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Quantum Chemical Theory Methods Study on Intrinsic Fluorescence Emission and Possible Mechanisms of PAMAM

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In recent decades, it have been found and determined that the poly-amidoamine (PAMAM) can give fluorescence emission in some conditions. PAMAM have amide, primary amine, and tertiary amine, which were not the traditional typical fluorescence emission groups. The fluorescence emission center or mechanisms of PAMAM were cared. This paper used quantum chemical TD-DFT method to calculate the absorption and emission states of chemical group parts of PAMAM, which including amide, amide resonance structure imidic acid, amine and ammoniums. The theory calculation show the imidic acid and tertiary ammonium can give emission. The mechanisms of amide resonance structure imidic acid and tertiary ammonium were discussed. The calculation results show the imidic acid and tertiary ammonium was the fluorescence emission groups of PAMAM, which might help to explain the intrinsic-fluorescent phenomena.

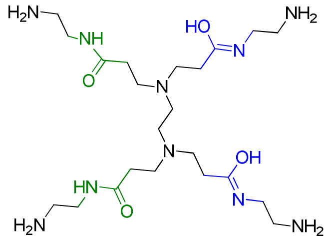
Introduction

Poly-amidoamine (PAMAM) dendrimers were firstly synthesized by Tomalia in 1985.[1] In recent years, the fluorescence emission phenomena of PAMAM have been proved[2]. PAMAM dendrimers have water dissolvable and inside holes[3], several modifiable chemical groups[4], well biocompatible[5], nano particles packaged able [6], and small molecules or drugs delivery abilities[7], and with the fluorescence properties, which will cause the cares and interests. And some other dendrimers such as Poly(amino ester)s[8b], Poly(propylether imine)[8e], poly(propylene-imine) (PPI) dendrimer, and poly(ethyleneimine) (PEI) dendrimer[9] can gave fluorescence emission, which were called as intrinsic-fluorescent emission phenomena.[10] And many related influences of PAMAM emission elements have been considered, such as staled in air[9], pH[11], oxidation[12], the amine groups' distances [13] and some other influences(sizes, shape)[14]. Until recent years, there were some common views but no determined conclusions on intrinsic-fluorescence.[15]

The PAMAM dendrimers have primary amine, amide, and tertiary amine. There were no traditional typical fluorescence emission groups in PAMAM. So the fluorescence emission center and mechanism of PAMAM have been studied by many research groups [8]. The PAMAM produced amide resonance structure imidic acid (HO-C=N) in PAMAM under some situations [16]. The 15N NMR, 1H NMR, 13C NMR, N-H 2D NMR, and IR spectra have determined this amide resonance structure imidic acid and tertiary ammonium [16]. In this paper, a new mechanism of fluorescence emission phenomena of PAMAM has been proposed. The quantum chemical calculations prove this resonance structure imidic acid can give fluorescence emission. The amide resonance structure imidic acid mechanisms were also discussed to explain the PAMAM fluorescence emission. And the tertiary ammonium exits in the structure of PAMAM, which also takes part in fluorescence emission. The emission and absorption states of chemical parts in PAMAM were calculated to test the fluorescence centers of PAMAM by quantum chemical theory methods, which might help for explain the intrinsic-fluorescent phenomena.

Results and Discussions

1. Fluorescence of PAMAM



PAMAM-G1

Amide / Imidic Acid (HO-C=N)

Fig. 1 The PAMAM-G1 include amide structure / amide resonance structure imidic acid.

PAMAM (Figure 1) gave weak fluorescence when synthesized initially. But the PAMAM dendrimers staled in air or added acid, and then PAMAM can give fluorescence emission. The fluorescence emission phenomena of PAMAM have been proved by many research groups [7-15]. Figure 2 gave the fluorescence emission spectrum of PAMAM-G1 in CH_2Cl_2 solution, which shows PAMAM-01 gave strong fluorescence. The photographs in Figure 3 show the PAMAM 1, 2, 3G, and Hyper-branch gave blue-green color fluorescence under 365 nm UV light after staled in air. Figure 4 gave UV-vis absorption peaks at 229 nm and 286 nm. These all show the PAMAM dendrimers can give fluorescence emission in some conditions. The fluorescence of PAMAM was called intrinsic-fluorescent, and the PAMAM fluorescence centers and mechanism need to be determined.

