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Fluorescence Characteristics of Naphthalene Dendrimers at Low Concentration in Aqueous Solution

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Water-soluble naphthalene dendrimers WN**1**, WN**2**, and WN**3**, together with the lipophilic compounds N**1**, N**2**, and N**3** were prepared and their photochemical properties were examined. Whereas lipophilic dendrimers N**1**, N**2**, and N**3** gave monomer emission peaking at 330–340 nm, water-soluble dendrimers WN**1**, WN**2**, and WN**3** gave not only the monomer emission at 330–340 nm but also excimer emission peaking at 400 nm in aqueous solution under considerably diluted conditions. The relative intensity of the excimer fluorescence at longer wavelengths compared to the monomer emission depended on the dendrimer generation and the concentration of dendrimer and added salt (KCl). In particular the excimer emission of the second generation dendrimer is considerably higher than those of the first and the third generation dendrimers. Based on these experimental results, the aggregation and the excimer formation of water-soluble naphthalene dendrimers in aqueous solution depending on the generation and the conditions were discussed.

Dendrimers are expected to have unusual chemical and/or physical properties and many studies concerning dendrimer effects have been reported.[1–5] We have prepared several kinds of dendrimers exhibiting photochemical and photophysical properties, which could be explained by usual analytical processes. Among these, stilbene dendrimers having large substituents of benzyl ether dendrons or polyphenylene dendrons exhibited either fluorescence or photochemical isomerization and almost no effect of the large dendron substituents was observed.[6–8] However, the introduction of hydrophilic groups such as carboxylate anion at the periphery of the benzene ring of the benzyl ether stilbene dendrimers enabled these compounds to be soluble in water and to exhibit unusual ultrafast photoisomerization of the C=C double bond (in the range of tens of nanoseconds) and rather slow molecular structural change (ca. ms) due to the reorientation of surrounding dendron groups after the geometric isomerization of the C=C double bond of the stilbene core.[9,10] Thus, photochemical properties of water-soluble photoresponsive dendrimers seem to be interesting.

We have already prepared water-soluble dendrimers of polyaromatic hydrocarbon such as pyrene and observed fluorescence emission due to the excimer or aggregated form of the core pyrene group even at relatively low concentration of ca. 10^{-4} M.[11] Thus, the water-soluble fluorescent molecules may give aggregates showing characteristic fluorescence at longer wavelength in contrast to the monomer emission. Because of the shorter singlet lifetime and smaller aromatic skeleton of naphthalene compared to pyrene, it is not easy to observe the fluorescence emission of naphthalene in excimer or aggregated form in solution at low concentrations. In contrast to this, naphthalene excimer was observed by fluorescence emission in solid state,[12] polymers,[13] photodimers,[14] and dendrimers having several naphthalene chromophores at the periphery.[15] However, naphthalene excimer formed by intermolecular interaction in very dilute solution has not yet been reported. Accordingly, we are interested in preparing and studying the photochemical properties of water-soluble naphthalene dendrimers WN**1**, WN**2**, and WN**3**, together with the lipophilic compounds N**1**, N**2**, and N**3**. In this case, the effect of aromatic ring size on fluorescence properties arising from intermolecular interaction can be expected. In this report, typical fluorescence spectra at longer wavelength due to the excimer was explored with water-soluble naphthalene dendrimers in connection to both concentration and salt effects on the fluorescence properties, especially for the second generation of dendrimer.

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra of N**1**, N**2**, and N**3** in THF. The absorption edge for these compounds was observed at slightly shorter than 320 nm. The absorption spectrum of N**1** showed vibrational structures

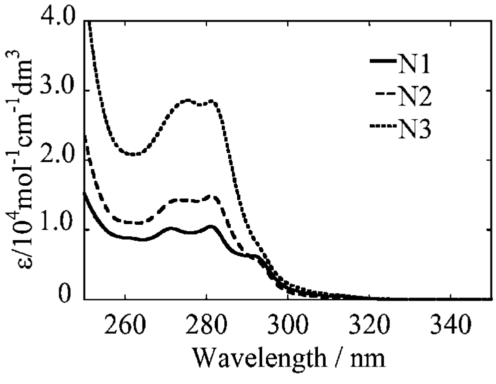


Figure 1. Absorption spectra of N**1**, N**2**, and N**3** in THF.

Table 1. Spectroscopic Parameters of Naphthalene Dendrimers

Compound	$\lambda_{\max \mathrm{UV}}$ /nm	ε /$M^{-1}\,cm^{-1}$ c)	$\lambda_{\max \mathrm{FL.}}$ /nm	Φ_f
N1[a)]	271, 281, 292	10300	329, 338	3.5×10^{-3}
N2[a)]	271, 281, 292	14200	328, 338	3.0×10^{-3}
N3[a)]	274, 281	28200	328, 338	2.1×10^{-3}
WN1[b)]	270, 280, 290	7800	328, 338	1.1×10^{-3}
WN2[b)]	273	12400	329–340	2.9×10^{-3}
WN3[b)]	275	22100	329–340	4.0×10^{-3}

a) In THF. b) In 0.1 M KOH aqueous solution. c) At 280 nm.

