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pH Dependent One-/Two-photon Fluorescence Emission and Mechanism of Dendrimer: PAMAM Triphenylamine Imine

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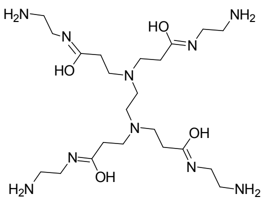
Dendrimer PTS-G0 based on poly-amidoamine (PAMAM) functionalized by triphenylamine imine (C=N), and reference compound ETS base on ethylenediamine triphenlyamine imine was synthesized. PTS-G0's one-/two-photon (2PA σ_2=75 GM) fluorescence emission increased at low pH and keep high fluorescence at large pH, which emission ranges were different with that of NH_2- or HO- terminated PAMAM in references report. PTS-G0 and ETS pH related fluorescence emission were compared. The independent chemical groups emsssion properties were calculated by quantum chemical theory methods. The imidic acid (HO-C=N), imine (C=N), and tertiary ammonium have the fluorescence phenomena in different pH ranges. The possibility fluorescence emission mechanisms of PTS-G0 was discussied, which can help for explain the fluorescence emission of PAMAM and benefit for understand the intrinsic-fluorescent phenomena.

Introduction

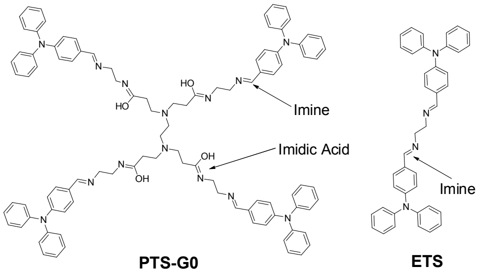
Poly-amidoamine (PAMAM) dendrimers (Scheme 1) were firstly synthesized by Tomalia[1] in 1985. Since then these dendrimers have been caused interests for their water dissolvable, inside holes[2], functional or modified able chemical groups[3], biocompatible[4], nano particles packagedable[5], and small molecules or drugs delivery abilities[6]. In recent years, the fluorescence emission phenomena of PAMAM have been observed[7]. The PAMAM dendrimers have amide, primary amine, and tertiary amine, which were not traditional typical fluorescence emission groups. And many PAMAM emission related influence factors have been considered, such as pH[8], oxidation[9], staled in air[10], and the other influences (size, shapes, distances)[11]. The fluorescence emission phenomena and mechanism of PAMAM has been cared.



PAMAM-G0

Scheme 1 The structure of PAMAM

The pH-dependent fluorescence emissions of PAMAM were researched by several groups[12]. It was show the NH_2-terminated and HO- terminated PAMAM can give strong fluorescence emission at low pH values[13]. The mechanisms need to be determined. The PAMAM fluorescence emission phenomena were attributed to intrinsic-fluorescence. Although the intrinsic-fluorescent macromolecules have been paid attentions[14], so far the intrinsic-fluorescent mechanism has not been studied systemically[15]. Our group have studied the fluorescence emission phenomena of PAMAM[16], to find there exit imidic acid (HO-C=N) and ammoniums structures in PAMAM dendrimers, which take part in the fluorescence emissions of PAMAM. The study of PAMAM dendrimers and their modified derivatives will help for finding the mechanism of intrinsic-fluorescent emissions.



PTS-G0 ETS

Scheme 2 The structure of PTS-G0 and ETS

In order to understand the pH dependent fluorescence emission of PAMAM dendrimers, the dendrimer PTS-G0 (PAMAM_Triphenylamine_Schiff-base imine Generation 0) (Scheme 2) was synthesized out, which was from PAMAM-G0 modified by triphenylamine aldehyde with imine (Schiff base C=N) linked. The PTS-G0 has tertiary amine, amide, imine, and

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aromatic tertiary amine groups. The pH related one-photon and two-photon fluorescence emission of PTS-G0 was test. The results show the PTS-G0 gave strong fluorescence at pH>2 and gave weak fluorescence at pH<2. The two-photon excited fluorescence (2PEF) spectra of PTS-G0 gave the similar situation. The PTS-G0 pH related fluorescence gave the different phenomena from the NH_2- terminated PAMAM and HO- terminated PAMAM in reference report[12]. PAMAM show the strong fluorescence at low pH values and weak fluorescence at high pH values. But the PTS-G0 including PAMAM core gave strong fluorescence emission at neutral or high pH values, and weak at low pH. These differences were discussed and some related mechanisms were given.