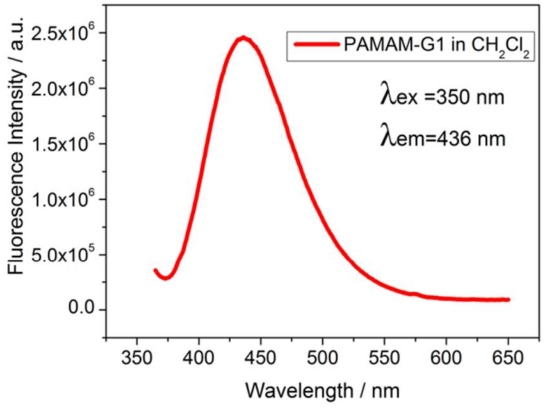


Fig. 2 The fluorescence emission spectrum of PAMAM-G1 in CH_2Cl_2 solution.

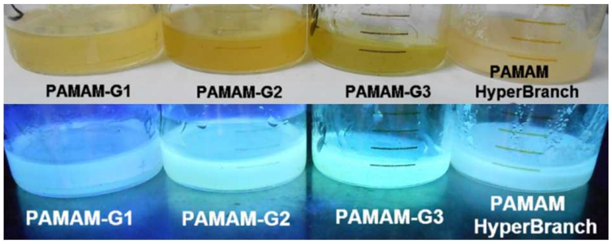


Fig. 3 The (fluorescence) photographs of PAMAM-G1, PAMAM-G2, PAMAM-G3, and PAMAM Hyper-Branch. The above was in room light and the below was in 365 nm UV light.

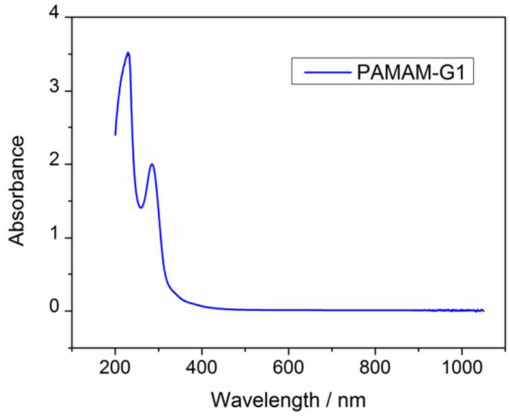


Fig. 4 The UV-vis absorption spectrum of PAMAM-G1 in water solution.

The spectra data[16] have been determined that amide resonance structure imidic acid exits in the PAMAM. This imidic acid structure (Figure 5 **P-02**) might be the fluorescence emission group, which was rigid co-plane structure, has C=N double bonds, p-π conjugated structure, and exits donor electronic group hydroxyl. The imine C=N double bonds can give fluorescence emission in some conditions.[17] The C=N in imidic acid was similar to C=N in imine, which may give fluorescence emission. There exit amide; imidic acid[16], primary amine; primary ammonium; tertiary amine; tertiary ammonium; and amidium in PAMAM. The quantum chemical theory calculation methods were used to test the fluorescence emission properties of these structure units in PAMAM.

2. Theory Calculations

P-01 and **P-02** (Figure 5) were small parts of key groups from PAMAM, which can make the quantum chemical calculation easy. **P-01** was the amide part of PAMAM, which was divided out from PAMAM chains. **P-02** was the amide resonance structure imidic acid part of PAMAM. The quantum chemical calculation results of **P-01** and **P-02** were list in Table 1, 2.

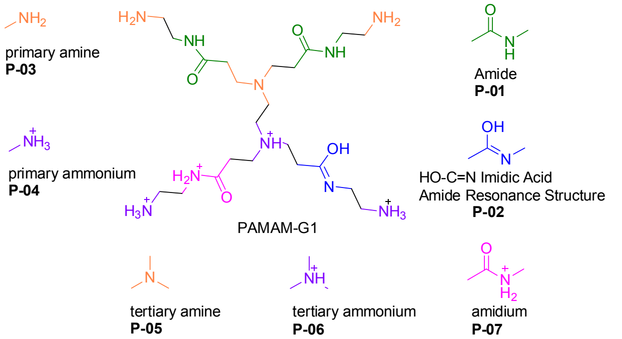


Fig. 5 The parts of amide (P-01); imidic acid (P-02); primary amine (P-03); primary ammonium (P-04); tertiary amine (P-05); tertiary ammonium (P-06); and amidium (P-07) in PAMAM (Ref. 16) prepared for theory calculation.

