

Article

## Formation of Zwitterionic Fullerodendron Using a New DBN-Focal Dendron

Yutaka Takaguchi <sup>1,\*</sup>, Maki Hosokawa <sup>1</sup>, Masatoshi Mayahara <sup>1</sup>, Tomoyuki Tajima <sup>1</sup>, Takahiro Sasamori <sup>2</sup> and Norihiro Tokitoh <sup>2</sup>

<sup>1</sup> Graduate School of Environmental Science, Okayama University, Tsushima-Naka 3-1-1, Kita-Ku, Okayama 700-8530, Japan; E-Mails: gev19374@cc.okayama-u.ac.jp (M.H.); gev17371@cc.okayama-u.ac.jp (M.M.); tajimat@cc.okayama-u.ac.jp (T.T.)

<sup>2</sup> Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan; E-Mails: sasamori@boc.kuicr.kyoto-u.ac.jp (T.S.); tokitoh@boc.kuicr.kyoto-u.ac.jp (N.T.)

\* Author to whom correspondence should be addressed; E-Mail: yutaka@cc.okayama-u.ac.jp; Tel.: +81-86-251-8903; Fax: +81-86-251-8903.

Received: 16 November 2009; in revised form: 30 December 2009 / Accepted: 6 January 2009 / Published: 14 January 2010

---

**Abstract:** A new poly(amidoamine) dendron having 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) at the focal point was synthesized. Interestingly, formation of zwitterionic fullerodendrons ( $\lambda_{\max} = 930$  nm for C<sub>60</sub> and 795 nm for C<sub>70</sub>) were observed by Vis-NIR spectroscopy upon the reaction of C<sub>60</sub> or C<sub>70</sub> with the DBN-focal dendron. In particular, the C<sub>70</sub> anion was effectively stabilized by the site isolation effect of the dendritic wedge. The half-life of fullerodendron **12b** having C<sub>70</sub> anion at the focal point reaches 7,345 min, which is 20 times longer than that of complex between C<sub>60</sub> and pristine DBN. Furthermore, in order to confirm the structure of the zwitterionic complex, fullerodendron **12a** was reprecipitated from benzonitrile/1,2,4-trimethylbenzene, and was observed using IR spectroscopy and APPI-MS.

**Keywords:** dendrimer; fullerodendron; fullerene; DBN; fullerene anion

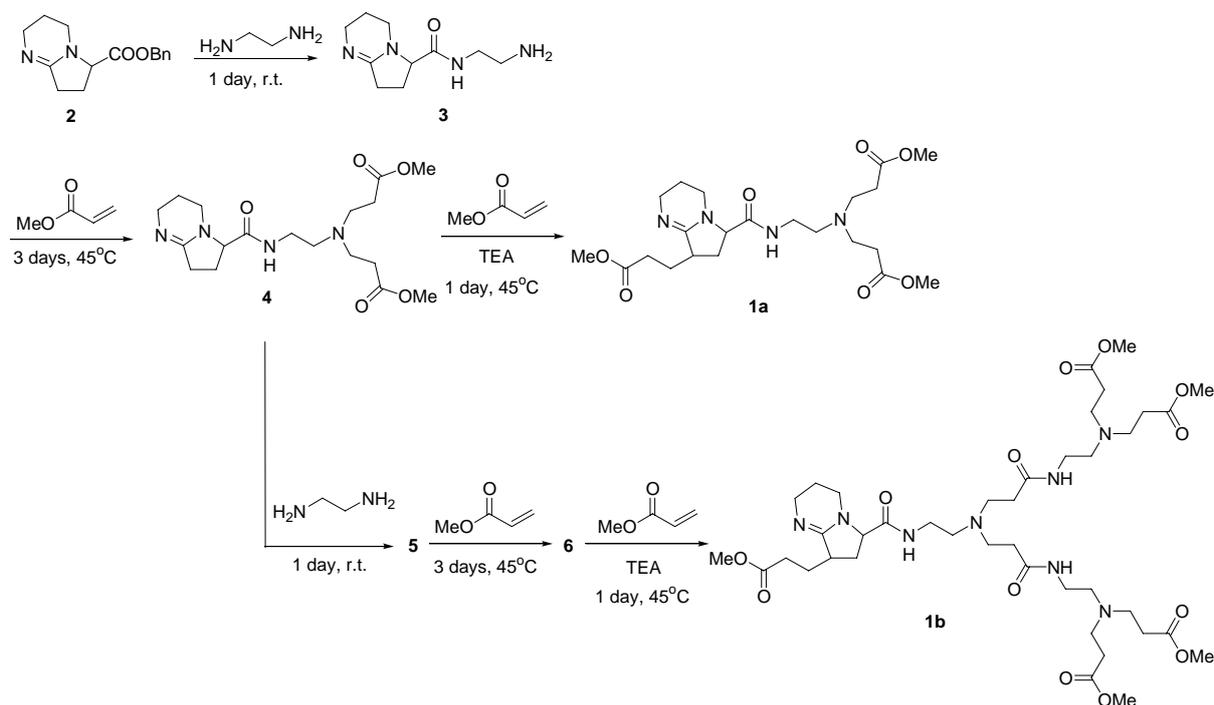
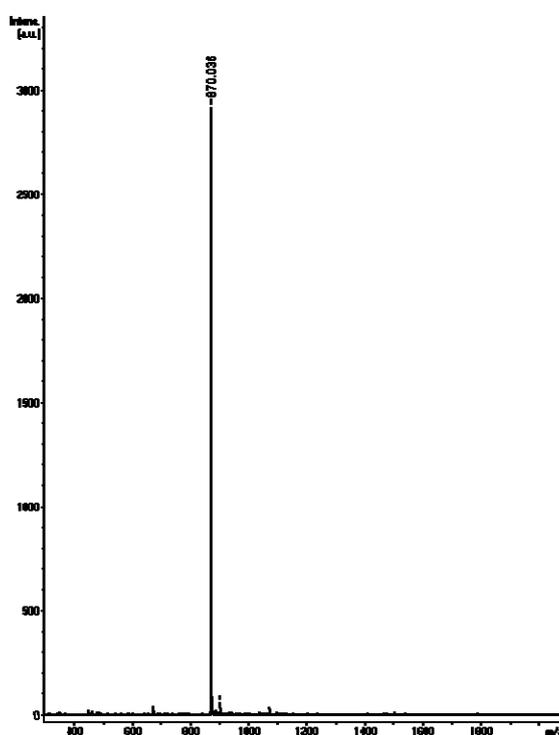
---

