Synthesis and Photophysical Properties of Poly(ester−amine) Dendrimers with Focal 4-Amino-*N*-benzylphthalimide, as Sensitive Media Probes and Switchable Proton Sensors

Daxin Shi, Yaowu Sha,* Feng Wang, and Qingyong Tian

The Key Laboratory of Bioorganic Phosphorous Chemistry and Chemical Biology, Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, P.R. China

Received April 14, 2008; Revised Manuscript Received August 9, 2008

ABSTRACT: Synthesis and photophysical properties of different generations of poly(ester−amine) dendrimers with focal 4-amino-*N*-benzylphthalimide (4-ANBP) as the core were studied. The $\lambda_{max}{}^{abs}$ of dendronized 4-ANBP was nonsensitive to the solvents used and located at 334 nm, while that of bare 4-ANBP was very sensitive. The fluorescence behaviors of dendronized 4-ANBPs showed much dependence on the generation of the dendrimers used and the media. As compared with bare 4-ANBP, the fluorescence intensity of **3** (G1.0), **5** (G2.0), **7** (G3.0), and **9** (G4.0) in methanol was reduced to 6.2-, 26-, 50-, and 56.5-fold, respectively, and had a 83 nm blue shift. The corresponding fluorescence quantum yields were also measured (4-ANBP-0.12, **3**-0.017, **5**-0.0042, **7**-0.0028, **9**-0.0016). Addition of sulfuric acid to the methanol solution of **9** (3.27×10^{-5} M/L), resulted in a strong fluorescence, and the fluorescence intensity was amplified 181 times. Acid titration experiments showed that all of the tertiary amines in **3**, **5**, and **7** were protonated, but only 12 in 15 of the tertiary amines in G4.0∂9 were protonated. Repeated acid−base titrations caused the fluorescence to switch on and off. After many cycles of acid−base titration, slight changes in fluorescence intensity were observed.

1. Introduction

Acidity plays significant roles in numerous chemical and biological processes.[1] There is also a close dependence between the pH values of natural water and the kinds of animals and plants living within.[2] Thus, research in pH sensing is attracting more and more attention in recent years.[3] Among the recommended none-invasive approaches of pH detection, fluorescent techniques have been extensively employed due to the great sensitivity and high spatial resolution they provide. It is still necessary to develop new sensors with higher sensitivity. Much efforts have been made in recent yeas to discover new fluorophores and improve the properties of well-known ones.[4] Fluorophore dendrimerization is one of the new, unique approaches designed for this purpose.

Dendrimers[5] are regularly branched macromolecules with precious structures. Functional groups can be site-specific positioned in the core, in the branches, and on the surface[6] for use as light-harvesters,[7] nanoscale containers,[8] and sensors.[9] A few dendrimers have also been designed as pH-sensors.[10] However, no exciting results with respect to sensitivity have been found for fluorophores and dendritic structures.

4-Aminophthalimide is a polarity probe.[11] However, its poor solubility in common solvents and simplicity of structure have limited its otherwise wider application. Poly(ester−amine) dendrimer (PESAM), first designed in our group,[12] is a new type of structure whose potentials still need to be revealed. The dendritic structure can improve the solubility and affect on the photophysical properties of focal fluorophore. There are some tertiary amines in the dendritic branch which can be protonated and then give effects on the original photophysical properties. Therefore we designed PESAM with 4-amino-*N*-benzylphthalimide (4-ANBP) at the focal point as potential switchable fluorescent proton sensors.

* Corresponding author: E-mail: shayw@tsinghua.edu.cn. Telephone: +86-10-6279-5866. Fax: +86-10-6279-5866.

2. Results and Discussion

2.1. Synthesis of Dendrimers. Scheme 1 shows the synthesis of the designed dendrons. First, 4-ANBP 1 was acrylated using 1.1 equiv of acrylic chloride and 1.1 equiv of Et_3N. The crude product was washed with diluted $NaHCO_3$ and brine to yield **2** (G0.5-acrylate), 85%) as a yellow powder. The Michael reaction of **2** with diethanolamine was carried out with 3-fold excess of diethanolamine in methanol, followed by the recrystallization of the crude product from acetone to yield **3** (G1.0-$(OH)_2$, 83%) as a yellow powder. A further acrylation reaction of **3** with acrylic chloride proceeded in dry $CHCl_3$ to give **4** (G1.5-$(acrylate)_2$) as a yellow powder with a yield of 93% after column chromatography (silica gel). The G2.0-$(OH)_4$, **5**, was prepared by reaction of 2.2 equiv of diethanolamine with **4** in THF, and then the residual diethanolamine was removed by extraction with saturated brine (82% yield). Likewise, G2.5-$(acrylate)_4$, **6**, was obtained in 94% yield through esterification of **5** with 4.4 equiv of acrylic chloride in dry chloroform. G3.0-$(OH)_8$, **7**, was obtained in 80% yield by the Michael addition of **6** with 4.4 equiv of diethanolamine in THF. Reiteration of the esterification with **7** produced G3.5-$(acrylate)_8$ (dendrimer 8, 65% yield). G4.0-$(OH)_{16}$, **9**, was obtained in 73% yield by the Michael addition of **8** with 8.8 equiv of diethanolamine in THF, with the excessive diethanolamine being removed by washing with brine. All structures were confirmed by ESI−MS, ^1H NMR, ^{13}C NMR and elemental analysis. These dendrimers were readily soluble in common solvents.

2.2. UV−Vis Absorption Properties. The UV and fluorescence spectral data of the dendrimers with hydroxyl terminals and bare 4-ANBP are collected in Table 1. In Figure 1 were shown the UV spectra of bare 4-ANBP and the dendrimers derived from it. The position of the UV absorption maximum of bare 4-ANBP exhibits high sensitivity toward solvents used. The spectrum as a whole does not change, only a shift in the characteristic maximum occurs. The $\lambda_{max}{}^{abs}$ of bare 4-ANBP was at 380nm in methanol, 369nm in THF and 361 nm in chloroform. In contrast, the $\lambda_{max}{}^{abs}$ of the dendronized 4-ANBPs

10.1021/ma8008228 CCC: $40.75
Published on Web 09/24/2008

Scheme 1. Synthesis of Poly(ester−amine) Dendronized 4-Amino-*N*-benzylphthalimide

