama, M.; Maruo, N.; Arai, T.; Nishino, N. *Chem. Lett.* **2000**, 144−145. (c) Kato, T.; Maruo, N.; Akisada, H.; Arai, T.; Nishino, N. *Chem. Lett.* **2000**, 890−891.
(28) Arai, T.; Ishibashi, K.; Tomizaki, K.-y.; Kato, T.; Nishino, N. *Tetrahedron* **2005**, *61*, 4023−4030.
(29) Meiboom, S.; Gill, D. *Rev. Sci. Instrum.* **1958**, *29*, 688−691.
(30) (a) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1−13. (b) Arai, T.; Araki, K.; Maruo, N.; Sumida, Y.; Korosue, C.; Fukuma, K.; Kato, T.; Nishino, N. *New J. Chem.* **2004**, *28*, 1151−1159.
(31) (a) Gulari, E.; Gulari, E.; Tsunashima, Y.; Chu, B. *J. Chem. Phys.* **1979**, *70*, 3965−3972. (b) Tsunashima, Y.; Nemoto, N.; Kurata, M. *Macromolecules* **1983**, *16*, 584−589. (c) Sehgal, A.; Seery, T. A. P. *Macromolecules* **1999**, *32*, 7807−7814.
(32) Crespo, L.; Sanclimens, G.; Pons, M.; Giralt, E.; Royo, M.; Albericio, F. *Chem. Rev.* **2005**, *105*, 1663−1681 and references therein.
(33) (a) Yusa, S.-i.; Sakakibara, A.; Yamamoto, T.; Morishima, Y. *Macromolecules* **2002**, *35*, 5243−5249. (b) Arai, T.; Inudo, M.; Ishimatsu, T.; Akamatsu, C.; Tokusaki, Y.; Sasaki, T.; Nishino, N. *J. Org. Chem.* **2003**, *68*, 5540−5549. (c) Williams, G. D. P.; Scales, J. C. W.; McCormick, C. L. *Macromolecules* **2004**, *37*, 2603−2612. (d) Spevácek, J.; Hanyková, L.; Starovoytova, L. *Macromolecules* **2004**, *37*, 7710−7718.
(34) Tomiyama, T.; Uchiyama, S.; Shinohara, H. *Chem. Phys. Lett.* **1997**, *264*, 143−148.
(35) Li, W.-S.; Jiang, D.-L.; Suna, Y.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 7700−7702.
(36) (a) Armaroli, N.; Marconi, G.; Echegoyan, L.; Bourgeois, J.-P.; Diederich, F. *Chem.—Eur. J.* **2000**, *6*, 1629−1645. (b) Guldi, D. M.; Hirsch, A.; Scheloske, M.; Dietel, E.; Troisi, A.; Zerbetto, F.; Prato, M. *Chem.—Eur. J.* **2003**, *9*, 4968−4979.
(37) Maiti, N. C.; Mazumdar, S.; Periasamy, N. *J. Phys. Chem. B* **1998**, *102*, 1528−1538.
(38) (a) Kano, K.; Kitagishi, H.; Tamura, S.; Yamada, A. *J. Am. Chem. Soc.* **2004**, *126*, 15202−15210. (b) Kano, K.; Nishiyabu, R.; Doi, R. *J. Org. Chem.* **2005**, *70*, 3667−3673 and references therein.
(39) (a) Guo, X.; An, W.; Shuang, S.; Cheng, F.; Dong, C. *J. Photochem. Photobiol. A: Chem.* **2005**, *173*, 258−263. (b) Wu, J.-J.; Ma, H.-L.; Mao, H.-S.; Wang, Y.; Jin, W.-J. *J. Photochem. Photobiol. A: Chem.* **2005**, *173*, 296−300.
(40) Liu, Y.; Wang, H.; Chen, Y.; Ke, C.-F.; Liu, M. *J. Am. Chem. Soc.* **2005**, *127*, 657−666 and references therein.

MA0522817