Electronic Supplementary Information (ESI)

Up-converted Fluorescence Emission under Linear Common Spectrofluorometer from PAMAM Pyridine Derivatives and with QDs Nanoparticles

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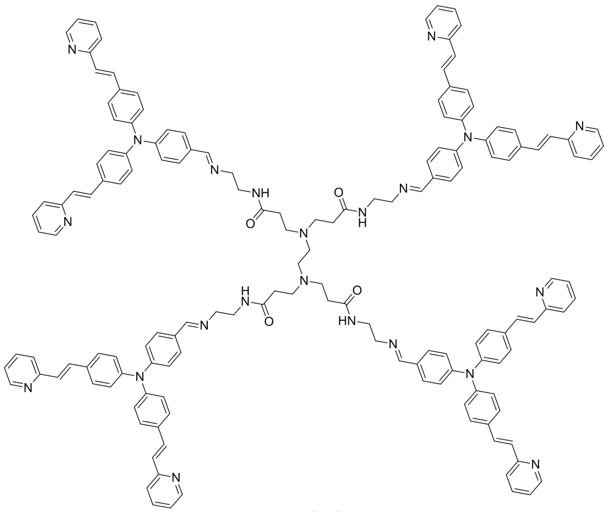
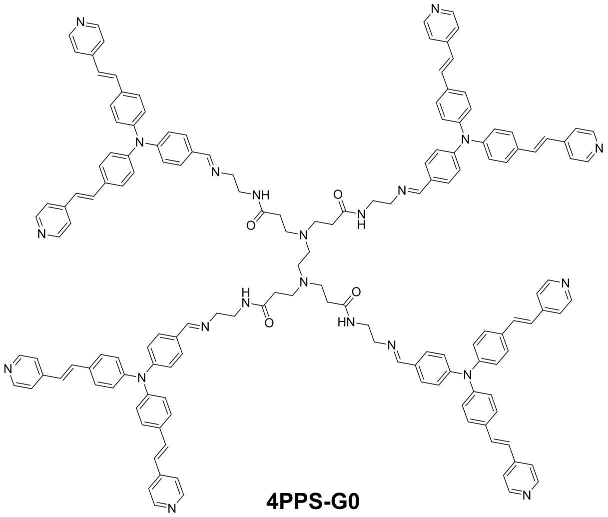


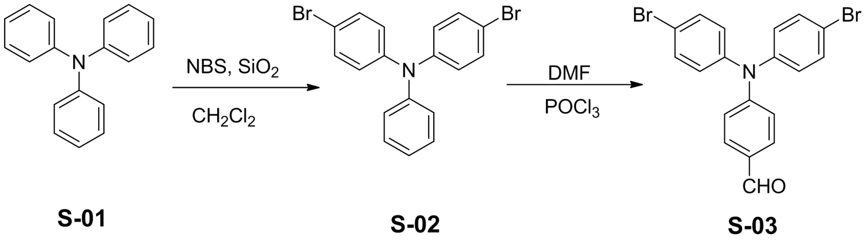
2PPS-G0



4PPS-G0

S-Figure 1 the structures of dendrimers 2PPS-G0 and 4PPS-G0

1. Experiment Synthesis



S-Figure 2 the reaction of molecules **S-02** and **S-03**

1.1 Synthesis of 4-bromo-N-(4-bromophenyl)-N-phenylaniline **(S-02)**

500mL round-bottom flask add in triphenylamine (**S-01**) 0.5 g (2.04 mmol)，1g SiO_2， NBS 0.73 g (4.08 mmol)， and 280mLCH_2Cl_2. Keep in dark place, room temperature, stiring24h. After reaction, filtration， washing by water three times, washing by salt water three times, add anhydrous Na_2SO_4 to dry. rotary evaporation then purify by silicagel column (petroleum ether elution), got thick liquid.

IR (KBr) cm^{-1}: 3025, 1584, 1489, 1335, 1225, 554

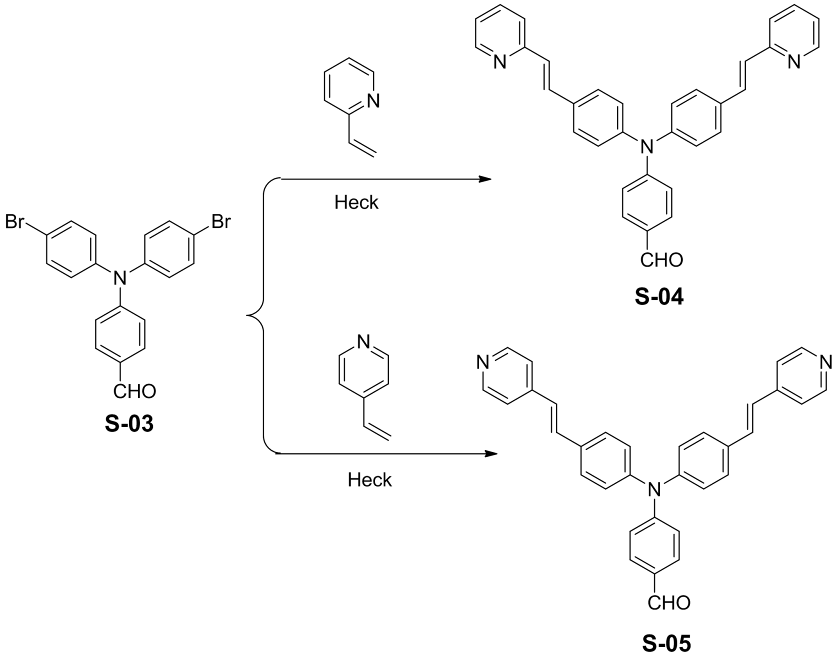
1.2 Synthesis of 4-(bis(4-bromophenyl)amino)benzaldehyde **(S-03)**

At N_2 protecting, add mixture 4-bromo-N-(4-bromophenyl)-N-phenylaniline **(S-02)** 12 g (30 mmol)，1,2-dichloroethane (100 mL)，and DMF 3.3 g (45 mmol) into $POCl_3$7.0 g (46 mmol). Deepred solution reflux 18h. cooling to room temperature, and pour into ice water (200 mL), stirring 1h, then adjust pH to 7 by $NaHCO_3$. dark green solution extract by CH_2Cl_2 (4×80 mL). organic layer washed by water (3 × 50 mL), then drying by anhydrous Na_2SO_4. rotary evaporation then purify by silicagel column (elution solvent: petroleum ether/ ethyl acetate=1:4). m.p.: 167~168.5℃.

IR (KBr) cm^{-1}: 3024, 2724, 1694, 1584, 1487, 1330, 1224.

^1H NMR (300 MHz, CDCl3): δ9.82 (s, 1H, -CHO), 7.68 (d, 2H, ph-H), 7.41 (d, 4H, ph-H), 6.97-7.03(m, 6H, ph-H).

MS (m/z): 431.5 [M^+] (cal: 431.1)



S-Figure 3 the reaction of molecules **S-04** and **S-05**

1.3 Synthesis of 4-(bis (4-(2-(pyridin-2-yl)vinyl)phenyl)amino)benzaldehyde **(S-04)**

4-(bis(4-bromophenyl)amino)benzaldehyde **(S-03)** 0.216 g (0.5 mmol), 2-vinylpyridine 0.13 g (1.2 mmol,), tri-o-tolylphosphine 0.1 g, $Pd(OAc)_2$0.01 g, triethylamine 6 mL, DMF 6 mL, added into 50 mL two-necks flask. Keep no water and no oxygen situation, and in N_2 atmosphere， heat 110℃, reaction 96 h. cooling to room temperature. Filtrate the catalyst, pour in methanol， separate out lots of yellow precipitate, filtration and recrystallization by methanol. vacuum drying and purify by silicagel column.