The (Ethylenediamine triphenlyamine Schiff base) ETS was synthesized out as reference compound (Scheme 2), which were from ethylenediamine modified by triphenylamine aldehyde with imine (Schiff base C=N) linked. ETS has imine and triphenylamine groups. So the ETS's pH related fluorescence emissions have reference meaning to that of PTS-G0.

Two-photon absorption (2PA)[17] is a nonlinear optical process wherein a molecule simultaneously absorbs two photons of energy *hv* (or of energy *hv1* and *hv2*) via middle virtual state to access an excited state in the presence of intense laser pulse. 2PA is corresponding to third-order nonlinear optical process. The 2PA was excited by near-infrared lamp-house that has longer wavelength. Therefore, the scatter of the light decreased and the light's penetration in the material increased, which can make deep observation of the materials. The two-photon process is in direct ratio with the square of incidence light intensity, so the better modulate properties can be obtained. In recent years, a considerable amount of effort has been devoted to 2PA materials and devices. A variety of compounds including donor-bridge-acceptor (D-π-A) dipoles, donor-bridge-donor (D-π-D) quadrupoles, multi-branched compounds, dendrimers, and octupoles have been synthesized and researched. A number of factors influence the 2PA magnitude, which include electronic delocalization and intramolecular charge-transfer (ICT) phenomena, long conjugated system.[18]

This paper test PTS-G0 one/two photon pH dependent fluorescence emission properties. The pH dependent fluorescence of PTS-G0 and ETS was compared, and try to get some information about intrinsic-fluorescent emissions phenomena.

Results and Discussions

Structure characterized

The structure of PTS-G0 was determined by ^1H NMR, ^{13}C NMR, IR, and MS, which connected with the fluorescence properties. The characterized structure show there exist imidic acid (HO-C=N) and imine (C=N) in PTS-G0. ^1H NMR (Figure S4) of PTS-G0 has chemical shifts (δ) 3.53 ppm peak was show as water, but there were DMSO-d6 solvent and not water in sample. So this peak was attributed to hydroxyl of imidic acid (HO-C=N). The ^{13}C NMR (Figure S5) show the δ peak 171.87 ppm, which should be attributed to C atom of imidic acid (HO-C=N). And there was no amide ^{13}C NMR δ peak that should be at about 175.6 ppm. The ^{13}C NMR peak at 161.46 ppm was C atom signal of the C=N. The IR (Figure S6) show the 1640 (cm^{-1}) peak that was absorption from C=N of imine end group or C=N from imidic acid. The amide carbonyl peak should be at about 1700 cm^{-1}, but this 1700 cm^{-1} peak was not appear in IR spectra, which show the amides in PTS-G0 have changed. The MS (Figure S7) show the molecules ions peaks (1537.02 [M], 1537.91$[M+H]^+$) and some fragments peaks. The MS show that there have no other new chemical structure produced, which cannot exclude the possibilities of imidic acid exists in PTS-G0. The ^1H NMR, IR, and MS show that there were imidic acid (HO-C=N) structure exist in PTS-G0 (Scheme 2). The TLC of PTS-G0 (Figure S13) shows the long tails of sample, which means the different ratios of amide/imidic acid exists in PTS-G0 to forming tailing band. The imidic acid (HO-C=N) and imine (C=N) influence the fluorescence of PTS-G0 together.

pH related fluorescence properties

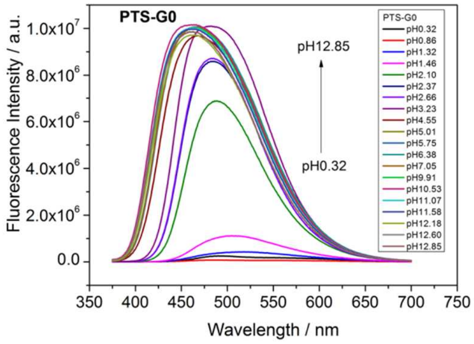


Figure 1 the fluorescence emission spectra of (1×10^{-5} mol/L) PTS-G0 (ethanol/water = 1/9 volume ratio) at different pH (λex= 360 nm)

