

Electronic Supplementary Information (ESI)

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

Yan Ji\* <sup>a,b</sup>, and Ying Qian\* <sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, China

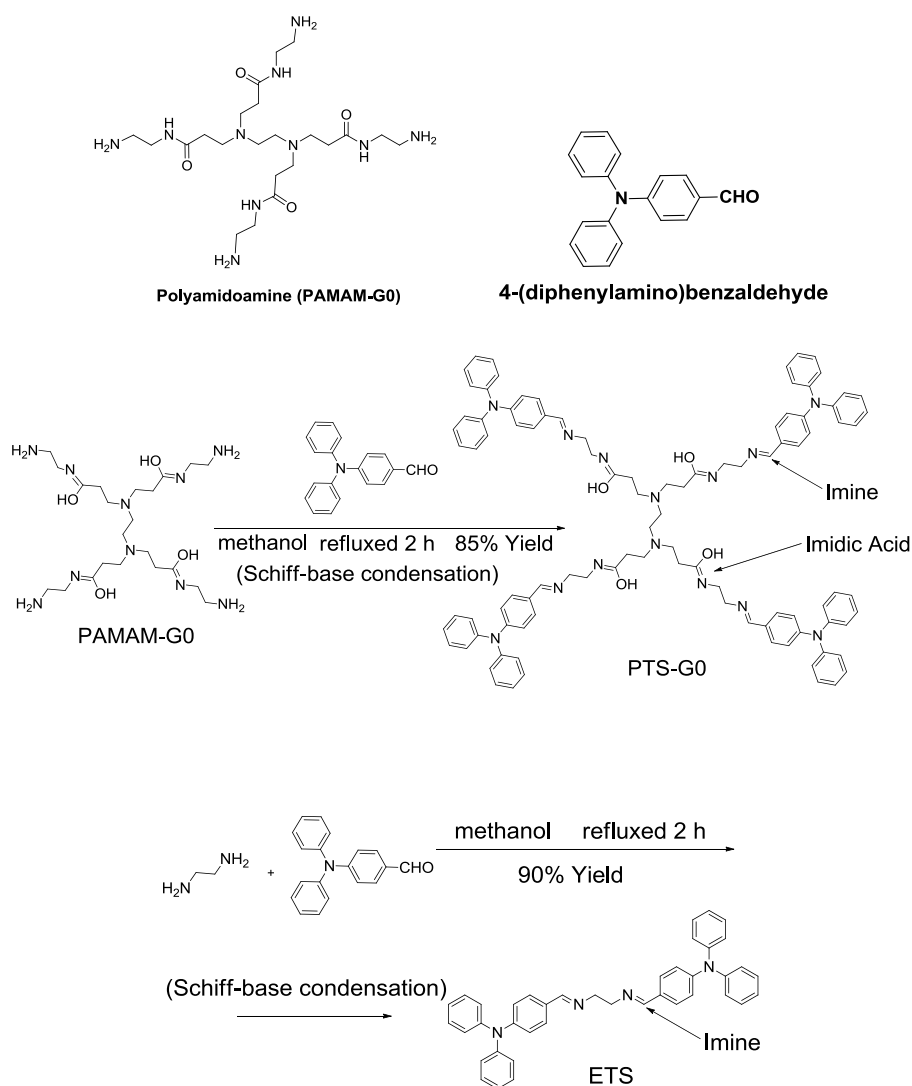
<sup>b</sup> School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China.

Email: [jiyan98@163.com](mailto:jiyan98@163.com)

1. **Experimental**
  - 1.1 **Materials**
  - 1.2 **Instruments**
  - 1.3 **Procedures**
- 2 **The UV-vis absorption and fluorescence spectra**
- 3 **<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MS**
- 4 **Fluorescence decay curves and fluorescence life time**
- 5 **2PA cross-sections ( $\sigma_2$ )**
- 6 **TLC**
- 7 **Parameters**
- 8 **Quantum chemical theory calculations**

# 1. Experimental

## 1.1 Materials



The dendrimers polyamidoamine(PAMAM-G0) were prepared refer to the previously method. Methyl acrylate (MA) and ethylenediamine (EDA) were used as substrates. The processes: (1) the Michael-addition of amine groups in EDA to MA under 50 °C 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 0.5 G dendrimer from dissolving in methanol solution by excessive EDA under 50 °C. Affords the 1.0 G dendrimers with terminal amine groups. (3) And distillation of exceeded EDA under reduced pressure, and gives the purified dendrimers PAMAM-G0.

The preparation of 3,3',3'',3'''-(ethane-1,2-diylbis(azanetriyl))tetrakis (N-(2-((4-(diphenylamino) benzylidene)amino)ethyl)propanamide) (PTS-G0): PAMAM-G0 0.52 g (1mmol) and 4-(diphenylamino) benzaldehyde 1.4 g (5 mmol excessive), sodium sulphate anhydrous 0.5 g, methanol 30 mL, refluxed 2 h, cooled and filtrated, removed methanol in rotary evaporation. The solid washed by water twice and filtrated, vacuum drying, 1.3 g yellow powder got, and yield 85%. m.p.>280 °C, IR (KBr):  $\nu$ ,  $\text{cm}^{-1}$  3416(N-H) 1640(C=N), 1590(Ar-H), 1494, 1277, 756, 695.  $^1\text{H-NMR}$ ( $\text{CDCl}_3$ , 300 MHz): $\delta$ , 8.143 (s, 4H, H-C=N), 7.706,7.678(d,  $J=8.4\text{Hz}$ , 8H, Ar-H), 7.515,7.492(d,  $J=6.9\text{Hz}$ , 4H, N-H),7.357,7.334(d,  $J=6.9\text{Hz}$ , 12H, Ar-H), 7.202,7.181(d,  $J=6.3\text{Hz}$ , 12H, Ar-H), 7.046,7.017 (d,  $J=8.7\text{Hz}$ , 24H, Ar-H), 3.66(t, 8H, N-H), 3.509(t, 8H, N-H), 3.295(t, 8H, N-H), 2.598(t, 8H, N-H), 2.375(t, 4H, N-H). MS m/z: (Calculate 1537.81 [M]) Found: 1537.02 [M], 1537.91[M+H] $^+$ )

## 1.2 Instruments

All chemicals purchased from Agents of Country Inc. The  $^1\text{H}$  NMR data recorded in  $\text{CDCl}_3$  solution with Bruker AM-300/500 MHz spectrometers. The chemical shifts reported relative to TMS in  $\text{CDCl}_3$ . UV-vis spectra obtained from a Shimadzu UV-2450 spectrophotometer. IR spectra obtained from Nicolet 750 IR spectrometers. MS measured on TSQ QUANTUM ULTRA and Finnigan LCQ advantage MAX+ mass spectrometer. Melting points were determined on X4 melting point apparatus. Melting points not corrected. The fluorescence spectra obtained from FluoMax-4 fluorescence meter. The pH values obtained from PHS-3C pH-meter. The fluorescence quantum yields were obtained by comparing with the sulfate quinine solution. The gel-permeation chromatography (GPC) was tested on the PL-220 instrument.

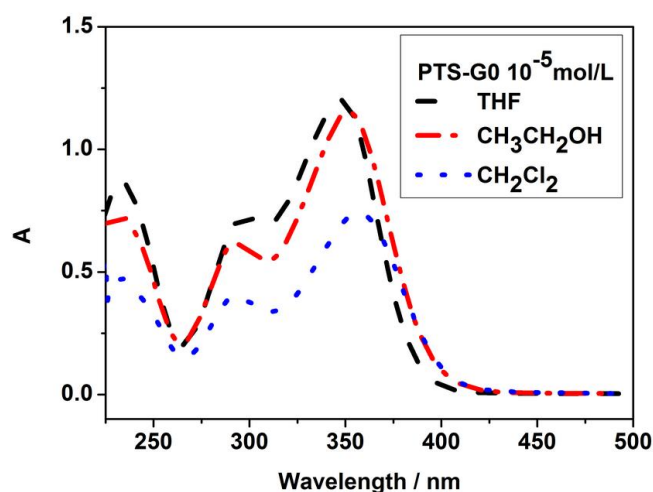
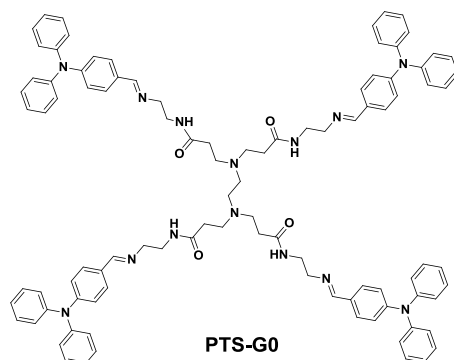
The two-photon absorption was measured by optic multi-channel analyze apparatus and Ti:Sapphire laser apparatus (150fs)+Panther OPO provide harmony adjustable laser (model Mira900-F, Legend-F, OperA, Coherent Int.). The 2PA cross-sections of chromophore were measured by the two-photon induced fluorescence (TPIF) method under a femto-second Ti:Sapphire laser. The Rhodamine B ( $2 \times 10^{-5} \text{ mol/L}$ ) used as a standard, which  $\sigma_1$  was 150 GM by TPIF method and  $\Phi$  was 0.71 The basic parameters of the laser out put were 800nm (for 2PA) wavelength, 150 fs pulse width, and 1–2mJ

pulse energy. Here, the incident laser pulses were focused via  $f = 15\text{cm}$  lens onto the center of the sample cell, while intensity levels of the input laser pulses could be varied by rotating a polarization prism with out changing the pulse shape and laser operation levels.