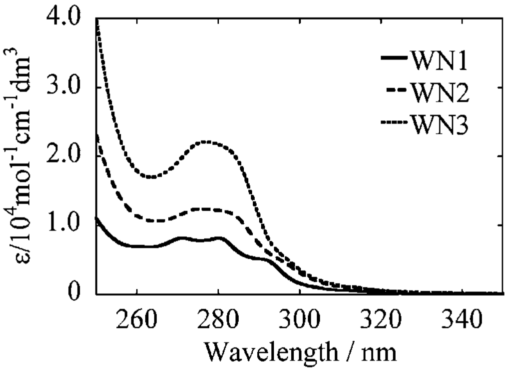


Figure 2. Absorption spectra of WN**1**, WN**2**, and WN**3** in 0.1 M KOH aqueous solution.

peaking at 271, 281, and 292 nm (Table 1). With increasing generation, the molar extinction coefficient of the absorption maxima at 271 and 281 nm increased, resulting in a broadened spectrum. This increase is explained by the increase of benzyl ether dendron groups with increasing generation. The small absorbance around 310 nm is almost the same among these compounds.

Figure 2 shows absorption spectra of WN**1**, WN**2**, and WN**3** in 0.1 M KOH aqueous solution. In this case, WN**1** showed vibrational structure peaking at 270, 280, and 290 nm. The spectral profile of the absorption spectra of WN**2** became broad and the molar extinction coefficient increased in comparison with those of WN**1**, indicating that the conformation or molecular environment of WN**2** is different from that of WN**1**. The extinction coefficient of WN**3** shorter than 295 nm was greater than that of WN**2** indicating that the molecular structure seems to be similar between WN**2** and WN**3**, because the observed band shorter than 295 nm is due to the benzyl ether dendron groups and the number of the benzyl ether groups is almost double in WN**3** compared to WN**2**.

As shown in Figure 3, addition of KCl to the solution slightly changed the absorption spectra leading to decrease of absorbance at the maximum wavelength and broadening the spectral profile. In particular the absorbance at 280 nm in WN**2** in 0.001 M KOH aqueous solution slightly decreased and the absorbance at 300 nm increased with increasing concentration of KCl, in contrast to WN**1** and WN**3**.

Fluorescence Spectra. Figure 4 shows absorption, fluorescence, and fluorescence excitation spectra of 1-methylnaphthalene, N**1**, N**2**, and N**3** in THF. Dendrimers N**1**–N**3** exhibited similar spectral profile and intensity in fluorescence spectra peaking at 330 and 340 nm and are assigned to naphthalene monomer emission. The edge of fluorescence spectra was observed at 420 nm for all the compounds. The singlet excitation energy is calculated from the fluorescence maximum (330 nm) to be 87 kcal mol^{-1} (1 kcal = 4.184 kJ). While the fluorescence excitation spectra of 1-methylnaphthalene has quite similar spectral profile to the absorption spectra, those of N**1**–N**3** are different from their absorption spectra, but are similar to the spectral profile of 1-methylnaphthalene. The dendron groups of N**1**–N**3** absorb light at similar spectral region to the naphthalene, but the dendron groups with carbomethoxy substituents at the terminal of the benzene ring could not transfer the excitation energy to the core naphthalene as already observed for stilbene-cored dendrimers.[16] Therefore, the excitation spectra of the dendrimers should exhibit a different spectral profile from their absorption spectra. Thus, the observed differences could be explained by the overlap of the absorption spectra between the dendrons and the core

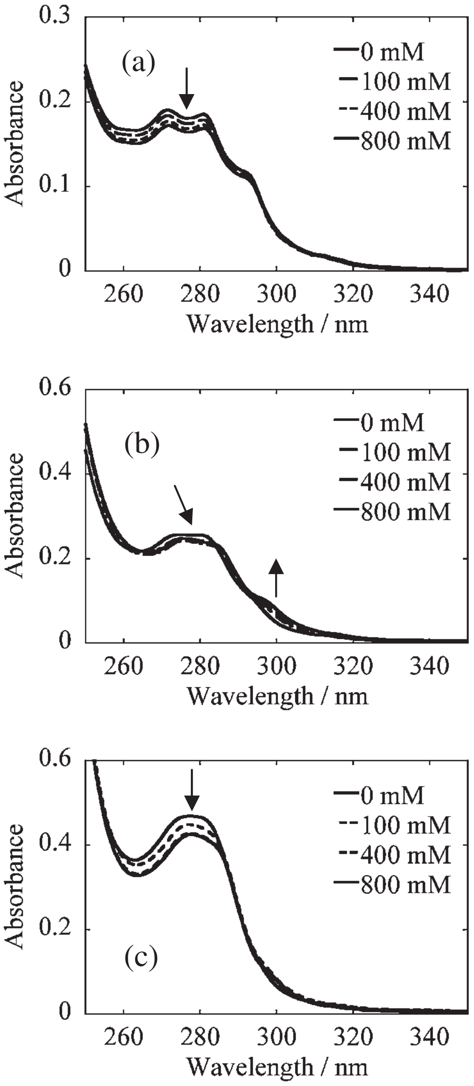


Figure 3. Change in the absorption spectra upon the addition of KCl for (a) WN**1**, (b) WN**2**, and (c) WN**3** in 0.001 M KOH aqueous solution.