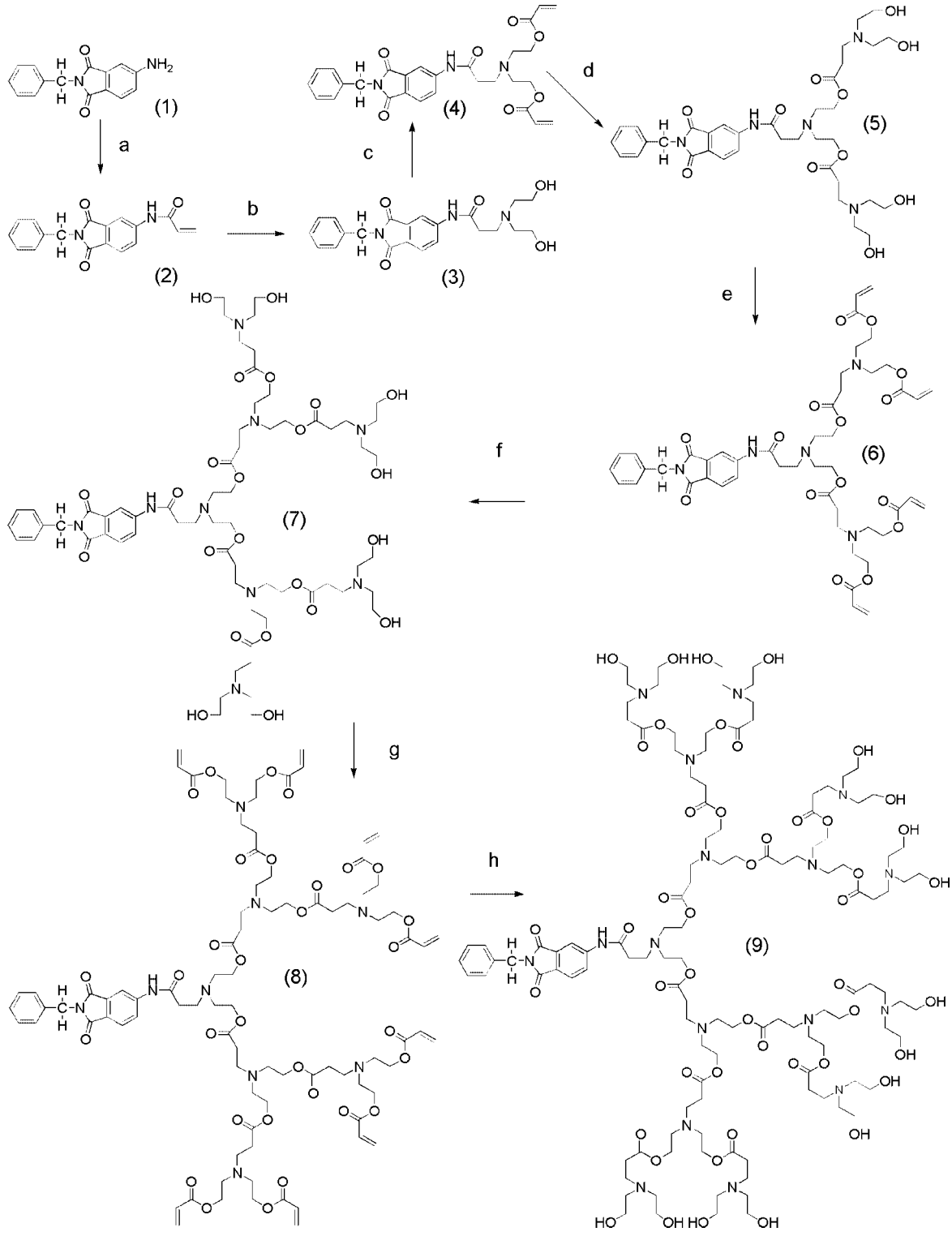

Table 1. Photophysical Properties of 4-ANBP and Dendrimers G1.0−G4.0 (3, 5, 7, 9)

	chloroform $\varepsilon = 4.8$				THF $\varepsilon = 7.52$			methanol $\varepsilon = 33.0$		
compd	λ_{max}^{abs} (nm)	λ_{max}^{flu} (nm)	ϕ_f	τ_f/ns	λ_{max}^{abs}(nm)	λ_{max}^{flu}(nm)	ϕ_f	λ_{max}^{abs}(nm)	λ_{max}^{flu}(nm)	ϕ_f
ANBP	361	490	0.46	12.3	369	466	0.69	380	525	0.12
G1.0-**3**	329	422	0.32	9.8	333	409	0.11	334	445	0.017
G2.0-**5**	329	422	0.30	8.5	334	409	0.074	334	443	0.0042
G3.0-**7**	334	426	0.21	4.4 (31%) 3.9 (69%)	334	415	0.070	334	441	0.0028
G4.0-**9**	334	427	0.19	1.1 (21%) 9.7 (79%)	334	412	0.041	334	442	0.0016

were nonsensitive to the changes of solvent and remained at 334 nm for all three solvents.

In methanol (Figure 1a), the UV-spectral patterns of these dendrimers are very similar to each other and there is little

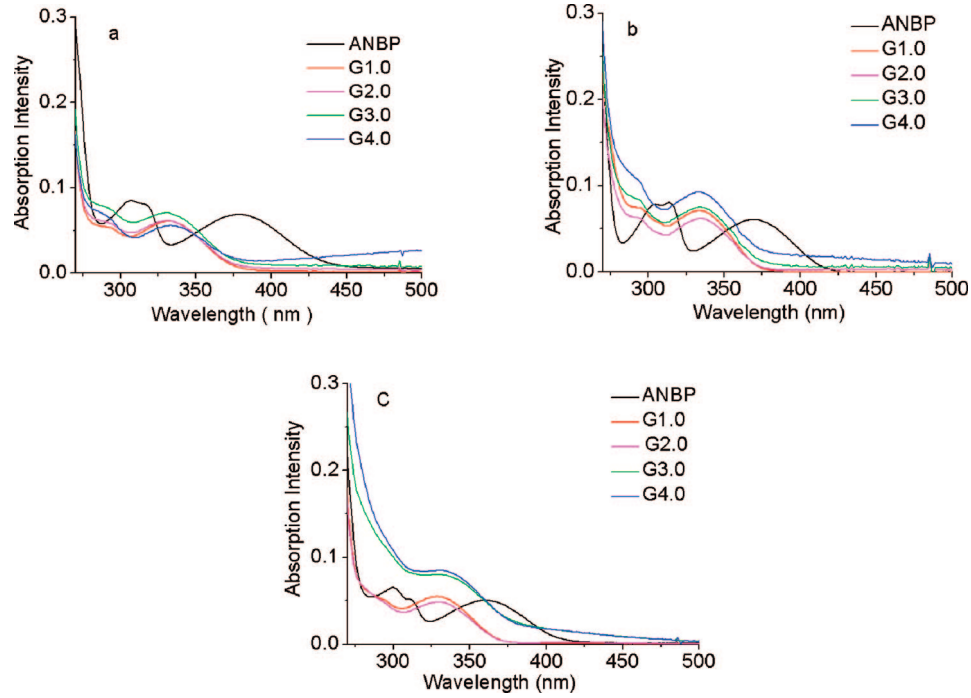

Figure 1. Absorption spectra of 1×10^{-5} mol/L G1.0-**3**, G2.0-**5**, G3.0-**7**, and G4.0-**9** in methanol (a), THF (b) and chloroform (c).

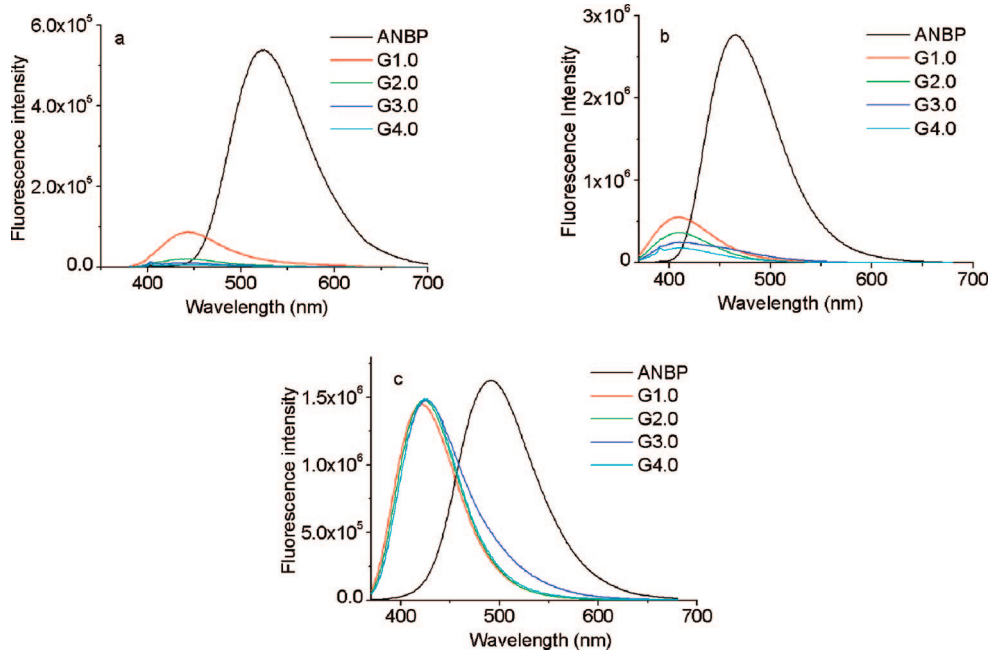

Figure 2. Fluorescent spectra of 1×10^{-5} mol/L G1.0, G2.0, G3.0, G4.0 in methanol (a), THF (b), and chloroform (c).

