PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/pccp

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Controllable Photophysical Properties and Self-Assembly of Siloxane–Poly(Amidoamine) Dendrimers

Hang Lu, Jie Zhang, and Shengyu Feng*

Poly(amidoamine) dendrimers are typical luminescent polymers containing unconventional chromophores. A series of novel siloxane-poly(amidoamine) (Si-PAMAM) dendrimers was synthesized and investigated in this study. Their structures and properties were determined by NMR, XPS, LC/MS, and fluorescence spectra. The introduction of Si-O-Si units in Si-PAMAM changed the photophysical properties of the dendrimers. The luminescence of Si-PAMAM was associated with the aggregation of its carbonyl groups, which was caused by N \rightarrow Si coordination bonds. The strong blue luminescence of Si-PAMAM was also studied in detail, and it was found to be quite different from the ethanediamine-based poly(amidoamine). Results indicated that the luminescence of Si-PAMAM could be controlled by solvents, acids, metal ions, temperature, or degree of aggregation of the carbonyl groups. Moreover, micron-sized tubes composed of Si-PAMAM found in water/methanol molecules generated and first solution. were

Introduction

In recent years, polymers containing unconventional chromophores have attracted a great deal of interest 1^{-7} . Compared with conventional chromophores, unconventional chromophores are not composed of π -aromatic building blocks or constructed by a conjugated main chain. Unconventional chromophores include aliphatic tertiary amine, amide, C=O, C=S, C=N, N=O, and N=N in hyperbranched or dendrimer molecules and aggregated polymers^{8,9}. These polymers containing unconventional chromophores are environmentally friendly, easy to prepare, bio-compatible, and hydrophilic. Therefore, these polymers have broad applications in biological materials, sensors¹⁰, and drug delivery¹¹. Polymers with unconventional chromophores have been recently designed and synthesized successfully. Such polymers can emit strong fluorescence under proper conditions. Zhao et al. recently studied poly[(maleic anhydride)-alt-(vinyl acetate)] (PMV)⁸, a pure oxygenic nonconjugated polymer. The strong fluorescence of PMV was emitted from the clustering of the carbonyl groups. The oxidized hydrolyzate of poly(Nvinylpyrrolidone) exhibited a stimulus response to metal ions and acid-base, and the formation of secondary amine oxide $(N \rightarrow O)$ enhanced fluorescence¹². An unusual aggregationinduced emission phenomenon was also observed in some

Key Laboratory of Special Functional Aggregated Materials & Key Laboratory of Colloid and Interface Chemistry (Shandong University), Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China

E-mail fsy@sdu.edu.cn (S.F.).

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See

polymers with unconventional chromophores, such as PMV⁸, polyisobutene succinic anhydrides and imides¹³, and poly(amidoamine) (PAMAM) dendrimers⁷.

PAMAM dendrimers are the most investigated luminescent polymers because of their commercial availability, biocompatibility, globular structure, and strong luminescent emission¹⁴⁻¹⁶. For example, PAMAM can be applied in absorbing heavy metal ions from water pollution¹⁷. The fluorescence intensity of PAMAM increases with the decrease in pH because of the protonation of nitrogen atoms¹⁸. However, the exact chromophore is still under debate. Peroxy radicals or excimers (the oxygen–amine "contact" donor–acceptor complex) are generally accepted to be responsible for their light emission^{5,19,20}.

Siloxane-poly(amidoamine) dendrimers (Si-PAMAM) were first synthesized in our previous work^{7,21}. The structures of Si-PAMAM dendrimers are presented in Scheme S1 (Supporting Information). In our research, the fluorescence intensity of hexamethylenediamine-based PAMAM (H-PAMAM) was much weaker than that of Si-PAMAM dendrimers under the same conditions. In a further study, N \rightarrow Si coordination bonds were found and proven to exist in Si-PAMAM. Meanwhile, an unusual aggregation-enhanced emission phenomenon was observed in the Si-PAMAM solution. The hypothesis that peroxy radicals or excimers are responsible for the emission cannot explain such phenomena. A new hypothesis was proposed according to the experimental phenomena and previous reports. The aggregation of carbonyl groups caused by N \rightarrow Si coordination bonds is responsible for the light emission of Si-PAMAM.