## 1. Introduction

The sensing of fullerenes ( $C_{60}$ ,  $C_{70}$ , and higher fullerenes) is gaining considerable interest because of their versatile applications in material science and nanotechnology, such as solar cells and field effect transistors (FETs). From this point of view, reversible formation of fullerodendrons is important [1-4], since the fullerodendron is known to be very soluble fullerene derivative. Meanwhile, Hirsch and co-workers reported that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) reacts with  $C_{60}$  to give a zwitterionic complex via single electron transfer and radical recombination [5]. Recently, Nagata and coworkers have reported that this reaction is useful for large scale separation of  $C_{60}$  from a fullerene mixture because of selective complexation of higher fullerenes with DBU [6]. This zwitterion formation is known to be reversible reaction. However, the resulting complexes are susceptible to air-oxidation; they must therefore be handled in an inert atmosphere. Although many studies on the fullerodendron having neutral  $C_{60}$  or  $C_{70}$  moiety at the focal point have been described [7-29], there are few examples of incorporation of unstable fullerene species into dendritic architectures. Meanwhile, several groups have reported that covalent incorporation of highly unstable subunits into the dendritic architecture is effective to obtain active-site mimics for enzymes [30] and/or highly reactive species as an isolable compound [31] because of site isolation effect of the dendrimer [32-34]. In this context, site-isolation of dendritic substituent expected to be effective to stabilize the unstable fullerene species, such as fullerene anion. These backgrounds prompted us to investigate stabilization of the zwitterionic complex between fullerene and bicyclic amidines using the site isolation effect of the dendron. Herein we report the synthesis of a new DBN-focal dendron, poly (amidoamine) dendron having 1,5-diazabicyclo [4.3.0] non-5-ene (DBN) at the focal point together with the formation of zwitterionic fullerodendrons via complexation of fullerene, either  $C_{60}$  or  $C_{70}$ , and DBN moiety of the dendron.