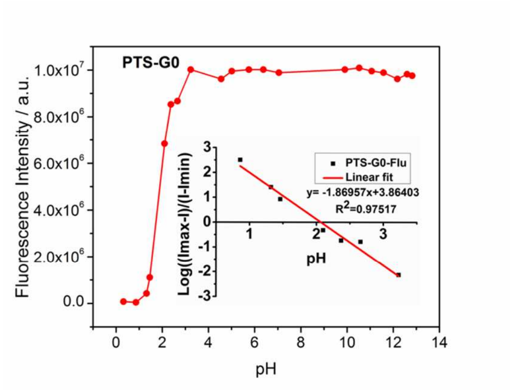


Figure 2 The relationship curve of fluorescence emission peak intensity vs. pH of PTS-G0 (insert line is the linear fit: log [(IFmax-IF)/(IF-IFmin)] vs. pH). (Solvent ethanol/water = 1/9 volume ratio)

Figure 1 gave the pH dependent fluorescence emission spectra and pH relationship in Figure 2. These figures show the fluorescence of PTS-G0 increased with the increasing of pH values. The (fluorescence) photograph of PTS-G0 at low/neutral/high pH values were show in Figure S14 (in Electronic Supplementary Information (ESI)), which show the yellow color low pH PTS-G0 solution gave very weak fluorescence, and the transparent neutral or high pH PTS-G0 solution gave strong fluorescence under UV light.

The pH-dependent fluorescence emission relationship (Figure 2) show the fluorescence intensity were increased from pH 1.5 to 3, and keep high fluorescence intensity at pH>3. The pH related fluorescence spectra (Figure 1) have blue shifts at pH≈4; and the pH related UV-vis absorbance spectra (Figure S3) also show the wavelength changed at pH≈4 (λabs wavelength from 480 to 450 nm). This show the pH≈4 was the point of fluorescence emission structure centres transformation point. pH related fluorescence spectra (Figure 4 in DMSO solvent) wavelength change at pH≈6 (λabs from 500 to 450 nm), which show PTS-G0's fluorescence structure centres change at pH≈6.

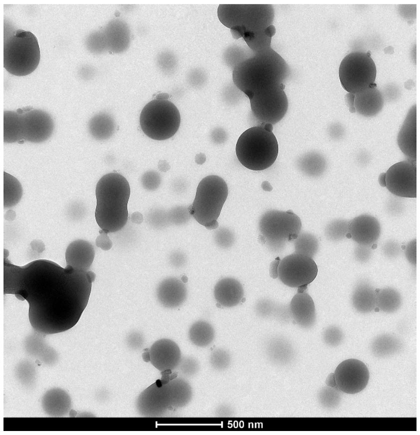


Figure 3 the TEM of PTS-G0 (test dry sample in ethanol /water = 1/9 volume ratio)

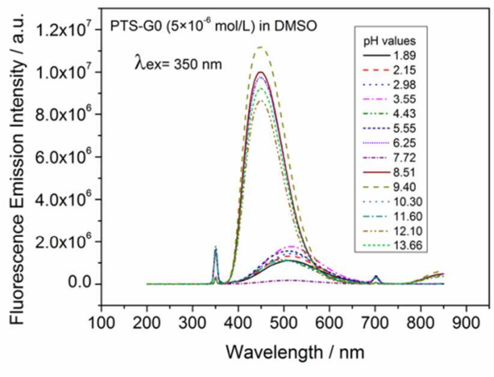


Figure 4 the fluorescence emission spectra of (5×10^{-6} mol/L) PTS-G0 (in DMSO) at different pH (λex= 350 nm).