To further understand the physical properties of Si-PAMAM and reveal the essence of the fluorescence emitted from Si-PAMAM, the photophysical properties of Si-PAMAM



DOI: 10.1039/x0xx00000x

ARTICLE

dendrimers were investigated and analyzed by fluorescence spectra, X-ray photoelectron spectroscopy, and nuclear magnetic resonance spectra. Results showed that different solvents altered the fluorescence of Si-PAMAM by changing its polarity, solubility, and configuration. Meanwhile, Si-PAMAM was found to be sensitive to Fe^{3+} and Hg^{2+} in different mechanisms. Inorganic and organic acids could influence the fluorescence behavior of Si-PAMAM. H⁺ first lowered and then increased the fluorescence intensity of Si-PAMAM. However, multivariate acid radical increased the fluorescence intensity Si-PAMAM. Moreover, 3-aminopropyl-methylof diethoxysilane-based hydrolyzed Si-PAMAM dendrimers (P-G'1.0) were designed and synthesized. The fluorescence intensity of P-G'1.0 was stronger than that of G1.0 because of the aggregation degree of the carbonyl groups. These results implied that the change in the aggregation of carbonyl groups could adjust the fluorescence behavior of Si-PAMAM. Simultaneously, self-assembly of Si-PAMAM was first observed in a further study. Micron-sized tubes from Si-PAMAM selfassembly were generated and found in water/methanol solution.

Experimental

Materials and Methods

CuCl₂•2H₂O, CoCl₂•6H₂O, CrCl₃•6H₂O, PbCl₂, ZnCl₂, FeCl₃•6H₂O, Hg(NO₃)₂•H₂O, hydrochloric acid, sulfuric acid (98%), phosphoric acid, acetic acid (98%), oxalic acid, citric acid, phloroglucinol, and pyromellitic acid were purchased from Tianjin Kermel Chemical reagents Development Centre. Methyl acrylate (MA), methanol, ethanol, tetrahydrofuran (THF), cyclohexane, acetone, CCl₄, toluene, and petroleum ether were purchased from Tianjin Fuyu Chemical Co., Ltd. 1,3-Bis(3-aminopropyl)-tetramethyldisiloxane (BAPTMDS) and APMDES were obtained as commercial products. All materials were used as received.

Proton nuclear magnetic resonance (¹H NMR) spectra, carbon nuclear magnetic resonance (¹³C NMR) spectra, and silicon nuclear magnetic resonance (²⁹Si NMR) spectra were recorded on a Bruker AVANCE 400 spectrometer at 25 °C using CDCl₃ as the solvent and without tetramethylsilane as an interior label. Molecular weights were determined by an Agilent HP1100 LC-Applied Biosystems API 4000 TQ mass spectrometer (LC/MS). Morphology of Si-PAMAM was observed by an "Axio Scope.A 1" A Pol optical microscope. The luminescence (excitation and emission) spectra of the samples were determined with a Hitachi F-7000 fluorescence spectrophotometer using a monochromatic Xe lamp as an excitation source. The excitation and emission slits were both set at 5 nm. X-ray photoelectron spectroscopy was performed using a Thermo Fisher Scientific Escalab 250 spectrometer with a monochromatic Al Ka X-ray source at a residual pressure of 10^{-7} Pa. The survey and high-resolution scans were generated at 100 eV pass energy with a 1 eV step and 20 eV pass energy with a 0.05 eV step, respectively.

Synthesis

APMDES-based Si-PAMAM dendrimers were synthesized in high yield by aza-Micheal reaction, amidation reaction, and hydrolysis.

The synthetic routes are shown in Scheme 1.



Scheme 1. Synthetic routes of APMDES-based Si-PAMAM dendrimers

Synthesis of APMDES-based Si-PAMAM dendrimers (G'0.5)

Approximately 1.95 g (10.05 mmol) of APMDES and 2.45 g (28.45 mmol) of MA were added to 25 mL of ethanol and then stirred at 50 °C for about 2 days. After the reaction was completed, the excess MA and ethanol were removed by distillation under reduced pressure at 50 °C. Subsequently, 3.58 g (9.84 mmol) of G'0.5 was obtained (yield: 97.9%). ¹H NMR (CDCl₃): δ (ppm) 0.08 (s, 3H, SiCH₃), 0.51 (t, 2H, SiCH₂CH₂CH₂N), 1.15 (t, 6H, SiOCH₂CH₃), 1.39–1.49 (m, 2H, SiCH₂CH₂CH₂N), 2.35–2.43 (m, 12H, SiCH₂CH₂CH₂NCH₂), 2.73 (t, 4H, NCH₂CH₂CO), 3.62 (s, 6H, OCH₃), 3.73-3.75 (m, 4H, SiOCH₂CH₃).