change in the maximum absorption wavelength (around 334nm) for dendrimers **3** (G1.0), **5** (G2.0), **7** (G3.0), and **9** (G4.0). Their UV absorption intensities are also close. When dissolved in THF (Figure 1b), the absorption patterns of dendronized 4-ANBPs did not change as much as they did for 4-ANBP, but the absorption intensities increased in the order of G4.0 > G3.0 > G.2.0. Interesting UV absorption patterns were observed for the chloroform solutions of these dendrimers (Figure 1c). The UV absorptions of **3** and **5** were almost the same, and likewise, so were the absorptions for **7** and **9**.

Chloroform must have special actions with the chromophore and dendritic branches. The chromophore is sensitive to polarity. The higher generation dendritic branches can more efficiently prevent the freely access of chromophore by solvents and encapside more solvent molecules by the time. These factors together will change the chromophore energy gap between excited-state and ground state. So that the solvent and dendrimer generation related UV absorption properties were observed.

2.3. Fluorescence Emission Properties. The fluorescence emissions were more sensitive to the poly(ester−amine) dendritic architecture than the UV absorptions, as shown in Figure 2. In methanol, 4-ANBP showed a broad emission peak at 525 nm with $\lambda_{ex} = 380$ nm (Figure 2a). Attachment of the dendritic poly(ester−amine) architecture resulted in a dramatic decrease (6.2-fold-**3**, 26-fold-**5**, 50-fold-**7**, and 56.5-fold-**9**, respectively) in fluorescence intensity, and the shifts were from 525 to 442 nm (83 nm blue shift). The corresponding quantum yields (ϕ_f

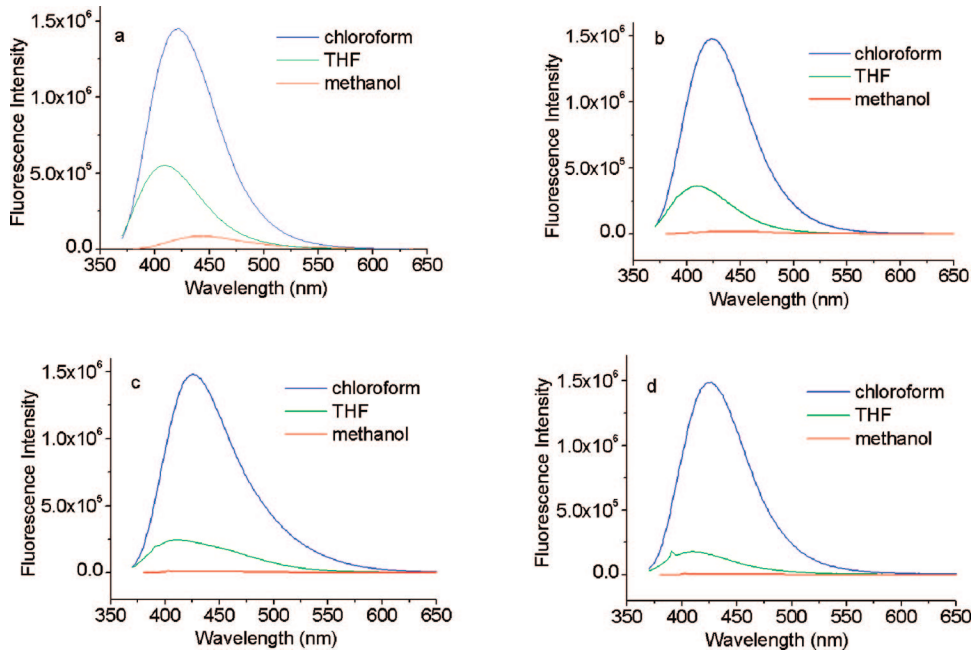

Figure 3. Fluorescence spectra of 1×10^{-5} mol/L G1.0-**3** (a), G2.0-**5** (b), G3.0-**7** (c), G4.0-**9** (d) in chloroform, THF, and methanol.

in methanol) were 0.017-**3**, 0.0042-**5**, 0.0028-**7**, 0.0016-**9**, which indicated a strong interaction between fluorophore 4-ANBP and the dendritic poly(ester−amine) architecture.

In THF, the maximum fluorescence emission of 4-ANBP was at 466 nm while that for the four dendrimers with hydroxyl terminals occurred at about 410 nm (Figure 2b). In addition, attachment of dendritic branch resulted in 5-fold-**3**, 7.5-fold-**5**, 11.1-fold-**7** and 15.5-fold-**9** decrease in the fluorescence intensity.

In chloroform (Figure 2c), the maximum emissions of the four dendrimers with hydroxyl terminals were all located at about 425 nm, which were blue-shifted by 65 nm as compared with bare 4-NBAP at 490 nm. The attachment of dendritic branches brought about only a 10% decrease in the intensity of luminescence, and there was almost no intensity difference among the dendrimers. Although their quantum yields decreased regularly, the differences were slight (ANBP-0.46, **3**-0.32, **5**-0.30, **7**-0.21, **9**-0.19). These results hinted that chloroform has obstructed the interactions between the dendritic poly(ester−amine) architecture and 4-ANBP, and that the original properties of bare ANBP were retained.

In order to get clearer insight into the effect of solvents on the fluorescence of different generations of dendrimer, the fluorescence behavior of each generation dendrimer was measured and shown in Figure 3. It is evident that as the dielectric constant of the medium ($\varepsilon = 4.8$ for chloroform, $\varepsilon = 7.52$ for THF and $\varepsilon = 33.0$ for methanol) increases, the fluorescence intensities decreased remarkably. For dendrimer **3**, the fluorescence intensities in THF and chloroform were 6.4 times and 16.7 times as large as those in methanol, respectively; For dendrimer **5**, these intensities were 17.6 times and 71.3 times greater; For dendrimer **7**, these intensities were 22.9 times and 136.7 times greater, and for dendrimer **9**, these intensities were 24.3 times and 156.0 times greater. There was an obvious trend that as the dendrimer generation and solvent polarity increased, the fluorescence intensity decreased dramatically. It is most likely that two simultaneous and overlapping processes occur in the system: the interaction of the dendritic shell, which expands or collapses with the change in the surrounding medium, and the solvation of the chromophore by the solvents of different polarity.

2.4. Proton Sensing Properties. Many papers revealed that fluorophores with amine groups as "receptors" are potential proton sensors.[13] Thus, we were motivated to investigate the proton sensing behavior of these dendrimers with focal 4-ANBP. Figure 4 shows the luminance changes of dendrimers on the addition of sulfuric acid. The increasing addition of protons caused the fluorescence intensities of the **3**, **5**, **7**, and **9** dendrimers to increase. In order to get a greater insight into the actions between the dendrimers and the added proton ions, quantitative relations between the intensity ratios I/I_o (I, observed emission intensity; I_o, the intensity without any addition of proton in the media.) via proton equivalents added were assessed by spectrophotometric titration. By addition of proton ions, the fluorescence intensities became 7.3, 12.6, 24.1 and even 181 times stronger for dendrimers **3**, **5**, **7**, and **9**, respectively, than their originals. Through the titration experiments, we found that all tertiary amines in dendrimers **3**, **5**, and **7** were protonated, but only 12 of the 15 tertiary amines in dendrimer **9** were protonated. The number 12 just corresponded to the sum of tertiary amines in the two outer shells. The three tertiary amines in the interior shells of 1 and 2 should remain free. This interesting result could be attributed to the strong state-electric field of protonated amines, in accordance with the reported solvation dynamics studies and titration of PMAM dendrimers.[14]

At higher H^+ concentration, the OH groups could also be protonated to form oxonium ions. However it prefers more, for OH group, to form hydrogen bond than form oxonium ions. At least, the concentration of oxonium ions and their effects on fluorescence intensity were not in the comparable scale as ammonium ions did.