IR(KBr) cm^{-1}: 3060, 2835,1692, 1631, 1602, 1575,1478,950.

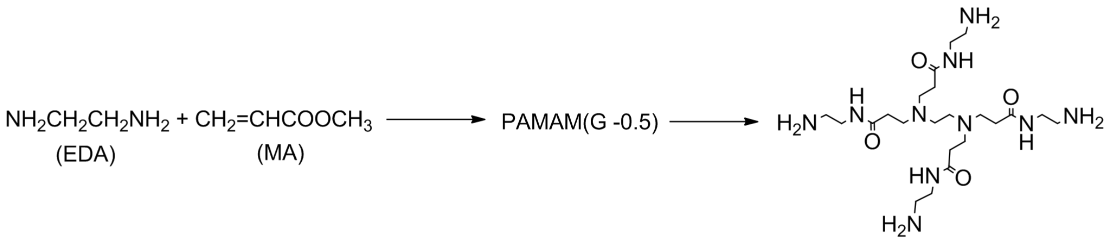
^{1}H NMR(300 MHz $CDCl_3$): δ9.87(s, 1H), 8.50(d, J=6.00 Hz, 2H), 7.74(d,J=6.00 Hz, 4H), 7.47 (d,J=9.00Hz, 2H),7.40(d, 2H), 7.38(d, J=9.00Hz, 2H), 7.36(d, J=6.00 Hz, 2H), 7.32(s, 2H), 7.14-.7.19(m, 4H), 6.95(d, J=18.00 Hz, 4H).

1.4 Synthesis of 4-(bis(4-(2-(pyridin-4-yl)vinyl)phenyl)amino)benzaldehyde **(S-05)**

4-(bis(4-bromophenyl)amino)benzaldehyde **(S-03)** 0.216 g (0.5 mmol), 4-vinylpyridine 0.13 g (1.2 mmol,), tri-o-tolylphosphine 0.1 g, $Pd(OAc)_2$ 0.01 g, triethylamine 6 mL, DMF 6 mL, added into 50 mL two-necks flask. Keep no water and no oxygen situation, and in N_2 atmosphere， heat 110℃, reaction 96 h. cooling to room temperature. Filtrate the catalyst, pour in methanol， separate out lots of yellow precipitate, filtration and recrystallization by methanol. vacuum drying and purify by silicagel column. m.p. 150~152 ℃.

IR(KBr) cm^{-1}: 3058, 2837,1690, 1628, 1603, 1572,1479,952.

^{1}H NMR(300 MHz $CDCl_3$): δ9.87(s, 1H), 8.57(d, J=6.00 Hz, 4H), 7.74(d,J=6.00 Hz, 2H), 7.50(d,J=9.00Hz, 4H), 7.37(d, J=9.00Hz, 4H), 7.32(s, 2H), 7.14-.7.19(m, 4H), 6.95(d, J=18.00 Hz, 4H).



S-06 PAMAM-G0

S-Figure 4 the reaction of molecules **S-06**

1.5 Synthesis of polyamides-amine (PAMAM-G0) dendrimers (**S-06**)[*]

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).

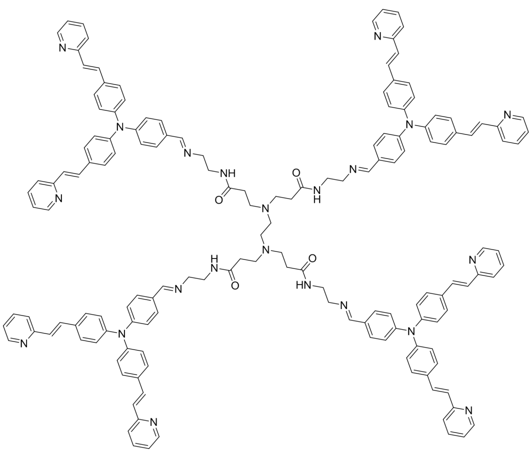
(2) the amidation of the terminal ester groups of -0.5*G* dendrimer from dissolving in methanol solution by excessive EDA under 50 ℃ (affords the 0*G* dendrimer with terminal amine groups).

(3) distillation of exceeded EDA under reduced pressure (gives the purified 0 *G* dendrimer). the PAMAM dendrimers are shown as yellow ropy liquid.

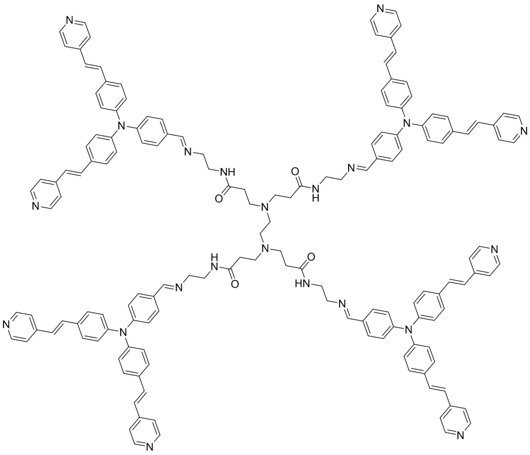
(PAMAM 0G). IR (KBr) cm^{-1}: 3325(NH), 2961, 1647(CO), 1563, 1465, 1307, 995, 687.

MS (m/z): found: 518.3 $[M+2H]^{2+}$ (cal: 518.6 $[M+2H]^{2+}$)

[*] D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder and P. Smith. *Polym J,* 1985, **17**, 117- 132



S-07 2PPS-G0



S-08 4PPS-G0

S-Figure 5 the structures of molecules 2PPS-G0 (**S-07**) [3,3',3'',3'''- (ethane-1,2-diylbis(azanetriyl)) tetrakis(N-(2-((4-(bis(4-((Z)-2-(pyridin-2-yl)vinyl)phenyl)amino) benzylidene) amino) ethyl)propanamide)] and 4PPS-G0 (**S-08**) [3,3',3'',3'''-(ethane-1,2-diylbis(azanetriyl))tetrakis(N-(2-((4-(bis(4-((Z)-2-(pyridin-4-yl)vinyl) phenyl) amino)benzylidene)amino)ethyl) propanamide)]

1.6 Synthesis of 2PPS-G0 (**S-07**) and 4PPS-G0 (**S-08**)

Take PAMAM(G0) **(S-06)** 1mmol, add 4-(bis(4-(2-(pyridin-2-yl)vinyl)phenyl)amino)benzaldehyde **(S-04)** or 4-(bis(4-(2-(pyridin-4-yl)vinyl)phenyl)amino)benzaldehyde **(S-05)** in to 100 mL flask. Add anhydrous Na_2SO_4 0.5 g, in methanol 30 mL, reflux 2 h， cooling and filtration， rotary evaporation to remove solven. Then wash by methanol two times, vacuum drying. Got 2PPS-G0 (**S-07**) or 4PPS-G0 (**S-08**) respectively.