Synthesis of Si-PAMAM dendrimers (G'1.0)

Approximately 4.96 g (13.36 mmol) of BAPTMBS and 2.43 g (6.68 mmol) of G'0.5 were added to 50 mL of ethanol and stirred at 50 °C for about 7 days. After the reaction was completed, the excess BAPTMBS was removed by extraction with petroleum ether. Upon removal of the solvent by distillation under reduced pressure at 50 °C, 4.30 g (5.41 mmol) of G'1.0 was obtained (yield: 81%). ¹H NMR (CDCl₃): δ (ppm) 0.05 (s, 27H, SiCH₃), 0.49 (t, 10H, SiCH₂CH₂CH₂N), 1. 21 (t, 6H, SiOCH₂CH₃), 1.44–1.50 (m, 10H, SiCH₂CH₂CH₂N), 2.15 (t, 4H, CH₂CONH), 2.59 (t, 2H, SiCH₂CH₂CH₂N), 2.65 (t, 4H, SiCH₂CH₂CH₂NH₂), 2.85 (t, 4H, NCH₂CH₂CONH), 3.19 (t, 4H, SiCH₂CH₂CH₂NHCO)., 3.66–3.71 (m, 4H, SiOCH₂CH₃). LC/MS (C₃₄H₈₁N₅O₆Si₅): m/z 796.5 [M]⁺ (calcd. 795.5).

Hydrolysis of Si-PAMAM dendrimers

G'1.0 and excess water were added to ethanol and stirred at 50 °C for 12 h. After the reaction was over, water and ethanol were distilled off under reduced pressure at 60 °C. The crude product was dried in a vacuum oven at 60 °C overnight. Hydrolyzed Si-PAMAM dendrimers (P-G'1.0) were obtained.

RESULTS AND DISCUSSION

Journal Name

Relative to PAMAM, the introduction of Si-O-Si units changed the internal configuration of Si-PAMAM because of the flexibility of Si-O-Si and N \rightarrow Si coordination bonds. Thus, Si-PAMAM could emit strong blue fluorescence in the visible region by transforming UV light. Fluorescence emission strongly depends on the environment, so the photophysical characteristics of the dendrimer were investigated in various organic solvents.



Figure 1. Fluorescence spectra of G2.0 Si-PAMAM dendrimers excited at 363 nm: (a) G2.0 Si-PAMAM dendrimers dissolved in different organic solvents, (b) G2.0 Si-PAMAM dendrimers dissolved in methanol/hexamethylene mixture solvents, and (c) G2.0 Si-PAMAM dendrimers dissolved in acetone.

Figure 1(a) shows the fluorescence spectra of G2.0 Si-PAMAM dendrimers in different organic solvents excited at 363 nm. The emission regions of the dendrimers were almost the same, but their fluorescence intensity varied in different solvents. The fluorescence emission became weaker in the order of methanol, acetone, THF, ethyl acetate, toluene, and CCl₄. Among these organic solvents, methanol exhibits the biggest polarity²², and the fluorescence intensity of the dendrimers changed almost in the order of solvent polarity. The quantum yield data of Si-PAMAM in different solvents (see Supporting Information Table S1) also showed a similar emission trend. The results suggested that the polarity of solvents influenced energy transformation during excitation and emission. Figure 1(b) illustrates the fluorescence spectra of G2.0 Si-PAMAM dendrimers in hexamethylene/methanol. The fluorescence intensity increased with the decrease in the volume fraction of hexamethylene. The results also implied that the fluorescence intensities were lower in non-polar media.

The fluorescence emissions of Si-PAMAM were quite different in water and acetone. Figure 1(c) shows the fluorescence spectra of G2.0 Si-PAMAM dendrimers in acetone. The samples were dissolved in acetone for 0–5 days. The color of Si-PAMAM turned from yellow to brown (see Supporting Information Figure S1), and the emission region red shifted gradually. The fluorescence intensity of Si-PAMAM initially decreased and then increased when Si-PAMAM was dissolved in acetone. The emission region red-shifted after the samples were dissolved in acetone for days. The fluorescence intensity of Si-PAMAM decreased first because of the weak polarity of acetone. According to the mechanism of fluorescence emission and the experiment data, we supposed that acetone could participate in or influence the aggregation of the carbonyl groups and change the configuration of Si-PAMAM physically. Therefore, the color of Si-PAMAM and the fluorescence spectra changed.