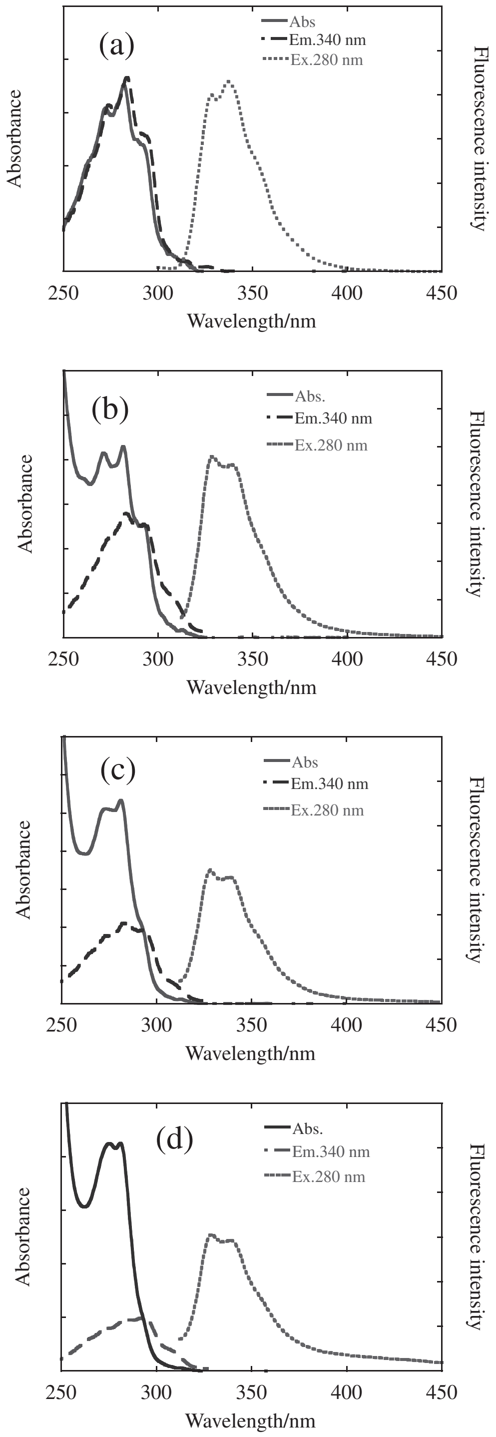


Figure 4. Absorption, fluorescence, and fluorescence excitation spectra of (a) 1-methylnaphthalene, (b) N**1** (7.7×10^{-6} M), (c) N**2** (3.2×10^{-6} M), and (d) N**3** (1.5×10^{-6} M) in THF.

naphthalene and the lack of singlet energy transfer from the dendron group to the core.

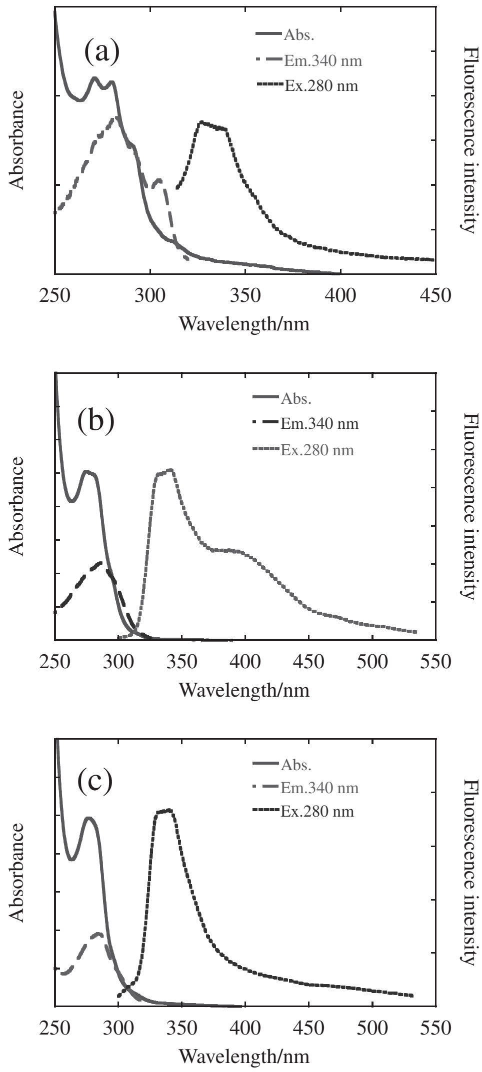


Figure 5. Absorption, fluorescence, and fluorescence excitation spectra of (a) WN**1** (7.7×10^{-6} M), (b) WN**2** (3.2×10^{-6} M), and (c) WN**3** (1.5×10^{-6} M) in 0.1 M KOH aqueous solution.

Figure 5 shows absorption, fluorescence, and fluorescence excitation spectra of WN**1**, WN**2**, and WN**3** in 0.1 M KOH aqueous solution. WN**1** and WN**3** show fluorescence spectra similar to N**1** peaking at around 330 and 340 nm, while broad fluorescence up to 500 nm was observed with low intensity. However, in WN**2** an apparent shoulder peak at around 400 nm was observed. The fluorescence at around 330–340 nm was assigned to the monomer fluorescence of the naphthalene ring and the broad fluorescence at longer wavelength ($\approx$400 nm) could be assigned to the fluorescence from the excimer or aggregated form. In these compounds the fluorescence excitation spectra and the absorption spectra are also different, which also indicate the lack of energy transfer from the surrounding dendron group to the core naphthalene.

