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Yan Ji, and Ying Qian*

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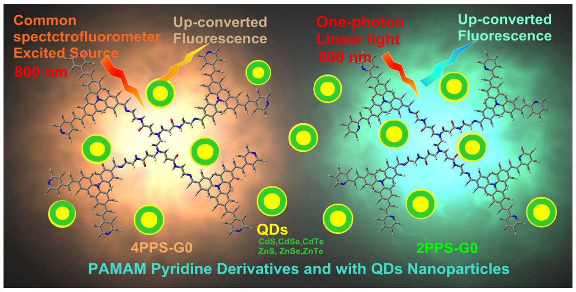

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ARTICLE TYPE

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

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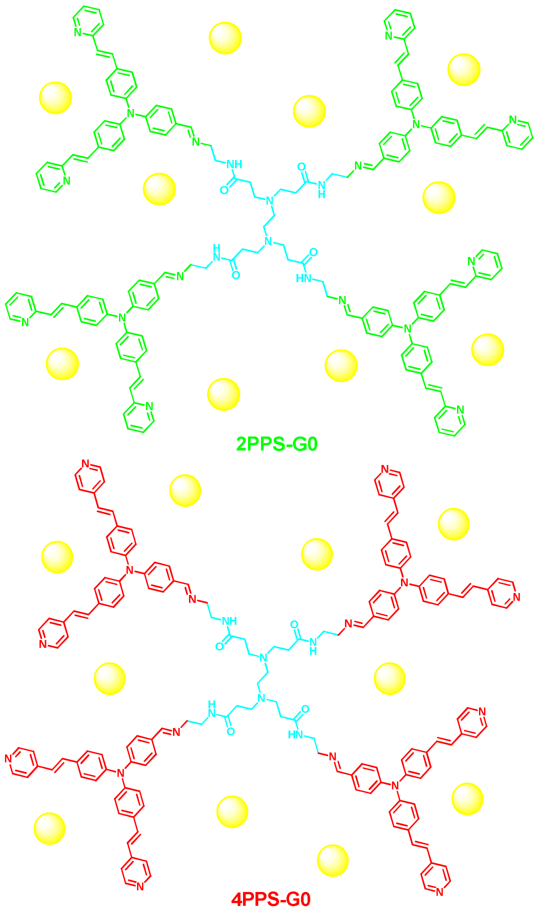
Organic dyes two-photon absorption-induced frequency up-converted fluorescence (UCF) excited under laser have been used in biological imaging and optical physics. Laser need higher level equipments that limit the application of UCF dyes. The experimental observation that the poly-amidoamine (PAMAM) pyridine derivatives 2PPS-G0, 4PPS-G0 and mixed with quantum dots (QDs) nanoparticles realized UCF by common spectrofluorometer. The low-energy linear one-photon light source also can excite some organic molecules or QDs to give UCF emission, which replaced the laser. The UCF related mechanism: second harmonic generation; two-photon absorption induced, and linear excited-states shifts (LESS) mechanisms were discussed to explain the linear one-photon light source excited UCF.

1. Instructions

The simultaneous absorption of two photons by the same molecule was analyzed theoretically in the 1930s by Göppert-Mayer [1] and was demonstrated experimentally in 1961 [2] . The up-converted fluorescence (UCF) emission (anti-Stokes emissions) realized long wavelength excitation and short wavelength emission. The up-conversion was proposed from quantum calculation by N. Bloembergen [3] in 1959, and the experimental observation was got by F. Auzel [4] in 1966. UCF has three mechanisms [5]: One was second-harmonic generation, the second was two-photon absorption, and the third was photon avalanche [6] process. After the advent of lasers, the two-photon absorption-induced frequency UCF in organic dye materials could be observed by using pulsed laser excitation [7]. The light sources of two-photon UCF were the black-body excitation or spontaneous diode emission before that the laser sources become commonly available [8]. Laser high-density IR excitations make UCF become easy phenomena [9].

Organic dyes multi-photon (two-/three-photon) up-converted processes have been studied by using laser pulse. And the multi-photon excitation based laser scanning microscopy realized frequency-upconversion imagings [10], which have been used in bio-imaging, chemical sensors, and optical physics [11].