ARTICLE



Figure 2. (a) ²⁹Si NMR spectra of Si-PAMAM dendrimer G1.0 and A-G1.0; (b) ¹³C NMR spectra of Si-PAMAM dendrimer G1.0 and A-G1.0.

To further confirm the abovementioned hypothesis, NMR was performed to analyze the structure of Si-PAMAM. The ¹H NMR data of G1.0 and acetone-treated G1.0 (A-G1.0) suggested that no chemical reaction occurred between G1.0 and acetone. Figure 2 shows the ¹³C NMR and ²⁹Si NMR spectra of G1.0 and A-G1.0. Figure 2(a) shows three different ²⁹Si signals in G1.0 located at 7.28, 7.05, and 6.96 ppm, belonging to the three kinds of N \rightarrow Si coordination bonds⁷. The ratio of Si signals at 7.28, 7.05, and 6.96 ppm was 1:2:2. However, the ²⁹Si signals of A-G1.0 shifted to a higher field, and the integral area ratio of the peaks changed. This change suggested that the environments of silicon atoms were altered after G1.0 was dissolved in acetone for days. In the ¹³C NMR spectra of G1.0, only one peak was observed between 160 and 180 ppm. However, two peaks between 160 and 180 ppm and one peak at 206 ppm were observed in the ¹³C NMR spectra of A-G1.0. The signals at 166 and 172 ppm represented the carbonyl groups in Si-PAMAM. The peak at 166 nm suggested that the environments of the carbonyl groups also changed. The formation of a hydrogen bond between the amino and carbonyl made the complete removal of acetone difficult, so a signal located at 206 ppm was observed. The ¹³C NMR data showed that the environments of carbon atoms also changed. Thus, the addition of acetone did not change the chemical structure of Si-PAMAM chemically but influenced the configuration of Si-PAMAM, thereby changing the aggregation of the carbonyl groups in acetone.



Figure 3. Fluorescence spectra of Si-PAMAM dendrimers (G2.0)/methanol solution (concentration of G2.0 was 4 mg/mL): (a) excited at 363 and (b) 285 nm.

According to the mechanism of the fluorescence emission of Si-PAMAM and the characteristics of solubility, an aggregationenhanced emission phenomenon was observed. Figure 3 illustrates that the fluorescence intensity increased with the increase in volume fraction of water. Figure 3(a) shows the spectral region of 435 nm under excitation at 363 nm, whereas Figure 3(b) shows the spectral region of 338 nm under excitation at 285 nm.

Si-PAMAM is not soluble in water because of the introduction of Si-O-Si, whereas ethanediamine-based PAMAM (E-PAMAM) can dissolve in water. Si-PAMAM became less soluble in the water-methanol system with the increase in water volume fraction, but the solution remained hyaline and clear. Si-PAMAM finally separated as white precipitate when the water volume fraction increased. When water was continuously added, Si-PAMAM became insoluble and aggregated in water/methanol. However, the carbonyl groups were much more aggregated. In addition, the fluorescence intensity increased until the mixture became non-transparent.

In a further study, the self-assembly of Si-PAMAM was observed in the non-transparent mixture. Water was added into the Si-PAMAM (G2.0)/methanol solution until the mixture became non-transparent. The sample was then observed after stewing for 1 day. One drop of the mixture was dropped on a glass slide and observed under a microscope. The results are shown in Figure 4.



Figure 4. Morphology of Si-PAMAM in the water-methanol system: (a-c) Si-PAMAM was dissolved in water-methanol; (d) Si-PAMAM was dissolved in water-methanol-H⁺

Figure 4(a) shows that some wirelike matters were generated in the mixture. Figures 4(b) and (c) illustrate that micron-sized tubes were obtained in the self-assembly of Si-PAMAM. The tubes had a diameter of 5–10 m and a thickness above 1 μ m. The surface of the tube was smooth. The morphology of micron-sized tubes was destroyed after the addition of H⁺ [Figure 4(d)].