The fluorescence intensity increasment caused by protonation indicated that the tertiary amines played important roles in the fluorescence quenching. When the acidified solution was neutralized with sodium hydroxide, the fluorescence became invisible. When treated with acid again, the strong fluorescence recovered. Repeated acid−base titration caused the fluorescence to switch on and off. After many cycles of acid−base titration, slight changes in fluorescence intensity were observed. The protonation and deprotonation of tertiary amines can switch the fluorescence emission on and off. Therefore, poly(ester−amine)

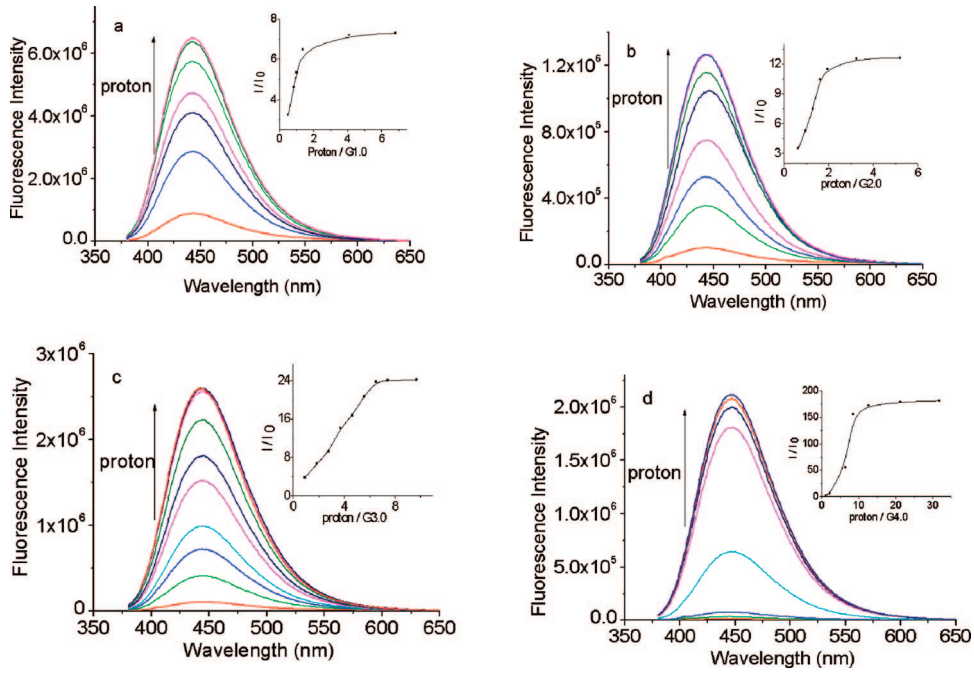

Figure 4. Luminescence spectra of G1.0 (8.16×10^{-5} mol/L (a)), G2.0 (4.28×10^{-5} mol/L (b)), G3.0 (3.72×10^{-5} mol/L (c)), and G4.0 (3.27×10^{-5} mol/L (d)) by titration with sulfuric acid.

dendrimers with focal 4-ANBP, especially higher generations, are highly sensitive and switchable fluorescent proton sensors.

3. Experimental Section

3.1. Materials. 4-ANBP was synthesized by literature methods. Other reagents were purchased from Alfa Aesar, TCI, or Aldrich and used without further purification. Chloroform was dried with anhydrous Na_2SO_4 and distilled. Tetrahydrofuran was distilled over sodium under N_2. Methanol was distilled before used. Spectral-grade $CHCl_3$, THF, and methanol were used for UV−vis absorption and fluorescence spectroscopy measurements.

3.2. Instruments. ^{1}H NMR and ^{13}C NMR spectra were recorded as solutions in $CDCl_3$ or DMSO-d_6 on a JEOL JNM ECA-300 (300 MHz) spectrometer with TMS as the internal standard. IR spectra were recorded with a Nicolet AVATAR-360 FT-IR spectrometer with KBr pellets or film on KBr plates. ESI−MS were recorded with a Perkin-Elmer ESQUIRE in the positive ion mode.

UV−vis absorption spectra were recorded with a Perkin-Elmer spectrophotometer. Fluorescence spectra were obtained with a Perkin-Elmer spectrofluorimeter. Fluorescence quantum yields were measured following the methods of Demas and Crosby (standard used: 4-aminephthalimide in THF ($\Phi = 0.70$)). Fluorescence lifetimes were measured by time-correlated single-photon counting (0.1 ns time resolution) with an Edinburgh Instruments (D_2 lamp, $\lambda_{exc} = 330$ nm), and a spectrofluorimeter FLUOROLOG equipped with a phase-shift Tau 3 unit capable of measuring luminescence lifetimes with a 10 ps time resolution.

The titrations of dendrimers with H_2SO_4 in methanol were performed in a quartz cell with a Perkin-Elmer spectrofluorimeter. The solutions were excited at 334 nm and the emission spectra were recorded over the range of 375–650 nm. Slits with nominal band-pass of 4 nm were used for both excitation and emission beam. The emission spectra were recorded at 25 °C by incremental addition of concentrated H_2SO_4 to dendrimers at the concentrations of 8.16×10^{-5}mol/L (G1.0), 4.28×10^{-5} mol/L (G2.0), 3.72×10^{-5} mol/L (G3.0), and 3.27×10^{-5} mol/L (G4.0). After each addition, the system was allowed to equilibrate for 10 min, and then the emission spectrum was recorded. The fluorescence intensity was measured as a function of the H^+/dendrimer ratio. Fluorescence intensities were corrected for the contribution of light scattering by subtraction of the appropriate vesicle blank.

The experimental results showed that the dendrimers (G ≥ 3.0) have good solubility in most common organic solvents, such as CH_3OH, CH_2Cl_2, $CHCl_3$, THF, CH_3CN, and EtOAc. The G0.5−G2.5 dendrimers are readily soluble in aprotic polar solutions, such as $CHCl_3$, THF, CH_3CN, and EtOAc, but exhibit poor solubility in protic solvents and nonpolar solvents, for example, petroleum ether, methanol, and ethanol.