Table 1 The absorption spectra of **P-01** (amide) in gas phase vacuum calculated by TD_DFT b3lyp/6-31g method.

Electron transition [a]	Energy (eV)	Calculated wavelength (nm)	Main transition configuration	Oscillator strength *f*
S0→S1	3.195	388.01	HOMO→LUMO: 0.70656	0.0007
S0→S1	5.106	242.82	HOMO-1→LUMO: 0.68179 HOMO-3→LUMO: 0.15224	0.0797
S0→S1	6.883	180.11	HOMO→LUMO+1: -0.44445 HOMO-2→LUMO: 0.28272 HOMO-3→LUMO: 0.45577	0.0092
S0→S1	7.009	176.89	HOMO→LUMO+1: -0.52148 HOMO-1→LUMO+1: 0.24424 HOMO-2→LUMO: -0.29636 HOMO-3→LUMO: -0.25948	0.0691
S0→S1	7.560	164.00	HOMO→LUMO+2: 0.11041 HOMO-2→LUMO: -0.51492 HOMO-3→LUMO: 0.41561	0.0809

[a] Footnote: S0→S1 was the absorption states of **P-01** (Singlet)

The gas phase vacuum states of parts were set for calculation. The calculation of whole dendrimer PAMAM-G0 can be carried out, but which can not easy analysis the every group (Figure 5) parts' contributions to the fluorescence emission. The calculation of every part without set the solvent environments, for the solvent act on parts can not equal the solvent action on whole dendrimers. Then the gas phase vacuum state were set to calculate and consider the fluorescence contribution of every part without set solvent environments.

Table 2 The absorption and emission spectra of **P-02** (imidic acid) in gas phase vacuum calculated by TD_DFT b3lyp/6-31g method.

Electron transition [a]	Energy (eV)	Calculated wavelength (nm)	Main transition configuration	Oscillator strength *f*
S0→S1	0.663	1868.03	HOMO→LUMO:0.72495	0.0000
S0→S1	4.017	308.61	HOMO→LUMO: 0.19054 HOMO-1→LUMO: 0.67201	0.0434
S0→S1	4.912	252.39	HOMO→LUMO+1: -0.67133 HOMO-1→LUMO: 0.16858 HOMO-2→LUMO: 0.12149	0.0334
S0→S1	5.693	217.76	HOMO-2→LUMO: -0.66739 HOMO-3→LUMO: 0.15285	0.0220
S0→S1	6.425	192.96	HOMO→LUMO+2: 0.68424 HOMO-3→LUMO: -0.11371	0.0405
S0→S1	6.920	179.16	HOMO-3→LUMO: 0.13505 HOMO-1→LUMO+1: 0.68841	0.0110
S1→S0	0.663	1868.03	LUMO→HOMO: -0.16421	0.0000
S1→S0	4.017	308.61	LUMO→HOMO-1: -0.10986	0.0434

[a] Footnote: S0→S1 was the absorption states of **P-02**; the S1→S0 was the emission states of **P-02** ((Singlet), S0 was ground states, S1 was excitation states.

The absorption and emission spectra of **P-01** and **P-02** were calculated out by time-dependent density functional theory (TD_DFT) b3lyp/6-31g method in *Gaussian 09* [18] software package. Until now, TD_DFT [19] was the best method for excitation energies, frequency-dependent response properties, photoabsorption spectra, and emission calculations. DFT methods need large resources of computer, so the small parts (Figure 5) can make calculations efficient. The calculation data listed in Table 1, 2, and 3. The **P-01** amide only gave absorption spectra without giving emission spectra from calculation data. The amide resonance structure imidic acid **P-02** gave emission at 308.61 nm. The traditional amide structure gave no fluorescence emission. The amide resonance structure imidic acid including C=N double bonds, which was the key fluorescence emission group determined from these calculation results.

Table 3 The emission spectra of **P-03**; **P-04**; **P-05; P-06**; and **P-07** in gas phase vacuum calculated by TD_DFT b3lyp/6-31g method.