This self-assembly of Si-PAMAM may be attributed to the following reasons. The introduction of Si-O-Si units made the Si-PAMAM insoluble in water, whereas E-PAMAM and H-PAMAM could dissolve in water. The Si-O-Si units were hydrophobic in Si-PAMAM. The amido and amine groups played a hydrophilic role in Si-PAMAM. The self-assembly of Si-PAMAM is shown in Scheme 2.



Scheme 2. Diagram of the self-assembly of Si-PAMAM in water-methanol.

The terminal groups of G2.0 were -NH₂, which is hydrophilic. The solubility of Si-PAMAM in water/methanol became poor with the increase in water volume fraction. The obtained molecules aggregated in the solution. According to the lipid bilayer in the cells, we presumed that similar parts aggregated together and formed multilayers. The surface of the multilayers was -NH₂, and each molecule was linked by NH₂. At the end of the multilayer, Si-O-Si was exposed to water/methanol, which was unstable. The multilayers were curly, and tubes were generated for more stability. When H⁺ was added into the solution, the amido and amine groups were protonated. The protonated nitrogen atoms were much soluble in water, which changed the solubility of Si-PAMAM in water/methanol. The influence of Si-O-Si on solubility became weaker with the addition of H⁺. The morphology of the micronsized tube was destroyed because of the protonation of amine groups. The morphology of Si-PAMAM with H^{\dagger} is shown in Figure 4(d).

PAMAM can form complexes with several metal cations^{23,24}. The configuration of PAMAM dendrimers exhibits global geometry. Several cavities and high-density functional groups are found in PAMAM, such as amino and amide. The oxygen and nitrogen atoms can provide lone pair electrons that can form complexes with metal cations. Niu et al. synthesized a series of amino- and ester-terminated silica-gel supported hyperbranched PAMAM dendrimers to remove the heavy metal ions from water²⁵. The stimulus response of metal cations of the fluorescence emitted from modified PAMAM dendrimers was investigated by Staneva²².

The photophysical properties of Si-PAMAM may be influenced because of the PAMAM/cation complexes that changed the aggregation of the carbonyl groups.

Journal Name

Journal Name



Figure 5. Fluorescence spectra of Si-PAMAM dendrimer (G2.0)/methanol solution (concentration of G2.0 was 4 mg/mL): (a) with different metal ions, (b) Fe^{3+} , and (c) Hg^{2+} .

The stimulus response of the fluorescence of the Si-PAMAM dendrimer was investigated with different metal cations (CoCl₂, CrCl₃, PbCl₂, ZnCl₂, CuCl₂, FeCl₃, and Hg(NO₃)₂) in the solutions. Hg(NO₃)₂ was dissolved in 1 mol/L HNO₃ water solution, whereas the other metal salts were dissolved in methanol. Figure 5(a) shows the fluorescence spectra of G2.0 Si-PAMAM dendrimers with different cations. The decrease in fluorescence intensity was very small for Zn²⁺, Pb²⁺, and Co²⁺, but became more significant for Cu²⁺, Fe³⁺, and Cr³⁺. Compared with E-PAMAM, Si-PAMAM was not sensitive to mental cations. The structure of Si-PAMAM was larger and the N atoms formed N \rightarrow Si coordination bonds with Si, so density functional groups were lower than E-PAMAM in the same generation. Therefore, the metal complexes in Si-PAMAM were not as stable as those in E-PAMAM.

However, Fe^{3+} and Hg^{2+} are strong fluorescence quenchers in the Si-PAMAM solution. The stability of the metal complexes increases with increasing metal ion charge/radius ratio¹². Fe³⁺ has the largest charge/radius ratio among the above metal ions; thus, it has the strongest interaction with Si-PAMAM. An obvious decrease was found at 10⁻⁴ mol/L. The fluorescence of Si-PAMAM added with Hg²⁺ decreased to nearly zero, suggesting that the fluorescence of Si-PAMAM was extremely sensitive to Hg^{2^+} . The quenching for Hg^{2^+} was probably due to the heavy atom effect²⁶, whereas the metal cation complexes led to quenching. Generally, heavy atoms quench the fluorescence. The high nuclear charge of heavy atoms can induce or increase the spin-orbit coupling effect of the solute, which increases the probability of the transitions of $SO \rightarrow T1$ and S1 \rightarrow T1, thereby increasing the quantity of T1 particles and the quantum yield of phosphorescence.