### 1.3 Procedures

The UV-vis absorption and fluorescence emission ( $\lambda_{\text{ex}}=360\text{nm}$ ) spectra of PTS (G0) were got in different solvent (THF,  $\text{CH}_2\text{Cl}_2$ , ethanol, toluene, DMF,  $\text{CHCl}_3$ ) at  $1 \times 10^{-5}$  mol/L concentration. Moreover, optical related pH sense (the UV-vis absorption and fluorescence emission) of PTS (G0) were investigated. The solvent was ethanol: water =1:9(volume ratio). The pH values demarcated through dripping NaOH or HCl solutions measured by PHS-3C pH-meter. The solutions of PTS (G0) in different pH values were prepared by using 10mL volumetric flask. The UV-vis absorption and fluorescence emission( $\lambda_{\text{ex}}=360\text{nm}$ ) pH sense related spectra were undertook in  $4\text{cm} \times 1\text{cm} \times 1\text{cm}$  fluorometric quartz cuvettes.

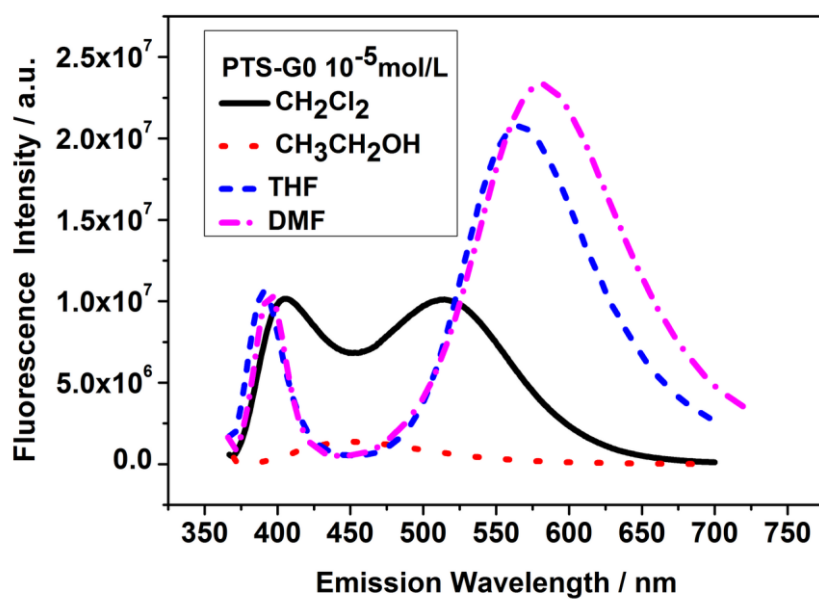
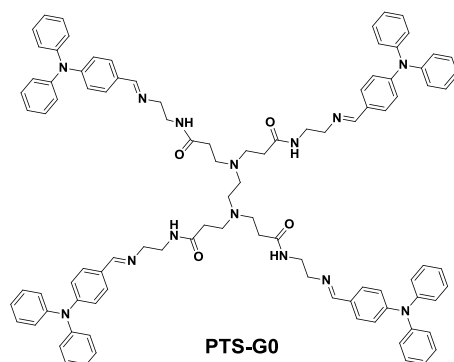
## 2 The UV-vis absorption and fluorescence spectra



**Figure S1** the UV-vis spectra of PTS (G0) in different solvents. The concentrations of solutions were all  $1 \times 10^{-5}$  mol/L.

The Figure S1 gave the UV-vis absorption of dendrimers PTS (G0) in different solvents. The concentrations of solutions were all  $1 \times 10^{-5}$  mol/L. The Figure S 1 showed the maximum UV-vis absorption peaks of PTS (G0) were about at 340 nm – 360 nm. The PTS (G0) in solvent THF gave the maximum UV-vis absorption peaks. The UV-vis absorption peaks at about 300 nm were corresponding to the absorption of PAMAM

cores. The branches of dendrimers dispersed and spreaded out in the solutions forming the space-structures might affect the absorption.

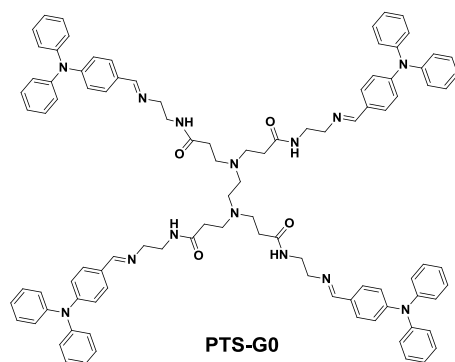


**Figure S2** The fluorescence emission spectra of PTS (G0) in different solvents. The concentrations of solutions were all  $1 \times 10^{-5}$  mol/L.

The Figure S2 gave the fluorescence emission spectra of PTS (G0) in different solutions and the concentrations were all  $1 \times 10^{-5}$  mol/L. The excited wavelength was  $\lambda_{ex}=360$  nm. The fluorescence spectra of two dendrimers were all showed the double

peaks. The PTS (G0) in ethanol in  $\text{CH}_2\text{Cl}_2$  gave only single fluorescence emission peak. The peaks at 400nm were corresponding to the fluorescence emission peaks of PAMAM cores, which gave the fluorescence emission intensity were at about  $1 \times 10^7$  a.u.. The PTS (G0) fluorescence emission peaks were mainly at about 600 nm except the G0 in the solvent  $\text{CH}_2\text{Cl}_2$  giving peak at 500nm. The maximum fluorescence intensity of G0 was at about  $2.5 \times 10^7$  a.u. The triphenylamine conjugated Schiff-base end groups of the two dendrimers were the mainly fluorescence parts. The end groups' number increased but the proportion reduced and the PAMAM cores affect the fluorescence emission in different generations, which might reduce the fluorescence intensity. The branches' space spreading degrees in the solution with different generation might also affect the intensity and emission wavelength.

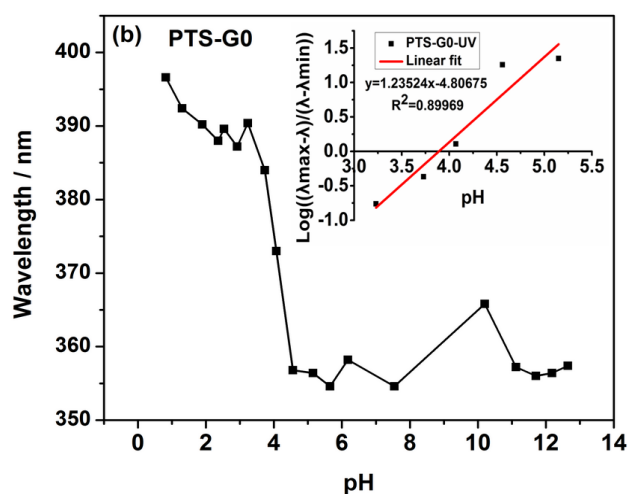
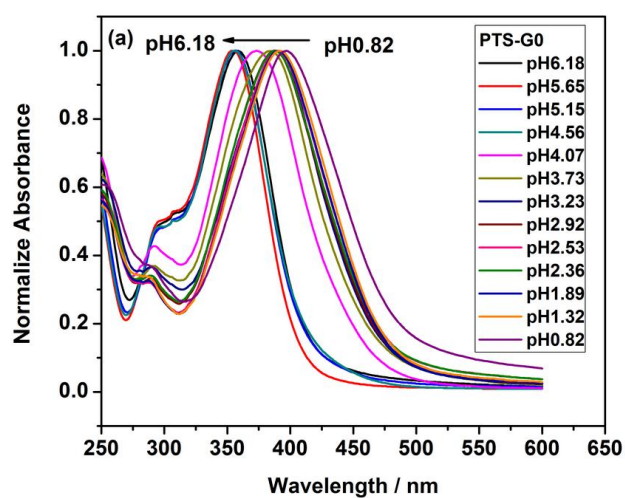
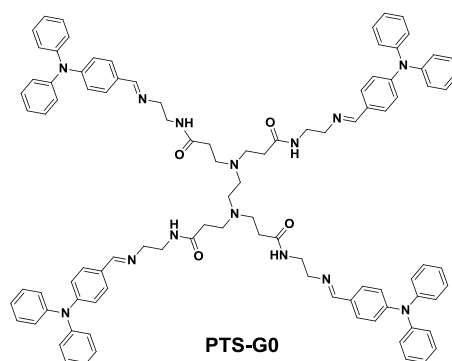