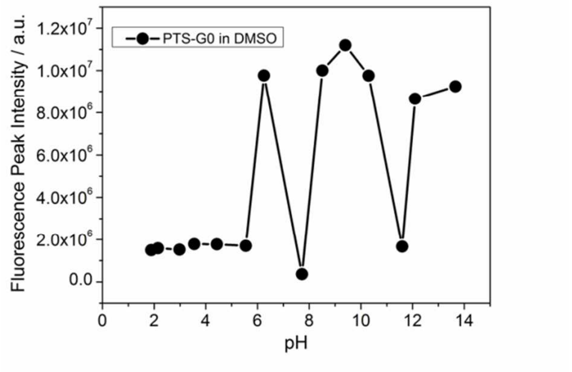


Figure 5 the relationship curve of fluorescence emission intensity vs. pH of PTS-G0 in DMSO

PTS-G0 in water/ethanol system have aggregation phenomena, the TEM photograph (Figure 3) show the nano liquid balls formed in the water/ethanol mixed solvent. So the pH related fluorescence in water/ethanol system gave aggregation induced emission (AIE) [19]. So to test pH dependent fluorescence without AIE, the DMSO solvent was used to test the pH related fluorescence of PTS-G0. The Figure 4 gives the PTS-G0 pH dependent fluorescence in DMSO, which excluded the AIE or J- aggregation possibility. The Figure 5 show the PTS-G0 gives low fluorescence at low pH and give high fluorescence at high pH, which was similar to the Figure 2.

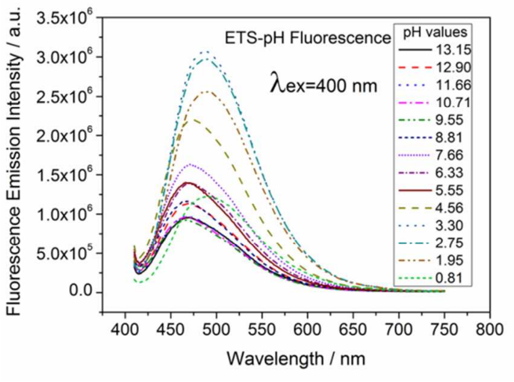


Figure 6 the fluorescence emission spectra of (1×10^{-5} mol/L) ETS (ethanol/water = 1/9 volume ratio) at different pH (λex= 400 nm)

The pH dependent fluorescence emission spectra (Figure 6) and pH relationships (Figure 7) of ETS show high fluorescence emission at low pH values and weak at high pH values. The peak was at about pH=3. The pH dependent fluorescence reduce and be low at range pH=5~13. Compared the PTS-G0 and ETS pH dependent situation, they all high emission at about pH=3, but different in high pH values range. From pH=6 to pH=13, PTS-G0 kept high fluorescence, but ETS fluorescence reduced and low. ETS has triphenlyamine and imine groups.

PTS-G0 has imidic acid and tertiary amine, which more have than ETS. The structure different make the pH dependent fluorescence different.

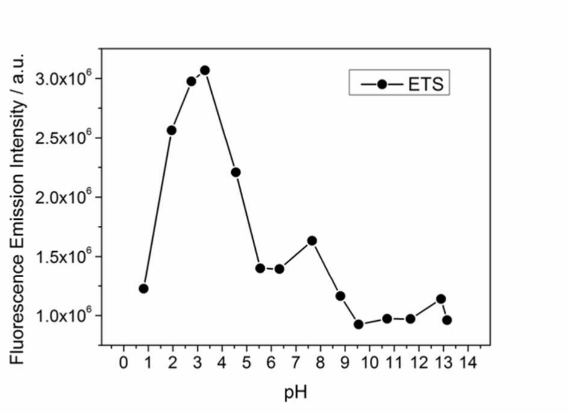


Figure 7 The relationship curve of fluorescence emission intensity vs. pH of ETS (in ethanol/water = 1/9 volume ratio)