2PPS-G0 (**S-07**):

^{1}H NMR (300 MHz DMSO-d$_6$): δ8.55 (s, 4H, H-C=N), 8.17(s, 8H, Ar-H), 7.61~7.86 (m, 48H, Ar-H), 7.55(d, J=9.00Hz, 8H, H-C=C), 7.52 (m, 4H, H-N), 7.22 (d, J=9.00Hz, 8H, H-C=C), 7.00~7.32(m, 24H, Ar-H), 3.23(m, 24 H, H-C), 2.50 (t, 8H, H-C), 1.23 (t,4H,H-C)

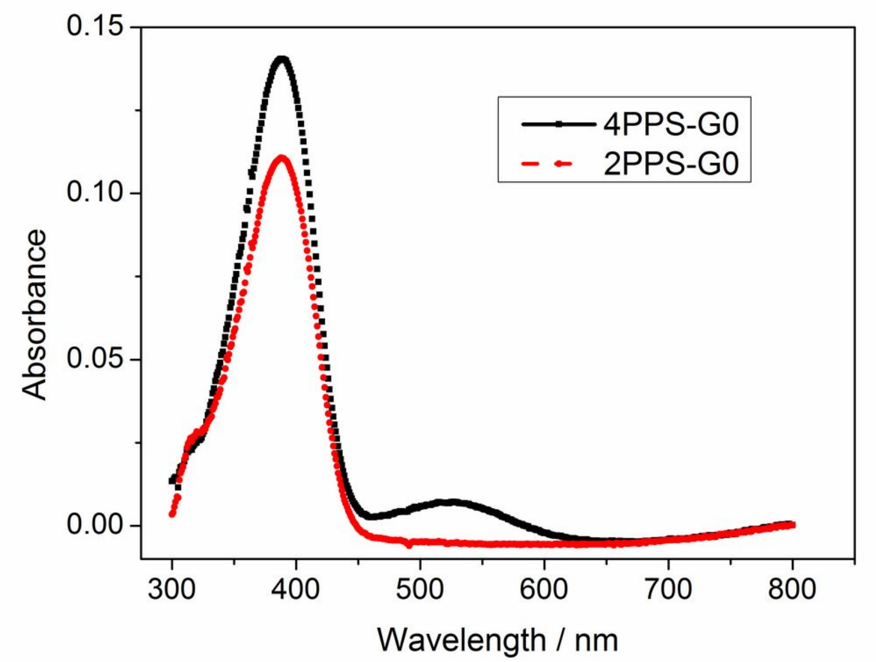
HRMS (m/z) found: 2363.9257 $[M+H]^+$(cal: 2363.9123 $[M+H]^+$)

4PPS-G0 (**S-08**):

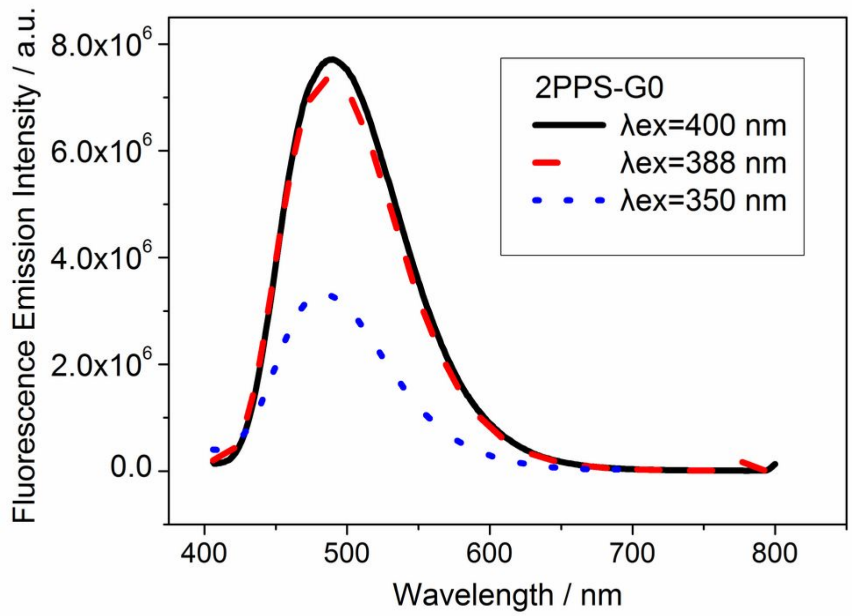
^{1}H NMR (300 MHz DMSO-d$_6$): δ8.53 (s, 4H, H-C=N), 8.15 (d, J=9.00Hz, 16H, Ar-H), 7.70 (s, 8H, H-C=C), 7.61~7.68 (m, 40H, Ar-H), 7.50 (m, 4H, H-N), 7.21 (d, J=9.00Hz, 8H, H-C=C), 7.08~7.28(m, 24H, Ar-H), 3.23(m, 24 H, H-C), 2.50 (t, 8H, H-C), 1.23 (t,4H,H-C).

HRMS (m/z) found: 2363.9257 $[M+H]^+$ (cal: 2363.9123 $[M+H]^+$)

2. UV and Fluorescence Spectra.



S-Figure 6 UV absorption spectra of dendrimers 2PPS-G0 and 4PPS-G0 (3×10^{-5} mol/L in CH_2Cl_2)



S-Figure 7 The fluorescence emission spectra of dendrimers 2PPS-G0 (3×10^{-5} mol/L in CH_2Cl_2