Table 1 summarizes the photochemical properties, absorption maxima ($\lambda_{\text{max UV}}$), molar extinction coefficient (ε) at $\lambda_{\text{max UV}}$, fluorescence maxima ($\lambda_{\text{max FL}}$), and fluorescence quantum yield (Φ_f) of naphthalene dendrimers.

Figure 6 shows the fluorescence spectra of WN**1**, WN**2**, and WN**3** at varying concentration in 0.1 M KOH aqueous solution. These spectra were normalized respectively by fluorescence intensity at 340 nm. The peaks at around 340 nm are fluorescence from naphthalene monomer. The broad spectra

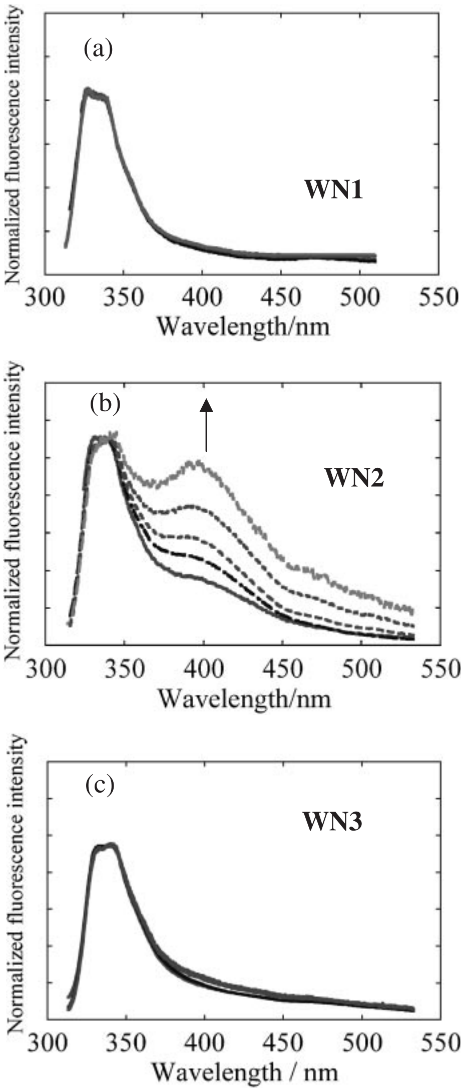


Figure 6. Effect of dendrimer concentration (1.0×10^{-5}–1.0×10^{-4} M) on the fluorescence spectra of (a) WN**1**, (b) WN**2**, and (c) WN**3** in 0.1 M KOH aqueous solution. Excitation wavelength is 280 nm for all the experiments.

peaking around 400 nm are attributed to the fluorescence from the naphthalene excimer or aggregated form. The relative intensity of the excimer fluorescence to monomer from WN**2** increased with increasing concentration.

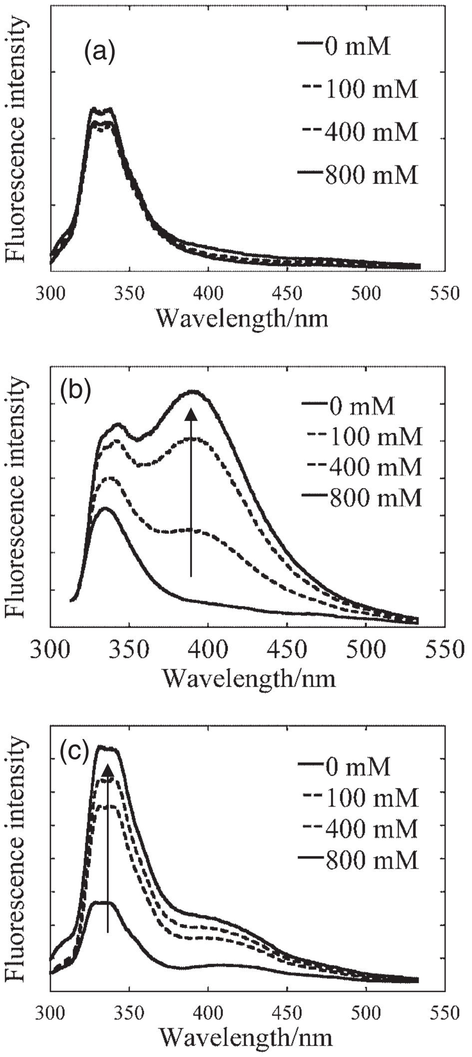


Figure 7. Change in the fluorescence spectra upon the addition of KCl for (a) WN**1**, (b) WN**2**, and (c) WN**3** in 0.001 M KOH aqueous solution. Excitation wavelength is 280 nm for all the experiments.

Figure 7 shows the change in the fluorescence spectra of WN**1**, WN**2**, and WN**3** in 0.001 M KOH aqueous solution upon addition of KCl. The intensity of the fluorescence of WN**1** is almost independent of the concentration of KCl, but a small decrease of the monomer fluorescence at 340 nm and small increase of the excimer fluorescence intensity at 400 nm were observed. On the other hand, the fluorescence spectra greatly changed with increasing concentration of KCl in WN**2** and WN**3**. In the case of WN**3**, an increase of fluorescence intensity over the whole spectral range was observed accompanying a shoulder at 400 nm. In WN**2**, KCl affected the fluorescence spectra remarkably. Whereas the intensity at 340 nm attributed to the monomer fluorescence increased almost two times with addition of KCl at 800 mM, the 400 nm fluorescence due to the excimer increased more than ten times with addition of 800 mM KCl.