The semiconductor nano-particles were known as quantum dots (QDs) [12]. QDs are characterized by large Stokes shifts, broad absorption bands, and narrow, size-dependent emission bands without a significant red tail. The multiple color QDs can be excited using a single laser excitation wavelength [13]. The size-dependent emission of QDs is the result of a quantum confinement effect (QCE) [14]. The two-photon processes of QDs have been investigated by laser instruments [15].



Scheme 1 The structures of dendrimers 2PPS-G0, 4PPS-G0 and added with CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe quantum dots nanoparticles.

This experiment observed UCF emission from PAMAM pyridine organic dyes (2-Pyridine Poly-amidoamine Schiff-base generation 0) 2PPS-G0, (4-Pyridine Poly-amidoamine Schiff-base generation 0) 4PPS-G0, and with mixed quantum dots (QDs) nanoparticles (Scheme 1). The tests were taken by FluoroMax-4 spectrofluorometer, which was excited at 800 nm wavelength common linear light source. This experimental finding that realized UCF by organic dyes or added with QDs excited under one-photon light source spectrofluorometer, which can replace laser to extend the application of UCF materials. There was still no report on UCF of organic dyes and added with QDs under common linear light sources.

2. Results and Discussion

2.1 Up-converted Fluorescence

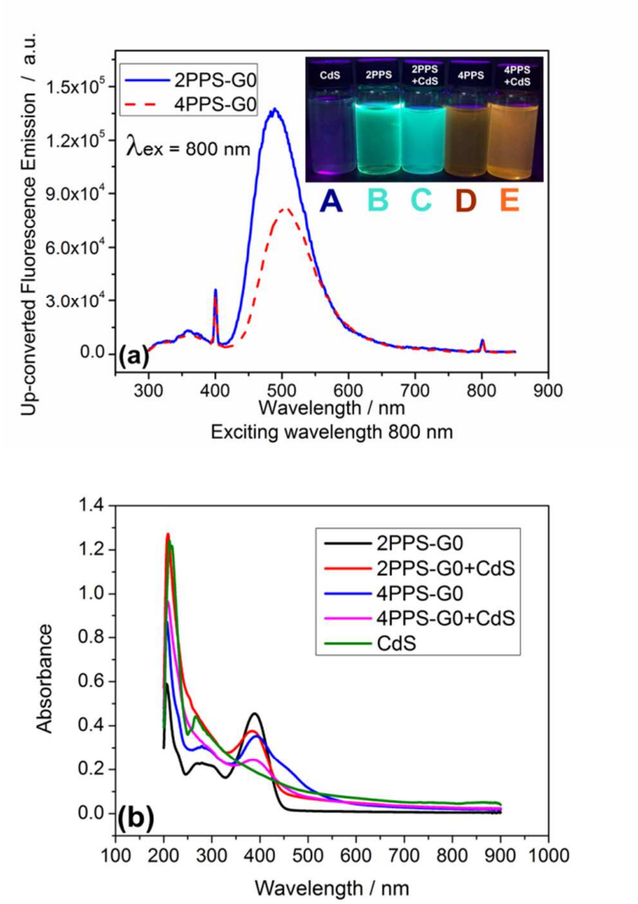


Fig. 1(a) Up-converted fluorescence emission spectra of molecules 2PPS-G0 and 4PPS-G0 (3×10^{-5} mol/L in CH_2Cl_2) excited at 800 nm wavelength one-photon light source by linear spectrofluorometer. Insert fluorescence photograph (at 365 nm UV light) of (A) CdS, (B) 2PPS-G0, (C) 2PPS-G0+CdS, (D) 4PPS-G0, (E) 4PPS-G0+CdS in ethanol. (b) The UV absorption spectra of dendrimers 2PPS-G0, 4PPS-G0, 2PPS-G0+CdS, 4PPS-G0+CdS, and CdS (range from 200 nm to 900 nm).

Figure 1 show fluorescence emission peaks were at 490.7 nm (2PPS-G0) and 506.2 nm (4PPS-G0) in CH_2Cl_2 solution, which were excited at 800 nm wavelength light source. The fluorescence intensity was 1.36×10^5 a.u. (2PPS-G0) and 8.01×10^4 a.u. (4PPS-G0). The spectra show the realizing UCF under common linear light source by organic dyes. The fluorescent photographs insert in Figure 1 were from 2PPS-G0, 4PPS-G0, and with added CdS nanoparticles ethanol solutions.