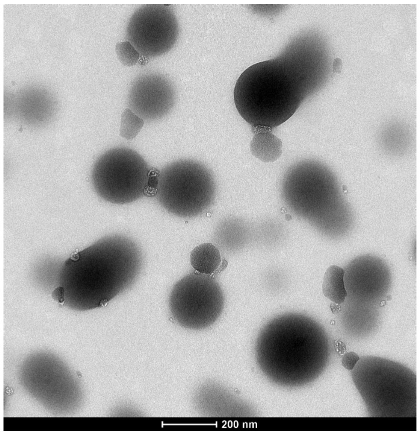


Figure 8 the TEM of ETS (test dry sample in ethanol/water = 1/9 volume ratio)

Figure 8 give the TEM of ETS test dry sample in ethanol/water mixed solvent. The nano particles show that the ETS was aggregation in solvent. It can be concluded that the ETS pH dependent fluorescence emission show AIE effect in these ethanol/water mixed solvent. The Figure 3 and Figure 8 show the PTS-G0 and ETS were all show AIE effect in ethanol/water mixed solvent. The DMSO was used as solvent to test the pH dependent fluorescence without AIE effect.

The Figure 9 gave the ETS pH dependent fluorescence emission spectra in DMSO. And the Figure 10 gave the relationship of ETS fluorescence peak intensity versus pH, which display same situation with the PTS-G0 in DMSO in Figure 5. The situations in Figure 5 and Figure 9 were show low fluorescence in pH 1~5, show high fluorescence in pH 6~13, and gave low fluorescence point in pH=8 and pH=12.

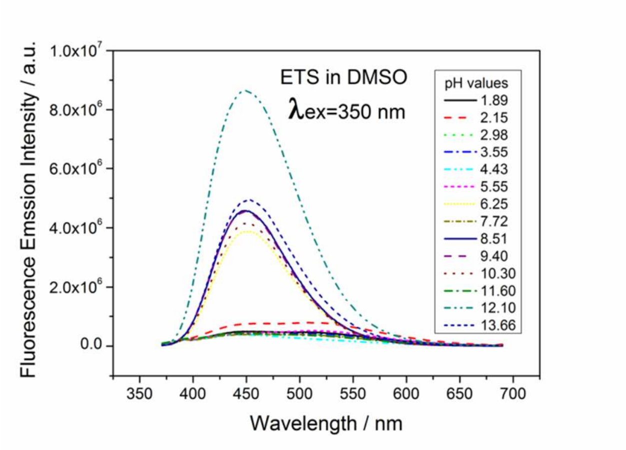


Figure 9 the fluorescence emission spectra of (1×10^{-5} mol/L) PTS-G0 (in DMSO) at different pH (λex= 350 nm);

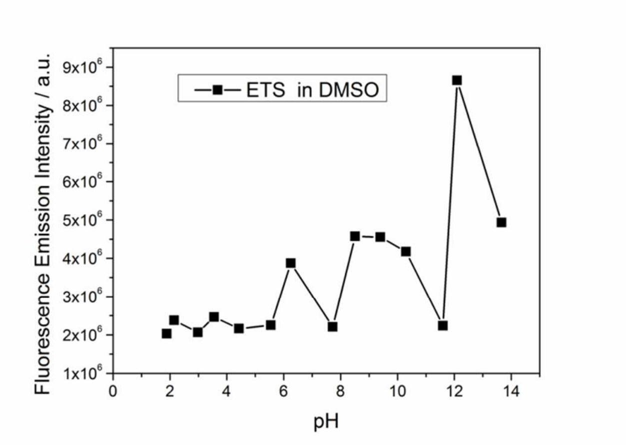


Figure 10 the relationship curve of fluorescence emission intensity vs. pH of PTS-G0 in DMSO

Figure 5 and 10 show pH 8 and pH 12 structure change points. The reason need to be determined, while the possibility reasons may connect to the chemical groups structure change at this two pH values. At pH=8, solution was the weak base, which might be fit for the C=N exits. The imine C=N has isomerization phenomena, which double bonds produce isomerisation resonance to absorb the energy of system, to low the fluorescence emission intensity of PTS-G0 or ETS at pH=8. The pH=12 low point might be imine connected with TPA. The $^{-}$OH act on N atom of triphenylamine (TPA), to form a new the imine N=C-TPA isomerisation system to consume energy of PTS-G0 or ETS fluorescence. Then the pH=12 values gave low fluorescence intensity. The system (in Scheme 3) has base OH act on N atom of TPA to form -N=C-TPA-OH, that to gave high fluorescence at pH>13. The PTS-G0 and ETS all have C=N and TPA, which might be give the similar fluorescence situation in DMSO shown in Figure 5 and Figure 10.