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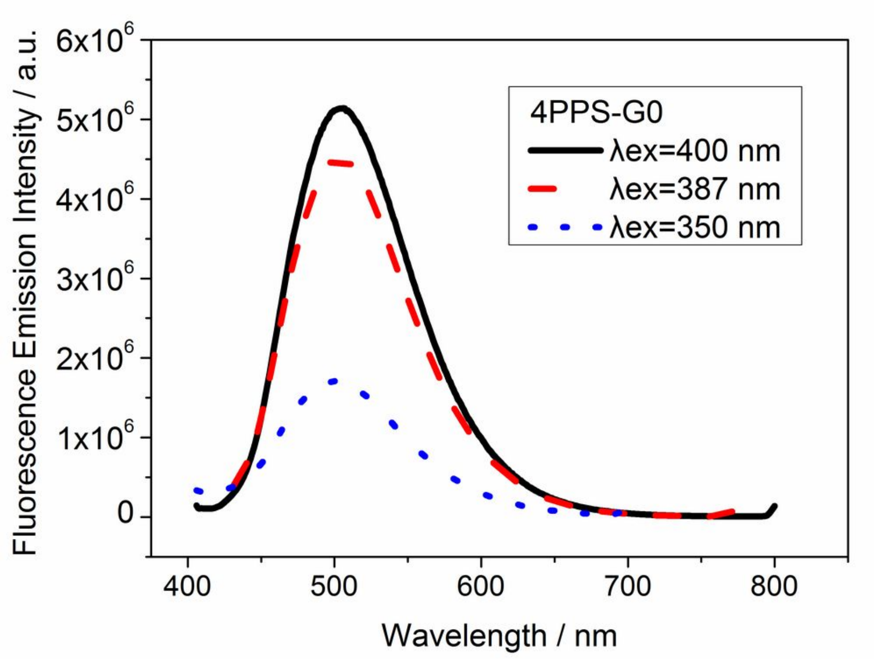
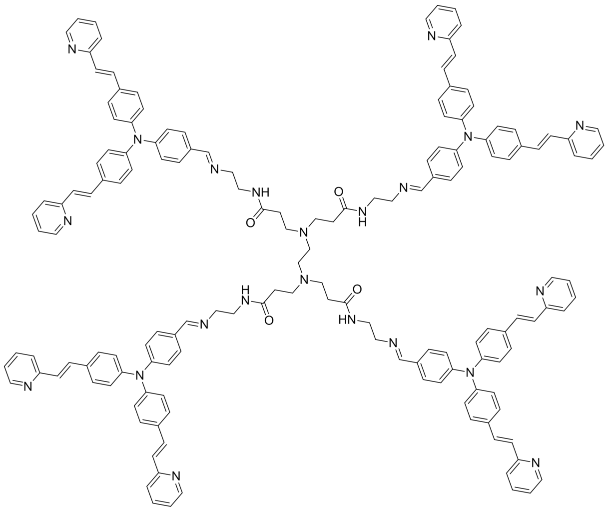
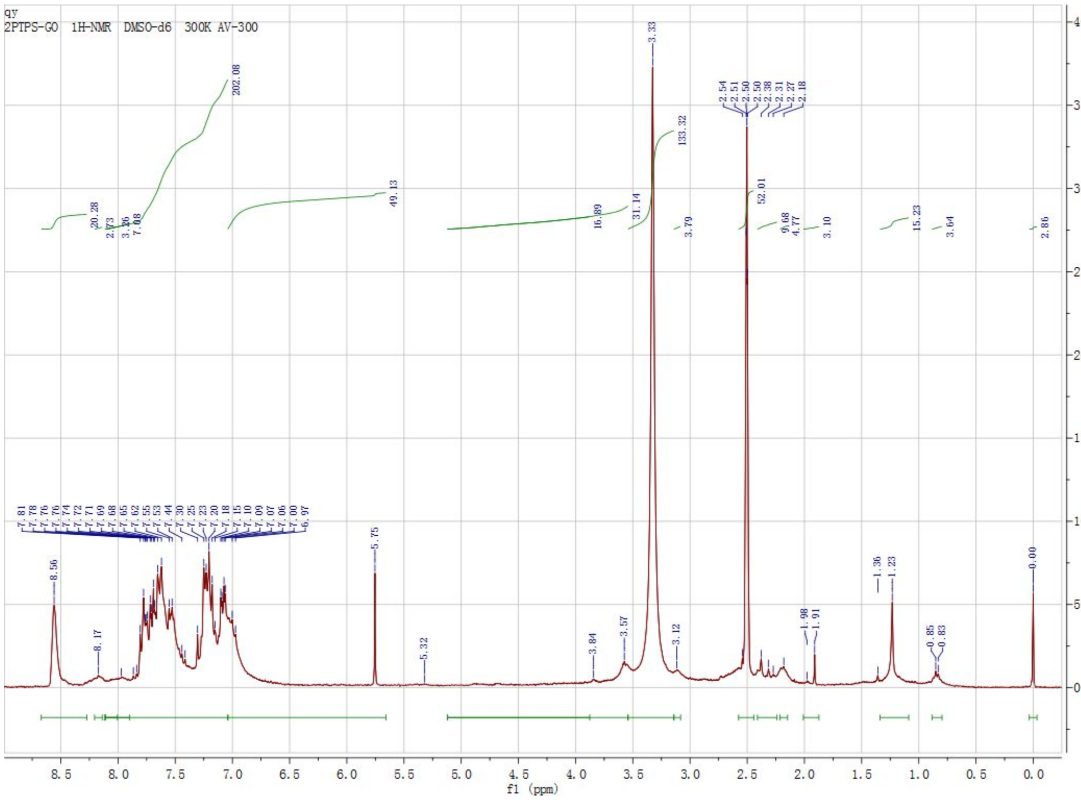


S-Figure 8 The fluorescence emission spectra of dendrimers 4PPS-G0 (3×10^{-5} mol/L in CH_2Cl_2)