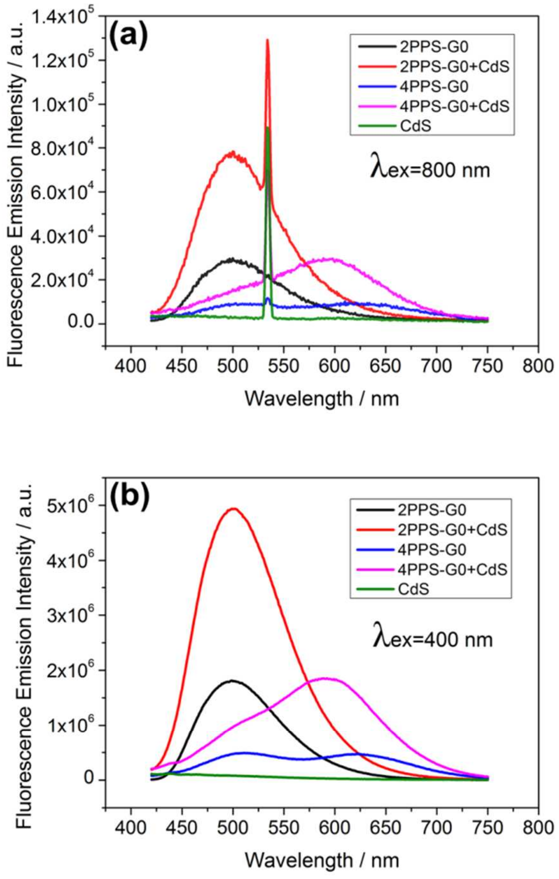


Fig. 2 (a) Up-converted fluorescence emission spectra of dendrimers 2PPS-G0, 4PPS-G0, 2PPS-G0+CdS, 4PPS-G0+CdS, and CdS in ethanol (excited wavelength 800 nm, range from 420 nm to 750 nm). (b) The fluorescence emission spectra (excited wavelength 400 nm).

Figure 2 gave the UCF emission spectra of 2PPS-G0, 4PPS-G0, and with added CdS nanoparticles ethanol solutions at range from 420 nm to 750 nm. The UCF peaks of 2PPS-G0 and 2PPS-G0+CdS were at about 500 nm. The UCF peaks of 4PPS-G0 and 4PPS-G0+CdS were at about 600 nm. The UCF of CdS has sharp peak at about 533 nm. The UCF peaks of 2PPS-G0+CdS and 4PPS-G0+CdS also have sharp peaks at about 533 nm. But the UCF peaks of 2PPS-G0 and 4PPS-G0 have no peaks at about 533 nm. These mean the 533 nm peaks were the character peaks of CdS nano particles. Another phenomenon can be noticed that the UCF of 2PPS-G0 and 4PPS-G0 were enhanced after adding the CdS nano particles. These show the CdS nano particles have action with the two dendrimers. Figure 1 (test in CH_2Cl_2) and Figure 2 were in two different solvent (test in ethanol). The solvent fects make the spectra having some different in emission wavelength. The polar, refractive, dielectric contant, these all act on the dyes to give different optical physical properties.

2PPS-G0 and 4PPS-G0 have poly-(amidoamine) (PAMAM) dendrimer [16] core and pyridine triphenylamine surface groups.

These two dendrimers have PAMAM flexible chains with many amines (tertiary amine, amide, aryl-amine, and imine), which can complex metal ions, package nanoparticles, or deliver drugs. The PAMAM can emission fluorescence after store or oxidation in the air [17], which extended the application of these two dendrimers in fluorescence areas. The N atom of pyridine form ions under exciting, which connected with triphenylamine by double bonds. The pyridine N ions attract electron to be "Accepter" and the triphenylamine give electron to be "Donor", which form push-pull electronic conjugated dipole unit. This dipole unit has intramolecular charges transfer (ICT) phenomenon, which can improve nonlinear optical properties (such as two-photon absorption) of molecules.