Effect of Dendrimer Generation on Fluorescence Spectra. The absorption and fluorescence spectra in THF solution for all the dendrimers examined (N**1**, N**2**, and N**3**) exhibited normal spectra from the monomer, indicating that these dendrimers exist as monomer in THF solution. Water-soluble dendrimers WN**1**, WN**2**, and WN**3** in aqueous solution show similar absorption spectra to N**1**, N**2**, and N**3** except for a slightly different absorption profile at longer wavelength. The remarkable difference between the fluorescence spectra of N**2** in THF solution and of WN**2** in aqueous solution was observed. Especially, the increase of fluorescence intensity was observed upon the addition of KCl in aqueous solution. Although the effect of KCl on the spectral profile for WN**2** and WN**3** is different, these results indicate that the added KCl accelerates the formation of the excimer-like structure due to the aggregation of dendrimers. The effect on the excimer fluorescence is considerably larger for WN**2** than for WN**3**

indicating that the intramolecular interaction between the naphthalene ring of dendrimer depends on the size of the surrounding dendron group: the second generation dendrimer is more appropriate for the formation of the excimer-like structure due to the interaction of the naphthalene ring. The smaller effect on the excimer fluorescence of WN**3** can be explained by the following discussion. Because of the relatively small aromatic ring size of the naphthalene dendrimers, intramolecular interaction of the naphthalene rings in WN**3** is less favorable than that in WN**2**. In the aggregated form, naphthalene rings can exist either with the surrounding dendron groups of the different dendrimers or with naphthalene rings of the different dendrimers. With increasing generation, the size of the surrounding dendron group increases and the core naphthalene ring can find more room at the surrounding dendron groups of the other dendrimers.

It should be mentioned here that the experiments in this paper were performed at concentrations as low as 10^{-5}–10^{-6} M and even at these very low concentrations naphthalene emission of the excimer (or aggregated form) was effectively observed with the aid of dendrimer structures with hydrophobic interiors and hydrophilic exteriors to form molecular aggregate with novel fluorescence properties.

In summary, the excimer fluorescence of naphthalene was successfully observed for water-soluble dendrimers, which depends on the generation of the dendrimers. Furthermore, the effect of KCl salt to accelerate the formation of the dimer or the aggregate to form excimer-like fluorescence was observed, where the second generation dendrimer WN**2** suffered the highest effect on formation of excimer-like fluorescence.

Experimental

Dendrimers used in this study were synthesized as summarized in Scheme 1. The structure of the dendrimers was determined by several analytical data, as shown below, but the ^{1}H NMR spectra are summarized in Figure 8. Dendrons were synthesized according to a reported procedure.[17]

Synthesis of the Core (Scheme 2).[18] 1-(Bromomethyl)naphthalene (0.957 g, 4.33 mmol) and K_2CO_3 (2.02 g, 14.6 mmol) were suspended in 8 mL of DMF under nitrogen atmosphere at room temperature. Phloroglucinol (1.22 g, 9.68 mmol) in 50 mL of DMF was then added to the solution and the mixture was stirred for 10 h at room temperature. The solution was filtered and evaporated to dryness. Water (30 mL) and CH_2Cl_2 (30 mL) were then added to the residue and the products were extracted three times with CH_2Cl_2. The combined extracts were dried with $MgSO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography eluting with hexane–dichloromethane (1:1) to give 0.260 g of the core (22.6%) as a white powder.

^{1}H NMR (270 MHz, $CDCl_3$): δ 4.99 (s, 2H, Ar–OH), 5.43 (s, 2H, Ar–CH_2), 6.00 (t, $J = 2.0$ Hz, 1H, ArH), 6.15 (d, $J = 2.0$ Hz, 2H, ArH), 7.43–7.56 (m, 4H, Nap–H), 7.84–7.91 (m, 2H, Nap–H), 7.99–8.02 (m, 1H, Nap–ArH).

Synthesis of Dendrimers, N1, N2, and N3 (Scheme 1). Synthesis of N1: G1–Br (178 mg, 0.778 mmol), core (90.3 mg, 0.339 mmol), 18-crown-6-ether (42.5 mg, 0.160 mmol), and K_2CO_3 (185 mg, 1.34 mmol) were added and suspended in 14 mL of THF under nitrogen atmosphere. The mixture was heated under reflux for 5 h. The solution was filtered and evaporated to dryness. The crude product was purified by silica gel column chromatography eluting with hexane–dichloromethane (1:1) to give 137 mg of N**1** (71.7%) as a white powder.

Mp: 190–192 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.90 (s, 6H, den–COOMe), 5.03 (s, 4H, den–Ar–CH_2), 5.40 (s, 2H, Ar–CH_2), 6.20 (d, $J = 2.2$ Hz, 2H, Phl–H), 6.23 (t, $J = 2.2$ Hz, 1H, Phl–H), 7.40–7.55 (m, 8H, Nap + den–ArH), 7.84–7.90 (m, 2H, Nap–ArH), 7.99–8.02 (m, 5H, Nap + den–ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.09, 68.70, 69.35, 94.97, 95.08, 123.57, 125.26, 125.89, 126.46, 126.63, 126.93, 128.67, 129.07, 129.64, 129.82, 131.44, 131.91, 133.72, 141.89, 160.36, 160.76, 166.76; MALDI-TOF-MS (*m*/*z*) calcd for $C_{35}H_{30}O_7Na$ $[M + Na]^+ = 585.19$; found, 585.66.