**Table S1** the UV and Fluorescence parameters of PTS-G0

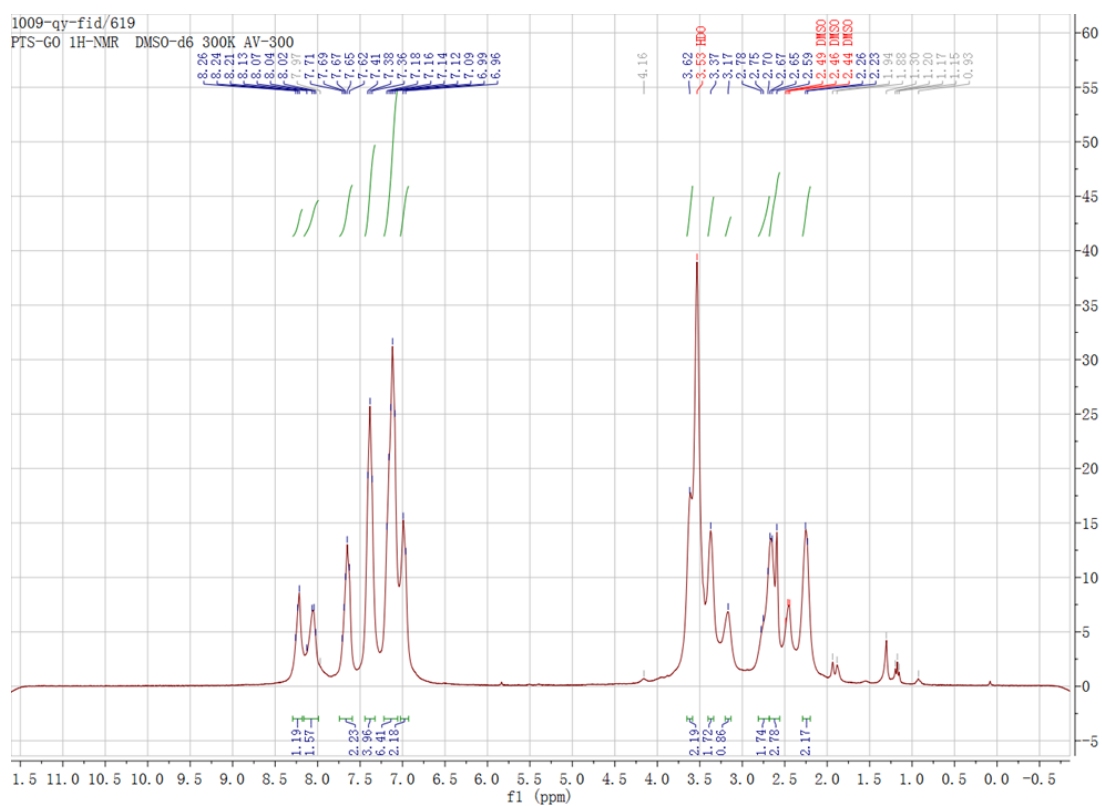
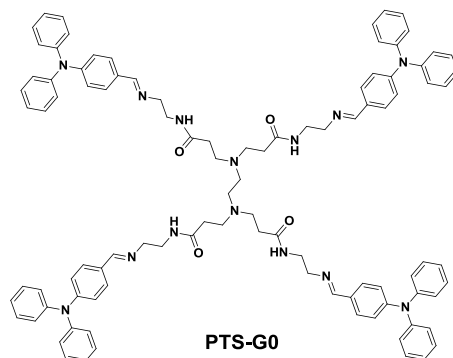
(Stokes shifts= $\nu_{abc} - \nu_{em}$ )

PTS-G0	UV	Flu	stokes
CH <sub>2</sub> Cl <sub>2</sub>	354	488	77567.84
toluene	366	450	51001.82
ethanol	350	452	64475.35
THF	347	515	94009.68
DMF	346	582	117196

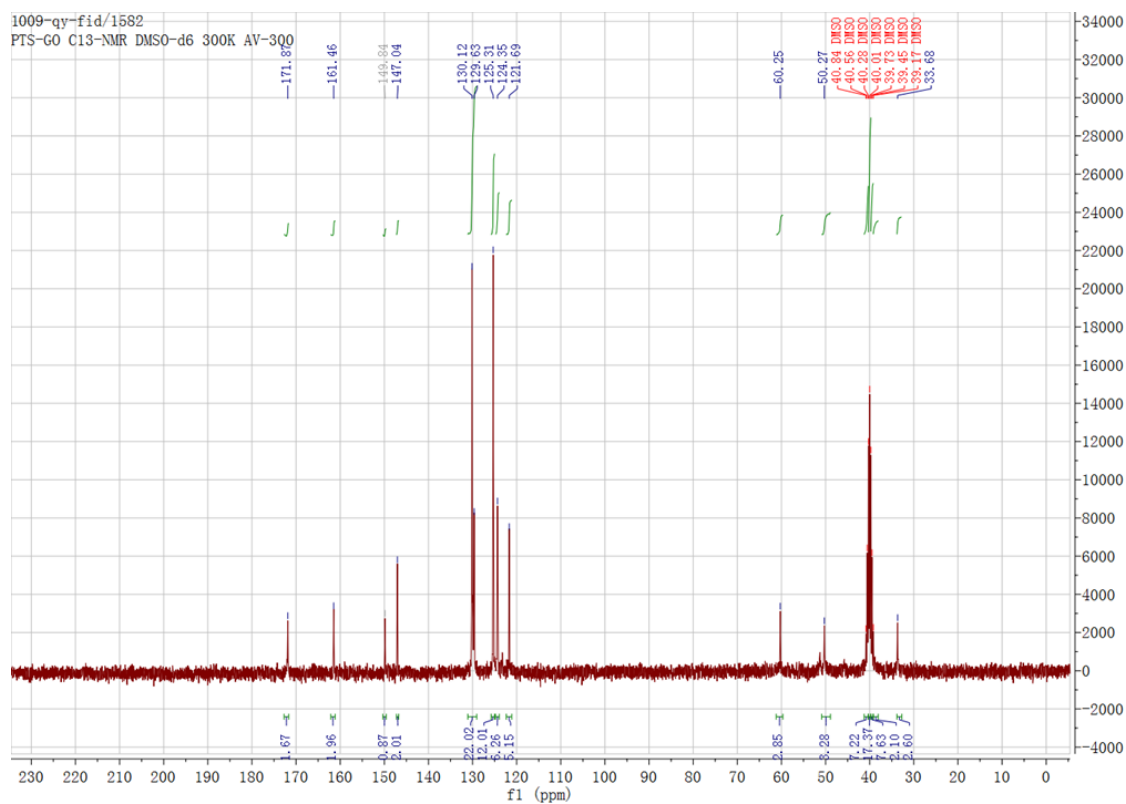
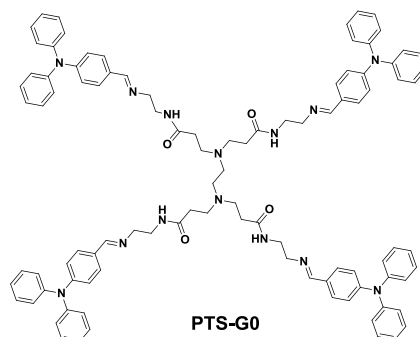


**Figure S3** (a) normalized UV-vis spectra of ( $1 \times 10^{-5}$  mol/L) PTS-G0 (EtOH:water = 1:9 volume ratio) vs pH. (b) relationship of UV-vis absorption peaks wavelength vs. pH (insert line is the linear fit:  $\log[(\lambda_{\text{max}}-\lambda)/(\lambda-\lambda_{\text{min}})]$  vs. pH )

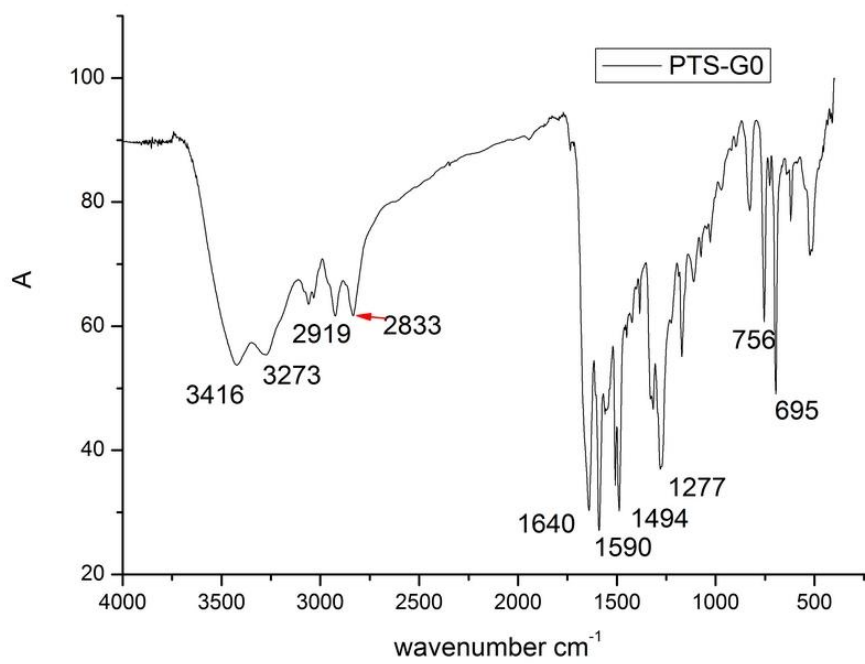
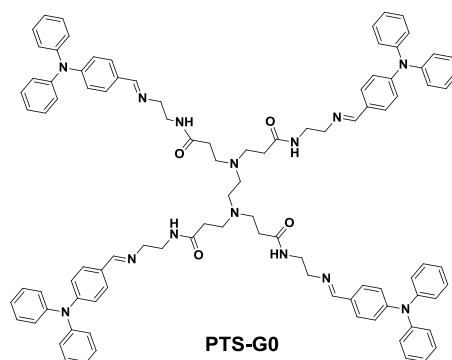
### 3. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, IR, MS