3.3. Syntheses. *Synthesis of G0.5-(acrylate),* **2**. Acrylic chloride (1.98 g, 22.0 mmol) in dry $CHCl_3$ (10 mL) was added dropwise to a solution of **4-ANBP 1** (5.04 g, 20.0 mmol) and triethylamine (2.22 g, 22.0 mmol) in dry $CHCl_3$ (50 mL) at 0−5 °C under nitrogen. The mixture was then stirred for 30 min at 0−5 °C and 90 min at 20 °C and washed with diluted $NaHCO_3$ (3%, 3 × 30 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4. The filtrate was evaporated under vacuum, and the residue was recrystallized from methanol to give a yellow powder (85% yield). IR (KBr): 3338, 3075, 1701, 1684 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 1H, aryl-H), 7.97 (d, 1H, aryl-H, $J = 6.3$ Hz), 7.82 (d, 1H, aryl-H, $J = 6.3$ Hz), 7.55 (s, 1H, CONHAr), 7.40 (d, 2H, aryl-H, $J = 6.0$ Hz), 7.20−7.35)m, 3H, aryl-H, $J = 6.0$ Hz), 6.50 (d, 1H, =CH_2, $J = 16.8$ Hz), 6.26 (dd, 1H, =CH−, $J = 16.8$, $J' = 7.2$ Hz), 5.87 (d, 1H, =CH_2, $J = 10.2$ Hz), 4.83 (s, 2H, =N−CH_2−Ar). ^{13}C NMR (75 MHz, DMSO): δ 168.0, 167.8, 164.4, 144.9, 137.1, 133.5, 131.5, 129.2, 129.1, 127.97, 127.8, 126.0, 125.0, 124.1, 113.6, 41.6. ESI−MS: calcd for (M + H)/z, 307; found, m/z 307 (M + H$^+$), 329 (M + Na$^+$), 345 (M + K$^+$).

Synthesis of G1.0-(OH)$_2$, **3**. Diethanolamine (1.72 g, 16.4 mmol) was added to a solution of G0.5-(acrylate), **2** (1.26 g, 4.1 mmol), in methanol (10 mL) and THF (20 mL) at 5 °C. After being stirred at 15 °C for 24 h, the mixture was evaporated and partitioned between chloroform and water. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was dried and evaporated. The crude product was purified by recrystallization from acetone to give a yellow powder (83% yield). IR (KBr): 3390, 3035, 2830, 1707 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.29 (s, 1H, CONHAr), 8.02 (m, 2H, aryl-H), 7.67 (d, 1H, aryl-H, $J = 9.0$ Hz), 7.40 ((d, 1H, aryl-H, $J = 7.2$ Hz), 7.20−7.33 (m, 3H, aryl-H, $J = 6.3$ Hz), 4.79 (s, 2H, =N−CH_2−Ar), 3.76 (t, 4H, −CH_2CH_2OH, $J = 4.8$ Hz), 3.37 (br, 2H, −OH), 2.94 (t, 2H, =N−CH_2CH_2CO, $J = 6.0$ Hz), 2.77 (4H, HOCH_2CH_2N−, $J = 4.8$ Hz), 2.59 (t, 2H, −N−CH_2CH_2CONH−Ar, $J = 6.0$ Hz), ^{13}C NMR (75 MHz, DMSO): δ 172.0, 168.1, 167.9, 145.1, 137.2, 133.4, 129.1, 127.9, 127.8, 125.5, 124.9, 123.9, 113.4, 59.1, 56.3, 50.8,

41.3, 34.7. ESI−MS: calcd for (M + H)/*z*, 412; found, *m*/*z* 412 (M + H$^+$), 434 (M + Na$^+$), 450 (M + K$^+$).

Synthesis of G1.5-(acrylate)$_2$, **4**. Acrylic chloride (1.74 g, 19.2 mmol) in dry $CHCl_3$ (15 mL) was added dropwise to a solution of G1.0-(OH)$_2$, **3** (3.65 g, 9.0 mmol) and triethylamine (1.80 g, 22.0 mmol) in dry $CHCl_3$ (40 mL) at 0 °C under nitrogen. The solution was then stirred for 30 min at 0 °C and 90 min at 10 °C. After washing with diluted $NaHCO_3$ (3%, 3 × 30 mL) and brine (30 mL), the organic layer was dried over Na_2SO_4, and filtered. The filtrate was evaporated under vacuum, and the residue was purified by silica gel column chromatography (ethyl acetate:petroleum ether = 1:1). The product was obtained as a yellow power (93% yield). IR (KBr): 3331, 3030, 2956, 2851, 1724, 1704 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.57 (s, 1H, CONHAr), 8.00 (s, 1H, aryl-H), 7.82 (d, 1H, aryl-H, J = 8.1 Hz), 7.70 (d, 1H, aryl-H, J = 8.1 Hz), 7.40 (d, 2H, aryl-H, J = 7.5 Hz), 7.20−7.35 (m, 3H, aryl-H, J = 7.5 Hz), 6.33 (d, 2H, =CH$_2$, J = 17.1 Hz), 6.02 (dd, 2H, =CH−, J = 17.1, J' = 10.2 Hz), 5.74 (d, 2H, =CH$_2$, J = 10.2 Hz), 4.81 (s, 2H, =N−CH$_2$−Ar), 4.34 (t, 4H, CH$_2$=CHCOO*CH$_2$*-, J = 4.8 Hz), 2.98 (m, 6H, CH$_2$=CHCOOCH$_2$*CH$_2$*N− + =N−*CH$_2$*CH$_2$CO), 2.57 (t, 2H, −N−CH$_2$*CH$_2$*CO−NH−Ar, J = 5.4 Hz). ^{13}C NMR (75 MHz, DMSO): δ 171.7, 168.0, 167.3, 166.0, 145.1, 137.2, 133.5, 131.9, 129.1, 128.6, 127.9, 127.8, 125.5, 124.9, 123.7, 113.3, 62.8, 52.4, 50.6, 41.6, 35.1. ESI−MS: calcd for (M + H)/*z*, 520; found, *m*/*z* 520 (M + H$^+$), 542 (M + Na$^+$), 558 (M + K$^+$).

Synthesis of G2.0-(OH)$_4$, **5**. Diethanolamine (1.28 g, 12.2 mmol) was added to a solution of G1.5-(acrylate)$_2$, **4** (2.67 g, 5.1 mmol), in dry THF (30 mL) at 0 °C. The mixture was stirred at 10 °C for 4 days. Then, the mixture was evaporated and partitioned between chloroform and water. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was dried and evaporated. The crude product was purified by silica gel column chromatography(ethyl acetate:methanol = 4:1). The product was obtained as a yellow oil (82% yield); IR (KBr): 3359, 3029, 2952, 2833, 1708 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.40 (s, 1H, CONHAr), 8.05 (d, 1H, aryl-H, J = 8.1 Hz), 7.96 (s, 1H, aryl-H), 7.77 (d, 1H, aryl-H, J = 8.1 Hz), 7.40 (d, 2H, aryl-H, J = 7.2 Hz), 7.15−7.33 (m, 3H, aryl-H, J = 7.2 Hz), 4.80 (s, 2H, =N−CH$_2$−Ar), 4.22 (t, 4H, −CH$_2$COO*CH$_2$*−, J = 5.1 Hz), 3.56 (t, 8H, −CH$_2$*CH$_2$*OH, J = 5.1 Hz), 3.25 (br, 4H, −OH), 2.91 (t, 2H, =N−*CH$_2$*CH$_2$-CONH−Ar, J = 6.0 Hz), 2.84 (t, 4H, =N−*CH$_2$*CH$_2$COO, J = 6.0 Hz), 2.75 (t, 4H, =N−*CH$_2$*CH$_2$COO, J = 6.0 Hz), 2.56 (t, 10H, −N−*CH$_2$*CH$_2$OH + =N−CH$_2$*CH$_2$*CONH−Ar, J = 5.1 Hz), 2.44 (t, 4H, =N−CH$_2$*CH$_2$*COO, J = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 171.1, 168.1, 168.0, 144.3, 136.5, 133.5, 128.7, 128.6, 127.8, 126.4, 125.8, 125.3, 124.6, 123.9, 114.1, 62.2, 59.3, 56.2, 53.0, 51.2, 49.6, 41.6, 35.0, 32.8. ESI−MS: calcd for (M + H)/*z*, 730; found, *m*/*z* 730 (M + H$^+$), 752 (M + Na$^+$), 768 (M + K$^+$).