Wang et. al found that the fluorescence intensity of ethanediamine-based PAMAM increased with the decrease in pH^{18} . The protonation of the tertiary amine groups was responsible for the increase in fluorescence intensity. The strong charge-charge repulsion between the dendritic interior made the globular configuration of the PAMAM much tighter

and the structure of the PAMAM more rigid. The peroxy radicals or excimers are the key reasons for the fluorescence of PAMAM. According to this hypothesis, the peroxy radicals or excimers should be protonated when the pH decreases, which leads to a decrease in fluorescence intensity.

In our previous work⁷, we found that blue photoluminescence is produced by the aggregation of carbonyl groups induced by $N \rightarrow Si$ coordination bonds in Si-PAMAM, which can explain how pH influences the photoluminescence of Si-PAMAM. Different kinds of acids were used in the experiments, including hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, oxalic acid, and citric acid.





Figure 6. Fluorescence spectra of Si-PAMAM dendrimer (G2)/methanol solution with acids (concentration of G2.0 was 4 mg/mL): (a) HCl, (b) H_2SO_4 , and (c) organic acid.

Figure 6 shows the fluorescence of Si-PAMAM/acid in different conditions. Figure 6(a) shows that the fluorescence intensity of Si-PAMAM decreased with increasing HCl concentration. Figure 6(b) illustrates that the fluorescence intensity of Si-PAMAM decreased first and then increased with increasing H₂SO₄ concentration.

According to the hypothesis of the fluorescence proposed in our previous work, the change in fluorescence was reasonable. When the acid was monobasic, N was protonated with the addition of H^{\dagger} . The strong charge-charge repulsion between the dendritic interior made the globular configuration of the PAMAM much tighter and the structure of the PAMAM more rigid. However, the strong fluorescence was produced by the aggregation of carbonyl groups induced by N \rightarrow Si coordination bonds in Si-PAMAM. The N \rightarrow Si coordination bonds were replaced by protonation of N. The carbonyl groups became less aggregated in Si-PAMAM. Thus, the fluorescence intensity became weak. When the acid was polyatomic, the fluorescence intensity increased with increasing H^+ concentration. The acid radical could link the different quaternary amines like a bridge, which caused the aggregation of carbonyl groups. Scheme 3 illustrates this mechanism.





Scheme 3. Effects of the addition of acids to Si-PAMAM

More experiments were performed to further confirm the hypothesis mentioned above. Figure S2 (Supporting Information) shows the fluorescence of Si-PAMAM with the addition of phosphoric acid, acetic acid, oxalic acid, citric acid, and 1,2,4,5-benzenetetracarboxylic acid or phloroglucinol. All samples behaved as described above. Figure 6(c) shows the fluorescence of Si-PAMAM with different kinds of acids. The addition of COOH was the same in each sample. Figure 6(c) shows that the fluorescence intensity of Si-PAMAM/citric acid was stronger than that of Si-PAMAM/oxalic acid, and the fluorescence intensity of Si-PAMAM/oxalic acid was stronger than that of Si-PAMAM/acetic acid. Given that 1 mol citric acid molecule can bind to 3 mol quaternary amine, the degree of aggregation of the carbonyl groups was the greatest and the fluorescence intensity was stronger than the other two.

No N \rightarrow Si coordination bond was observed in E-PAMAM. The strong charge-charge repulsion made the configuration of the E-PAMAM much tighter, and the carbonyl groups became more aggregated with the increase in H⁺ concentration. Thus, the fluorescence intensity of E-PAMAM increased after the addition of H⁺.

A solid (S-G2.0) can be obtained after a volatile solvent from the mixture of Si-PAMAM and acid. To confirm the effect of H^{+} on Si-PAMAM, S-G2.0 was analyzed by X-ray photoelectron spectroscopy (XPS).



Figure 7. XPS spectra of S-G2.0: (a) XPS survey spectrum, (b) XPS of the Si 2p spectral region, (c) XPS of the N 1s spectral region, and (d) XPS of the O 1s spectral region.

Figure 7(a) shows the XPS survey spectrum of the Si-PAMAM/HCl solid. The peaks of Si 2p and N 1s are located at 103 and 400 eV, respectively. Compared with Si-PAMAM (G2.0), the peak of N 1s was divided into two peaks. The peak at higher binding energy (located at 401.7 eV) was attributed to radical cationic nitrogen atoms, whereas the one at the lower energy side (located at 399.9 eV) was assigned to the uncharged amine sites²⁷. Compared with Si-PAMAM (G2.0), the peak of Si 2p was also divided into two peaks. Part of the N \rightarrow Si coordination bonds in Si-PAMAM was broken by H⁺. The peak at lower binding energy (located at 101.8 eV) belonged to Si 2p of N \rightarrow Si coordination bonds, whereas the new peak at higher binding energy (located at 104.05 eV) belonged to Si without N \rightarrow Si coordination bonds.