	Electron transition a	Energy (eV)	Calculated wavelength (nm)	Main transition configuration	Oscillator strength *f*
P-03	S1→S0	0.3934	3151.86	LUMO→HOMO: 0.36520	0.0002
	S1→S0	0.5777	2146.18	LUMO→HOMO: 0.10708	0.0006
P-04	S1→S0	1.2726	974.23	LUMO→HOMO: -0.37303	0.0099
	S1→S0	0.7101	1746.11	LUMO→HOMO: -0.26941	0.0016
P-05	S1→S0	-	-	-	-
P-06	S1→S0	3.3368	371.56	LUMO→HOMO: -0.12593	0.0150
	S1→S0	6.4936	190.93	LUMO→HOMO: -0.10599	0.1388
	S1→S0	1.5639	792.78	LUMO→HOMO:-0.44768	0.0176
	S1→S0	1.4019	884.43	LUMO→HOMO:-0.31141	0.0177
	S1→S0	1.4154	875.96	LUMO→HOMO:0.30283	0.0182
	S0→S1	3.3368	371.56	HOMO→LUMO: 0.71123	0.0150
P-07	S1→S0	0.1259	9845.10	LUMO→HOMO:0.37008	0.0008

Footnote: a) the primary amine (**P-03**); primary ammonium (**P-04**); tertiary amine (**P-05**); tertiary ammonium (**P-06**); and amidium (**P-07**) in PAMAM (structures in Figure 5). b) the S1→S0 was the emission states of the parts. (Singlet) ,S0 was ground states, S1 was excitation states.

Table 3 lists the data of calculation emission spectra of the primary amine (**P-03**); primary ammonium (**P-04**); tertiary amine (**P-05**); tertiary ammonium (**P-06**); and amidium (**P-07**) in PAMAM (structure in Figure 5). The primary amine and primary ammonium gave fluorescence emission, the emission wavelengths were all larger than 900 nm, which were at infrared ranges. The amidium also gave emission at infrared ranges. The tertiary amine gave no emission by theory calculation data. The tertiary ammonium gave emission at 370 nm, 190 nm, 790 nm, 870 nm, 880 nm, and 980 nm, which show the tertiary ammonium have strong fluorescence emission abilities from the theory calculated results.

Ref. 9 show the blue emission of oxygen-doped tertiary amine (triethylamine) was a key unit of fluorescent poly(amido amine) dendrimer. Ref. 13 show the distance of tertiary amine affect on the fluorescence emission of PAMAM. It was demonstrated that the tertiary amine in branching units of hyperbranched polymers is a key group for keeping high fluorescence efficiency[20]. These all show the tertiary amine or tertiary ammonium has taken part in the fluorescence emission. From Table 3 data, it can show the tertiary ammonium can give emission.

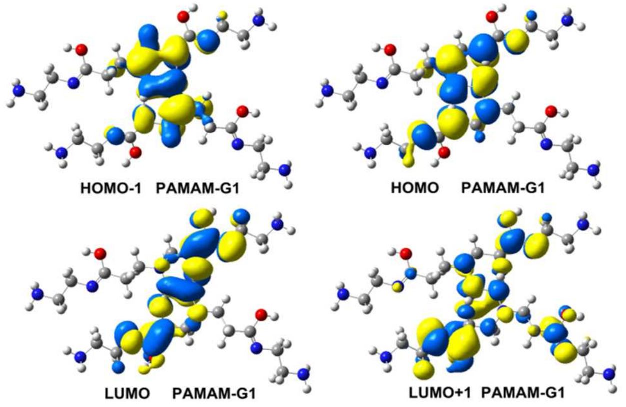


Fig. 6 The molecules orbits HOMO-1, HOMO, LUMO, and LUMO+1 of PAMAM-G1 (imidic acid structure)

Figure 6 gave the molecules orbits HOMO-1, HOMO, LUMO, and LUMO+1 of PAMAM-G1 in imidic acid structure. The HOMO-1 show the electronic clouds put together at the center of the PAMAM-G1. The HOMO show the ground states electronic clouds gathered at the center of the PAMAM-G1, which electronic clouds spread to four branches compared with HOMO-1 clouds. The LUMO show the excitation states electronic clouds gathered at the center of the PAMAM-G1, which were mainly on tertiary amine parts and spread to the imidic acid structures parts. The LUMO+1 show the excitation states electronic clouds gathered mainly at the imidic acid and tertiary parts of the PAMAM-G1. From HOMO to LUMO, the molecules orbits ground state electronic clouds were spread and expand from tertiary amine center to imidic acid parts, and the excitation electronic clouds were mainly gather on the imidic acid structures. It can be deduced from the Figure 6 and the data in Table 1, 2, 3, that imidic acid structures and tertiary ammonium were the fluorescence emission center of PAMAM-G1.

