NOTE

Synthesis of PAMAM Dendrimers Possessing [2.2]Paracyclophane on Their Surface

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KEY WORDS: PAMAM Dendrimer / [2.2]Paracyclophane / π - π Interaction / CT Complex / Photoluminescence /

Cyclophane compounds, particularly those comprising intramolecular face-to-face-oriented π -conjugated systems, have been well-acknowledged in the field of organic chemistry.¹ Among them, benzene rings of [2.2]paracyclophane are rigidly held with two ethylenes at *para* positions, and a distance between two benzene rings is 2.8–3.1 Å. This class of cyclophanes has been central to the cyclophane chemistry since the first synthesis of [2.2]paracyclophane.² A number of cyclophane compounds have been synthesized till date, and their unique structural, optical, and electronic properties have been investigated in detail.^{1–3} However, there were a few studies on cyclophane-containing polymers^{4–9} in spite of the remarkable progress in cyclophane chemistry except for our reports on conjugated polymers containing cyclophane units in the main chain;^{9,10} additionally, there have been no studies on the synthesis of cyclophane-containing dendrimers.

On the other hand, dendrimers¹¹ are well-defined macromolecules that are distinct from the corresponding linear polymers due to their unique spherical and symmetric architecture.¹² Functionalization of the dendrimer core, branch, and surface are readily carried out, and properties of the resulting dendrimers have been extensively studied. Cyclophanes have optically, electrically, and topologically various intriguing features, which arise from characteristic transannular π - π interactions between two co-facial π -electron systems. Thus, we decided to install cyclophane compounds into the dendrimer framework.

Herein we report synthesis and properties of [2.2]paracyclophane-containing dendrimers based on the polyamidoamine dendrimer (PAMAM dendrimer). In this work, we succeeded in the first synthesis of third- and fourth-generation PAMAM dendrimers possessing [2.2]paracyclophane on their surface.

EXPERIMENTAL

General

¹H and ¹³C NMR spectra were recorded on a JEOL EX400 instrument at 400 and 100 MHz, respectively. Samples were analyzed in CDCl₃ or CD₃OD, and the chemical shift values were expressed relative to Me₄Si as an internal standard. FT-IR spectra were obtained on a Perkin-Elmer 1600 spectrometer in

KBr pellets. UV-vis spectra were obtained on a JASCO V-530 spectrophotometer or a SHIMADZU UV-3600 spectrophotometer at room temperature. Photoluminescence and excitation spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer at room temperature. Gel permeation chromatography (GPC) was carried out on TOSOH UV-8020 and RI 8020 equipped with TSKgel α -3000 column using DMF (containing 10 mM of LiBr) as an eluent after calibration with standard polystyrene samples. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Gel filtration chromatography was performed with Sephadex LH-20. Column chromatography was performed with Wakogel C-300 silica gel. MALDI-TOF-MS analysis was performed on an Axima-CFR instrument from Shimadzu Biotech Kratos Analytical. The device is a high resolution, floor-standing instrument equipped with a pulsed N₂ laser (wavelength 337 nm, pulse width 4 ns); a mixture of 2,5-dihydroxybenzoic acid (DHB) and D-(+)-fucose (v/v = 1:1) was used as a matrix.¹³ High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer.

Materials

All solvents and chemicals were of reagent grade quality, obtained commercially, and used without further purification except as noted below. Et₂O and THF were distilled from sodium benzophenoneketyl. Triethylamine (NEt₃), toluene, and dichloromethane were distilled from KOH, CaH₂, and CaCl₂, respectively. Propylamine was distilled from zinc dust. Ethylenediamine core amine-terminated PAMAM dendrimer G = 3.0 (CAS number 153891-46-4) and G = 4.0 (CAS number 163442-67-9), 1,3-dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide, thionyl chloride (SOCl₂), propylamine, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetone were obtained commercially. [2.2]Paracyclophane-4-carboxylic acid **3** was prepared as described in the literature.¹⁴ All of the reactions were performed under a nitrogen or argon atmosphere.