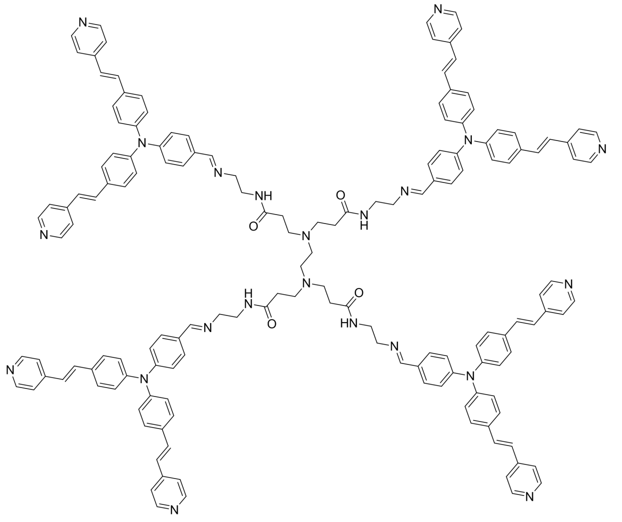
3. NMR, HRMS, MS



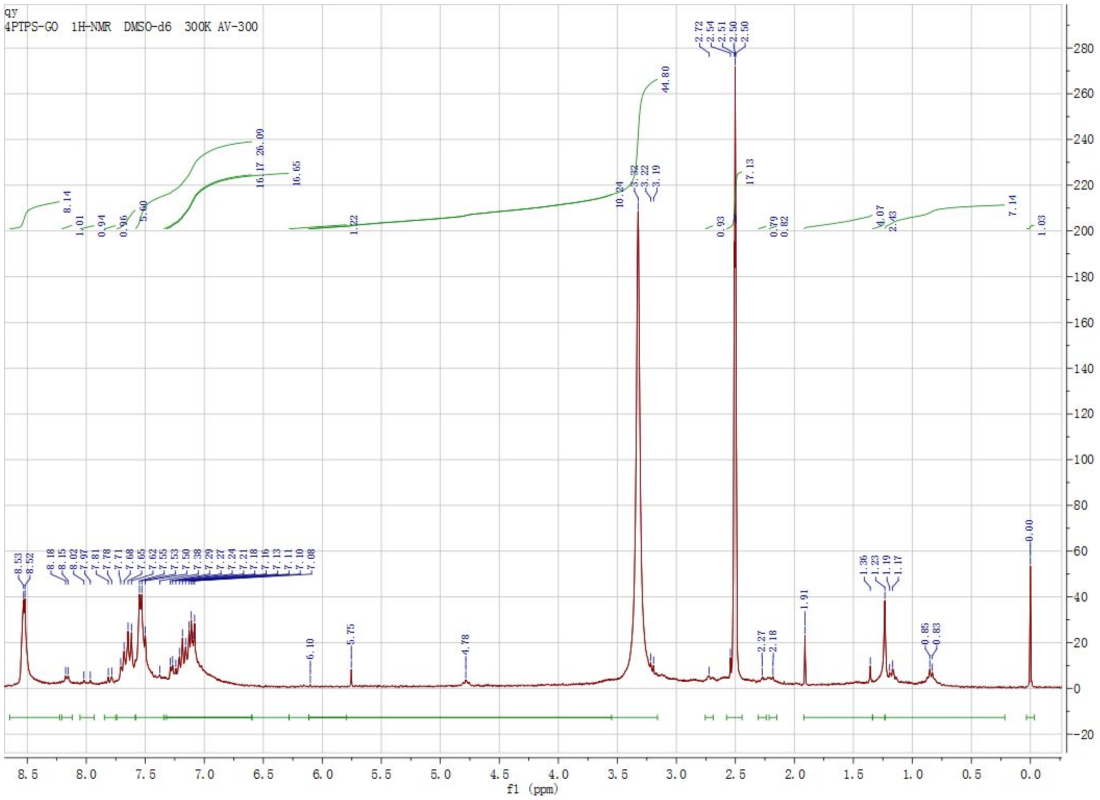
S-07 2PPS-G0



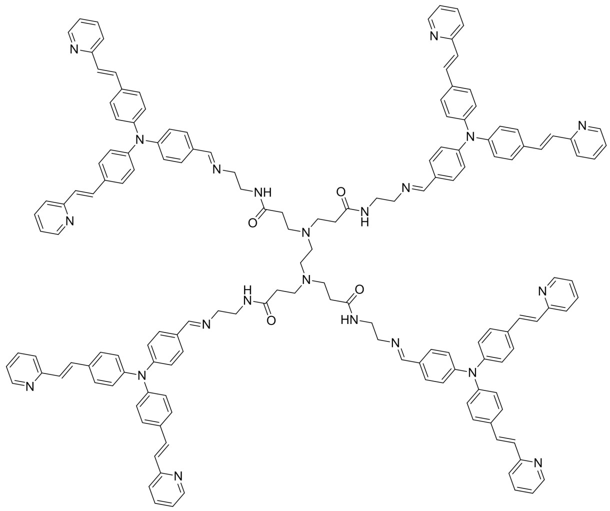
S-Figure 9 the ^{1}H NMR of molecules 2PPS-G0 (**S-07**)



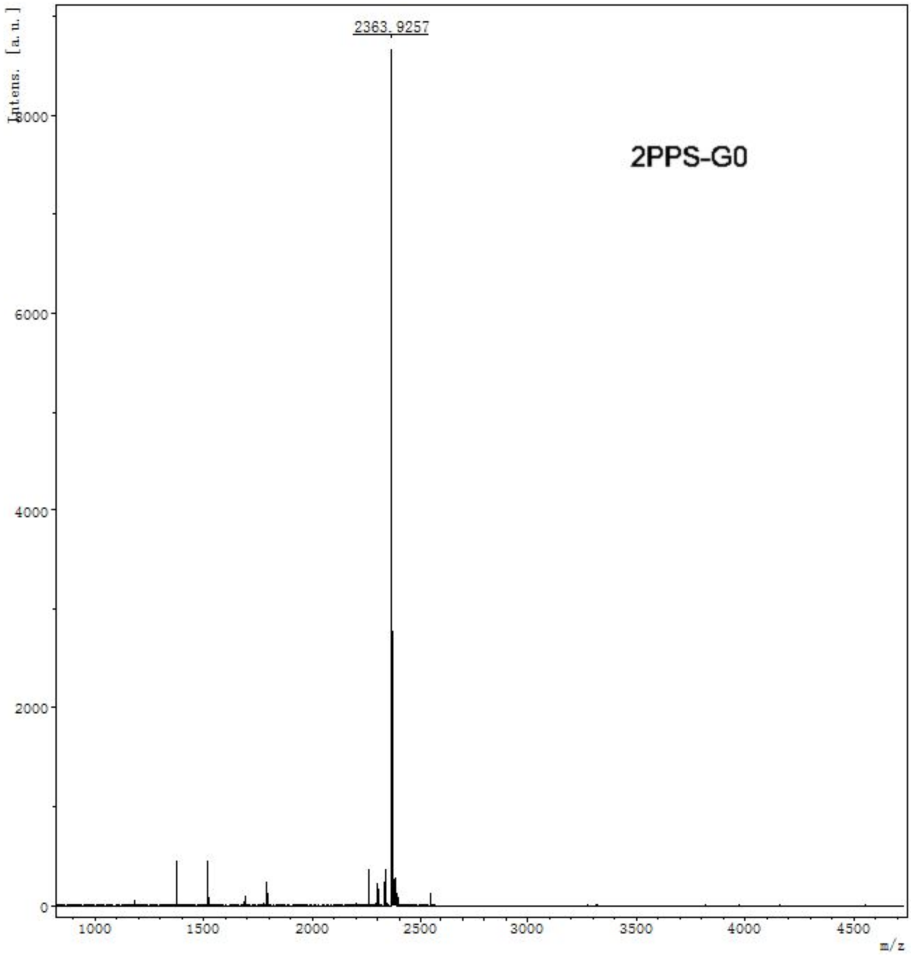
S-08 4PPS-G0



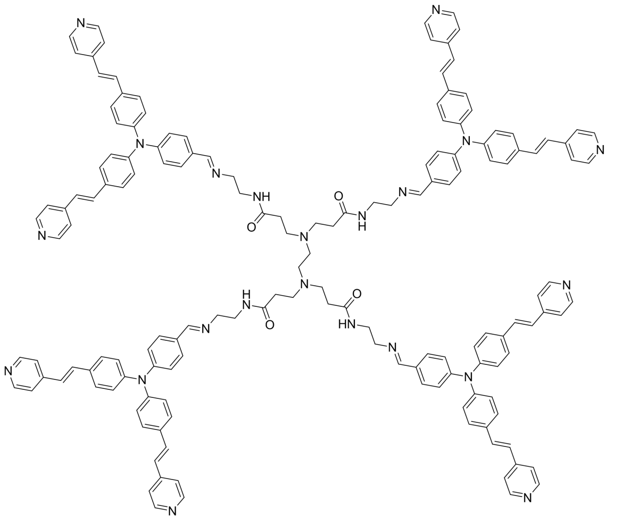
S-Figure 10 the ^{1}H NMR of molecules 4PPS-G0 (**S-08**)