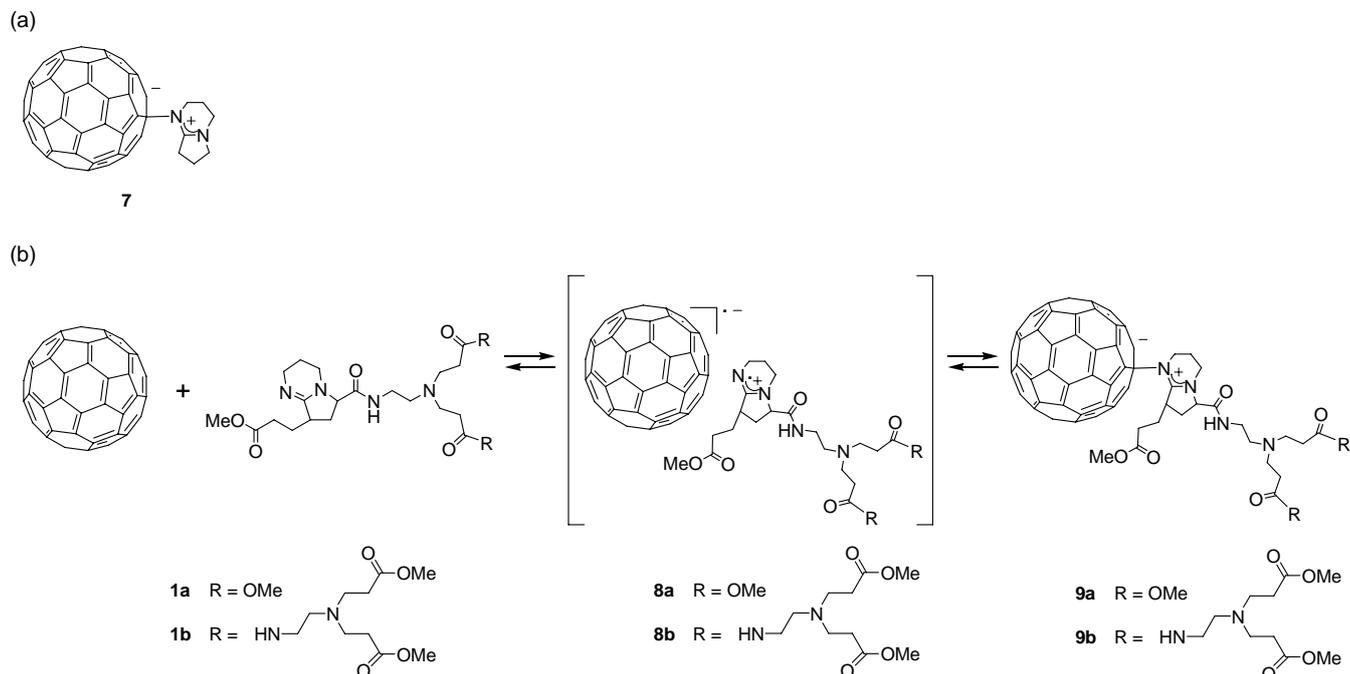
## 2. Results and Discussion

DBN-focal poly(amidoamine) dendrons **1a** and **1b** were synthesized by the use of the divergent method shown in Scheme 1. A focal point of the dendron, 9-benzyloxycarbonyl-1,5-diazabicyclo [4.3.0] non-5-ene (**2**), was prepared as described by Kumagai *et al.* [35]. Compound **2** was allowed to react with ethylenediamine to afford DBN derivative **3**. Then, treatment of **3** with methyl acrylate produced dendron **4**. Subsequent reaction of **4** with methyl acrylate in the presence of triethylamine (TEA) produced dendron **1a** in 40% yield. This three-step process can be repeated to prepare dendron **1b** in 26% yield. The structures of dendrons **1a** and **1b** were confirmed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopies and MALDI-TOF-MS. In the  $^1\text{H}$ -NMR spectra of dendron **1a**, multiplet peaks around 4.9 ppm are attributable to the methine proton of DBN's 9-position of diastereomeric mixture of dendron **1a**. Furthermore, a broad peak around 3.2 ppm, which represents the methine proton of DBN's 7-position, was observed. In the  $^{13}\text{C}$ -NMR spectra of dendron **1a**, the chemical shift at  $\delta$  166.7 is the imine carbon signal of the focal point. The MALDI-TOF-MS spectrum of **1a** showed a molecular ion peak at  $m/z$  469.27 (**1a**,  $C_{22}H_{37}N_4O_7$  requires  $m/z$  469.26) using positive-ion mode. Figure 1 shows that the MALDI-TOF-MS spectrum of **1b** exhibits a molecular ion peak at  $m/z$  870.04 (**1b**,  $C_{40}H_{69}N_8O_{13}$  requires  $m/z$  869.49) using positive-ion mode.

Scheme 1. Syntheses of dendrons **1a** and **1b**.Figure 1. MALDI-TOF MS spectrum of dendron **1b**.

The formation of zwitterionic complex of dendrons **1a** or **1b** with  $\text{C}_{60}$  was observed by Vis/NIR spectrum, as reported by Hirsch *et al.* (Scheme 2) [5]. In a typical experiment,  $\text{C}_{60}$  ( $0.200 \text{ mg}$ ,  $0.278 \times 10^{-3} \text{ mmol}$ ) was dissolved in benzonitrile ( $3 \text{ mL}$ ), to which dendron **1b** ( $9.49 \text{ mg}$ ,  $0.0109 \text{ mmol}$ ) was added under an Ar atmosphere. Subsequently, the Vis/NIR spectrum of the solution was recorded.

**Scheme 2.** (a) Structure of zwitterionic complex **7**. (b) Formation of zwitterionic fullerodendrons **9a** or **9b**.



**Figure 2.** Vis-NIR spectra of the zwitterion **9b** and radical ion pair **8b** in benzonitrile. Inset: Vis-NIR spectrum of zwitterion **7**.

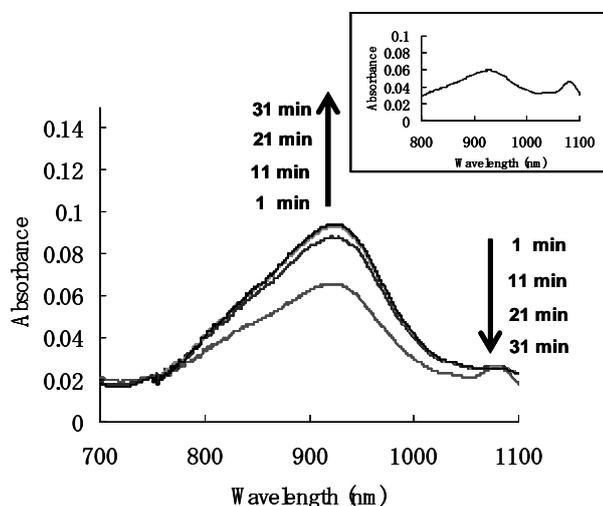
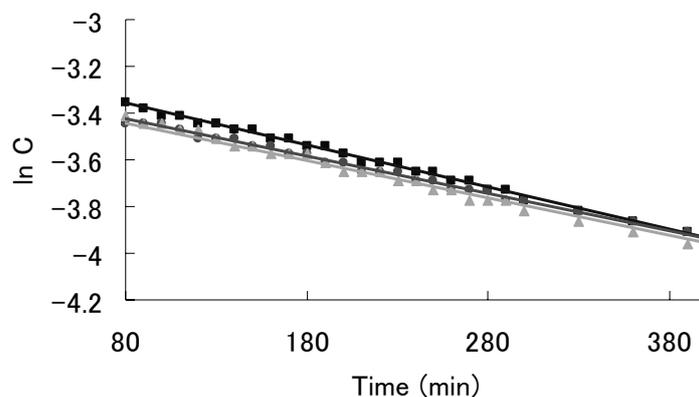


Figure 2 shows the Vis/NIR spectrum of the reaction of dendron **1b** with C<sub>60</sub>. The decay of the absorbance of C<sub>60</sub> anion radical (λ<sub>max</sub> = 1083 nm) is accompanied by the evolution of the zwitterion (λ<sub>max</sub> = 930 nm) [5]. These assignments were confirmed by the reaction of C<sub>60</sub> with pristine DBN, in which radical ion pair (λ<sub>max</sub> = 1083 nm) and zwitterionic complex **7** (λ<sub>max</sub> = 930 nm) were also observed. Although the zwitterionic fullerodendrons **9a** and **9b** were stable under an Ar atmosphere for 24 h at room temperature, they slowly decomposed on exposure to air, as reported by Nagata *et al.* [6]. We examined the time course of the absorbance of zwitterionic complexes **7**, **9a** and **9b** (λ<sub>max</sub> = 930 nm) in the presence of atmospheric oxygen (Figure 3). The half-lives of the zwitterion complexes **7**, **9a** and **9b**