Synthesis of Cp-PAMAM-G3 **4**

N-Hydroxysuccinimide (89 mg, 0.78 mmol) and DCC (0.17 g, 0.82 mmol) were added to [2.2]paracyclophane-4-

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Scheme 1.

carboxylic acid **3** (0.16 g, 0.65 mmol) dissolved in DMF (4.0 mL) at 0 °C and the resulting mixture was stirred for 4 h. Then, PAMAM-G3 dendrimer (88 mg, 12.8 μ mol) was dissolved in DMSO (2.0 mL). NEt₃ (0.13 mL, 0.95 mmol) was added to the solution, and the reaction mixture was stirred for 14 d at room temperature. The precipitated solid was filtered, and the filtrate was evaporated *in vacuo*. The residue was purified using Sephadex LH-20 column with DMF as an eluent. The dendrimer having [2.2]paracyclophane was further purified by reprecipitation from DMF/Et₂O (1.5 mL/30 mL). The precipitate was collected and dried *in vacuo* at 45 °C for 72 h to give the target dendrimer **4** (0.15 g, 10.2 μ mol, 80%) as a pale yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ 2.33 (br), 2.53 (br), 2.75 (br), 2.82–3.35 (br), 3.35–3.50 (br), 3.68 (br), 6.40–6.68 (br), 6.71 (br), 7.21 (br) ppm. IR (KBr) 3295, 3080, 2928, 2848, 1645, 1558, 719 cm⁻¹.

Synthesis of Cp-PAMAM-G4 5

Cp-PAMAM-G4 **5** was synthesized in the same manner as Cp-PAMAM-G3 **4**. Yield: 76%. ¹H NMR (CDCl₃, 400 MHz) δ 2.34 (br), 2.53 (br), 2.76 (br), 2.82–3.35 (br), 3.35–3.50 (br), 3.68 (br), 6.40–6.68 (br), 6.71 (br), 7.62 (br) ppm. IR (KBr) 3289, 3074, 2931, 2856, 1662, 1558, 720 cm⁻¹.

Synthesis of *N*-propyl[2.2]paracyclophane-4-carboxamide 6

To [2.2]paracyclophane-4-carboxylic acid **3** (0.13 g, 0.50 mmol), SOCl₂ (8.2 g, 5.0 mL, 68.8 mmol) was added at room temperature, and the mixture was brought to 60 °C and stirred for 4 h. Excess amount of SOCl₂ was removed under reduced pressure. The resulting [2.2]paracyclophane-4-carboxylic acid chloride was dissolved in CH₂Cl₂ (10 mL) and cooled to 0 °C. To this solution the mixture of propylamine (60 mg, 0.080 mL, 1.0 mmol) and NEt₃ (0.10 g, 0.14 mL, 1.0 mmol) was added dropwise over 5 min. The solution was allowed to warm to room temperature and then stirred for 12 h. CH₂Cl₂ (10 mL) was added, and the reaction mixture was washed with NaHCO₃ and brine. The organic layer was dried over MgSO₄. After filtration of MgSO₄, the solvent was evaporated and dried *in vacuo*. The residue was subjected to column chromatography on SiO₂ with CHCl₃ as an eluent to give compound **6** (60 mg, 0.21 mmol, 42%) as a white solid. ¹H NMR (CDCl₃, 400 MHz) δ 0.98 (t, J = 7.5 Hz, 3H), 1.61 (sextet, J = 7.5 Hz, 2H), 2.83–2.90 (m, 1H), 2.90–3.18 (m, 5H), 3.18–3.27 (m, 1H), 3.36 (t, J = 7.5 Hz, 2H), 3.65 (m, 1H), 5.57 (br, 1H), 6.40 (d, J =

8.0 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 6.53 (m, 2H), 6.56 (d, J = 8.0 Hz, 1H), 6.63 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 100 MHz) δ 11.48, 23.03, 34.77, 35.11, 35.27, 35.41, 41.50, 131.52, 131.94, 132.43, 132.55, 134.87, 134.97, 135.23, 135.89, 139.00, 139.12, 139.83, 140.17, 169.22 ppm. IR (KBr) 3328, 2928, 2853, 1628, 1538, 718 cm⁻¹. HRMS (FAB) calcd for C₂₀H₂₃NO, 294.1858 [M + H⁺]; found, 294.1856.

Synthesis of Ph-PAMAM-G4 7

A solution of benzoyl chloride (0.13 g, 0.11 mL, 0.91 mmol) in DMF (2.5 mL), and NEt₃ (0.13 g, 0.19 mL, 1.33 mmol) were added dropwise to PAMAM-G4 dendrimer (67 mg, 4.73 μ mol) dissolved in DMSO (3.0 mL) over 5 min. Then, the resulting solution was stirred at room temperature for 5 d. The precipitated solid was filtered off, and the filtrate was evaporated *in vacuo*. The residue was purified using Sephadex LH-20 column with methanol as the eluent. The resultant dendrimer having the benzene ring was further purified by reprecipitation from DMF/Et₂O (1.5 mL/30 mL). The precipitate was collected and dried in a vacuum at 45 °C for 72 h to obtain target dendrimer **7** (74 mg, 3.55 μ mol, 75%) as a pale yellow solid. ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (br), 2.75 (br), 2.94 (br), 3.23–3.42 (br), 3.42–3.53 (br), 7.39 (br), 7.47 (br), 7.62 (br), 7.80 (br) ppm. IR (KBr) 3272, 3067, 2944, 2839, 1651, 1558, 1435, 708, 697 cm⁻¹.