Synthesis of N2: G2–Br (131 mg, 0.262 mmol), core (31.8 mg, 0.119 mmol), 18-crown-6-ether (19.9 mg, 0.0752 mmol), and K_2CO_3 (60.2 mg, 0.435 mmol) were suspended in 11 mL of THF under nitrogen atmosphere. The mixture was heated under reflux for 8 h. The solution was filtered and evaporated to dryness. The crude product was purfied by silica gel column chromatography eluting with hexane–dichloromethane (1:1) and GPC column chromatography eluting with chloroform to give 46.2 mg of N**2** (36.7%) as a white powder.

Mp: 110–112 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.90 (s, 12H, den–COOMe), 4.92 (s, 4H, den–Ar–CH_2), 5.06 (s, 8H, den–Ar–CH_2), 5.41 (s, 2H, Ar–CH_2), 6.23 (t, $J = 2.2$ Hz, 1H, Phl–H), 6.31 (d, $J = 2.2$ Hz, 2H, Phl–H), 6.52 (t, $J = 2.2$ Hz, 2H, den–ArH), 6.67 (d, $J = 2.2$ Hz, 4H, den–ArH), 7.34–7.57 (m, 12H, Nap + den–ArH), 7.82–8.04 (m, 11H, Nap + den–ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.11, 68.69, 69.38, 69.81, 94.90, 94.94, 101.58, 106.48, 123.62, 125.28, 125.90, 126.47, 126.67, 126.89, 126.96, 128.67, 129.09, 129.64, 129.69, 129.78, 129.84, 132.00, 139.44, 141.86, 159.83, 160.48, 166.76; MALDI-TOF-MS (*m*/*z*) calcd for $C_{67}H_{58}O_{15}Na$ $[M + Na]^+ = 1125.28$; found, 1125.49.

Synthesis of N3: G3–Br (347 mg, 0.330 mmol), core (43 mg, 0.161 mmol), 18-crown-6-ether (16.0 mg, 0.06 mmol), and K_2CO_3 (83 mg, 6.00 mmol) were suspended in 14 mL of THF under nitrogen atmosphere. The mixture was heated under reflux for 46 h. The solution was filtered out and evaporated to dryness. The crude product was purfied by silica gel column chromatography eluting with hexane–dichloromethane (1:9) and GPC column chromatography eluting with chloroform to give 164 mg of N**3** (46.5%) as a white powder.

Mp: 120–124 °C; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.87 (s, 24H, den–COOMe), 4.88–4.90 (m, 12H, den–Ar–CH_2), 5.00 (s, 16H, den–Ar–CH_2), 5.35 (s, 2H, Ar–CH_2), 6.25 (t, $J = 2.2$ Hz, 1H, Phl–H), 6.29 (d, $J = 2.2$ Hz, 2H, Phl–H), 6.52 (t, $J = 2.2$ Hz, 6H, den–ArH), 6.67 (d, $J = 2.2$ Hz, 12H, den–ArH), 7.34–7.57 (m, 20H, Nap + den–ArH), 7.82–8.04 (m, 19H, Nap + den–ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.07, 68.63, 69.32, 69.77, 69.89, 94.90, 94.96, 101.46, 101.56, 106.35, 106.42, 123.59, 125.24, 125.87, 126.44, 126.62, 126.90, 128.63, 129.04, 129.64, 129.68, 129.74, 129.80, 133.69, 139.25, 139.39, 141.82, 159.80, 159.91, 160.51, 160.66, 166.70; MALDI-TOF-MS (*m*/*z*) calcd for $C_{131}H_{114}O_{31}Na$ $[M + Na]^+ = 2205.63$; found, 2206.20.

Synthesis of WN1, WN2, and WN3. WN1: To the solution of N**1** (269 mg, 0.478 mmol) in tetrahydrofuran (11 mL) was added 1 M KOH aqueous solution (3 mL). Methanol (2 mL) was then added to this two-phase system to give a homogeneous solution and the solution was heated at reflux for 10 h during which time precipitates formed. The reaction mixture was then evaporated to dryness and the residue was dissolved in water. In order to continue the hydrolysis the solution was heated at reflux for another 12 h. After cooling to room temperature, the mixture was