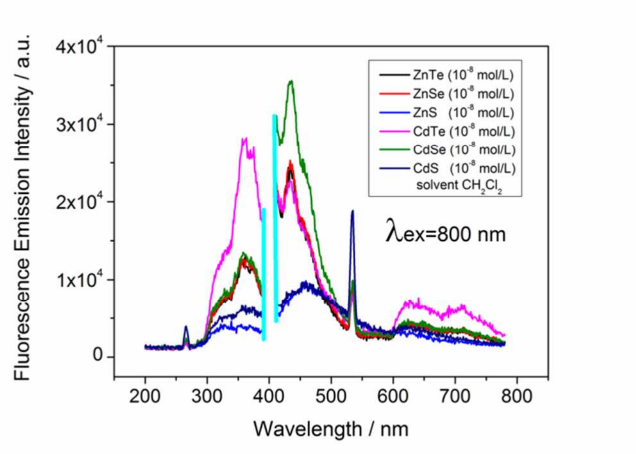


Fig. 3 Up-converted fluorescence emission spectra of QDs (CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe) in CH_2Cl_2 (excited wavelength 800 nm, range from 200 nm to790 nm, cut off 390-410 nm) (10^{-8} mol/L in CH_2Cl_2.)

Figure 3 gave the up-converted fluorescence emission under 800 nm excitation wavelengths by common spectrofluorometer, which show the QDs gave UCF under linear light source. Some quantum dots [18] can give multi-photon absorption induced frequency up-converted emission. The observed experiment QDs mixed with 2PPS-G0 and 4PPS-G0 can enhance UCF emission. The actions between QDs and dyes in solutions were the fluorescence resonance energy transfer (FRET)[19]. The Figure 3 shown the QDs have emission at about range from 300 nm to 500 nm. The UV spectra insert Figure 2 shown the 2PPS-G0 and 4PPS-G0 have absorption at about 400 nm. The overlap of QDs emission and absorbance of two dendrimers show there exits FRET phenomena in the QDs+dyes system. The energy transferred between QDs nanoparticles and pyridine triphenylamine groups at close distances (about <10 nm) in the solutions, which increased the UCF emission of the QDs+dyes system.

The fluorescence spectra of gradient concentrations of QDs (CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe) added 2PPS-G0 and 4PPS-G0 was test (Figure 4, S-Figure 14, and S-Figure 15). The QDs added 2PPS-G0 and 4PPS-G0 gave emission wavelength 570 nm and 580 nm. The emission wavelength of 2PPS-G0 was 570 nm, and that of 4PPS-G0 was 580 nm. These two emission wavelength were not the key emission peaks areas of QDs. From Figure 4 show the 2PPS-G0 and 4PPS-G0 fluorescence all enhanced after added QDs. The emission wavelength changed little.