Two-photon fluorescence properties

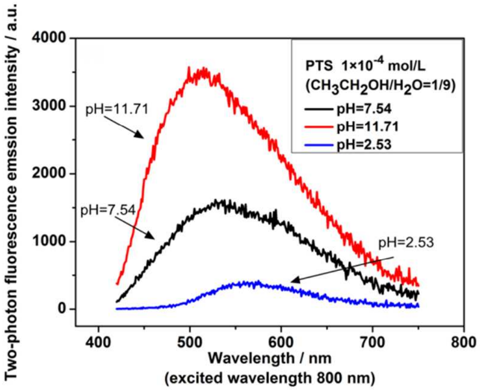


Figure 11 Two-photon excited fluorescence (2PEF) emission spectra of PTS-G0 at different pH values. λex=800 nm by femtosecond Ti: Sapphire laser. (Solvent ethanol/water = 1/9 volume ratio)

The PTS-G0 modified dendrimer has pH related two-photon absorption (2PA) properties, which show in Figure 11. The two-photon absorption cross sections (σ_2) were test by two-photon induces fluorescence (TPIF) method. The two-photon excited fluorescence (2PEF) of PTS-G0 was tested on three pH values (pH = 7.54; 11.71; 2.53) PTS-G0 solutions. The σ_2=75 GM at pH 11.71, σ_2=38 GM at pH 7.54, and not test out at pH 2.53. The two-photon excited fluorescence spectra of PTS-G0 show that the PTS-G0 gave weak 2PEF intensity at low pH values; gave middle 2PEF intensity at neutral pH values; and gave strong 2PEF intensity at high pH values. The 2PEF of PTS-G0 show the similar situations of the one-photon fluorescence. The parameters of PTS-G0 were list in Table S2.

Quantum chemical calculations

MOPAC [20] software was used to calculate the pKa of imidic acids in PAMAM-G0 and in PTS-G0 (structure show in Scheme 2). PTS-G0 pKa for four hydroxyl hydrogen of HO-C=N: 1.434; 3.128; 4.529; 6.083. PAMAM-G0 four hydrogen of HO-C=N pKa: 2.289; 2.310; 2.499; 2.555. These pKa data show the imidic acid structure forming at the ranges about pH 1.5 to 6, which can deduce the fluorescence centre was imidic acid (HO-C=N) of PTS-G0 (Figure 12). In this range (pH 1.5-6), the key structure turning points were about pH≈4, which was correspond to the UV spectra (Figure S3). The PTS-G0 pH related fluorescence ranges (pH 1.5-6) were similar to the fluorescence of PAMAM [12]. And at the low pH values, the ammonium formed, which may influence the fluorescence emission. At the ranges pH>6, the PTS-G0 were still keep strong fluorescence emission that was from imidic acid emissions, which were different with the fluorescence of PAMAM in reference report[12]. From the Figure S10 (abc) and Table S2, the fluorescent life time was 1.61 ns (at pH=7.54) and 1.80 ns (at pH=11.71), which show the fluorescent centres of PTS-G0 were different at neutral and high pH. The fluorescent life time was 0.99 ns (at pH=2.53), which show the fluorescent centres were different with the neutral and high pH values. These phenomena can be explained by amide/imidic-acid transfer mechanism in Scheme 3.

In order to test the mechanism of imidic acid and imine (in Scheme 3), the quantum chemical calculations of parts from PTS-G0 (Figure S15) were taken. The calculation used the time-dependent density functional theory (TD_DFT) b3lyp/6-31g methods by Gaussian 09 software package [22]. The parts from PTS-G0 were small key chemical groups to make the calculations taking efficient.