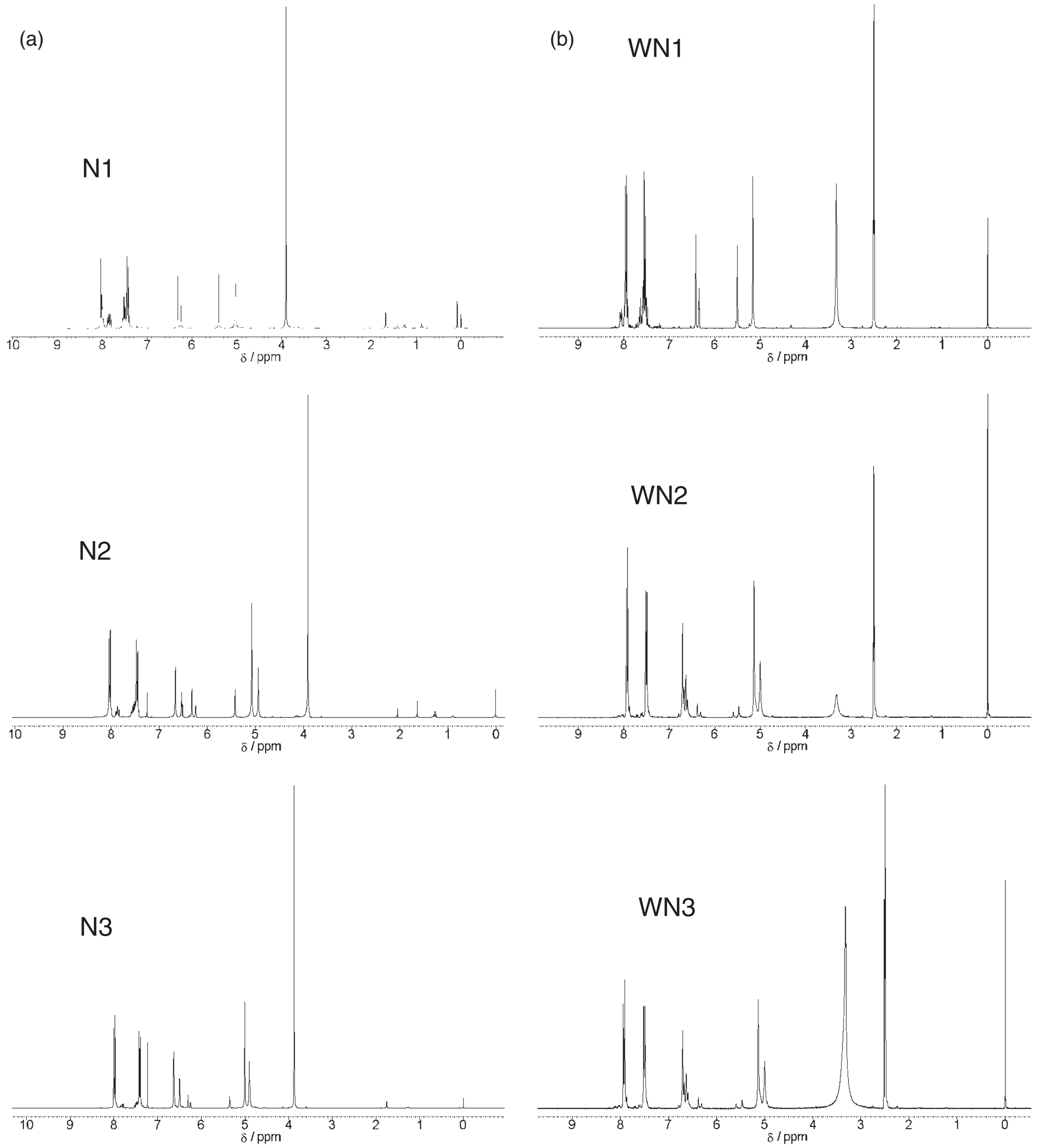


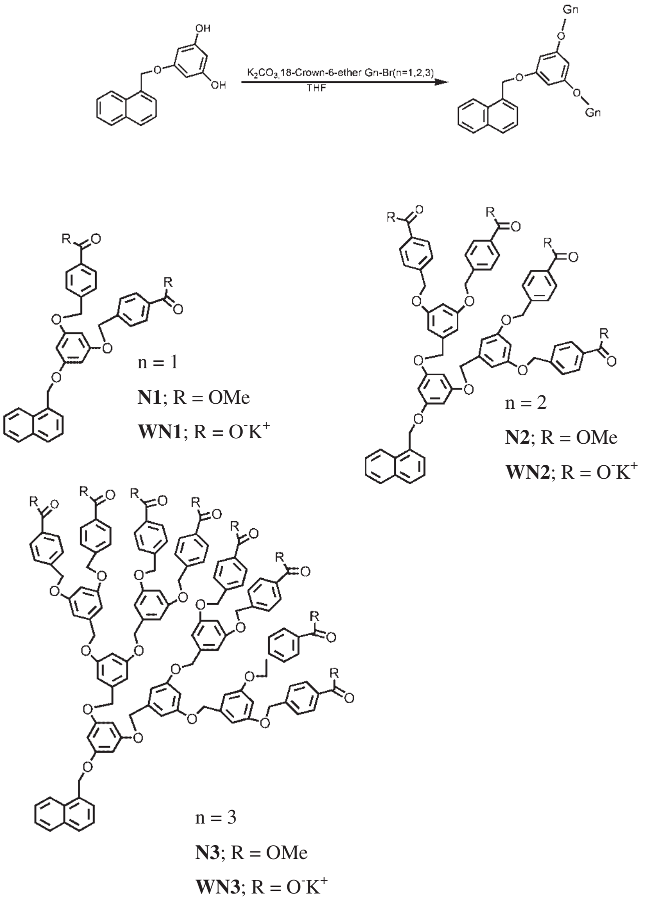
Figure 8. ^{1}H NMR spectra of (a) N**1**, N**2**, and N**3** in $CDCl_3$ and (b) WN**1**, WN**2**, and WN**3** in DMSO-d_6.

stirred at room temperature for 30 min. Then, fully protonated product at the peripheral carboxylate group was precipitated and was collected by suction filtration and was dried to give the acid form (226 mg, 88.6%).