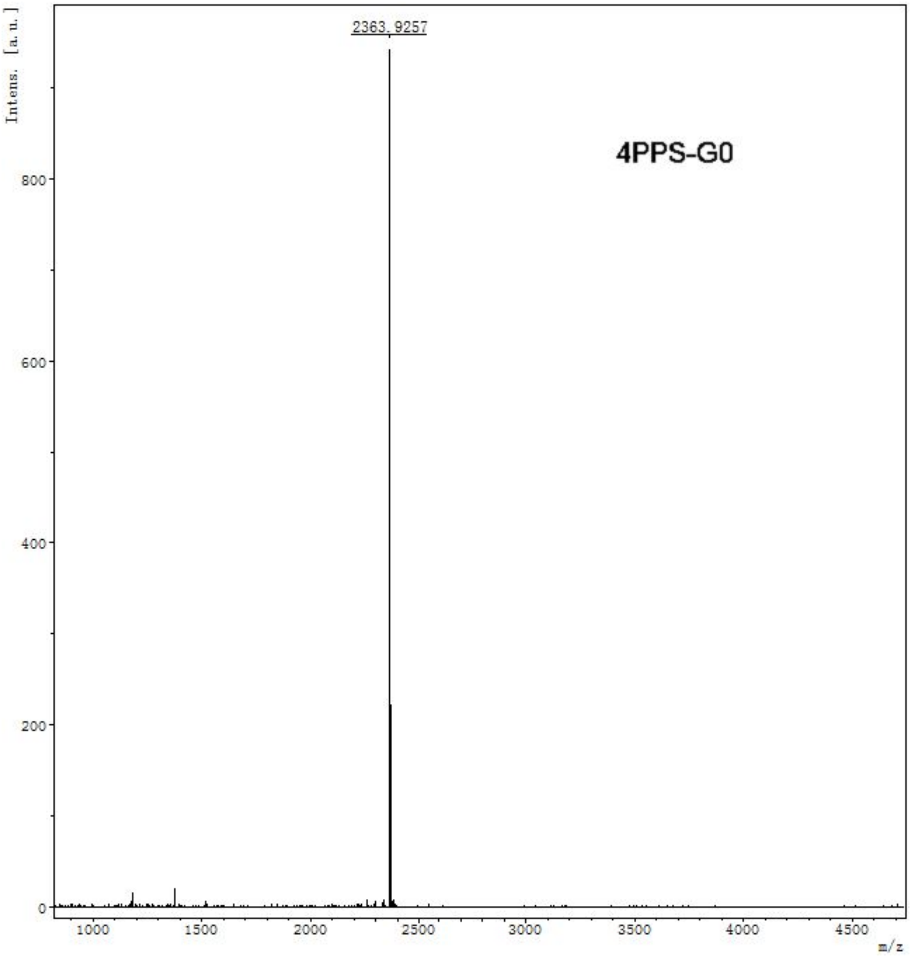
S-07 2PPS-G0



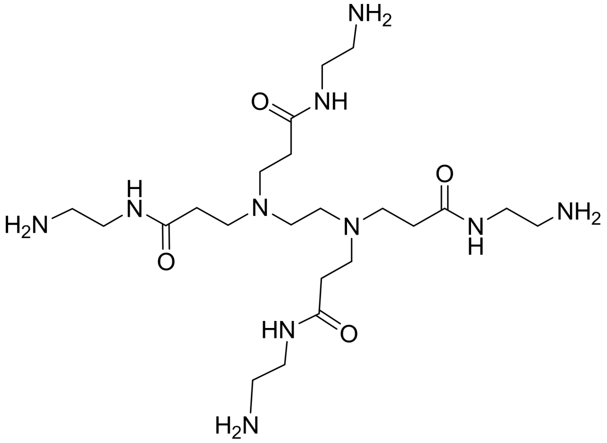
S-Figure 11 the HRMS of molecules 2PPS-G0 (**S-07**)



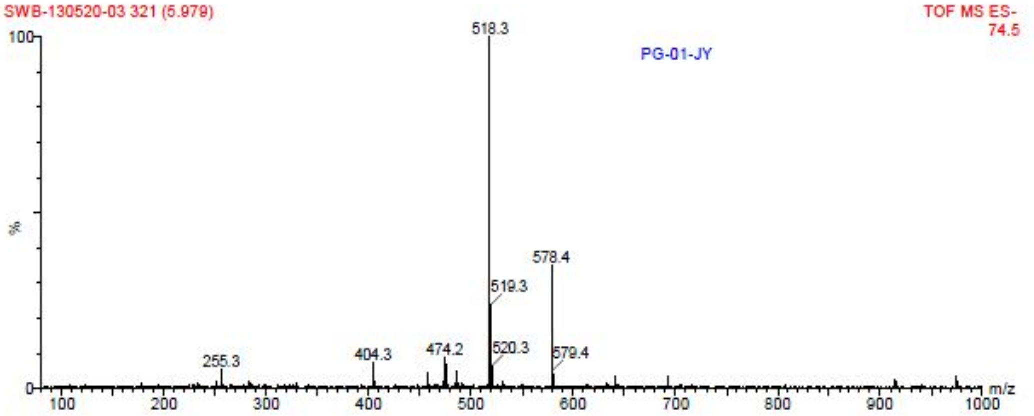
S-08 4PPS-G0



S-Figure 12 the HRMS of molecules 4PPS-G0 (**S-08**)



S-06 PAMAM-G0



S-Figure 13 the MS of molecules PAMAM-G0 (**S-06**)

4. Equipments:

Fluorescence: The up-converted fluorescence emission experiment were taken by FluoroMax-4 spectrofluorometer[**]:

The instruments parameters list follow:

At room temperature (~20℃) ;

The test samples were excited under wavelength 800 nm;

The emission wavelength ranges: 300 nm-850 nm;

At slit size 3 nm;

Range of spectrometer: the detector’s response ranges from 180–850 nm;

maximum scan speed 80 nm/s;

physical Range 0–950 nm;

accuracy ±0.5 nm;

resolution 0.3 nm;

excitation Source 150 W xenon, continuous output, ozone-free lamp.

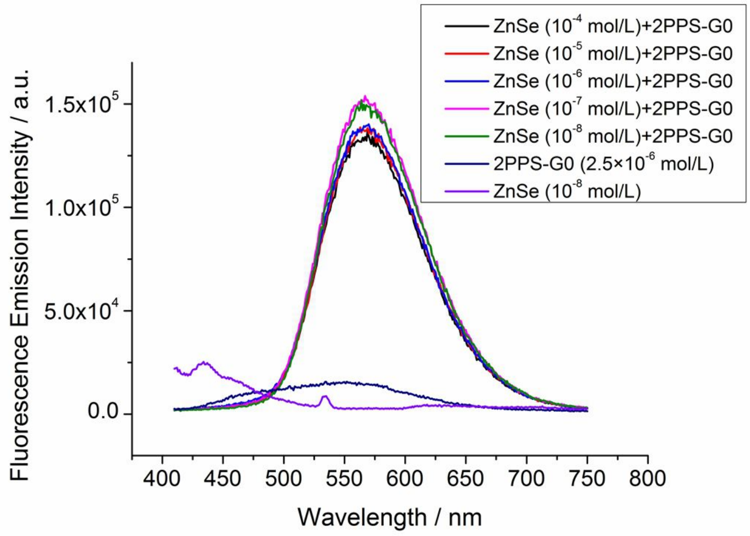
UV-vis: Shimadu UV-3600 spectrometer;

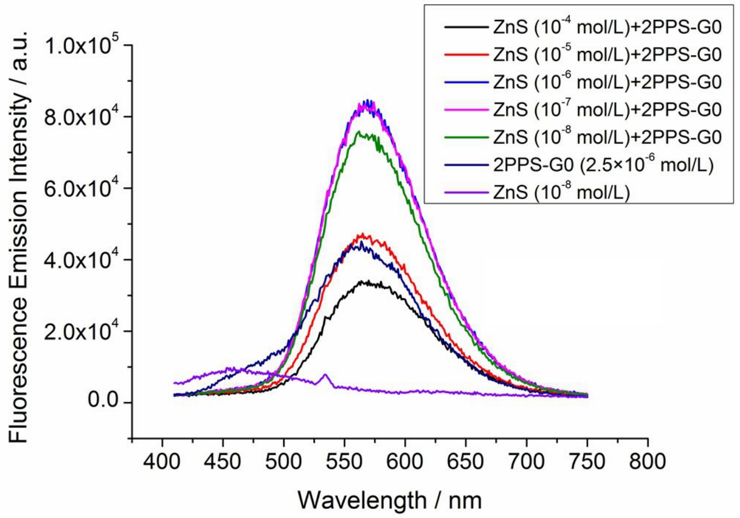
IR: Nicolet 750 IR spectrometer;