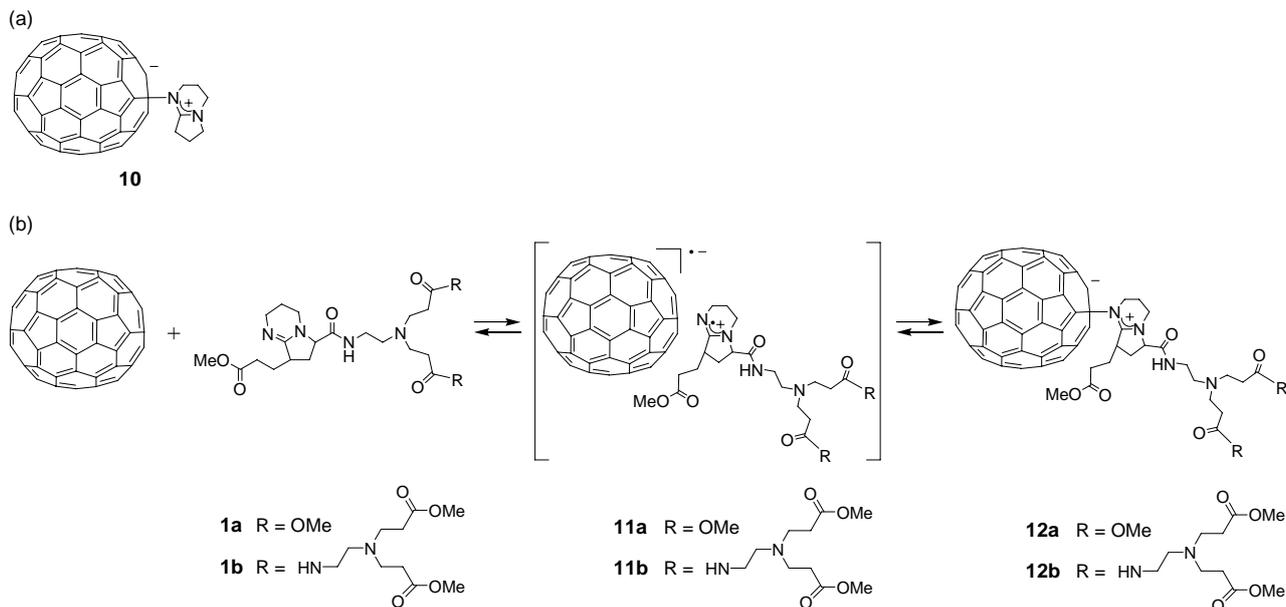
were estimated as 377, 397 and 463 min, respectively. Although a clear difference of half-lives between zwitterions **7** and **9a** could not be found, the highest generation **9b**, which might be stabilized by the site isolation effect of dendritic wedge, showed the longest half-life.

**Figure 3.** Time profile of the concentration of the zwitterions **7** (■), **9a** (●), and **9b** (▲).

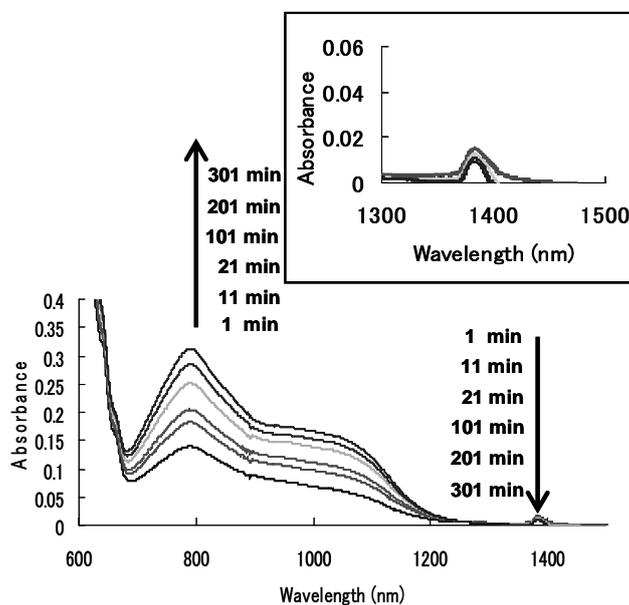


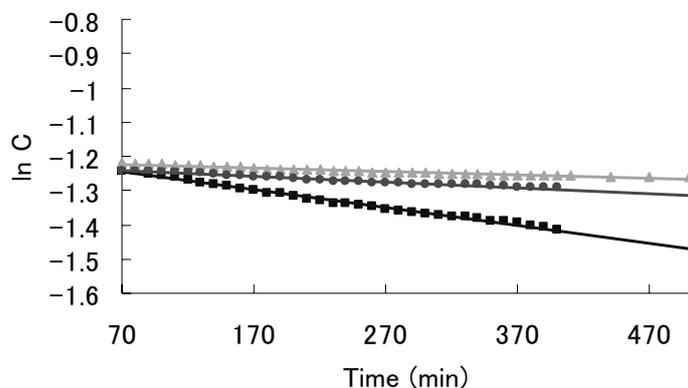
In order to obtain a more stable zwitterionic fullerodendron, we examined the respective reactions of dendrons **1a** and **1b** with  $C_{70}$ , which has higher electron affinity than  $C_{60}$  (Scheme 3). In a typical experiment,  $C_{70}$  (0.220 mg,  $0.262 \times 10^{-3}$  mmol) was dissolved in benzonitrile (3 mL), to which dendron **1b** (9.49 mg, 0.0109 mmol) was added under an Ar atmosphere. Subsequently, the Vis/NIR spectrum of the solution was observed. Figure 4 shows the Vis/NIR spectrum of the reaction of dendron **1b** with  $C_{70}$ . The decay of the absorbance at 1,380 nm is accompanied by the evolution of the absorbance at 795 nm. We interpreted that these absorbances were derived from a radical ion pair ( $\lambda_{\max} = 1,380$  nm) and zwitterionic complex ( $\lambda_{\max} = 795$  nm), as reported by Fukuzumi *et al.* [36]. These assignments were confirmed by the reaction of  $C_{70}$  with pristine DBN, in which a radical ion pair ( $\lambda_{\max} = 1,380$  nm) and zwitterionic complex **10** ( $\lambda_{\max} = 795$  nm) were also observed. Although the zwitterionic fullerodendrons **12a** and **12b** were stable under an Ar atmosphere for 5 days at room temperature, they decomposed slowly on exposure to air as well as in the case of  $C_{60}$ . We examined the time course of the absorbance of zwitterionic complexes **10**, **12a** and **12b** ( $\lambda_{\max} = 795$  nm) in the presence of atmospheric oxygen (Figure 5). The half-lives of the zwitterion complexes **10**, **12a**, and **12b** were estimated as 1445, 4800 and 7345 min, respectively. The half-lives of zwitterions having dendritic wedge, compounds **12a** and **12b**, were longer than that of **10**. Comparing half-lives of fullerodendrons **12a** and **12b**, it is obvious that the stability of zwitterions depends on the generation of the dendron unit. This result indicated that zwitterionic complexes **12a** and **12b** might be stabilized by the site isolation effect of the dendritic wedge.