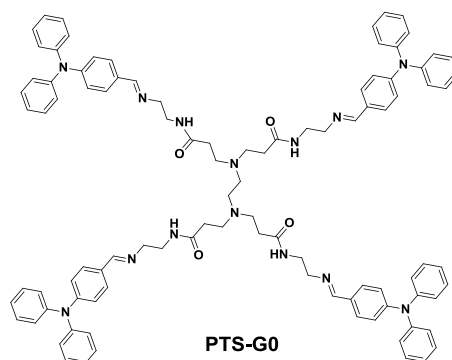
**Figure S4** the  $^1\text{H}$  NMR of PTS-G0



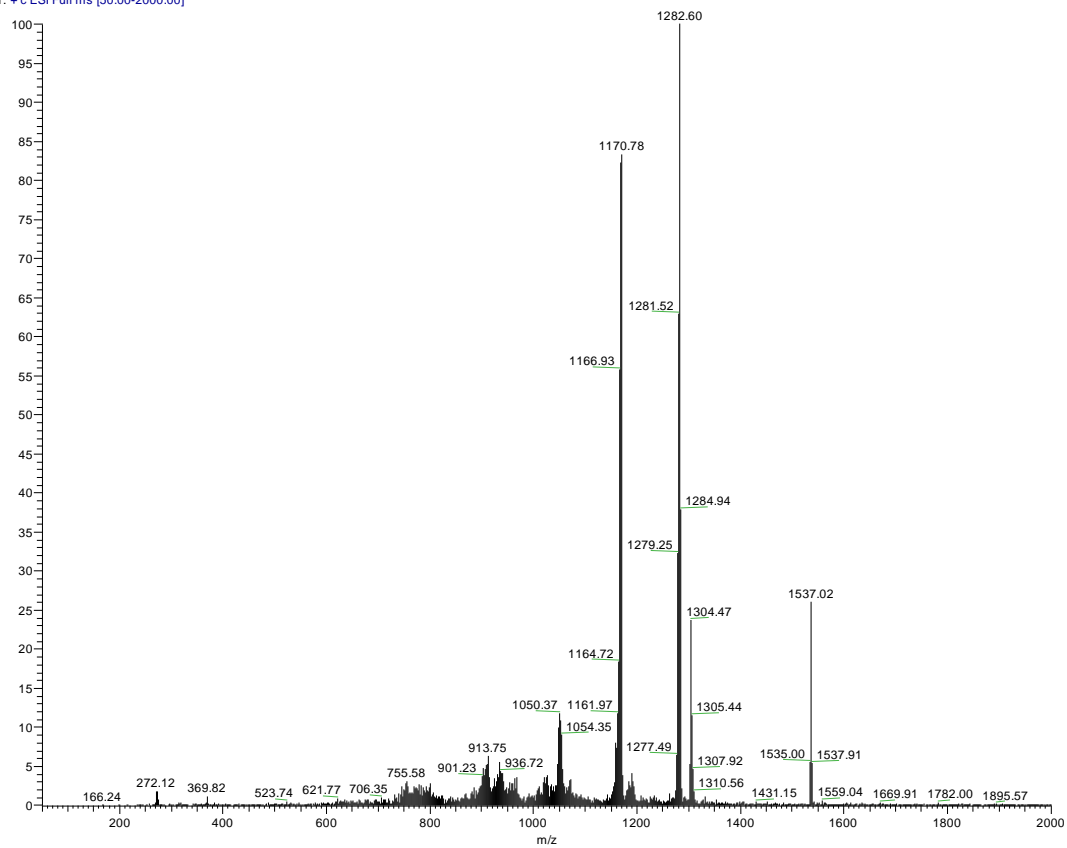
**Figure S5** the  $^{13}\text{C}$  NMR of PTS-G0



**Figure S6** IR of PTS-G0

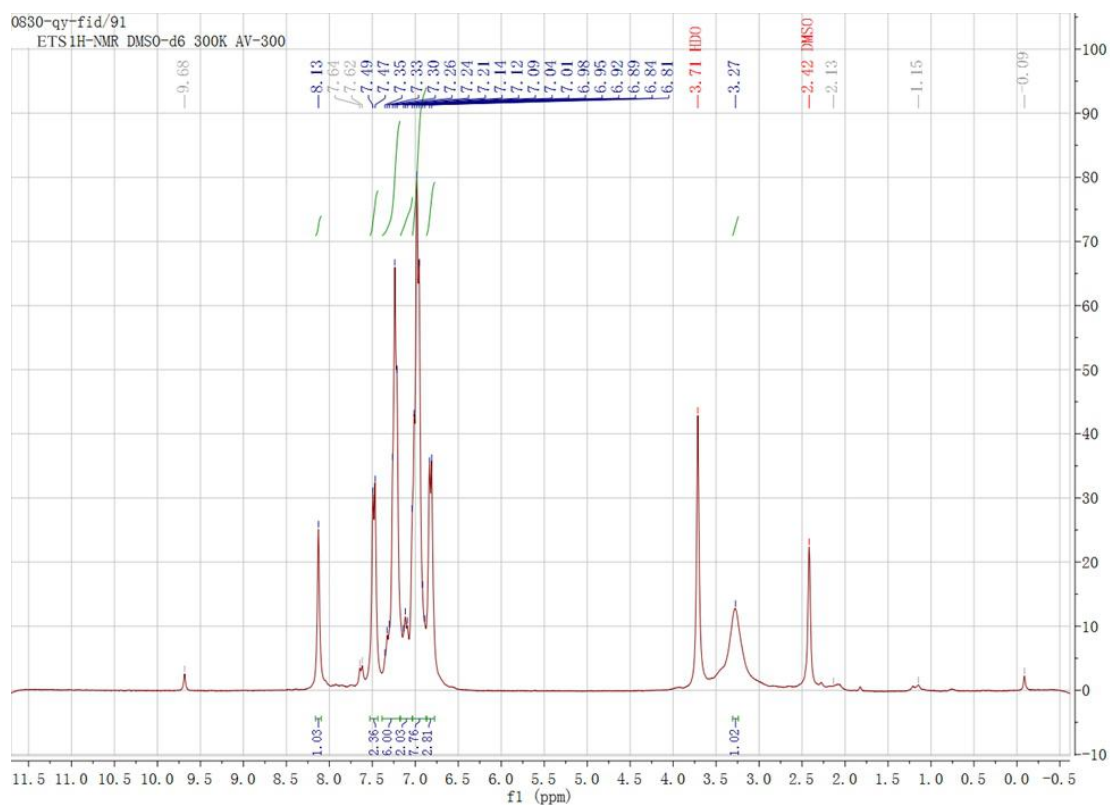
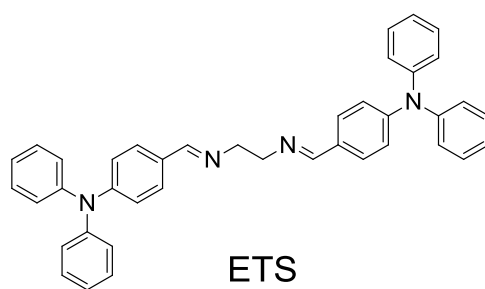


PTS #12 RT: 0.55 AV: 1 NL: 1.81E5  
T: + c ESI Full ms [50.00-2000.00]



**Figure S7** the MS of PTS-G0 (m/z: (Calculate 1537.81 [M]) Found: 1537.02 [M],

1537.91[M+H]<sup>+</sup>)