RESULTS AND DISCUSSION

Synthetic procedure of the target dendrimers is shown in Scheme 1. Ethylenediamine core amine-terminated PAMAM-G3 and G4 dendrimers **1** and **2** with [2.2]paracyclophane-4-carboxylic acid **3** were condensed to give the corresponding Cp-PAMAM-G3 and G4 dendrimers **4** and **5** in 80% and 76% yield, respectively, by using the DCC/*N*-hydroxysuccinimide system in NEt₃/DMF/DMSO at room temperature for 14 d. Dendrimers **4** and **5** were soluble in polar solvents such as MeOH, pyridine, DMF, DMSO, and partly soluble in CH₂Cl₂ and CHCl₃. The structures of dendrimers were characterized by IR and ¹H NMR spectra. The number of [2.2]paracyclophane in dendrimers was estimated from the ¹H NMR integral ratio between aromatic protons and aminomethylene protons, suggesting that almost all chain ends of dendrimers **4** and **5** had [2.2]paracyclophane units. According to GPC analysis using DMF as an eluent, a unimodal peak with a relatively narrow molecular weight distribution (M_w/M_n = 1.30 for **4** and 1.37 for **5**)¹⁵ was observed (Figure 1). It is considered that there are few defects in the structure. Their number-average molecular weights (M_n) were underestimated to be 8400 for **4** and 10400 for **5** using polystyrene standards (calculated M_n = 14406.4 for **4** and 29209.27 for **5**) due to their compact structure. MALDI-TOF-MS analysis was carried out, and a typical broad spectrum of high-generation-PAMAM dendrimers was obtained by using a mixture of DHB and D-(+)-fucose (v/v = 1:1) as a matrix.¹⁶ A parent peak was not observed for dendrimers **4** and **5** by MALDI-TOF-MS analysis, and thus we estimated the number

Figure 1. GPC charts of dendrimers **4** and **5** monitored by UV-8020 equipped with TSKgel α -3000 column; eluent: DMF containing LiBr (10 mM), flow rate: 1.0 mL/min, detection: UV 254 nm. Molecular weight distribution (M_w/M_n) was estimated by polystyrene standards.

Scheme 2.

of the cyclophane unit in the dendrimers by the UV titration study (vide infra).

The optical properties of dendrimers **4**, **5**, and compound **6** (Scheme 2) were examined, and the results are summarized in Table I. In addition, normalized UV-vis spectra of compounds **4–6** are shown in Figure 2. All compounds **4–6** exhibited absorption at around 225 nm, 275 nm, and 325 nm, which are derived from the 4-carbamoyl[2.2]paracyclophane unit. Molar absorption coefficient (ϵ) increased along with the number of the cyclophane unit (Table I). The wavelength of absorption shoulder and edge of dendrimers **4** and **5** were slightly red-shifted in comparison with those of compound **6** (Figure 2), indicating that π - π interaction among [2.2]paracyclophane units exists in the ground state. Figure 2 includes the absorption spectrum of G4 dendrimer **7** possessing phenyl groups in place of [2.2]paracyclophane. In the spectrum of **7**, clear absorption at around 275 nm was not observed, and only the peak at around 225 nm ($\log \epsilon = 4.80$) derived from the π - π^* transition of the phenyl group appeared (Figure 2).

7 Ph-PAMAM-G4

An installation efficiency of [2.2]paracyclophane was estimated by the UV titration study by taking advantage of

Table I. Optical data of dendrimers **4** and **5**, and model compound **6**

compound	UV λ /nm ^a	$\log \epsilon^a$	PL $\lambda_{\max}$ /nm ^{a,b}
4	225, 274, 325	4.89, 4.26, 3.20	399
5	226, 275, 325	5.26, 4.75, 3.76	403
6	224, 270, 325	3.40, 2.64, 2.41	395

^aAbsorption and emission spectra were recorded in dilute CH₃OH solution at room temperature. ^bExcited at 225 nm.