In the broad O 1s spectrum of S-G2.0, the O 1s peaks were centered at 532.8 and 533.15 eV, but they were difficult to distinguish.

 H^{*} broke the $N \rightarrow Si$ coordination bonds, and the acid radicals linked the different Ns. Both factors changed the configuration of Si-PAMAM, which altered the aggregation degree of the carbonyl groups. The fluorescence intensity of Si-PAMAM changed with the variation in the aggregation degree of carbonyl groups.

According to our work, the fluorescence intensity of Si-PAMAM could be adjusted by changing the aggregation degree of the carbonyl groups.

A new kind of Si-PAMAM (P-G'1.0) was obtained after hydrolytic condensation of G'1.0. The EtO-Si bonds became Si-O-Si after hydrolytic condensation and then linked Si-PAMAM together. The carbonyl groups in P-G'1.0 were much more aggregated than those in G1.0.



Figure 8. (a) Fluorescence spectra of Si-PAMAM dendrimer P-G1.0 and (b) Si-PAMAM dendrimers G1.0 and P-G1.0

Figure 8(a) shows the excitation and emission fluorescence spectra of P-G'1.0 Si-PAMAM dendrimers. P-G'1.0 Si-PAMAM dendrimer emitted fluorescence in the spectral region of 448 nm under excitation at 368 nm. Compared with G1.0, the spectral region slightly red-shifted because the aggregation degree of the carbonyl groups changed. Figure 8(b) shows the emission fluorescence spectra of P-G'1.0 and G1.0. These two samples were tested under the same conditions, with the same amount of carbonyl groups. The fluorescence intensity of P-G'1.0 was stronger than that of G1.0 because the carbonyl

groups of P-G'1.0 were much more aggregated than those of G1.0.



Figure 9 Fluorescence spectra of Si-PAMAM dendrimers at different temperatures (concentration of G2.0 was 4 mg/mL)

The influence of temperature on the fluorescence intensity of Si-PAMAM was investigated in methanol. The sample was first heated in hot water and then tested immediately. Figure 9 shows the emission fluorescence spectra of G2.0 Si-PAMAM dendrimers excited at 363 nm. The fluorescence intensity of Si-PAMAM decreased with the increase in temperature. In addition, the amount of energy was reduced in a non-radiative decay manner, whereas the collision between molecules and internal rotation of the dendrimer increased with increasing temperature. Thus, the fluorescence intensity decreased because of the high non-radiative decay rate of the excited state at high temperatures¹².

Conclusions

This study investigated the photophysical properties and selfassembly of silioxane-PAMAM dendrimers. Results showed that the fluorescence of Si-PAMAM could be adjusted by solvents, acids, metal ions, temperature, and aggregation degree of carbonyl groups. The fluorescence intensity of Si-PAMAM decreased with decreasing solvent polarity. However, the fluorescence of Si-PAMAM was different in acetone or water. Acetone changed the aggregation of the carbonyl groups and influenced the configuration of Si-PAMAM physically. Water aggregated Si-PAMAM because of its solubility. The protonation of nitrogen atoms broke the formation of $N \rightarrow Si$ coordination bonds when acid was added into Si-PAMAM, which changed the aggregation of the carbonyl groups and decreased the fluorescence intensity of Si-PAMAM. Nevertheless, the multivariate acid radical could act as a bridge, linking different nitrogen atoms and causing the aggregation of carbonyl groups. The stimulus response to metal cations was not ultrasensitive because of the large space and low density of coordination sites in Si-PAMAM. However, Si-PAMAM was sensitive to Fe^{3+} and Hg^{2+} because of the large charge/radius ratio and the heavy atom effect, respectively. In addition, the fluorescence intensity of Si-PAMAM was controlled by changing the aggregation of the carbonyl groups and temperatures. In a further study, the micron-sized tube

was generated in water/methanol solution because of the surfactivity and self-assembly of Si-PAMAM.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21274080) and Shandong Special Fund for Independent Innovation and Achievements transformation (No. 2014ZZCX01101).