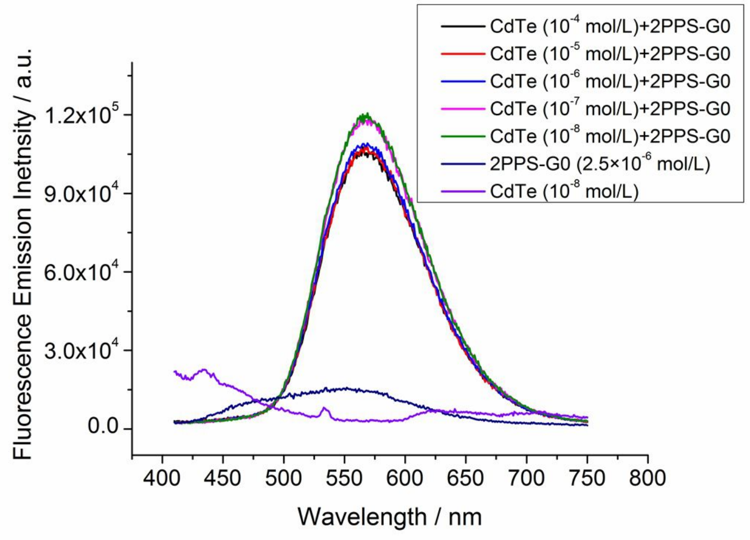
^{1}H NMR: Brucker 300 MHz/500MHz NMR spectrometer (TMS);

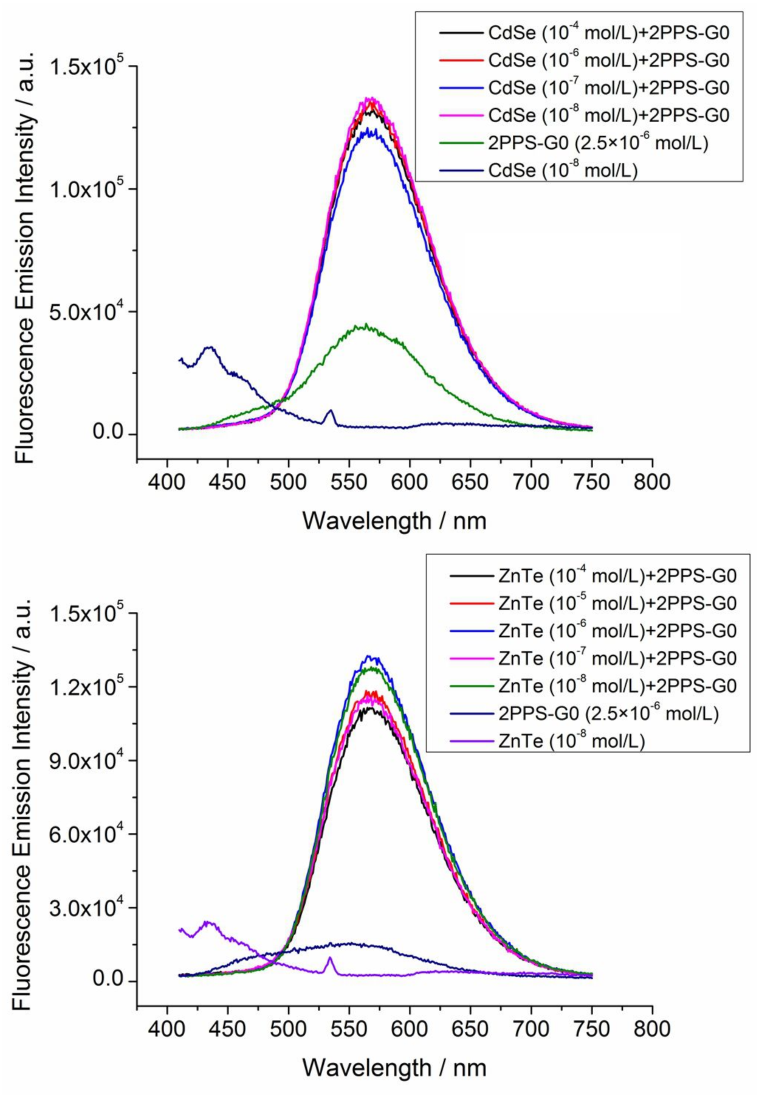
HRMS: Bruker daltonics: BRUKER BIFLEXIV MALDI-TOF

[**] Fluoromax-4 spectrofluorometer operation manual (part number 81110 version 1.0)(23 May 2006) HORIBA jobinyvon

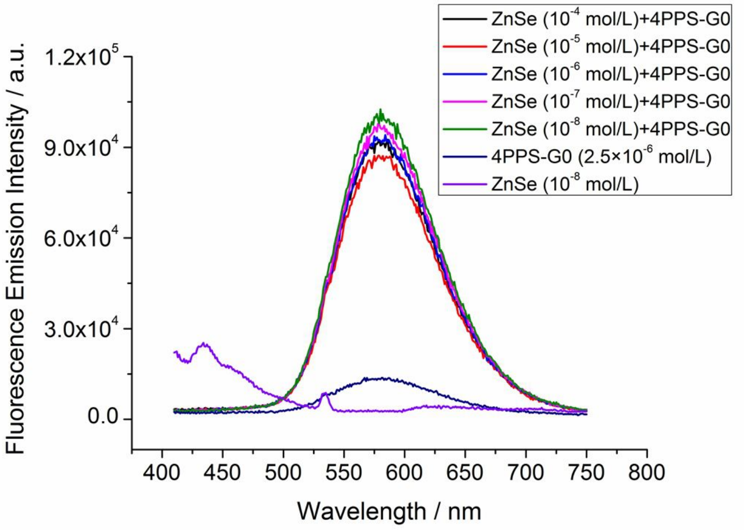

ZnSe (10^{-4} mol/L)+2PPS-G0
ZnSe (10^{-5} mol/L)+2PPS-G0
ZnSe (10^{-6} mol/L)+2PPS-G0
ZnSe (10^{-7} mol/L)+2PPS-G0
ZnSe (10^{-8} mol/L)+2PPS-G0
2PPS-G0 (2.5×10^{-6} mol/L)
ZnSe (10^{-8} mol/L)
Fluorescence Emission Intensity / a.u.
$1.5x10^5$
$1.0x10^5$
$5.0x10^4$
0.0
400 450 500 550 600 650 700 750 800
Wavelength / nm

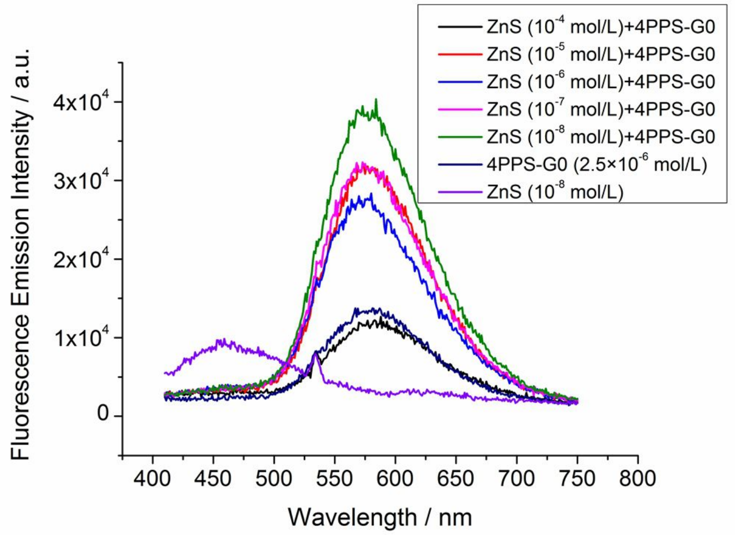

ZnS (10^{-4} mol/L)+2PPS-G0
ZnS (10^{-5} mol/L)+2PPS-G0
ZnS (10^{-6} mol/L)+2PPS-G0
ZnS (10^{-7} mol/L)+2PPS-G0
ZnS (10^{-8} mol/L)+2PPS-G0
2PPS-G0 (2.5×10^{-6} mol/L)
ZnS (10^{-8} mol/L)
Fluorescence Emission Intensity / a.u.
$1.0x10^5$
$8.0x10^4$
$6.0x10^4$
$4.0x10^4$
$2.0x10^4$
0.0
400 450 500 550 600 650 700 750 800
Wavelength / nm