Synthesis of G2.5-(acrylate)$_4$, **6**. Acrylic chloride (0.95 g, 10.0 mmol) in dry $CHCl_3$ (10 mL) was added dropwise to a solution of G2.0-(OH)$_4$, **5** (1.56 g, 2.1 mmol), and triethylamine (1.05 g, 10.0 mmol) in dry $CHCl_3$ (30 mL) at 0 °C under nitrogen. The solution was stirred at 0 °C for 30 min and then at 25 °C for 90 min. After being washed with diluted $NaHCO_3$ (3%, 3 × 30 mL) and brine (30 mL), the organic layer was dried over Na_2SO_4, and filtered. The filtrate was evaporated under vacuum, and the residue was purified by silica gel column chromatography (ethyl acetate). A yellow oil was obtained (94% yield); IR (KBr): 3346, 3034, 2959, 2836, 1720 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.48 (s, 1H, CONHAr), 7.96 (m, 2H, aryl-H), 7.74 (d, 1H, aryl-H, J = 8.4 Hz), 7.38 (d, 2H, aryl-H, J = 6.9 Hz), 7.20−7.33 (m, 3H, aryl-H, J = 6.9 Hz), 6.31 (d, 4H, =CH$_2$, J = 17.1 Hz), 6.07 (dd, 4H, =CH-, J = 17.1, J'= 10.2 Hz), 5.80 (d, 4H, =CH$_2$, J = 10.2 Hz), 4.78 (s, 2H, =N−CH$_2$−Ar), 4.20 (t, 4H, −CH$_2$CH$_2$COO*CH$_2$*CH$_2$-, J = 5.4 Hz), 4.11 (t, 8H, CH$_2$=CHCOO*CH$_2$*−, J = 6.0 Hz), 2.90 (m, 6H, =N−*CH$_2$*CH$_2$CO), 2.80 (t, 4H, −CH$_2$CH$_2$COOCH$_2$*CH$_2$*N−, J = 6.9 Hz), 2.72 (t, 8H, CH$_2$=CHCOOCH$_2$*CH$_2$*N−, J = 6.0 Hz), 2.55 (t, 2H, −N−CH$_2$*CH$_2$*CO−NH−Ar, J = 5.4 Hz), 2.34 (t, 4H, −CH$_2$*CH$_2$*COOCH$_2$CH$_2$−, J = 6.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 171.0, 167.6, 166.1, 144.1, 136.5, 133.7, 131.0, 128.7, 128.6, 128.3, 127.8, 126.4, 124.6, 123.7, 114.0, 62.6, 61.7, 52.7, 52.5, 51.0, 50.4, 41.6, 34.2, 33.1. ESI−MS: calcd for (M + H)/*z*, 947; found, *m*/*z* 947 (M + H$^+$), 969 (M + Na$^+$).

Synthesis of G3.0-(OH)$_8$, **7**. Diethanolamine (1.05 g, 10.0 mmol) was added to a solution of G2.5-(acrylate)$_4$, **6** (1.96 g, 2.1 mmol), in dry THF (45 mL) at 0 °C. The mixture was then stirred at 10 °C for 7 days. The reaction was monitored by ESI−MS. The mixture was evaporated and partitioned between chloroform and water. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was dried and evaporated. The crude product was purified by silica gel column chromatography (methanol) to yield a yellow oil (80% yield). IR (KBr): 3411, 2953, 2838, 1731 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.55 (s, 1H, CONHAr), 7.98 (m, 2H, aryl-H), 7.76 (d, 1H, aryl-H, J = 8.1 Hz), 7.40 (d, 2H, aryl-H, J = 7.5 Hz), 7.15−7.33 (m, 3H, aryl-H, J = 7.5 Hz), 4.79 (s, 2H, =N−CH$_2$−Ar), 4.20 (t, 4H, −CH$_2$CH$_2$COO*CH$_2$*-, J = 4.8 Hz), 4.05 (t, 8H, −CH$_2$CH$_2$COO*CH$_2$*−, J = 6.0 Hz), 3.57 (t, 16H, −CH$_2$*CH$_2$*OH, J = 5.1 Hz), 3.38 (br, 8H, −OH), 2.98 (t, 2H, =N−*CH$_2$*CH$_2$CONH−Ar, J = 6.0 Hz), 2.89 (t, 4H, =N−*CH$_2$*CH$_2$COO, J = 6.0 Hz), 2.80 (m, 12H, =N−*CH$_2$*CH$_2$COO + −CH$_2$COOCH$_2$*CH$_2$*N−), 2.66 (t, 8H, −CH$_2$COOCH$_2$*CH$_2$*N−, J = 6.0 Hz), 2.60 (m, 18H, −N−*CH$_2$*CH$_2$OH + −N−CH$_2$-*CH$_2$*CONH−Ar), 2.47 (t, 8H, =N−CH$_2$*CH$_2$*COO, J = 6.6 Hz), 2.35 (t, 4H, =N−CH$_2$*CH$_2$*COO, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 172.4, 171.1, 168.1, 144.3, 136.5, 133.5, 128.7, 128.6, 127.8, 126.4, 124.6, 123.9, 114.1, 62.8, 62.1, 59.5, 56.3, 52.7, 52.5, 50.5, 49.7, 41.6, 35.0, 32.9. ESI−MS: calcd for (M + H)/*z*, 1367; found, *m*/*z* 1367 (M + H$^+$).

Synthesis of G3.5-(acrylate)$_8$, **8**. Acrylic chloride (0.20 g, 2.2 mmol) in dry $CHCl_3$ (5 mL) was added dropwise to a solution of G3.0-(OH)$_8$, **7** (0.27 g, 0.2 mmol), and triethylamine (0.22 g, 2.2 mmol) in dry $CHCl_3$ (20 mL) at −5 °C under nitrogen. The solution was stirred for 30 min at −5 °C and then for 90 min at 0 °C. After washing with diluted $NaHCO_3$ (3%, 3 × 10 mL) and brine (20 mL), the organic layer was dried over Na_2SO_4, and filtered. The filtrate was evaporated under vacuum in ice-bath to give a yellow oil (65% yield). IR(KBr): 3350, 2996, 2847, 1723 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.47 (s, 1H, CONHAr), 7.98 (s, 1H, aryl-H), 7.93 (d, 1H, aryl-H, J = 7.8 Hz), 7.75 (d, 1H, aryl-H, J = 8.7 Hz), 7.38 (d, 2H, aryl-H, J = 8.7 Hz), 7.20−7.30 (m, 3H, aryl-H, J = 7.5 Hz), 6.37 (d, 8H, =CH$_2$, J = 8.7 Hz), 6.05 (dd, 8H, =CH−, J = 8.7, J' = 6.4 Hz), 5.76 (d, 8H, =CH$_2$, J = 8.7 Hz), 4.79 (s, 2H, =N−CH$_2$−Ar), 4.20(t, 16H, CH$_2$=CHCOO*CH$_2$*−, J = 5.4 Hz), 4.10 (t, 4H, −CH$_2$COO*CH$_2$*−, J = 5.4 Hz), 4.00 (t, 8H, −CH$_2$COO*CH$_2$*−, J = 5.4 Hz), 2.91(t, 14H, =N−*CH$_2$*CH$_2$CO, J = 6.9 Hz), 2.70−2.85 (m, 28H, CH$_2$=CHCOOCH$_2$*CH$_2$*N− + −CH$_2$COOCH$_2$*CH$_2$*N−), 2.65 (t, 8H, −N−CH$_2$*CH$_2$*COO−, J = 5.4 Hz), 2.55 (t, 2H, −N−CH$_2$*CH$_2$*CO−NH−Ar, J = 5.4 Hz), 2.32 (t, 4H, −N−CH$_2$*CH$_2$*COO−, J = 5.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1, 170.8, 167.6, 166.0, 144.1, 136.5, 133.6, 130.9, 128.5, 127.8, 126.3, 124.5, 123.6, 113.9, 62.7, 62.4, 61.8, 52.6, 50.4, 41.6, 33.0, 29.7. ESI−MS: calcd for (M + H)/*z*, 1799; found, *m*/*z* 1799 (M + H$^+$), 1821 (M + Na$^+$).