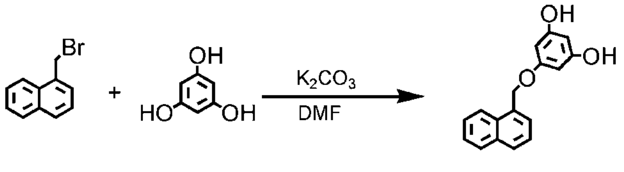
Mp: 58–60 °C; ^{1}H NMR (270 MHz, DMSO-d_6): δ 5.16 (s, 4H, den–Ar–CH_2), 5.50 (s, 2H, Ar–CH_2), 6.31–6.36 (m, 1H, Phl–H), 6.41 (d, $J = 1.9$ Hz, 2H, Phl–H), 7.52–7.66 (m, 8H, Nap + den–ArH), 7.93–8.01 (m, 7H, Nap + den–ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.30, 69.13, 95.31, 95.34, 124.23, 125.71, 126.30, 126.79, 127.00, 127.72, 128.84, 129.04, 129.87, 130.56, 131.49, 132.74, 133.63, 142.38, 160.44, 160.73, 167.53; MALDI-TOF-MS (m/z) calcd for $C_{33}H_{26}O_7Na$ $[M + Na]^+ = 557.06$; found, 557.67.

WN2: To the solution of N**2** (180 mg, 0.163 mmol) in tetrahydrofuran (10 mL) was added 1 M KOH aqueous solution (4 mL). Methanol (3 mL) was then added to this two-phase system to give a homogeneous solution and the solution was heated at reflux for 12 h during which time precipitates formed. The reaction mixture was then evaporated to dryness and the residue was dissolved in water. In order to continue the hydrolysis the solution was heated at reflux for another 12 h. After cooling to room temperature, the mixture was stirred at room temperature for 30 min. Then, fully protonated product at the peripheral carboxylate group was precipitated and was collected by suction filtration and was dried to give the acid form (152 mg, 89.4%).

Mp: 54–56 °C; ^{1}H NMR (270 MHz, DMSO-d_6): δ 5.00 (s, 4H, den–Ar–CH_2), 5.17 (s, 8H, den–Ar–CH_2), 5.49 (s, 2H, Ar–CH_2), 6.27 (t, $J = 2.2$ Hz, 1H, Phl–H), 6.37 (d, $J = 2.2$ Hz, 2H, Phl–H), 6.51 (t, $J = 2.2$ Hz, 2H, den–ArH), 6.71 (d, $J = 2.2$ Hz, 4H, den–



Scheme 1. Synthesis of dendrimer.



Scheme 2. Synthesis of core.

ArH), 7.47–7.66 (m, 12H, Nap + den–ArH), 7.93–8.07 (m, 11H, Nap + den–ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.79, 69.13, 94.94, 101.22, 106.67, 125.33, 125.91, 126.39, 126.64, 127.27, 127.35, 128.44, 128.65, 129.34, 129.41, 129.45, 130.21, 130.24, 131.13, 133.27, 139.60, 141.92, 159.42, 160.28, 167.05, 167.08; MALDI-TOF-MS (*m*/*z*) calcd for $C_{63}H_{50}O_{15}Na$ $[M + Na]^+ = 1069.29$; found, 1070.23.

WN3: To a solution of N**3** (120 mg, 0.0549 mmol) in tetrahydrofuran (7 mL) was added 1 M KOH aqueous solution (2 mL). Methanol (2 mL) was then added to this two-phase system to give a homogeneous solution and the solution was heated at reflux for 10 h during which time precipitates formed. The reaction mixture was then evaporated to dryness and the residue was dissolved in water. In order to continue the hydrolysis the solution was heated at reflux for another 12 h. After cooling to room temperature, the mixture was stirred at room temperature for 30 min. Then, fully protonated product at the peripheral carboxylate group was precipitated and was collected by suction filtration and was dried to give the acid form (91.0 mg, 80.0%).

Mp: 80–83 °C; ^{1}H NMR (270 MHz, DMSO-d_6): δ 4.88–4.90 (m, 12H, den–Ar–CH_2), 5.00 (s, 16H, den–Ar–CH_2), 5.35 (s, 2H, Ar–CH_2), 6.25 (t, $J = 2.2$ Hz, 1H, Phl–H), 6.29 (d, $J = 2.2$ Hz, 2H, Phl–H), 6.52 (t, $J = 2.2$ Hz, 6H, den–ArH), 6.67 (d, $J = 2.2$ Hz, 12H, den–ArH), 7.34–7.57 (m, 20H, Nap + den–ArH), 7.82–8.04 (m, 19H, Nap + den–ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.77, 69.16, 94.90, 101.23, 106.56, 106.69, 125.39, 125.97, 126.10, 126.35, 127.45, 127.40, 128.48, 129.50, 130.85, 131.14, 132.42, 133.24, 133.28, 139.48, 139.54, 141.96, 155.96, 156.07, 159.23, 159.42, 159.50, 159.55, 160.17, 160.29, 167.14; MALDI-TOF-MS (*m*/*z*) calcd for $C_{123}H_{98}O_{31}Na$ $[M + Na]^+ = 2093.59$; found, 2095.23.

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