**Scheme 3.** (a) Structure of zwitterionic complex **10**. (b) Formation of zwitterionic fullerodendrons **12a** or **12b**.



**Figure 4.** Vis-NIR spectra of the zwitterions **12b** and radical ion pair **11b** in benzonitrile. Inset: Expanded Vis-NIR spectrum of radical ion pair **11b**.



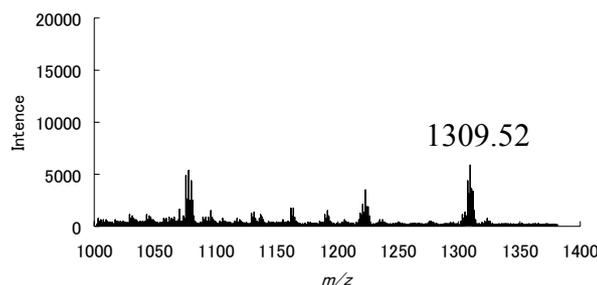
**Figure 5.** Time profile of the concentration of the zwitterions **10** (■), **12a** (●), and **12b** (▲).

The absorption maxima and half-lives of zwitterions **7**, **9**, **10** and **12** were summarized in Table 1. Comparing the half-lives of zwitterionic complexes **7**, **9**, **10** and **12**, we can conclude that anionic fullerene moieties of zwitterionic fullerodendrons **9b** and **12b** are stabilized by the site isolation effect of the dendritic wedge. In particular, zwitterionic fullerodendron **12b**, which has a C<sub>70</sub> moiety at the focal point, showed remarkable stability compared with **10**, which does not have a dendritic wedge, and fullerodendron **9b**, which contains C<sub>60</sub> moiety at the focal point. These observed results might be due to higher electron affinity of C<sub>70</sub> than C<sub>60</sub>, and the difference of anion delocalization between C<sub>60</sub> and C<sub>70</sub>. In marked contrast with the complete anion delocalization of C<sub>60</sub>, the localized anion of C<sub>70</sub> are known to be the reason of regioselective addition reactions [37]. Furthermore, the structure of zwitterionic fullerodendron **12a**, which could be isolated by reprecipitation from benzonitrile/1,2,4-trimethylbenzene, was confirmed by IR spectroscopy and APPI-MS. In the IR spectrum of fullerodendron **12a**, the  $\text{-C}=\text{N}$  absorbance (**1a**, 1,680 cm<sup>-1</sup>) of the DBN<sup>+</sup> moiety is split into two bands at 1,663 and 1,674 cm<sup>-1</sup>. This splitting occurs because the two nitrogens in the DBN<sup>+</sup> moiety are not identical; therefore two  $\text{-C}=\text{N}$  vibrations appeared as reported by Hirsch *et al.* [5]. The APPI-MS showed a molecular ion peak at  $m/z$  1,309.52 (C<sub>92</sub>H<sub>37</sub>N<sub>4</sub>O<sub>7</sub> requires  $m/z$  1,309.27 [MH<sup>+</sup>]) and fragment peaks at 1,223.49 ([MH<sup>+</sup>]-CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>) and 1,077.52 ([MH<sup>+</sup>]-CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>3</sub>-(CH<sub>2</sub>CH<sub>2</sub>COO)<sub>2</sub>) as shown in Figure 6.

**Table 1.** Absorption maxima and half-lives of the zwitterionic complexes **7–12** in air.

Compound	$\lambda_{\text{max}}$ [nm]	half-life [min] <sup>a</sup>
<b>7</b>	930	377
<b>9a</b>	930	397
<b>9b</b>	930	463
<b>10</b>	795	1445
<b>12a</b>	795	4800
<b>12b</b>	795	7345

<sup>a</sup> Half-lives were estimated using pseudo-first order decays of the absorption spectra.

**Figure 6.** APPI MS spectrum of zwitterionic fullerodendron **12a**.

### 3. Experimental Section

NMR spectra were measured using a spectrometer (AL 300; JEOL). Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was performed on a mass spectrometer (Autoflex; Bruker Daltonics Inc.) using dithranol (1,8-dihydroxy-9-anthrone) as a matrix. Atmospheric pressure photo ionization mass spectroscopy (APPI-MS) was performed on a BRUKER micrOTOF focus-Kci mass spectrometer equipped with an APCI ionization unit. The GPC experiments (LC-918V; Japan Analytical Industry Co.) were performed using JAIGEL 1H, 2H (eluent: chloroform). The UV/vis spectra ( $\lambda_{\max}$  in nm ( $\epsilon$ )) were measured using a spectrophotometer (UV-3150, Shimadzu Corp.). Infrared (IR) spectra were measured using a spectrophotometer (Avatar 360T2; Thermo Nicolet). The reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Kogyo Co. Ltd. Co., Aldrich Chemical Co. Inc., and Frontier Carbon Co. The reagents used as reaction solvents were further purified using general methods.