**Figure S8** the <sup>1</sup>H NMR of ETS

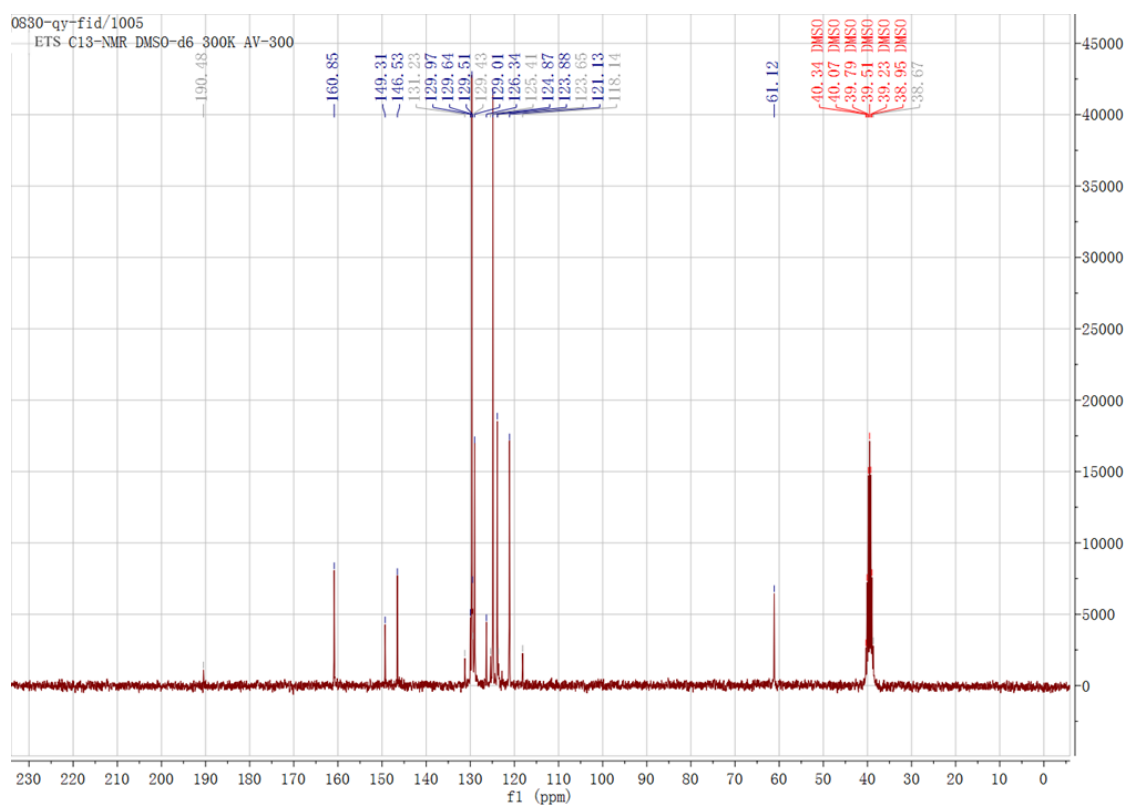
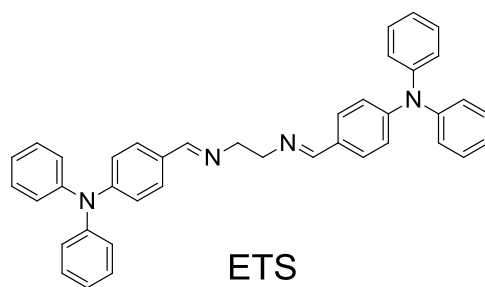
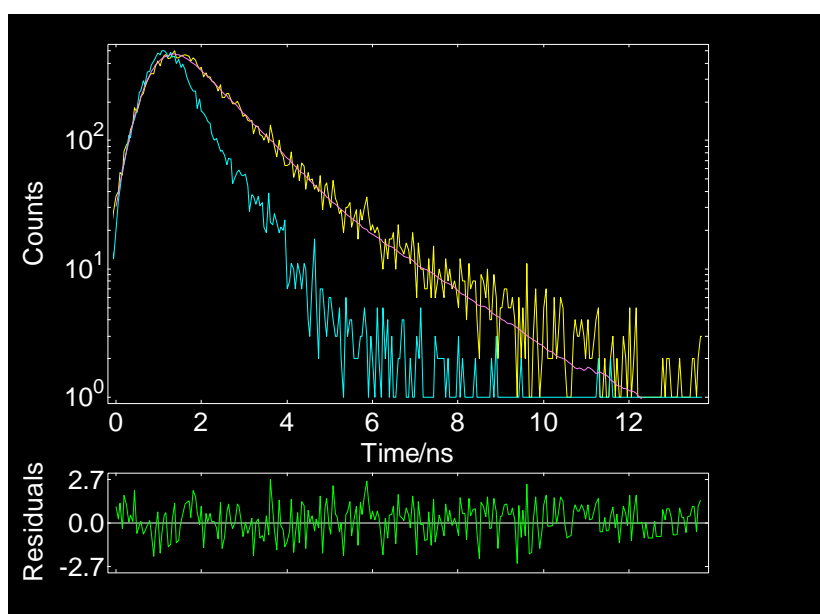
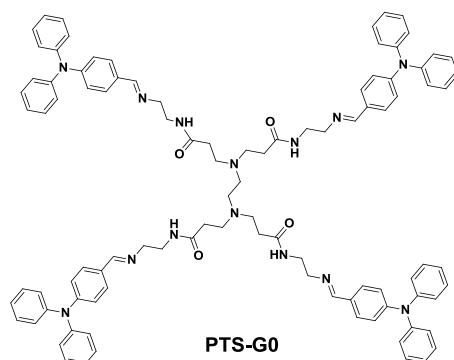


Figure S9 the  $^{13}\text{C}$  NMR of ETS

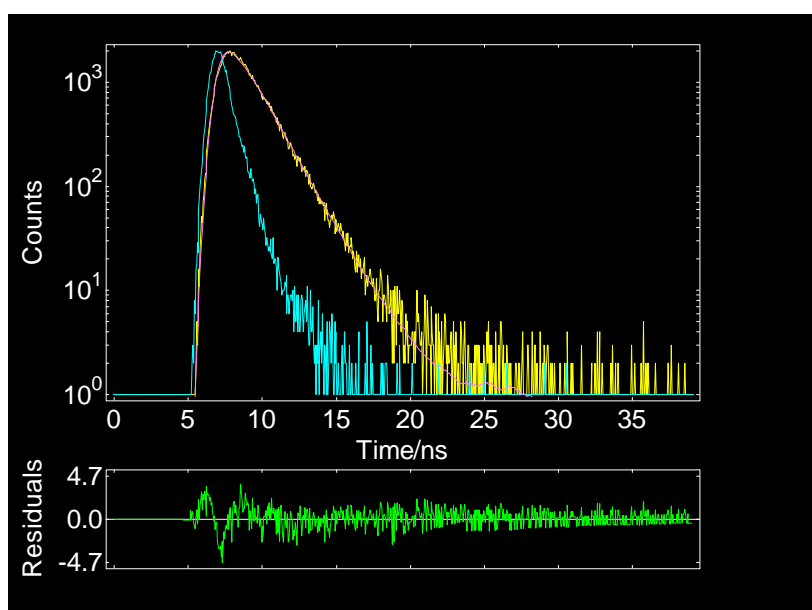
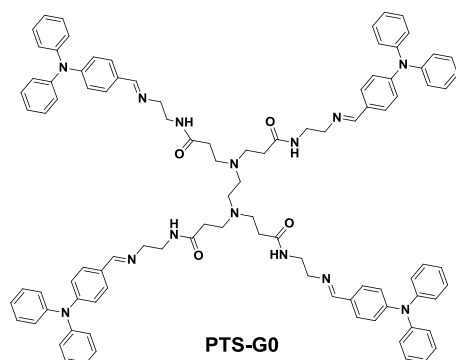


#### 4. Fluorescence decay curves and fluorescence life time



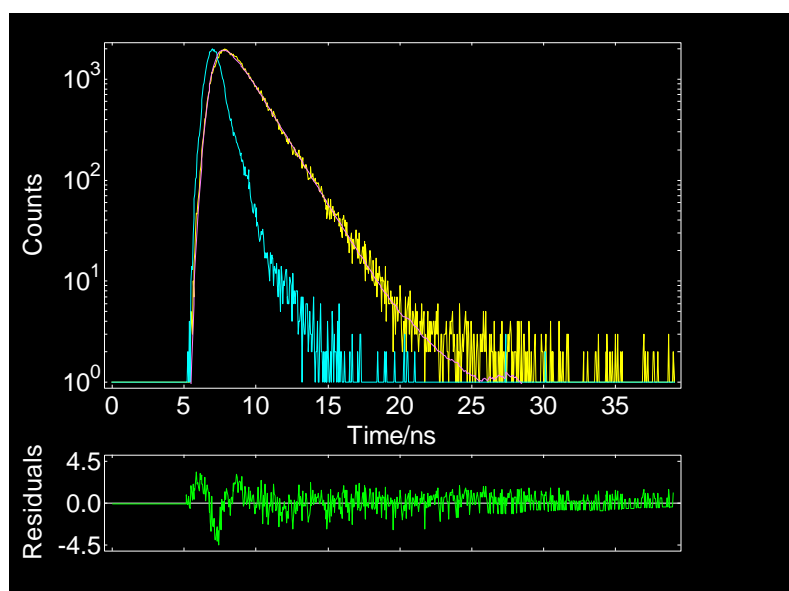
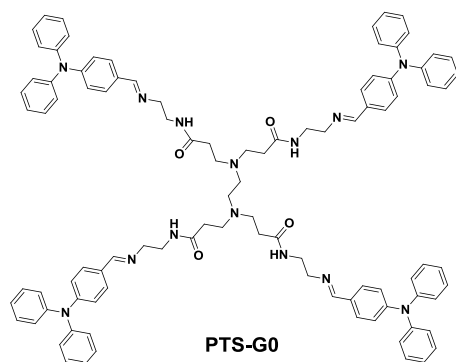
**Figure S10(a)** Fluorescence decay curves of PTS-G0 (at pH=2.53)  $1 \times 10^{-4}$