Synthesis of G4.0-(OH)$_{16}$, **9**. Diethanolamine (50 mg, 0.47 mmol) was added to a solution of G3.5-(acrylate)$_8$, **8** (100 mg, 0.056 mmol), in dry THF (10 mL) at 0 °C. The solution was stirred at 10 °C for 9 days. The reaction was monitored by ESI−MS. Then, the mixture was evaporated and partitioned between chloroform and water. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was dried and evaporated to yield a yellow oil (73% yield). IR (KBr): 3413, 2953, 2834, 1729 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.46 (s, 1H, CONHAr), 7.98 (s, 1H, aryl-H), 7.93 (d, 1H, aryl-H, J = 8.1 Hz), 7.72 (d, 1H, aryl-H, J = 8.1 Hz), 7.34 (d, 2H, aryl-H, J = 8.1 Hz), 7.15−7.25 (m, 3H, aryl-H, J = 7.8 Hz), 4.76 (s, 2H, =N−CH$_2$−Ar), 4.20(t, 4H, −CH$_2$COO*CH$_2$*−, J = 5.7 Hz), 4.10 (t, 16H, −CH$_2$COO*CH$_2$*−, J = 5.7 Hz), 4.00 (t, 8H, −CH$_2$COO*CH$_2$*−, J = 5.7 Hz), 3.55 (m, 48H, −OH + −CH$_2$*CH$_2$*OH), 2.80 (t, 30H, =N−*CH$_2$*CH$_2$CO, J = 6.0 Hz), 2.70 (16H, −CH$_2$COOCH$_2$*CH$_2$*N−), 2.63 (12H, −CH$_2$COOCH$_2$*CH$_2$*N−), 2.57 (t, 32H, −N−*CH$_2$*CH$_2$OH, J = 5.4

Hz), 2.35−2.50 (m, 26H, −N−$CH_2CH_2COOCH_2$− + −N−CH_2-CH_2CONH−Ar), 2.32 (t, 4H, −N−$CH_2CH_2COOCH_2$-, $J = 5.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.3, 172.5, 172.3, 171.2, 167.9, 144.1, 136.5, 133.6, 128.7, 128.5, 127.8, 126.3, 124.5, 114.0, 62.8, 62.6, 62.0, 59.5, 59.1, 56.4, 56.2, 52.7, 52.9, 50.4, 49.8, 41.6, 32.8, 29.7. ESI−MS: calcd for (M + H)/z, 2639; found, m/z 2639 (M + H^+).

Acknowledgment. We thank the Postdoctoral Foundation of China (No. 200436257).

Supporting Information Available: Figures showing ^1H NMR spectra and ESI−MS spectra of different generations of poly(ester−amine) dendrimers. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) McAnaney, T. B.; Shi, X.; Abbyad, P.; Jung, H.; Remington, S. J.; Boxer, S. G. *Biochemistry* **2005**, *44*, 8701–8711. (b) Miyawaki, A. *Curr. Opin. Neurobiol.* **2003**, *13*, 591–596. (c) Kermis, H. R.; Kostov, Y.; Harms, P.; Rao, G. *Biotechnol. Prog.* **2002**, *18*, 1047–1053.

(2) (a) Zhu, Q. Z.; Aller, R.; Fan, Y. Z. *Environ. Sci. Technol.* **2005**, *39*, 8906–8911. (b) Hulth, S.; Aller, R. C.; Engstrom, P.; Selander, E. *Limnol. Oceanogr.* **2002**, *47*, 212–220. (c) Wenzhofer, F.; Adler, M.; Kohls, O.; Hensen, C.; Strotmann, B.; Boehme, S.; Schulz, H. D. *Geochim. Cosmochim. Acta* **2001**, *65*, 2677–2690. (d) Borg, H.; Ek, J.; Holm, K. *Water, Air, Soil Pollut.* **2001**, *130*, 1757–1762.

(3) (a) Hippius, C.; Schlosser, F.; Vysotsky, M. O.; Bohmer, V.; Wurthner, F. *J. Am. Chem. Soc.* **2006**, *128*, 3870–3871. (b) Miao, Y. Q.; Chen, J. R.; Fang, K. M. *J. Biochem. Biophys. Methods* **2005**, *63*, 1–9. (c) Suzuki, Y.; Yokoyama, K. *J. Am. Chem. Soc.* **2005**, *127*, 17799–17802. (d) Grogan, M. J.; Kaizuka, Y.; Conrad, R. M.; et al. *J. Am. Chem. Soc.* **2005**, *127*, 14383–14387. (e) Sundararaman, A.; Victor, M.; Varughese, R.; Jakle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748–13749. (f) Komatsu, K.; Kikuchi, K.; Kojima, H.; Urano, Y.; Nagano, T. *J. Am. Chem. Soc.* **2005**, *127*, 10197–10204. (g) Zhao, W. L.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1677–1679. (h) Kikuchi, K.; Komatsu, K.; Nagano, T. *Curr. Opin. Chem. Biol.* **2004**, *8*, 182–191. (i) Zhu, C.; Hard, C.; Lin, C.; Gitsov, I. *J. Polym. Sci., Part. A: Polym. Chem.* **2005**, *43*, 4017–4029.

(4) (a) Zhao, W. L.; Carreira, E. M. *Org. Lett.* **2006**, *8*, 99–102. (b) Venkataramana, G.; Sankararaman, S. *Org. Lett.* **2006**, *8*, 2739–2742. (c) Miyata, K.; Tamamushi, R.; Ohkubo, A.; Taguchi, H.; Seio, K.; Santa, T.; Sekine, M. *Org. Lett.* **2006**, *8*, 1545–1548. (d) Ilhan, F.; Tyson, D. S.; Meador, M. A. *Org. Lett.* **2006**, *8*, 577–580. (e) Mei, X.; Martin, R. M.; Wolf, C. *J. Org. Chem.* **2006**, *71*, 2854–2861. (f) Wong, K.-T.; Ku, S.-Y.; Cheng, Y.-M.; Lin, X.-Y.; Hung, Y.-Y.; Pu, S.-C.; Chou, P.-T.; Lee, G.-H.; Peng, S.-M. *J. Org. Chem.* **2006**, *71*, 456–465. (g) Beinhoff, M.; Weigel, W.; Rettig, W.; Bruedgam, I.; Hartl, H.; Schlueter, A. D. *J. Org. Chem.* **2005**, *70*, 6583–6591. (h) Kimura, T.; Kawai, K.; Majima, T. *Org. Lett.* **2005**, *7*, 5829–5832. (i) Duan, X. F.; Wang, J. L.; Pei, J. *Org. Lett.* **2005**, *7*, 4071–4074. (j) Chiang, C. L.; Shu, C. F.; Chen, C. T. *Org. Lett.* **2005**, *7*, 3717–3720. (k) Lincker, F.; Bourgun, P.; Masson, P.; Didier, P.; Guidoni, L.; Bigot, J.-Y.; Nicoud, J.-F.; Donnio, B.; Guillon, D. *Org. Lett.* **2005**, *7*, 1505–1508. (l) Wang, Z.; Xing, Y.; Shao, H.; Lu, P.; Weber, W. P. *Org. Lett.* **2005**, *7*, 87–90. (m) Kurotobi, K.; Osuka, A. *Org. Lett.* **2005**, *7*, 1055–1058. (n) Wang, Z. X.; Zheng, G. R.; Lu, P. *Org. Lett.* **2005**, *7*, 3669–3672. (o) Nakamura, Y.; Yamazaki, T.; Nishimura, J. *Org. Lett.* **2005**, *7*, 3259–3262. (p) Goswami, S.; Mukherjee, R.; Ray, J. *Org. Lett.* **2005**, *7*, 1283–1285. (q) Golovkova, T. A.; Kozlov, D. V.; Neckers, D. C. *J. Org. Chem.* **2005**, *70*, 5545–5549. (r) Miyata, Y.; Nishinaga, T.; Komatsu, K. *J. Org. Chem.* **2005**, *70*, 1147–1153.