#### *Preparation of dendron 1a*

A suspension of 9-benzyl-1, 5-diazabicyclo [4.3.0] non-5-ene **2** (690 mg, 2.67 mmol) in methanol (18 mL) was added dropwise to a stirred solution of ethylenediamine (30.1 g, 534 mmol) in methanol (18 mL) at room temperature. The mixture was stirred continuously for 1 day. After removal of the solvent, the residue was washed with excess diethyl ether to obtain compound **3**, which was used for a following reaction without further purification. A mixture of **3** (530 mg, 1.88 mmol), methyl acrylate (3.24 g, 37.6 mmol), and methanol (50 mL) was stirred at 45 °C for 3 days. After removal of the solvent, the residue was purified using silica-gel column chromatography (eluent, chloroform/methanol = 15/1) to obtain compound **4**. Compound **4** (900 mg, 2.34 mmol), methyl acrylate (4.02 g, 46.8 mmol), triethylamine (0.240 g, 2.34 mmol), and methanol (63 mL) were stirred at 45 °C for 1 day. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 15/1) to afford dendron **1a** (720 mg, 1.54 mmol) as a yellow oil in 40% yield:  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.18–2.24 (m, 3H), 2.43–2.47 (t,  $J = 6.6$  Hz, 4H), 2.61–2.65 (dt,  $J = 4.8, 6.6$  Hz, 2H), 2.75–2.79 (t,  $J = 6.6$  Hz, 4H), 2.82–2.86 (m, 2H), 3.15–3.24 (m, 1H), 3.36–3.52 (m, 5H), 3.63–3.69 (m, 8H), 3.73 (s, 3H), 3.80–3.84 (t,  $J = 6.6$  Hz, 2H), 4.87–4.92 (m, 1H), 8.10 (t,  $J = 4.8$  Hz, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  18.9, 24.0, 30.7, 31.6, 32.6, 37.4, 41.8, 44.7,

49.0, 51.9, 52.3, 52.5, 68.2, 77.2, 166.7, 168.7, 171.0, 173.1; IR (neat)  $\nu_{\max}$  = 1,664, 1,731  $\text{cm}^{-1}$ ; MALDI-TOF Mass Found:  $m/z$  469.27. Calcd. for  $\text{C}_{22}\text{H}_{37}\text{N}_4\text{O}_7$ :  $[\text{MH}^+]$ , 469.26.

#### Preparation of dendron **1b**

A suspension of **4** (630 mg, 1.64 mmol) in methanol (11 mL) was added dropwise to a stirred solution of ethylenediamine (19.7 g, 328 mmol) in methanol (11 mL) at room temperature. The mixture was stirred continuously for 1 day. After removal of the solvent, the residue was washed with excess diethyl ether to obtain compound **5**, which was used for the following reaction without further purification. A mixture of **5** (560 mg, 1.28 mmol), methyl acrylate (4.40 g, 51.2 mmol), and methanol (69 mL) was stirred at 45 °C for 3 days. After removal of the solvent, the residue was purified using silica-gel column chromatography (eluent, chloroform/methanol = 10/1) to obtain compound **6**. A methanol solution (26 mL) of compound **6** (740 mg, 0.946 mmol), methyl acrylate (1.63 g, 19.0 mmol), and triethylamine (0.10 g, 0.989 mmol) was stirred at 45 °C for 1 day. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent, chloroform/methanol = 10/1) and GPC to afford the dendron **1b** (377 mg, 0.434 mmol) as a yellow oil in 26% yield:  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.00–2.20 (m, 3H), 2.35 (t,  $J$  = 6.0 Hz, 8H), 2.44 (t,  $J$  = 6.3 Hz, 4H), 2.43–2.44 (m, 1H), 2.49–2.54 (dt,  $J$  = 5.4, 6.0 Hz, 4H), 2.60–2.65 (dt,  $J$  = 4.5, 6.0 Hz, 2H), 2.69 (t,  $J$  = 6.0 Hz, 8H), 2.76 (t,  $J$  = 6.3 Hz, 4H), 3.07–3.15 (m, 2H), 3.26–3.45 (m, 8H), 3.53–3.59 (m, 3H), 3.60 (s, 12H), 3.73 (s, 3H), 3.84 (t,  $J$  = 6.0 Hz, 2H), 4.87–4.93 (m, 1H), 7.13 (t,  $J$  = 5.4 Hz, 2H), 8.49 (t,  $J$  = 4.5 Hz, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  18.5, 24.0, 25.6, 30.5, 32.7, 37.1, 37.6, 40.2, 41.9, 49.0, 49.2, 49.7, 50.8, 51.6, 52.3, 52.8, 67.6, 71.4, 166.5, 168.3, 171.0, 172.3, 173.1; IR (neat)  $\nu_{\max}$  = 1681, 1733  $\text{cm}^{-1}$ ; MALDI-TOF Mass Found:  $m/z$  870.04. Calcd. for  $\text{C}_{40}\text{H}_{69}\text{N}_8\text{O}_{13}$ :  $[\text{MH}^+]$ , 869.49.

#### Formation of zwitterionic fullerodendrons **9** or **12**

A solution of dendron **1a** or **1b** (5.16 mg/9.56 mg, 0.0110 mmol) in benzonitrile (1.5 mL) was added to a solution of  $\text{C}_{60}$  or  $\text{C}_{70}$  (0.18 mM) in benzonitrile (1.5 mL). The solution was investigated using Vis/NIR.

#### Preparation of zwitterionic fullerodendron **12a**

A solution of dendron **1a** (11.2 mg, 0.0239 mmol) in benzonitrile (2 mL) was added to a solution of  $\text{C}_{70}$  (1 mg) in 1,2,4-trimethylbenzene (5 mL). The mixture was stirred for 1 h at 25 °C under an Ar atmosphere. Centrifugation (4000 g) of the suspension for 30 min gave a brown precipitation: IR (neat)  $\nu_{\max}$  = 1,663, 1,674, 1,731  $\text{cm}^{-1}$ ; APPI MS Found:  $m/z$  1309.52. Calcd. for  $\text{C}_{92}\text{H}_{37}\text{N}_4\text{O}_7$ :  $[\text{MH}^+]$ , 1309.27.