$\text{CH}_3\text{CH}_2\text{OH}$  fluorescence life time 0.99 ns



**Figure S10(b)** Fluorescence decay curves of PTS-G0 (at pH=7.54)  $1 \times 10^{-4}$

$\text{CH}_3\text{CH}_2\text{OH}$  fluorescence life time 1.61 ns

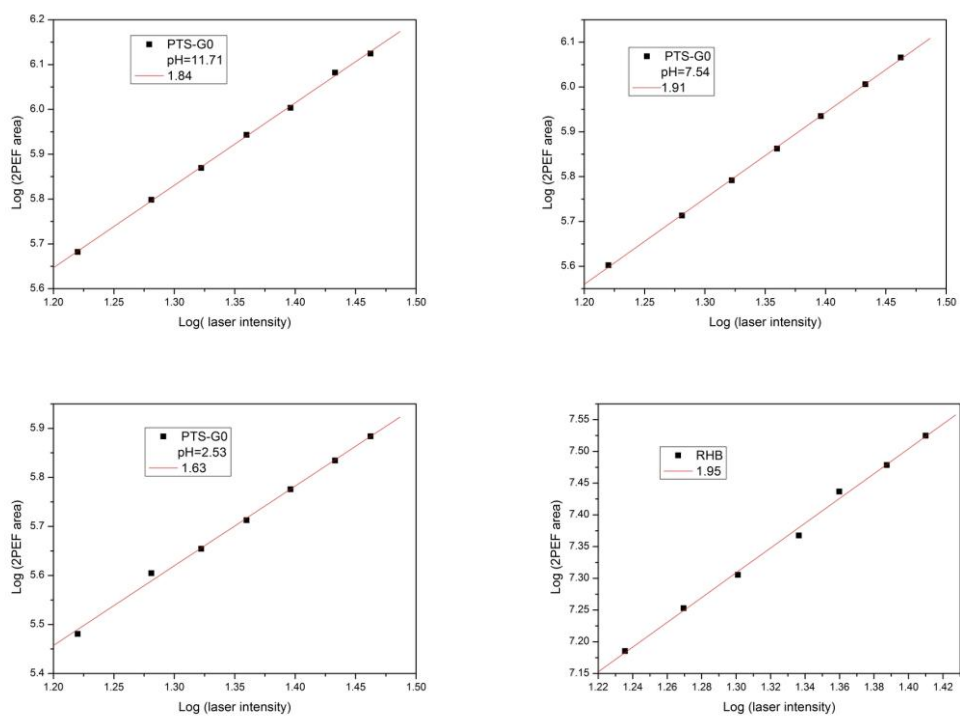
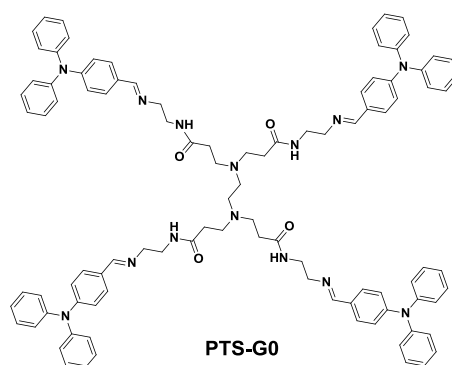


**Figure S10(c)** Fluorescence decay curves of PTS-G0 (at pH=11.71)  $1 \times 10^{-4}$

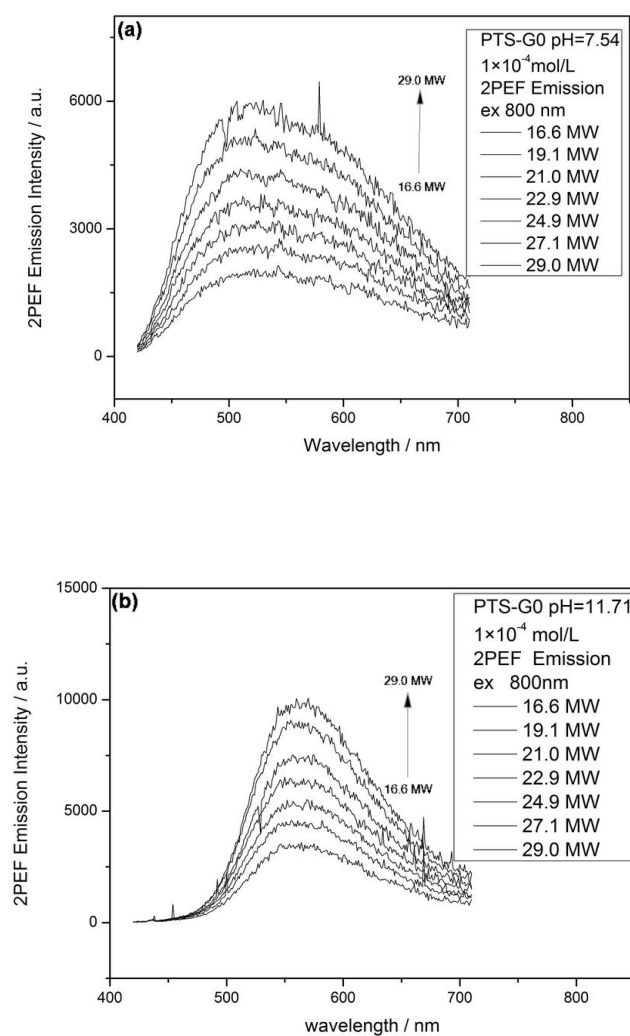
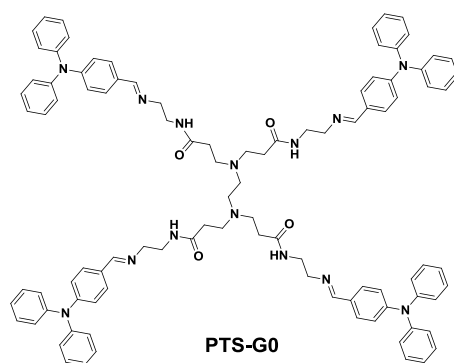
$\text{CH}_3\text{CH}_2\text{OH}$  fluorescence life time 1.80ns

## 5. 2PA cross-sections ( $\sigma_2$ )

RHB 800nm 150 GM (Two-Photon Induce Fluorescence method TPIF) in CH<sub>3</sub>OH  $\Phi=$   
0.71 for RHB in MeOH. Most important assumptions in this model are that one-photon  
and two-photon quantum efficiencies of the fluorophore are equal and that the  
fluorescence quantum efficiency is constant over the entire spectral range of the  
experiment We have also obtained quite close  $\sigma_1$  values, such as 150 GM, for RhB in  
MeOH at 800 nm from TPIF methods

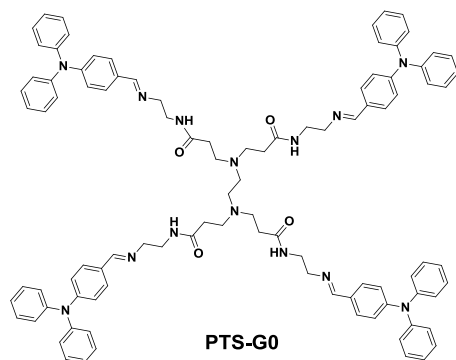


**Figure S11** Two-Photon Induce Fluorescence method fit line of PTS-G0 and RHB.



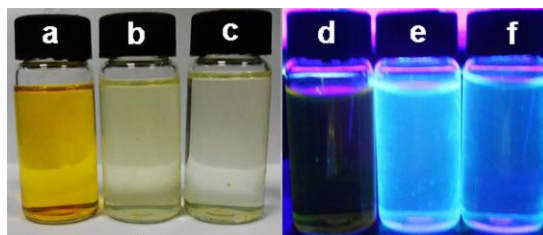
**Figure S12** two-photon fluorescence emission spectra of PTS-G0 ((a) at pH=7.54 and (b) at pH=11.71) under different laser power (excited wavelength 800 nm).