(5) (a) Vögtle, F. *Top. Curr. Chem.* **1998**, *197*, 210. (b) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (d) Newkome, G. R.; Mooreld, C. N.; Vögtle, F., Eds. *Dendrimers and Dendrons. Concepts, Syntheses, Applications*; Wiley VCH: Weinheim, Germany, 2001. (e) Frechet, J. M.J.; Tomalia, D. A., Eds. *Dendrimers and Other Dendritic Polymers*; Wiley: Chichester, 2001. (f) Jun, H.; Yuan, M.; Zhao, Y. F. *Progr. Chem.* **2005**, *17*, 468–476. (g) Gitsov, I.; Lambrych, K. R. *Dendrimers. Synthesis and Applications, "Microspheres, Microcapsules & Liposomes"*; Arshady, R., Ed.; Citus Books: London, 2002, Vol. *5*, p 31. (h) Trinchi, A.; Muster, T. H. *Supermol. Chem.* **2007**, *19*, 431–445.

(6) Gitsov, I.; Lin, C. *Curr. Org. Chem.* **2005**, *9*, 1025–1051.

(7) (a) Mery, D.; Astruc, D. *Coord. Chem. Rev.* **2006**, 1965–1979. (b) Bauer, R. E.; Grimsdale, A. C.; Mullen, K. *Top. Curr. Chem.* **2005**, *245*, 253–286. (c) DeSchryver, F. C.; Vosch, T.; Cotlet, M.; Van der Auweraer, M.; Mullen, K.; Hofkens, J. *Acc. Chem. Res.* **2005**, *38*, 514–522. (d) Nierengarten, J. F. *Top. Curr. Chem.* **2003**, *228*, 87–110.

(8) (a) Svenson, S.; Tomalia, D. A. *Adv. Drug Deliv. Rev.* **2005**, *57*, 2106–2129. (b) Tomalia, D. A. *Prog. Polym. Sci.* **2005**, *30*, 294–324. (c) Emanuele, A. D.; Attwood, D. *Adv. Drug Deliv. Rev.* **2005**, *57*, 2147–2161. (d) Dufes, C.; Uchegbu, I. F.; Schatzlein, A. G. *Adv. Drug Deliv. Rev.* **2005**, *57*, 2177–2202. (e) Jansen, J. F. G. A.; Meijer, E. W.; De Brabander-van den Berg, E. M. M. *J. Am. Chem. Soc.* **1995**, *117*, 4417–4418. (f) Gitsov, I.; Lambrych, K. R.; Remnant, V. A.; Pracitto, R. *J. Polym. Sci., Part. A: Polym. Chem.* **2000**, *38*, 2711–2727.

(9) (a) Chen, Q. Q.; Lin, L.; Chen, H. M.; Yang, S. P.; Yang, L. Z.; Yu, X. B. *J. Photochem. Photobiol. A. Chem.* **2006**, *180*, 69–74. (b) Balzani, V.; Bandmann, H.; Ceroni, P.; Giansante, C.; Hahn, U.; Klarner, F.-G.; Muller, U.; Muller, W. M.; Verhaelen, C.; Vicinelli, V.; Vogtle, F. *J. Am. Chem. Soc.* **2006**, *128*, 637–648. (c) Li, W. S.; Jiang, D. L.; Suna, Y.; Aida, K. *J. Am. Chem. Soc.* **2005**, *127*, 7700–7702. (d) Milosevic, P.; Hecht, S. *Org. Lett.* **2005**, *7*, 5023–5026. (e) Ohshima, A.; Momotake, A.; Nagahata, R.; Arai, T. *J. Phys. Chem. A* **2005**, *109*, 9731–9736. (f) Hawker, C. J.; Wooley, K. L.; Frćhet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 4375–4376.

(10) (a) Huang, J.-F.; Luo, H.; Liang, C.; Sun, I.-W.; Baker, G. A.; Dai, S. *J. Am. Chem. Soc.* **2005**, *127*, 12784–12785. (b) Finikova, O.; Galkin, A.; Rozhkov, V.; Cordero, M.; Hagerhall, C.; Vinogradov, S. *J. Am. Chem. Soc.* **2003**, *125*, 4882–4893. (c) Dirksen, A.; Zuidema, E.; Williams, R. M.; De Cola, L.; Kauffmann, C.; Vogtle, F.; Roque, A.; Pina, F. *Macromolecules* **2002**, *35*, 2743–2747.

(11) (a) Bucsiova, L.; Hedlovic, P. *J. Macromol. Sci., Part A−Pure Appl. Chem.* **2007**, *44*, 1047–1053. (b) Maciejewski, A.; Kubicki, J.; Dobek, K. *J. Colloid Interface Sci.* **2006**, *295*, 255–263. (c) Sankaran, N. B.; Sarkar, M.; Samanta, A. *J. Chem. Sci.* **2005**, *117*, 105–110. (d) Banthia, S.; Samanta, A. *Org. Biomol. Chem.* **2005**, *3*, 1428–1434. (e) Barja, B. C.; Chesta, C.; Atvars, T. D. Z.; Aramendia, P. F. *J. Phys. Chem. B* **2005**, *109*, 16180–16187. (f) Sahu, K.; Mondal, S. K.; Roy, D.; Karmakar, R.; Bhattacharyya, K. *J. Photochem. Photobiol. A* **2005**, *172*, 180–184. (g) Maciejewski, A.; Kubicki, J.; Dobek, K. *J. Phys. Chem. B* **2005**, *109*, 9422–9431. (h) Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, *109*, 15172–15177. (i) Mondal, S. K.; Roy, D.; Sahu, K.; Sen, P.; Karmakar, R.; Bhattacharyya, K. *J. Photochem. Photobiol. A* **2005**, *173*, 334–339.

(12) Shen, L.; Sha, Y. W.; Hong, X. Y. *Tetrahedron Lett.* **2002**, *43*, 9417–9419.

(13) (a) O'conner, N. A.; Sakata, S. T.; Zhu, H.; Shea, K. J. *Org. Lett.* **2006**, *8*, 1581–1584. (b) Grabchev, I.; Soumillion, J. P.; Muls, B.; Ivanova, G. *Photochem. Photobiol. Sci.* **2004**, *3*, 1032–1037. (c) Wang, D.; Imae, T. *J. Am. Chem. Soc.* **2004**, *126*, 13204–13205.

(14) (a) Maiti, P. K.; Cagin, T. C.; Lin, S. T.; Goddard, W. A., III *Macromolecules* **2005**, *38*, 979–991. (b) Niu, Y. H.; Sun, L.; Crooks, R. M. *Macromolecules* **2003**, *36*, 5725–5731. (c) Cakara, D.; Kleimann, J.; Borkovec, M. *Macromolecules* **2003**, *36*, 4201–4207. (d) van Duijvenbode, R. C.; Rajanayagam, A.; Koper, G. J. M.; Baars, M. W. P. L.; de Waal, B. F. M.; Meijer, E. W.; Borkovec, M. *Macromolecules* **2000**, *33*, 46–52.

MA8008228