## 4. Conclusions

The results described herein show the first example of a DBN-focal dendron and the formation of a zwitterionic fullerodendron, observed by UV-vis-NIR spectra, having an anionic fullerene moiety at

the focal point. In particular, the C<sub>70</sub> anion was effectively stabilized by the site isolation effect of the dendritic wedge. The lifetime of zwitterionic fullerodendron **12b** formed by the reaction of C<sub>70</sub> with the DBN-focal dendron **1b** is approximately 20 times longer than that of zwitterionic complex between C<sub>60</sub> and DBN. It is notable that the reversible formation of zwitterionic fullerodendrons potentially applicable to sensing fullerenes, because the absorption maximum of an anionic fullerene moiety should depend on the number of the carbon atoms in a fullerene. Further work is in progress to explore the selective sensing of the fullerene family using zwitterionic fullerodendrons.

### Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 21510103, 21750043) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

### References and Notes

1. Nierengarten, J.F. *Topics in Current Chemistry*; Schalley, C.A., Vögtle, F., Eds.; Springer: New York, NY, USA, 2003; Volume 228, pp. 87-110.
2. Rio, Y.; Accorsi, G.; Nierengarten, H.; Bourgoigne, C.; Strub, J.M.; van Dorsselaer, A.; Armaroli, N.; Nierengarten, J.F. A fullerene Core to Probe Dendritic Shielding Effects. *Tetrahedron* **2003**, *59*, 3833-3844.
3. Nierengarten, J.F.; Armaroli, N.; Accorsi, G.; Rio, Y.; Eckert, J.F. [60] Fullerene: A Versatile Photoactive Core for Dendrimer Chemistry. *Chem. Eur. J.* **2003**, *9*, 36-41.
4. Takaguchi, Y.; Tajima, T.; Ohta, K.; Motoyoshiya, J.; Aoyama, H.; Wakahara, T.; Akasaka, T.; Fujitsuka, M.; Ito, O. Reversible Binding of C<sub>60</sub> to an Anthracene Bearing a Dendritic Poly(amidoamine) Substituent to Give a Water-soluble Fullerodendrimer. *Angew. Chem. Int. Ed.* **2002**, *41*, 817-819.
5. Skiebe, A.; Hirsch, A.; Klos, H.; Gotschy, B. [DBU]C<sub>60</sub>. Spin Pairing in a Fullerene Salt. *Chem. Phys. Lett.* **1994**, *220*, 138-140.
6. Nagata, K.; Dejima, E.; Kikuchi, Y.; Hashiguchi, M. Kilogram-scale [60] Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with 1,8-Diazabicyclo [5.4.0] undec-7-ene (DBU). *Chem. Lett.* **2005**, *34*, 178-179.
7. Takaguchi, Y.; Sako, Y.; Yanagimoto, Y.; Tsuboi, S.; Motoyoshiya, J.; Aoyama, H.; Wakahara, T.; Akasaka, T. Facile and Reversible Synthesis of an Acidic Water-soluble Poly (amidoamine) Fullerodendrimer. *Tetrahedron Lett.* **2003**, *44*, 5777-5780.
8. Takaguchi, Y.; Katayose, Y.; Yanagimoto, Y.; Motoyoshiya, J.; Aoyama, H.; Wakahara, T.; Maeda, Y.; Akasaka, T. Photoinduced Dithiolation of Fullerene [60] with Dendrimer Disulfide. *Chem. Lett.* **2003**, *32*, 1124-1125.
9. Hirano, C.; Imae, T.; Fujima, S.; Yanagimoto, Y.; Takaguchi, Y. Fabrication and Properties of Fullerodendron Thin Films. *Langmuir* **2005**, *21*, 272-279.
10. Sandanayaka, A.S.D.; Zhang, H.; Takaguchi, Y.; Sako, Y.; Tamura, M.; Araki, Y.; Ito, O. Photoinduced Charge Separation and Charge Recombination of Fullerene Bearing Dendritic Poly (amidoamine) with Carboxylates at the Terminal in Aqueous Media. *Chem. Commun.* **2005**, *7*, 5160-5162.