## 6. TLC



**Figure S13** TLC photograph of PTS-G0

## 7. Parameters



**Figure S14** Photograph of PTS-G0 solution ( $1 \times 10^{-3}$  mol/L, EtOH/H<sub>2</sub>O = 1/9). Samples left in room light, right excited under UV lamp (365 nm) at room temperature. (a, d) low pH; (b,e) neutral pH; (c,f) high pH.

**Table S2** The parameters of PTS-G0

	$\lambda_{\text{abs}}/\epsilon^{\text{a}}$	$\lambda_{\text{em}}/I_{\text{max}}^{\text{b}}$	$\Delta\nu^{\text{c}}$	$\tau^{\text{d}}$	$\Phi\%^{\text{e}}$	$\lambda_{2\text{PEF}}/I^{\text{f}}$	$\sigma_{2\text{g}}$
<b>1</b>	356/1.3	476/9.16	7.21	1.61	12	532/3.5	38
<b>2</b>	355/1.2	475/9.65	7.34	1.80	13	512/1.5	75
<b>3</b>	401/1.1	485/8.76	4.87	0.99	—	563/0.3	—

Footnote: PTS-G0  $1 \times 10^{-4}$  mol·L<sup>-1</sup> in EtOH:H<sub>2</sub>O=1:9; (1) pH = 7.54; (2) pH=11.71; (3)

pH=2.53; a:  $\lambda_{\text{abs}}$  (nm) /  $\epsilon$  ( $\times 10^4$ ); b:  $\lambda_{\text{em}}$  (nm) /  $I_{\text{max}} \times 10^6$ (a.u.); c:  $\Delta\nu$  = Stokes shifts

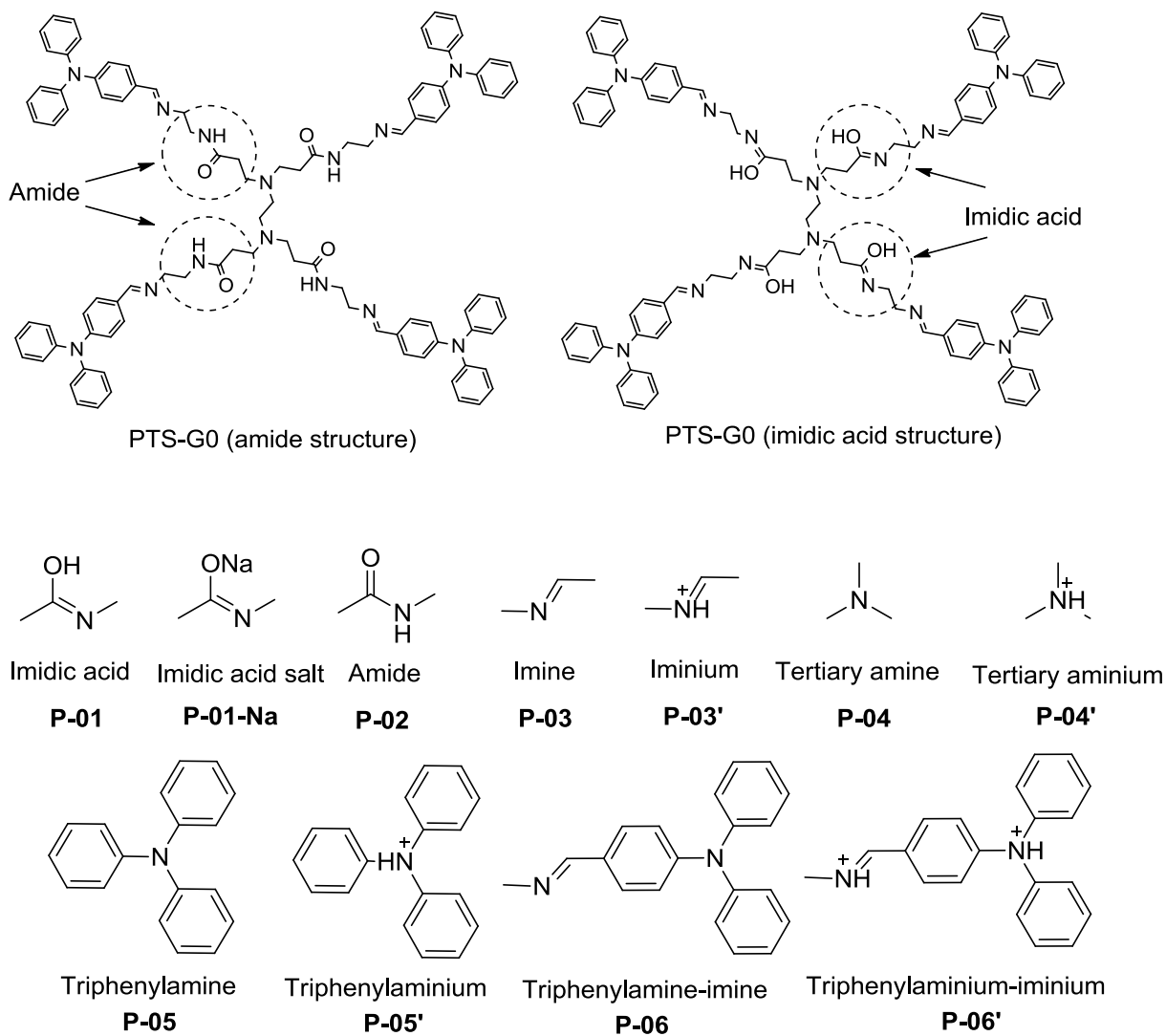
$(\nu_{\text{abc}} - \nu_{\text{em}}) \times 10^4$ (cm<sup>-1</sup>); d:  $\tau$  was the fluorescence lifetime (ns); e:  $\Phi$  was fluorescence

quantum yield; f:  $\lambda_{2\text{PEF}}$  (nm) /  $2\text{PEF } I_{\text{max}}$  ( $\times 10^3$  a.u.); g:  $\sigma_{2\text{g}}$  is two-photon absorption

cross-section at excited wavelength 800 nm (unit GM= $10^{-50}$ cm<sup>4</sup>·s·photon<sup>-1</sup>·molecule<sup>-1</sup>).