Table S3 lists emission spectra of P-01, P-02, P-03, P-03’, P-04, P-04’, P-05, P-05’, P-06, and P-06’ (Figure S15) in gas phase vacuum calculated by TD_DFT b3lyp/6-31g method. From calculated emission spectra data the Table S3, the main emission groups were P-01: imidic acid; P-03: imine; P-03’: iminium; P-04’: tertiary ammonium; P-05’: triphenyl-ammonium; P-06’: triphenyl ammonium-iminium. While the parts P-02: amide; P-04: tertiaryamine; P-05: triphenylamine; P-06: triphenylamine-imine gave no emissions. The theory calculations data in Table S3 give the emission data of the fluorescence emission groups of PTS-G0 in Figure S15 distributed by pH ranges. The imidic acid and ammoniums were the fluorescence emission groups at high pH values. The imine was the fluorescence emission group at low pH values.

Possibility mechanism analysis

PTS-G0 and ETS have several fluorescence groups. It was possible pH related fluorescence emission ranges gave in Figure 12. The PTS-G0 main fluorescence centres were imidic acid and ammoniums at 1.5<pH<6; the PTS-G0 main fluorescence centre were imidic acid salts at pH>6. The imine gave fluorescence emission at pH<6 and 8<pH<12. Triphenylamine gave fluorescence emission at pH>12. The Figure S16, S17 can determine from theory calculations that the mechanisms in Scheme 3 were reasonable and may explain the pH dependent one-/two-photon fluorescence emission of PTS-G0.

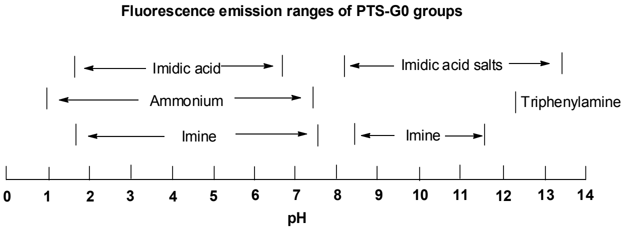
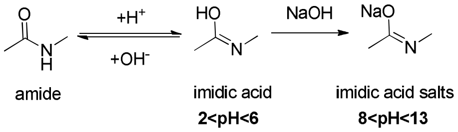
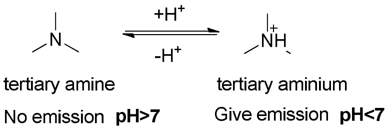


Figure 12 The fluorescence emission groups of PTS-G0 ranged by pH values

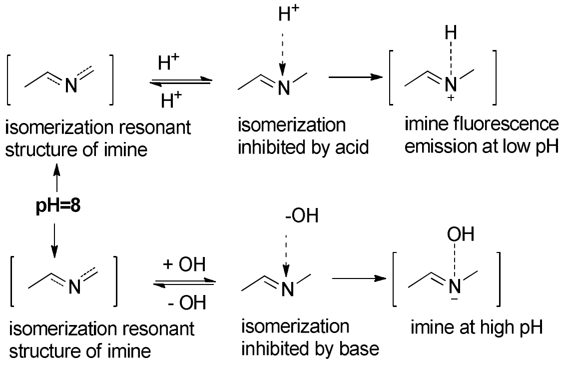
Imine group gave emission at the pH>6, and 8<pH<12. The end group imine of PTS-G0 connected with triphenylamine formed the fluorescence centre. The isomerization phenomena of imine make it gave weak fluorescence at about pH=8. There exit some conditions that inhibit the imine isomerization, then imine can give fluorescence[21]. PTS-G0 and ETS all have imines and triphenylamine. At acid situation pH<6, the ETS gave strong fluorescence emission. While at the base situations pH>8, the ETS gave weak fluorescence. The H^+ and OH^- acted on the imine of ETS, and inhibit the isomerization of imine, which make the ETS gave fluorescence at pH<6 (Figure 12). These may be explained by imine isomerization inhibited mechanism in Scheme 3.