11. Araki, Y.; Kunieda, R.; Fujitsuka, M.; Ito, O.; Motoyoshiya, J.; Aoyama, H.; Takaguchi, Y. Photoinduced Intermolecular Electron Transfer and Energy Transfer of C<sub>60</sub> Dendrimers. *C. R. Chimie.* **2006**, *9*, 1014-1021.
12. Takaguchi, Y.; Yanagimoto, Y.; Fujima, S.; Tsuboi, S. Photooxygenation of Olefins, Phenol, and Sulfide Using Fullerodendrimer as Catalyst. *Chem. Lett.* **2004**, *33*, 1142-1143.
13. Talukdar, B.; Takaguchi, Y.; Yanagimoto, Y.; Tsuboi, S.; Ichihara, M.; Ohta, K. Fabrication and Photocatalytic Activity of Fullerodendron/CaCO<sub>3</sub> Composites. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1983-1987.
14. Kawasaki, N.; Nagano, T.; Kubozono, Y.; Sako, Y.; Morimoto, Y.; Takaguchi, Y.; Fujiwara, A.; Chu, C.C.; Imae, T. Transport Properties of Field-effect Transistor with Langmuir-Blodgett Films of C<sub>60</sub> Dendrimer and Estimation of Impurity Levels. *Appl. Phys. Lett.* **2007**, *91*, 24351/1-24351/5.
15. Kusai, H.; Nagano, T.; Imai, K.; Kubozono, Y.; Sako, Y.; Takaguchi, Y.; Fujiwara, A.; Akima, N.; Iwasa, Y.; Hino, S. Fabrication of Field-effect Transistor Devices with Fullerodendron by Solution Process. *Appl. Phys. Lett.* **2006**, *88*, 173509/1-173509/3.
16. Takaguchi, Y.; Tamura, M.; Sako, Y.; Yanagimoto, Y.; Tsuboi, S.; Uchida, T.; Shimamura, K.; Kimura, S.; Wakahara, T.; Maeda, Y.; Akasaka, T. Fullerodendron-assisted Dispersion of Single-walled Carbon Nanotubes via Noncovalent Functionalization. *Chem. Lett.* **2005**, *34*, 1608-1609.
17. Hirano, C.; Imae, T.; Tamura, M.; Takaguchi, Y. Fabrication and Luminescent Properties of Silver Nanoparticles Passivated by Fullerodendrons. *Chem. Lett.* **2005**, *34*, 862-863.
18. Murata, Y.; Ito, M.; Komatsu, K. Synthesis and Properties of Novel Fullerene Derivatives Having Dendrimer Units and the Fullerenyl Anions Generated Therefrom. *J. Mater. Chem.* **2002**, *12*, 2009-2020.
19. Kunieda, R.; Fujitsuka, M.; Ito, O.; Ito, M.; Murata, Y.; Komatsu, K. Photochemical and Photophysical Properties of C<sub>60</sub> Dendrimers Studied by Laser Flash Photolysis. *J. Phys. Chem.* **2002**, *106*, 7193-7199.
20. Donnio, B.; Buathong, S.; Bury, I.; Guillon, D. Liquid Crystalline Dendrimers. *Chem. Soc. Rev.* **2007**, *36*, 1495-1513.
21. Campidelli, S.; Severac, M.; Scanu, D.; Deschenaux, R.; Vazquez, E.; Milic, D.; Prato, M.; Carano, M.; Marcaccio, M.; Paolucci, F.; Rahman, G.M.A.; Guldi, D.M. Photophysical, Electrochemical, and Mesomorphic Properties of a Liquid-crystalline [60]Fullerene-peralkylated Ferrocene Dyad. *J. Mater. Chem.* **2008**, *18*, 1504-1509.
22. Nierengarten, J.F.; Gutierrez-Nava, M.; Zhang, S.; Masson, P.; Oswald, L.; Bourgogne, C.; Rio, Y.; Accorsi, G.; Armaroli, N.; Setayesh, S. Fullerene-containing Macromolecules for Materials Science Applications. *Carbon* **2004**, *42*, 1077-1083.
23. Zhang, S.; Rio, Y.; Cardinali, F.; Bourgogne, C.; Gallani, J.L.; Nierengarten, J.F. Amphiphilic Diblock Dendrimers with a Fullerene Core. *J. Org. Chem.* **2003**, *68*, 9787-9797.
24. Choi, M.S.; Aida, T.; Luo, H.; Araki, Y.; Ito, O. Fullerene-Terminated Dendritic Multiporphyrin Arrays: Dendrimer Effects on Photoinduced Charge Separation. *Angew. Chem. Int. Ed.* **2003**, *42*, 4060-4063.
25. Negishi, N.; Ie, Y.; Tada, H.; Kaneda, T.; Aso, Y. Ambipolar Characteristics of Dendritic Oligothiophene/Fullerene Linkage Molecules. *Chem. Lett.* **2007**, *36*, 544-545.

26. Scanu, D.; Yevlampieva, N.P.; Deschenaux, R. Polar and Electrooptical Properties of [60] Fullerene-Containing Poly (benzyl ether) Dendrimers in Solution. *Macromolecules* **2007**, *40*, 1133-1139.
27. Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. Supramolecular Peapods Composed of a Metalloporphyrin Nanotube and Fullerenes. *J. Am. Chem. Soc.* **2003**, *125*, 13934-13935.
28. Nishioka, T.; Tashiro, K.; Aida, T.; Zheng, J.Y.; Kinbara, K.; Saigo, K.; Sakamoto, S.; Yamaguchi, K. Molecular Design of a Novel Dendrimer Porphyrin for Supramolecular Fullerene/Dendrimer Hybridization. *Macromolecules* **2000**, *33*, 9182-9184.
29. Iliopoulos, K.; Couris, S.; Hartnagel, U.; Hirsch, A. Nonlinear Optical Response of Water Soluble C<sub>70</sub> Dendrimers. *Chem. Phys. Lett.* **2007**, *448*, 243-247.
30. Bosman, A.W.; Janssen, H.M.; Meijer, E.W. About Dendrimers: Structure, Physical Properties, and Applications. *Chem. Rev.* **1999**, *99*, 1665-1688.
31. Takaguchi, Y.; Suzuki, S.; Ohta, K.; Motoyoshiya, J.; Aoyama H. Synthesis and Characterization of a Poly (benzyl ether) Dendron Sulfenyl Iodide. *Phosphor. Sulfur Silicon* **2001**, *176*, 61-67.
32. Hecht, S.; Fréchet, J.M.J. Dendritic Encapsulation of Function: Applying Nature's Site Isolation Principle from Biomimetics to Materials Science. *Angew. Chem. Int. Ed.* **2001**, *40*, 74-91.
33. Stefarn, B.; Marcel, K.; Volker, E.; Martin, B.; Klaus, M. Pyrene as Chromophore and Electrophore: Encapsulation in a Rigid Polyphenylene Shell. *Chem. Eur. J.* **2006**, *12*, 6117-6128.
34. Amore, A.; Heerbeek, R.V.; Zeep, N.; Esch, J.V.; Reek, J.N.H.; Hiemsta, H.; Maarseveen, J.H.V. Carbosilane Dendrimeric Carbodiimides: Site Isolation as a Lactamization Tool. *J. Org. Chem.* **2006**, *71*, 1851-1860.
35. Kumagai, N.; Matsunaga, S.; Shibasaki, M. An Efficient Synthesis of Bicyclic Amidines by Intramolecular Cyclization. *Angew. Chem. Int. Ed.* **2004**, *43*, 478-482.
36. Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Sakurada, N.; Arakawa, R.; Fujitsuka, M.; Ito, O. Enhanced Reactivity of C<sub>70</sub> in the Photochemical Reactions with NADH and NAD Dimer Analogues as Compared to C<sub>60</sub> via Photoinduced Electron Transfer. *J. Phys. Chem. A.* **1999**, *103*, 5935-5941.
37. Roduner, E.; Reid, I.D. Structure and Charge Distribution of Multiply Charged C<sub>70</sub>. *Chem. Phys. Lett.* **1994**, *223*, 149-154.

© 2010 by the authors; licensee Molecular Diversity Preservation International, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).