## 8. Quantum chemical theory calculations



**Figure S15** The chemical parts of PTS-G0 for quantum chemical calculation

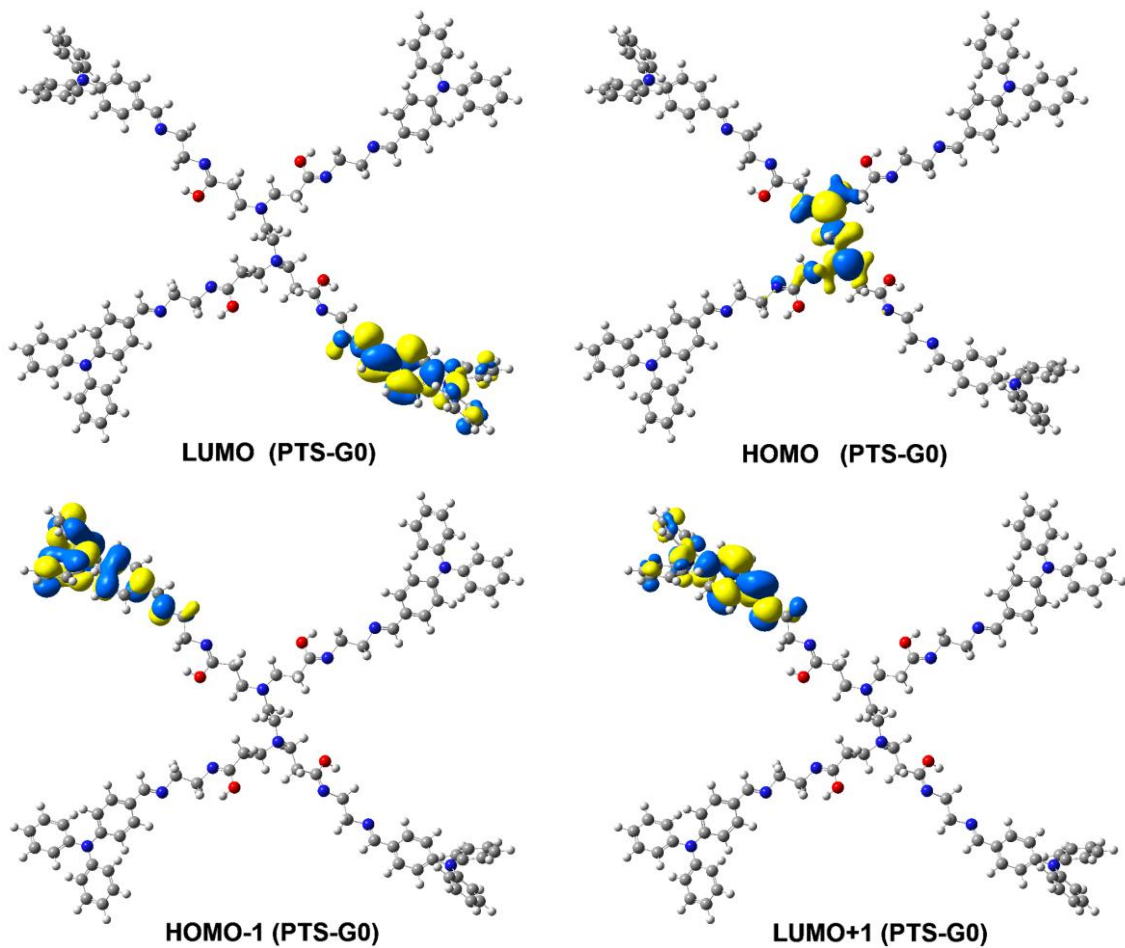
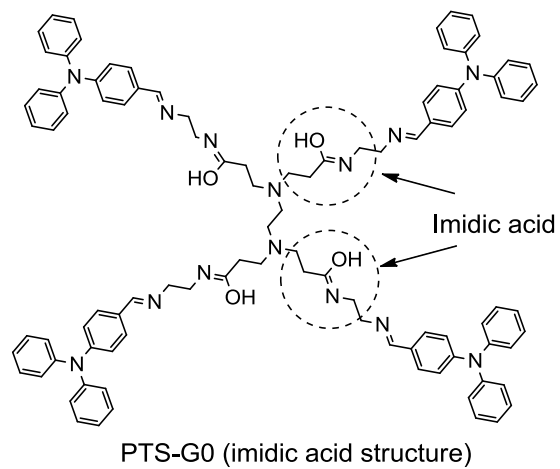
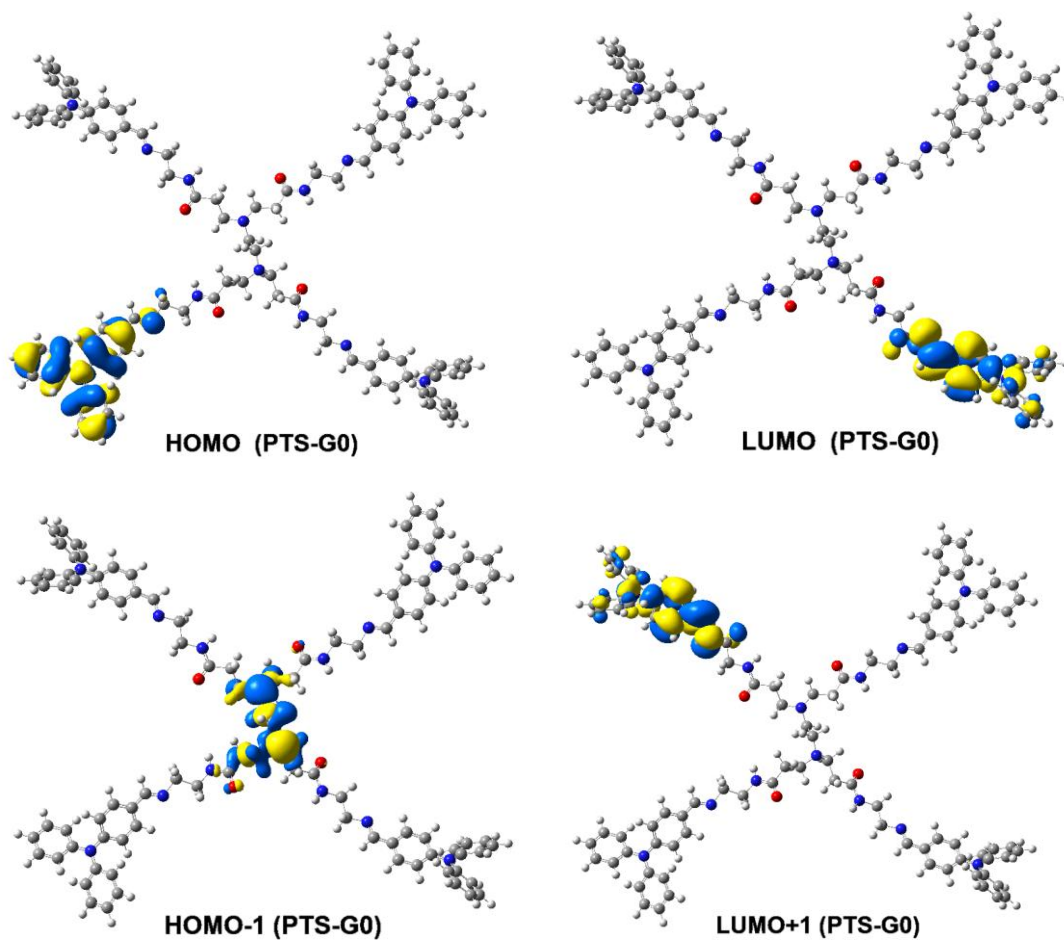
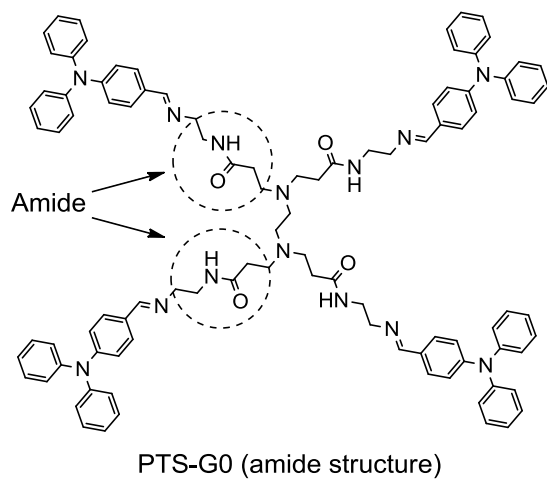


Figure S16 The molecules orbits of PTS-G0 (imidic acid structure)



**Figure S17** The molecules orbits of PTS-G0 (imidic acid structure)

**Table S3** The emissions and absorptions spectra of chemical groups in PTS-G0 in gas phase vacuum calculated by TD\_DFT b3lyp/6-31g method by Gaussian 09 <sup>S1</sup>

Parts	Electron transition	Energy [eV]	Calculated wavelength [nm]	Main transition configuration	Oscillator strength f
<b>P-01</b>	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
	S0→S1	4.017	308.61	HOMO→LUMO: 0.19054 HOMO-1→LUMO: 0.67201	0.0434
<b>P-01-Na</b>	S0→S1	0.4652	2665.15	LUMO→HOMO: -0.51605	0.0200
	S0→S1	0.7926	1564.33	LUMO→HOMO: 0.21388	0.0132
<b>P-02</b>	S1→S0	-	-	-	-
<b>P-03</b>	S1→S0	0.1785	6945.14	LUMO→HOMO: 0.50322	0.0000
	S1→S0	4.8833	253.89	LUMO→HOMO-1: -0.10164	0.0568
	S0→S1	4.8833	253.89	HOMO-1→LUMO: 0.66766 HOMO-2→LUMO: -0.19617	0.0568
<b>P-03'</b>	S1→S0	4.3491	285.08	LUMO→HOMO-1: 0.11646 HOMO→HOMO-2: -0.11788	0.0018
		4.5171	274.48	LUMO→HOMO-1: 0.11307 HOMO→HOMO-1: -0.11247	0.0001
		4.1986	295.30	LUMO→HOMO-1: 0.12355 HOMO→HOMO-1: -0.12266	0.0000
	0.0633	19576.05	LUMO→HOMO:0.21268	0.0000	
	S0→S1	4.1986	295.30	HOMO-6→ LUMO: 0.14308 HOMO-1→ LUMO: 0.69439 HOMO-6→ HOMO: -0.13611 HOMO-1→ HOMO: -0.70047	0.0000
<b>P-04</b>	S1→S0	-	-	-	-
<b>P-04'</b>	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
<b>P-05</b>	S1→S0	-	-	-	-
<b>P-05'</b>	S1→S0	0.0186	66733.24	LUMO→HOMO:-0.30168	0.0001
		0.2519	4920.99	LUMO→HOMO: -0.14677	0.0023
		0.7431	1668.54	LUMO→HOMO: 0.16563	0.0338
				LUMO+1→HOMO: 0.12028	
		0.9536	1300.11	LUMO→HOMO: 0.11940	0.0676
				LUMO+2→HOMO: -0.10278	
				LUMO+3→HOMO: -0.11185	
		0.9895	1253.04	LUMO+2→HOMO:-0.19585	0.0895
<b>P-06</b>	S1→S0	-	-	-	-
<b>P-06'</b>	S1→S0	1.3123	944.75	LUMO+2→HOMO: -0.13805	0.1595
	S1→S0	1.2826	966.66	LUMO+2→HOMO: -0.11496	0.1720

Footnote: a) **P-01** imidic acid; **P-02** amide; **P-03** imine; **P-03'** iminium; **P-04** tertiaryamine; **P-04'** tertiaryammonium; **P-05** triphenylamine; **P-05'** triphenylammonium; **P-06** triphenylamine-imine; **P-06'** triphenylammonium-iminium (Fig.5). b) The S1→S0 was the emission states of the parts. The S0→S1 was the absorptions states of the parts.