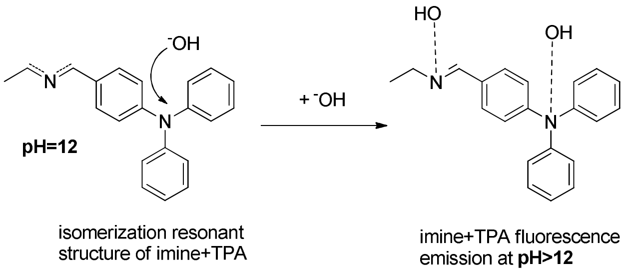
Amide/Imidic-acid Transfer Mechanism



Tertiary Aminium Emission Mechanism



Imine Isomerization-Inhibited Mechanism



Triphenylamine Fluorescence Emission Mechanism

Scheme 3 The possibility mechanism of pH dependent fluorescence emission chemical groups.

Imidic acid were in PTS-G0. The mechanisms show the transform of amide and (amide resonance structure) imidic acid under low pH or high pH in Scheme 3. The imidic acid formed by adds H^+ and can enhance the fluorescence emission of PTS-G0, which can enhance fluorescence at acid condition. The imidic acid structure was rigid co-plane structure, has C=N double bonds, p-π conjugated structure, and exits donor electronic group hydroxyl, which can enhance fluorescence at acid condition. At the base situation, the imidic acid form salts, this also gave fluorescence emission.

Tertiary ammonium can give fluorescence at acid situation. The triphenylamine-imine may form isomerization phenomena at some pH points, to consume energy of system to low the fluorescence intensity. The triphenylamine-imine conjugated structures have intramolecular charge transfer (ICT) that can enhance nonlinear optic (two-photon) properties.

The molecules orbits HOMO and LUMO of PTS-G0 were list in Figure S16 (imidic acid structure) and Figure S17 (amide structure). From Figure S16, the HOMO ground states electronic clouds gathered at triphenylamine parts, and the LUMO excitation electronic clouds gathered mainly at imine parts, which show the imine connected with triphenylamine were took part in the fluorescence emission. From Figure S17, the HOMO ground states electronic clouds gathered at centre of PTS-G0, and the LUMO excitation electronic clouds gathered nearly at imine and imidic acid parts. The HOMO and LUMO show the imidic acid took part in the fluorescence emission groups.

This paper data display interest pH dependent fluorescence emission phenomena of PTS-G0 and ETS. The mechanisms might be not accuracy determined by only analysed these data. The further experiments need designed to find mechanism of the intrinsic-fluorescent phenomena. The PAMAM dendrimers and their modified compounds will have wide application foreground through future research.

Conclusions

In conclusion, the pH related one/two photon fluorescence emission of PTS-G0 were increased with the increasing of pH values, which phenomena were different with the pH related fluorescence emission of NH_2- terminated or HO- terminated PAMAM in reference report. The pH related fluorescence of PTS-G0 increased at about 1.5<pH<13 (in ethanol/water mixed) and 6<pH<13 (in DMSO). And the pH related fluorescence of ETS increase at about 1<pH<6 (in ethanol/water mixed) and 6<pH<13 (in DMSO). The pH related fluorescence emissions of PTS-G0 and ETS has similar situation in solvent DMSO, but different in ethanol/water mixed solvent. It can be determined that groups imidic acid (HO-C=N), imine (C=N), and tertiary ammoniums took part in fluorescence emission. The possibility mechanisms explain these pH dependent fluorescence phenomena. These reports about PTS-G0 dendrimer and ETS can help to explain the fluorescence emission phenomena of PAMAM, and might help to understand the intrinsic-fluorescent phenomena of dendrimers.

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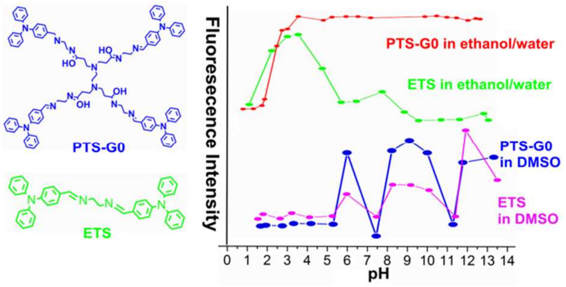

pH dependent fluorescence emission of PTS-G0 and ETS were compared to better understand intrinsic-fluorescent phenomena of PAMAM dendrimers.