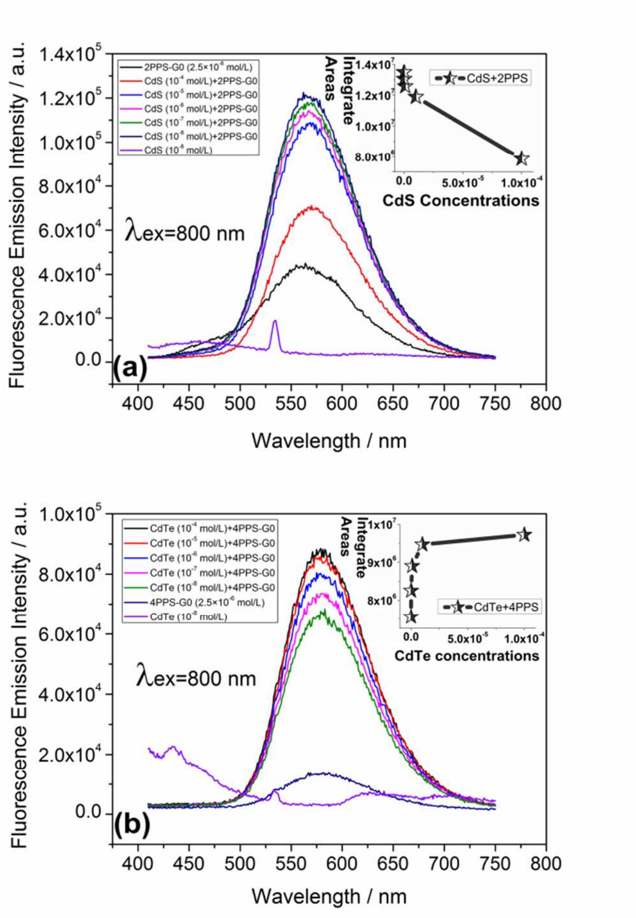


Fig. 4 (a) 2PPS-G0 (2.5×10^{-6} mol/L) and different concentrations CdS QDs up-converted fluorescence emission spectra (excitation wavelength 800 nm). Insert fluorescence integrate areas *vs.* CdS concentrations. (b) 4PPS-G0 (2.5×10^{-6} mol/L) and different concentrations CdTe QDs up-converted fluorescence emission spectra (excitation wavelength 800 nm). Insert fluorescence integrate areas *vs.* CdTe concentrations. QDs (1×10^{-8}, 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 1×10^{-4} mol/L). Solvent CH_2Cl_2.

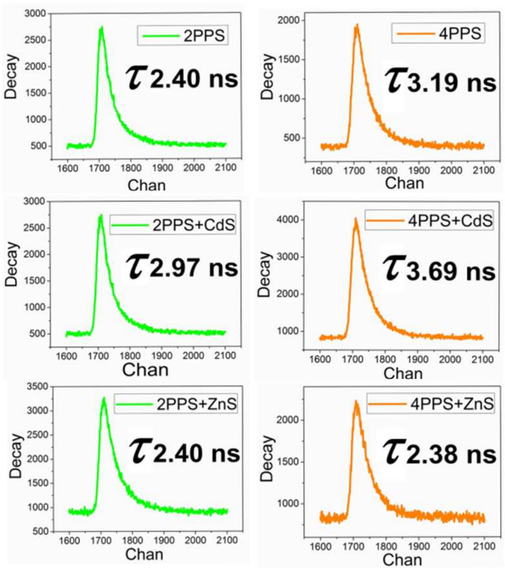


Fig. 5 The fluorescence lifetime (*τ*, unit nanoseconds) and fluorescence decay curves of 2PPS-G0 and 4PPS-G0 (2.5×10^{-6} mol/L), and added CdS and ZnS (1×10^{-5} mol/L in CH_2Cl_2.)

The Figure 5 gave the fluorescence lifetime and fluorescence decay curves, which show the fluorescence life time of 2PPS-G0 (2.40 ns) and 4PPS-G0 (3.19 ns), changed little after added QDs CdS (2.97 ns and 3.69 ns) and ZnS (2.40 ns and 2.38 ns). The Figure 4 show the fluorescence peaks positions kept at about 570 nm (2PPS-G0) and 580 nm (4PPS-G0) after added QDs. The Figure 4 and 5 can deduce that the fluorescence centers were not changed after added QDs. It may be QDs have FRET on 2PPS-G0 and 4PPS-G0, and then enhanced the fluorescence emission intensity of two dendrimers.

Another interest phenomenon: Figure 4a were that 2PPS-G0 added CdS, which fluorescence was decreased along with the increasing of CdS concentrations. Figure 4b 4PPS-G0 added CdTe, which fluorescence was increased along with the increasing of CdTe concentrations. The S-Figure 14, 15 show 2PPS-G0 and 4PPS-G0 added different concentrations QDs gave similar situations but not linear relationship. It was not clears that the reason why two dendrimers and added two kinds of QDs have inverse situations. These may be the further research directions.

2.2 Mechanism Possibilities

The mechanism of UCF emission excited by linear one-photon light source may have three possibilities: second-harmonic generation, two-photon absorption induced, and linear excites states shifts (LESS), which will be discussed follow.

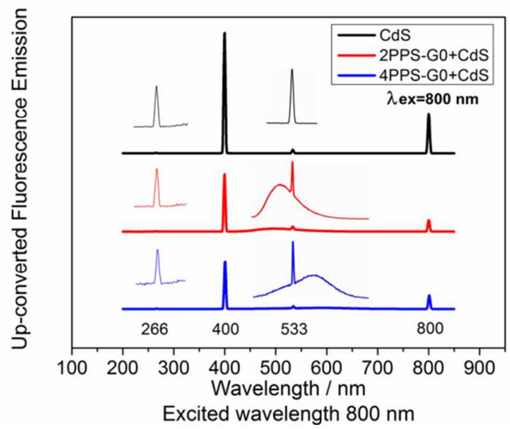


Fig. 6 Up-converted fluorescence emission spectra of 2PPS-G0+CdS, 4PPS-G0+CdS, and CdS in ethanol (excited wavelength 800 nm, range from 200 nm to 850 nm); Insert spectra were amplified peaks at about 266 nm and 533 nm.