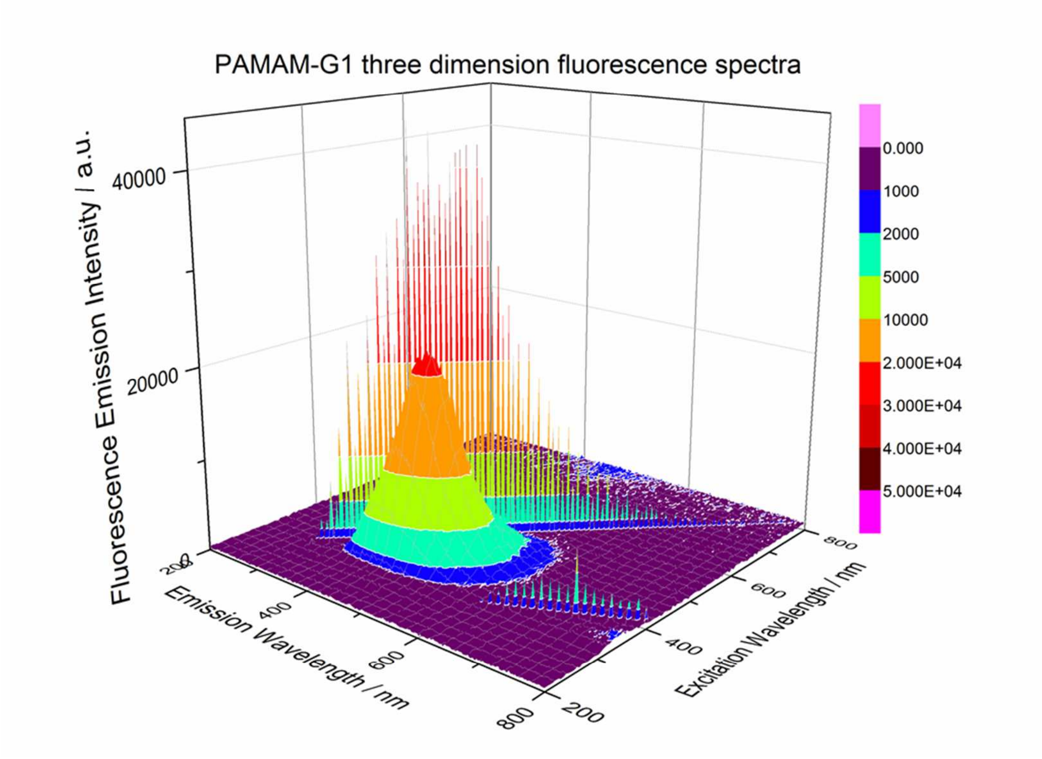


Fig.7 The three dimension fluorescence spectra of PAMAM-G1 in water solution (1×10^{-3} mol/L).

3. Possible mechanisms

The three dimension fluorescence excitation/emission spectra of PAMAM-G1 in water solution show in Figure 7. This show the PAMAM-G1 has fluorescence emission at about 400~600 nm range, and fluorescence emission peaks at about 450~500 nm. Figure 7 well illuminate the fluorescence phenomena of PAMAM dendrimers. And the fluorescence mechanism of PAMAM may be explained from the chemical groups' mechanisms, which include amide/imidc acid transfer and amine protonation.

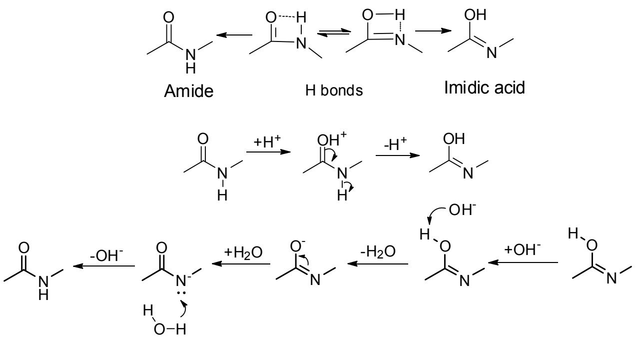


Fig. 8 The mechanisms of amide and resonance structure imidic acid.