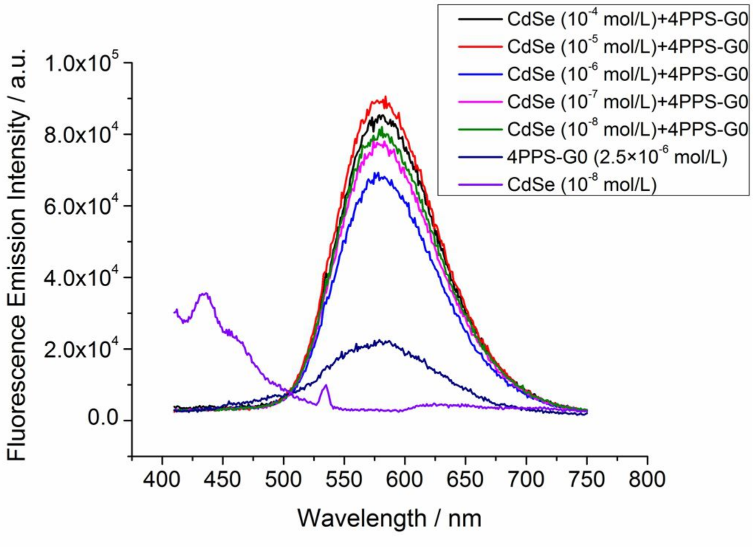

CdTe (10^{-4} mol/L)+2PPS-G0
CdTe (10^{-5} mol/L)+2PPS-G0
CdTe (10^{-6} mol/L)+2PPS-G0
CdTe (10^{-7} mol/L)+2PPS-G0
CdTe (10^{-8} mol/L)+2PPS-G0
2PPS-G0 (2.5×10^{-6} mol/L)
CdTe (10^{-8} mol/L)
Fluorescence Emission Inetnsity / a.u.
$1.2x10^5$
$9.0x10^4$
$6.0x10^4$
$3.0x10^4$
0.0
400 450 500 550 600 650 700 750 800
Wavelength / nm

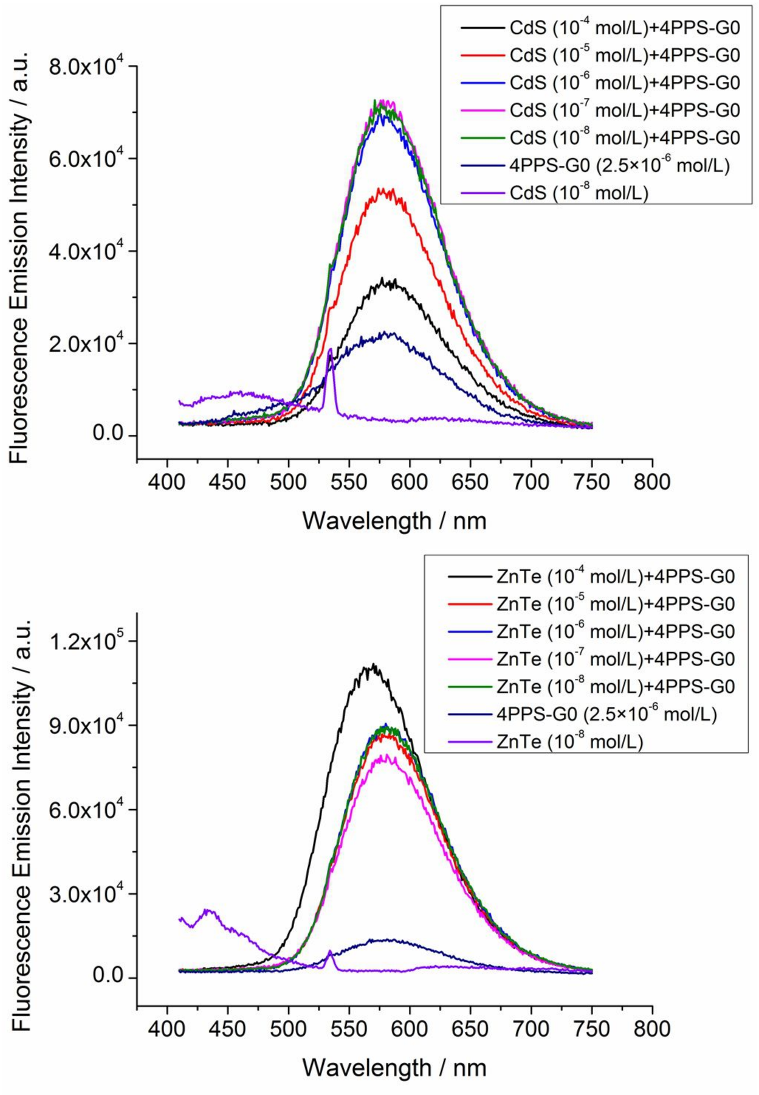


S-Figure 14 2PPS-G0 and different concentrations QDs (CdSe, CdTe, ZnS, ZnSe, ZnTe) up-converted fluorescence emission spectra (excitation wavelength 800 nm)


ZnSe (10^{-4} mol/L)+4PPS-G0
ZnSe (10^{-5} mol/L)+4PPS-G0
ZnSe (10^{-6} mol/L)+4PPS-G0
ZnSe (10^{-7} mol/L)+4PPS-G0
ZnSe (10^{-8} mol/L)+4PPS-G0
4PPS-G0 (2.5×10^{-6} mol/L)
ZnSe (10^{-8} mol/L)
Fluorescence Emission Intensity / a.u.
1.2×10^{5}
9.0×10^{4}
6.0×10^{4}
3.0×10^{4}
0.0
400 450 500 550 600 650 700 750 800
Wavelength / nm


ZnS (10^{-4} mol/L)+4PPS-G0
ZnS (10^{-5} mol/L)+4PPS-G0
ZnS (10^{-6} mol/L)+4PPS-G0
ZnS (10^{-7} mol/L)+4PPS-G0
ZnS (10^{-8} mol/L)+4PPS-G0
4PPS-G0 (2.5×10^{-6} mol/L)
ZnS (10^{-8} mol/L)
Fluorescence Emission Intensity / a.u.
4×10^{4}
3×10^{4}
2×10^{4}
1×10^{4}
0
400 450 500 550 600 650 700 750 800
Wavelength / nm


CdSe (10^{-4} mol/L)+4PPS-G0
CdSe (10^{-5} mol/L)+4PPS-G0
CdSe (10^{-6} mol/L)+4PPS-G0
CdSe (10^{-7} mol/L)+4PPS-G0
CdSe (10^{-8} mol/L)+4PPS-G0
4PPS-G0 (2.5×10^{-6} mol/L)
CdSe (10^{-8} mol/L)
Fluorescence Emission Intensity / a.u.
1.0×10^{5}
8.0×10^{4}
6.0×10^{4}
4.0×10^{4}
2.0×10^{4}
0.0
400 450 500 550 600 650 700 750 800
Wavelength / nm



S-Figure 15 4PPS-G0 and different concentrations QDs (CdS, CdSe, ZnS, ZnSe, ZnTe) up-converted fluorescence emission spectra (excitation wavelength 800 nm)