Firstly, the UCF mechanism of QDs may be the second-harmonic generation. Figure 6 gave UCF spectra of 2PPS-G0+CdS, 4PPS-G0+CdS, and CdS excited at 800 nm (the wide range from 200 nm to 850 nm). There were four main sharp peaks: 266 nm, 400 nm, 533 nm, and 800 nm. The 800 nm peaks were the scattering of excited light source. The UCF emission peaks at 266 nm, 400 nm, and 533 nm were produced for second-harmonic generation mechanism, which were third-harmonic generation, second-harmonic generation, one and half-harmonic generation respectively. The second-harmonic generation UCF was the character of the CdS quantum dots, which also produced by CdS mixed with 2PPS-G0 and 4PPS-G0 dendrimers.

Secondly, the 2PPS-G0 and 4PPS-G0 dendrimers mixed with CdS also have UCF peaks at 500 nm and 600 nm. These peaks were the character UCF of 2PPS-G0 and 4PPS-G0, which were attribute to two-photon induced UCF mechanism. The UV-vis absorbance spectra in Figure 1b show there were no linear absorbance at 800 nm, which means there exits nonlinear absorbance to produce fluorescence emission under 800 nm excited wavelength. It can be concluded that these two dendrimers excited at 800 nm wavelengths produce nonlinear absorbance and gave UCF emission peaks at about from 500 nm to 600 nm wavelengths. These phenomena were attributed to two-photon absorption-induced UCF mechanism.

The two dendrimers added with CdS nanoparticles have the UCF peaks at 266 nm, 400 nm, 533 nm were attributed to second-harmonic generation mechanism. The Figure 5 shown the UCF emission QDs+dyes system was combined second-harmonic generation mechanism and two-photon absorption-induced mechanism.

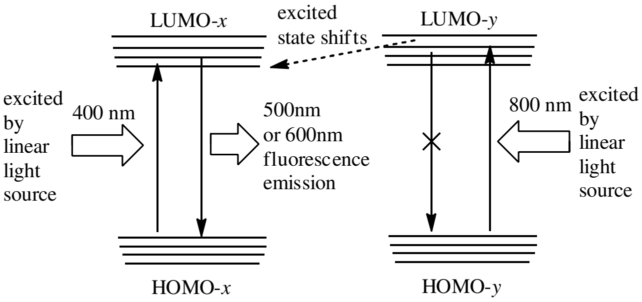


Fig. 7 The linear excited states shift (LESS) up-converted fluorescence emission mechanism.

Thirdly, the mechanism was proposed for this linear light source excited up-converted fluorescence, which was linear excited states shifts (LESS) up-converted fluorescence emission mechanism (Figure 7). This mechanism shows the 2PPS-G0 or 4PPS-G0 was excited under 400 nm to LUMO-*x* and gave fluorescence emission at 500 nm or 600 nm (Figure 2b). The 800 nm linear light source excited the molecules to LUMO-*y*, the LUMO-*y* shifts to LUMO-*x*, and then also can give fluorescence emission at 500 nm or 600 nm (Figure 2a). The excited states shifts may be the Triplet-Triplet or Triplet-Singlet. The LESS can explain the UCF emission excited by linear one-photon light source.

UCF dyes have potential and broad application foreground [20]. The experimental meaning of this finding was UCF can be tested in common linear spectrofluorometer without the laser instruments. Both this finding and these materials may improve low-intensity IR imaging, chemical sensors [21], biological imaging, biological fluorescence probes for cells, and drugs delivery trackers. The finding may further reduce the photo-damage in optical dynamical therapy or cell imaging by using linear lower-energy excited light source. The related chemical groups will be designed and synthesized in other molecules and can extend, even improved the application values in the UCF and multi-photon nonlinear optical areas, which will cause the interests.