The mechanism of amide and amide resonance structure imidic acid was list in Figure 8. The low pH values can help for the forming of imidic acid resonance structure from amide. The high pH values can help for the transfer imidic acid resonance structure to amide. The ratios of amide/imidic acid can be determined by NMR integrates areas. But the ratios were concerned with many elements, such as pH, temperature, or solvents. The pH related experiment of PAMAM show the low pH values or adding acids can enhance the fluorescence emission of PAMAM [9]. These mechanisms can explain the PAMAM give strong fluorescence when adding acids, for the forming of imidic acid structure. The PAMAM gave weak fluorescence when adding bases, for the imidic acid structure transfer to amide.

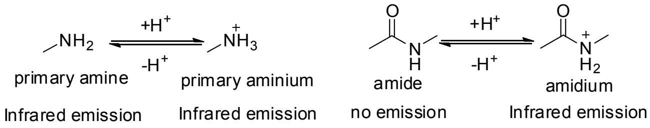


Fig. 9 The mechanisms of amine/ammonium and amide/amidium.

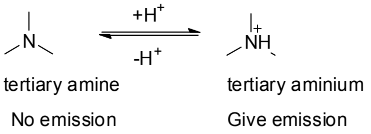


Fig.10 The mechanisms of tertiary-amine/tertiary-ammonium

The Figure 9 and Figure 10 gave the mechanisms of the mechanisms of primary-amine/ammonium, amide/amidium, and tertiary-amine/tertiary-ammonium. From the theory calculations results list in Table 3 show the ammoniums can give emissions. The primary-amine, primary-ammonium, and amidium gave emissions at about infrared ranges. Amide and tertiary-amine gave no emissions. The tertiary-ammonium can give emissions at visible light ranges. The ammoniums were formed often at low pH, and PAMAM gave high fluorescence emissions at low pH values. The Table 3 can deduce that the tertiary ammonium was one fluorescence emission center. So the fluorescence emission groups of PAMAM were imidic acid structure (that transferred from amide) and the tertiary ammonium structure, which can be explained by these mechanisms.

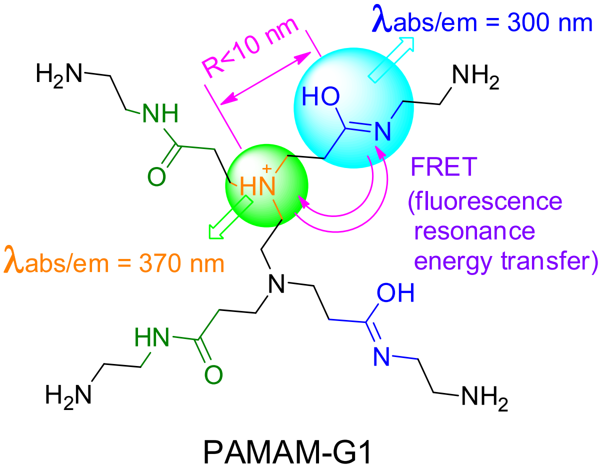


Fig.11 The illuminate of PAMAM-G1 fluorescence resonance energy transfer (FRET)

From the calculated data in Table 2, 3 show that there might be fluorescence resonance energy transfer (FRET)[21] among the chemical groups of PAMAM. FRET is a photo physical processes whereby individual chromophores communicate their electronic states, providing means for transferring excitations from a donor to an acceptor. FRET is sensitive to intra- and intermolecular distance in the range of <10 nm. From the Table 2, 3, the groups' emissions overlap with the other groups' absorptions. The distance R between groups were R <10 nm. These obey to the FRET conditions. It can be deduced that there was FRET in the PAMAM (Figure 11). For example, the imidic acid has absorption and emission at about 300 nm, and P-06 tertiary ammonium has emission and absorption at about 370 nm, which absorption and emission were close and have some overlap. There exit three bonds between the imidic acid and tertiary ammonium, which means the distance R was small than 10 nm. Figure 12 gave the calculated fluorescence emission wavelength positions. The **P-02**, **P-04**, and **P-06** have overlap on absorption/emission positions, which obey the FRET rules (absorption/emission have overlaps with the groups' distance small than 10 nm). These show the imidic acid, primary ammonium, and tertiary ammonium have FRET phenomena in PAMAM, which assisted the fluorescence emission of PAMAM.