REFERENCES

- T. Huang, Z. Wang, A. Qin, S. J. Zhi and T. B. Zhong, Acta Chimica Sinica, 2013, 71, 979.
- W. Li, J. Qu, J. Du, K. Ren, Y. Wang, J. Sun and Q. Hu, Chem. Commun., 2014.
- L. Pastor Pérez, Y. Chen, Z. Shen, A. Lahoz and S. E. Stiriba, Macromolecular rapid communications, 2007, 28, 1404-1409.
- 4. C. C. Chu and T. Imae, Macromolecular rapid communications, 2009, 30, 89-93.
- 5. M. Sun, C.-Y. Hong and C.-Y. Pan, Journal of the American Chemical Society, 2012, 134, 20581-20584.
- R. B. Restani, P. I. Morgado, M. P. Ribeiro, I. J. Correia, A. Aguiar Ricardo and V. D. Bonifácio, Angewandte Chemie International Edition, 2012, 51, 5162-5165.
- H. Lu, L. Feng, S. Li, J. Zhang, H. Lu and S. Feng, Macromolecules, 2015, 48, 476-482.
- E. Zhao, J. W. Y. Lam, L. Meng, Y. Hong, H. Deng, G. Bai, X. Huang, J. Hao and B. Z. Tang, Macromolecules, 2015, 48, 64-71.
- 9. Y. Chen, A. Spiering, S. Karthikeyan, G. W. Peters, E. Meijer and R.P. Sijbesma, Nature chemistry, 2012, 4, 559-562.
- 10. J. Satija, V. V. R. Sai and S. Mukherji, Journal of Materials Chemistry, 2011, 21, 14367-14386.
- 11. B. Kang, M. M. Afifi, L. A. Austin and M. A. El-Sayed, ACS Nano, 2013, 7, 7420-7427.
- G. Song, Y. Lin, Z. Zhu, H. Zheng, J. Qiao, C. He and H. Wang, Macromolecular rapid communications, 2014.
- A. Pucci, R. Rausa and F. Ciardelli, Macromolecular Chemistry and Physics, 2008, 209, 900-906.
- 14. G. Saravanan and T. Imae, Journal of nanoscience and nanotechnology, 2011, 11, 4838-4845.
- 15. W. I. Lee, Y. Bae and A. J. Bard, Journal of the American Chemical Society, 2004, 126, 8358-8359.
- 16. G. Rousseau, H. Fensterbank, K. Baczko, M. Cano, E. Allard and C. Larpent, Macromolecules, 2012, 45, 3513-3522.
- 17. Y. Niu, R. Qu, C. Sun, C. Wang, H. Chen, C. Ji, Y. Zhang, X. Shao and F. Bu, Journal of hazardous materials, 2013, 244, 276-286.
- D. Wang and T. Imae, Journal of the American Chemical Society, 2004, 126, 13204-13205.
- S. Y. Lin, T. H. Wu, Y. C. Jao, C. P. Liu, H. Y. Lin, L. W. Lo and C. S. Yang, Chemistry-A European Journal, 2011, 17, 7158-7161.
- 20. D. Wang, T. Imae and M. Miki, Journal of colloid and interface science, 2007, 306, 222-227.
- Y. Niu, H. Lu, D. Wang, Y. Yue and S. Feng, Journal of Organometallic Chemistry, 2011, 696, 544-550.
- D. Staneva, P. Bosch, A. M. Asiri, L. A. Taib and I. Grabchev, Dyes and Pigments, 2014, 105, 114-120.
- R. Qu, Y. Niu, J. Liu, C. Sun, Y. Zhang, H. Chen and C. Ji, Reactive and Functional Polymers, 2008, 68, 1272-1280.
- 24. R. Qu, Y. Niu, C. Sun, C. Ji, C. Wang and G. Cheng, Microporous and mesoporous materials, 2006, 97, 58-65.

ARTICLE

- 25. Y. Niu, R. Qu, H. Chen, L. Mu, X. Liu, T. Wang, Y. Zhang and C. Sun, Journal of hazardous materials, 2014, 278, 267-278.
- 26. K. Seehafer, M. Bender, S. T. Schwaebel and U. H. Bunz, Macromolecules, 2014, 47, 7014-7020.
- 27. J. Yue and A. Epstein, Macromolecules, 1991, 24, 4441-4445.

Page 8 of 8