The 800 nm linear light sources excited on two dendrimer and QDs gave high energy up-converted fluorescence emission, which realized long wavelength excitation and short wavelength emission by low energy light source without laser. CdS gave the 266 nm, 400 nm, 533 nm up-converted emission peaks were third-harmonic generation, second-harmonic generation, and one and half-harmonic generation respectively, which obey the second-harmonic generation mechanism. The up conversion spectra of 2PPS-G0 and 4PPS-G0 have 400 nm emissions. This 400 nm emission was excited by 800 nm was the double frequency peak, which can be explain by two-photon absorption and linear excited states shifts (LESS) mechanism or mixed. The LESS mechanism show the 800 nm excited states shift to 400 nm excited states, and then produce the up conversion. It was observed up-conversion phenomena excited by 800 nm wavelength linear source. The possible mechanisms may act on by one or mixed.

3. Experimental Methods

Materials synthesis: 2-vinylpyridine or 4-vinylpyridine reacted with 4-(bis(4-bromophenyl) amino)benzaldehyde by Heck reactions. And then the aldehyde reacted with poly-(amidoamine) (PAMAM-G0) dendrimer by Schiff-base reaction. The two dendrimers 2PPS-G0 and 4PPS-G0 (Scheme 1) were got. The CdS quantum dots were got by jetting Na_2S ethanol solutions into $Cd(OAc)_2$ ethanol solutions. The ZnS quantum dots were got by jetting Na_2S ethanol solutions into $Zn(OAc)_2$ ethanol solutions. The CdSe (ZnSe) quantum dots were got by jetting NaHSe CH_2Cl_2 solutions into $Cd(OAc)_2$ ($Zn(OAc)_2$) CH_2Cl_2 solutions.

The CdTe (ZnTe) quantum dots were got by jetting NaHTe CH_2Cl_2 solutions into $Cd(OAc)_2$ ($Zn(OAc)_2$) CH_2Cl_2 solutions.

Solutions sample: prepared 2PPS-G0 or 4PPS-G0 solutions in CH_2Cl_2 or ethanol at 2.5×10^{-6} or 3×10^{-5} mol/L. Take 10 mL 2PPS-G0 or 4PPS-G0 ethanol solutions and added with QDs (1×10^{-8}, 1×10^{-7}, 1×10^{-6}, 1×10^{-5}, 1×10^{-4} mol/L) nanoparticles CH_2Cl_2 or ethanol solutions to form the dyes+QDs mixed system.

Optic test: carry the solutions by using quartz color dish and test the fluorescence emission spectra at linear light source spectrofluorometer. The experiments were taken by FluoroMax-4 spectrofluorometer from excitation source xenon, continuous output, ozone-free lamp (150 W) at room temperature (~20℃). The excited wavelength set at 800 nm and test ranges set from 200 nm to 850 nm, slit 3 nm. The UCF spectra were got list in Figure1 (insert photograph), Figure 2, Figure 3, Figure 4, and Figure 6.

4. Conclusions

This experimental finding realized up-converted fluorescence (UCF) by organic dyes (2PPS-G0 and 4PPS-G0) and mixed with quantum dots QDs nanoparticles excited by 800 nm wavelength linear light source under common spectrofluorometer. The UCF emission peaks at about 500 nm or 600 nm were attributed to two-photon absorption-induced mechanism. The UCF emissions of QDs were the second-harmonic generation mechanism. The linear excited states shifts (LESS) mechanism also can explain this UCF emission phenomenon. These two dyes have poly-amidoamine (PAMAM) dendrimer core and pyridine triphenylamine surface groups, and have FRET with the QDs nanoparticles, which can improve nonlinear optical properties of molecules. This finding that low energy linear one-photon light source can replace laser to realize UCF, which can extend the application of this kind of organic dyes and QDs nano materials for UCF.

Notes and references

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† Electronic Supplementary Information (ESI) available: [The structures and synthesis of 2PPS-G0 and 4PPS-G0 were listed in S-Figure 1 to S-Figure 5. S-Figure 6 to S-Figure 8 was UV and Fluorescence spectra. The S-Figure 9 to S-Figure 12 lists the 1H NMR and HRMS of 2PPS-G0 or 4PPS-G0. The MS of PAMAM list in S-Figure 13, UCF of dyes+QDs in S-Figure 14, 15.]. See DOI: 10.1039/b000000x/

‡ Acknowledgment: The National Natural Science Foundation of China (No.61178057) and the Scientific Research Foundation of Graduate School of Southeast University (No.YBPY1209) were greatly appreciated for financial support.

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