The key fluorescence emission groups were imidic acid and tertiary ammoniums, which were got from the theory calculations. The FRET may take part in the fluorescence emission processes of PAMAM. The related mechanisms can partly explain the relationship between the fluorescence phenomena and the chemical structures of PAMAM dendrimers.

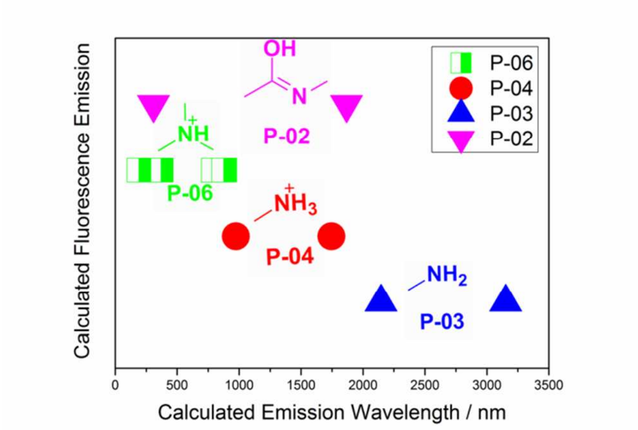


Fig.12 The calculated fluorescence emission wavelength positions of **P-02**, **P-03**, **P-04**, and **P-06** (data from Table 2, 3).

Experimental Methods

Synthesis

PAMAM 0.5G, 1.0G, 1.5G, 2.0G, 3.0G, hyper-branch[1].

Methyl acrylate (MA) and ethylenediamine (EDA) were used as substrates.

(1) The Michael-addition of amine groups in EDA to MA under 50 ℃ in methanol solution (affords the dendritic product of 0.5 generation (G) with ester groups terminated).

(2) The amidation of the terminal ester groups of 0.5G dendrimer from dissolving in methanol solution by excessive EDA under 50 ℃ (affords the 1G dendrimer with terminal amine groups).

(3) Distillation of exceeded EDA under reduced pressure and washed by ethyl ether (gives the purified 1 G dendrimer). The PAMAM dendrimers are shown as yellow sticky liquid.

(4) Repeated step (1), (2), and (3) can get 1.5G, 2.0G, and 3.0G

(5) The equal moles MA and EDA were added into methanol. Keep stirring at 50 ℃ 24 h. Distillation of methanol. The hyper-branch PAMAM was got.

Conclusions

The spectra data show PAMAM dendrimer have fluorescence emission phenomena. The amide of PAMAM exits resonance structure imidic acid. The tertiary amine transferred to ammonium at some conditions. It have been characterized that imidic acid and tertiary ammonium structures in PAMAM. The quantum chemical theory calculation show the imidic acid and tertiary ammonium can give fluorescence emission. The amide resonance structure imidic acid mechanism and tertiary amine/ammonium protonation mechanism were discussed, which can explain the high fluorescence emission phenomena of PAMAM in low pH or adding acids. It can be concluded that the imidic acid structure and tertiary ammonium in PAMAM have co-actions on the fluorescence emission group of PAMAM. These calculation results can help to explain and understand the intrinsic-fluorescent phenomena of dendrimers.

Notes and references

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Quantum Chemical Theory Methods Study on Intrinsic Fluorescence Emission and Possible Mechanisms of PAMAM

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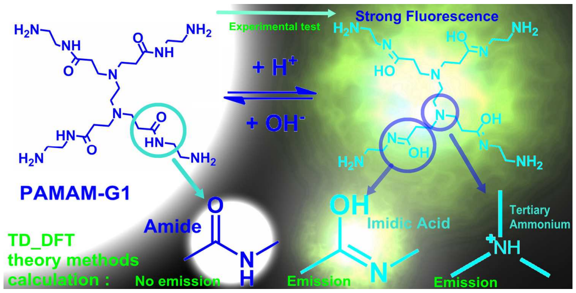

Structure units imidic acid (HO-C=N) and tertiary ammonium in PAMAM dendrimer were proved to emission fluorescence by TD_DFT method.