Figure 2. UV-vis absorption spectra of dendrimers **4**, **5**, **7**, and compound **6** in CH₃OH.

the formation of the charge-transfer (CT) complex between cyclophane units in the dendrimer and 7,7,8,8-tetracyanoquinodimethane (TCNQ).^{1a,17} Figure 3 shows the CT formation scheme and the dependence of the UV spectrum on the TCNQ feed ratio against the [2.2]paracyclophane unit of dendrimer **5** in DMSO. By the addition of TCNQ, the absorbance due to CT complexation with TCNQ increased. The peak intensity ranging 600–1000 nm was saturated at $x = 64$, and further increasing feed ratio of TCNQ did not affect the absorption of the anion radical of TCNQ (for example, $x = 128$). This result indicates that approximately sixty-four [2.2]paracyclophanes are incorporated onto the dendrimer surface; namely, almost all terminal units of G4 dendrimer **5** are substituted with [2.2]paracyclophane units.

The association constant (K_{CT}) of the formation of the CT complex was determined by using the Benesi–Hildebrand equation.¹⁸ According to the Benesi–Hildebrand plots of [cyclophane unit]/absorbance ($\lambda = 753$ nm) against $1/[TCNQ]$ and [cyclophane unit]/absorbance ($\lambda = 772$ nm) against $1/[TCNQ]$, the average of K_{CT} was found to be 14.7 (L mol⁻¹). It is reported that K_{CT} of 4-vinyl[2.2]paracyclophane with tetracyanoethylene (TCNE) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are 15.74 and 36.84 (L mol⁻¹), respectively.^{17d} The smaller K_{CT} (14.7 L mol⁻¹) value in the present system is considered to be derived from the carbamoyl unit on [2.2]paracyclophane.

The fluorescence emission spectra of compounds **4–6** were obtained in a dilute CH₃OH solution at room temperature, which were excited at 225 nm (Figure 4, right). All spectra

Figure 3. Scheme of the CT complex formation of dendrimer 5 with TCNQ, and UV-vis absorption spectra of CT complexes of dendrimer 5 with TCNQ (absorption of the typical anion radical of TCNQ) in DMSO ([2.2]paracyclophane unit = 2.2×10^{-3} M).

Figure 4. Fluorescence emission spectra of dendrimers 4 (---) and 5 (—) and compound 6 (···) in CH_3OH excited at 225 nm (right). Excitation spectra of dendrimer 5 in MeOH monitored at 400 and 435 nm.

Figure 5. (A) Fluorescence emission spectra of dendrimer 4 (—), model-emission fraction (---), and excimer fraction (···). (B) Fluorescence emission spectra of dendrimer 5 (—), model-emission fraction (---), and excimer fraction (···).

were featureless with weak emission at around 400 nm, which are assigned to emission from [2.2]paracyclophane (benzene excimer). Fluorescence quantum efficiencies of 4–6 were less than 0.1, calculated by using anthracene in EtOH as a standard. As shown in Figure 4, emission ranging from 400 to 500 nm increased with the increase of the generation number of the dendrimers. Excitation spectra at 400 nm and 435 nm of dendrimer 5 were completely overlapped by normalization (Figure 4, left), indicating that emission at 400 nm and around 435 nm are derived from the same emitting species. Those results imply that the interaction of the neighboring [2.2]paracyclophane units on the dendrimer surface in the excited state led to the increase of emission around longer wavelength. This interpretation was supported by the spectra in Figure 5. Emission spectrum of the dendrimer is considered to be the total emission spectrum of the cyclophane units and its excimers; and thus, the emission spectrum was divided into the model-emission and excimer fractions, as shown in Figure 5.¹⁹ The excimer fraction of G4 dendrimer 5 exhibited the broad peak with peak maximum at 432 nm, which possessed stronger emission with longer wavelength (λ_{max} 412 nm) than that of G3 dendrimer 4.

In conclusion, we succeeded in the incorporation of [2.2]paracyclophane on the surface of the third- and fourth-generation PAMAM dendrimers. These dendrimers are the first example of a [2.2]paracyclophane-containing dendrimer. The installation efficiency of the cyclophane units on the dendrimer surface is found to be high according to the NMR and UV titration studies. Investigation of their optical properties disclosed the intensity of emission from π - π interaction among [2.2]paracyclophane units in the excited state accompanying the increase of the generation number of dendrimers.

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- Molecular weight distribution (M_w/M_n) was 2.6 for both commercially available PAMAM dendrimers **1** and **2** under the same condition.
- Generally, in the MALDI-TOF-MS analysis, lower-generation-PAMAM dendrimers and higher-generation-PAMAM dendrimers show a complicated fragmentation and considerably broad peaks, respectively; therefore, it is quite difficult to detect a parent peak of higher-generation-PAMAM dendrimers. For example: J. Subbi, R. Agurauja, R. Tanner, V. Allikmaa, and M. Lopp, *Eur. Polym. J.*, **41**, 2552 (2005), and reference 13c.
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