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Two-photon Up-conversion Luminescent Properties of HMASPS and HEASPS in Three Different Polymer Matrices

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Abstract: Three dye-doped polymer rods in different matrices were synthesized in which weak hydrogen bond, strong hydrogen bond and covalent bond existed between the dye and the polymer chain. And the two-photon up-conversion luminescent properties of HMASPS and HEASPS[1] in three different microenvironments were studied.

Keywords: Two-photon,up-conversion lasing,solid-state laser dye.

Materials with considerably high two-photon pumped (TPP) up-conversion lasing efficiency have received close attention partly due to their prospective applications in laser device fabrication[2-3]. From the practical viewpoint, solid-state laser dye is compact, free of toxic organic solvent, easy to handle. Several qualifications, however, are required for matrix, such as compactness, transparency, homogeneity of dye scattered and high optical damage threshold.

In this article, in order to search the qualified matrix mentioned above, three polymer matrices including linear homogeneous polymer, cross-linked copolymer and linear copolymer were synthesized in which weak hydrogen bond, strong hydrogen bond and covalent bond existed respectively between the dye and the polymer chain. The two-photon excited fluorescence, two-photon pumped lasing and two-photon up-conversion lasing efficiency were measured. And the influence of the microenvironment of different matrices on the two-photon up-conversion properties was discussed.

Synthesis

A. 0.01 mol/L dye-doped linear homogeneous polymer

5 mL 2-hydroxyethyl methacrylate (HEMA), 0.0229 g HMASPS or 0.0227 g HEASPS, 0.0459 g 2,2'-Azo-bis-iso-butyronitrile (AIBN) were added into a 10 mL flask. The

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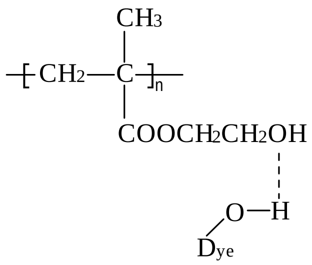
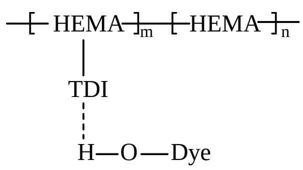
above mixture was stirred until the dye was solved. Then the reaction mixture was poured into a clean 1-cm path glass cuvette and heated to 40°C for a week for polymerization.



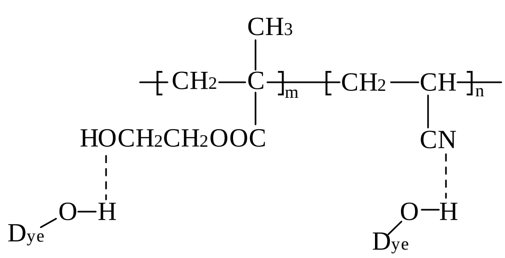
B. 0.01 mol/L dye cross-linked copolymer

4.5 mL HEMA, 0.0229 g HMASPS or 0.0227 g HEASPS were added into a 10 mL flask. The mixture was stirred for about half an hour until the dye was solved. 0.6 mL toluene-2,4-diisocyanate (TDI) was injected dropwise into the above solution and the resulting solution was stirred for another half an hour. Again 0.5 mL HEMA and 0.0287 g AIBN were added. When AIBN was solved, the reaction mixture was poured into a clean 1-cm path glass cuvette and heated to 40°C for a week for polymerization.



C. 0.01 mol/L dye-doped

5 mL HEMA, 0.375 mL acrylonitrile and 0.0402 g AIBN were added into a 10 mL flask. Then the reaction mixture was poured into a clean 1-cm path glass cuvette and heated to 40°C for a week for polymerization.

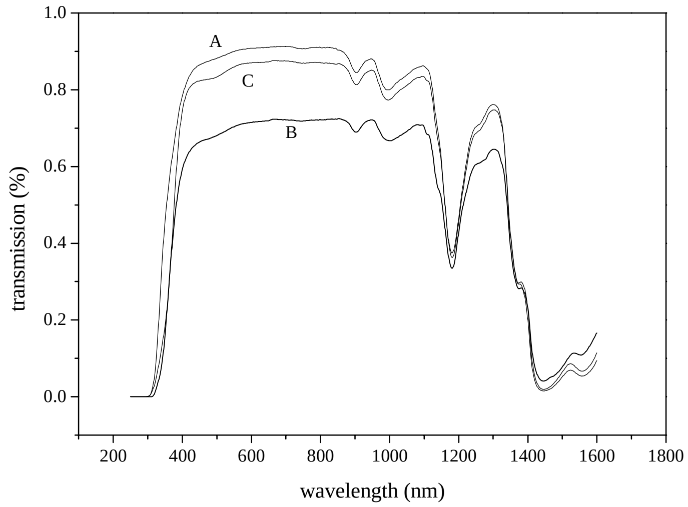


Two-photon pumped fluorescence and lasing test

The transmission ratios of three matrices were measured before the two-photon pumped fluorescence and lasing test (see **Figure 1**). Much higher transmission ratio can be obtained in linear homogeneous polymer and linear copolymer. The transmission ratio of the cross-linked copolymer was the lowest among three matrices.

The up-conversion fluorescence and lasing spectra were recorded by a passively mode-locked Nd:YAG laser as a pump source, and a single-scan streak camera together

Figure 1 The transmission spectra of three polymer matrices (A: linear homogeneous polymer B: cross-linked copolymer C: linear copolymer).



with a monochromator as the recorder. **Table 1** is the two-photon excited fluorescence and lasing peak positions of HEASPS and HMASPS in three matrices. One can see that the fluorescence peak positions for two dyes are similar both in linear homogeneous polymer and in linear copolymer matrices. And their fluorescence in cross-linked copolymer is blue-shifted in comparison with that in the other two matrices. Same characteristic can be seen in their two-photon up-conversion lasing.

Table 1 The two-photon excited fluorescence and up-conversion lasing peak positions (in parenthesis) of HMASPS and HEASPS doped or cross-linked polymer rods with the same concentration of 0.01mol/L.

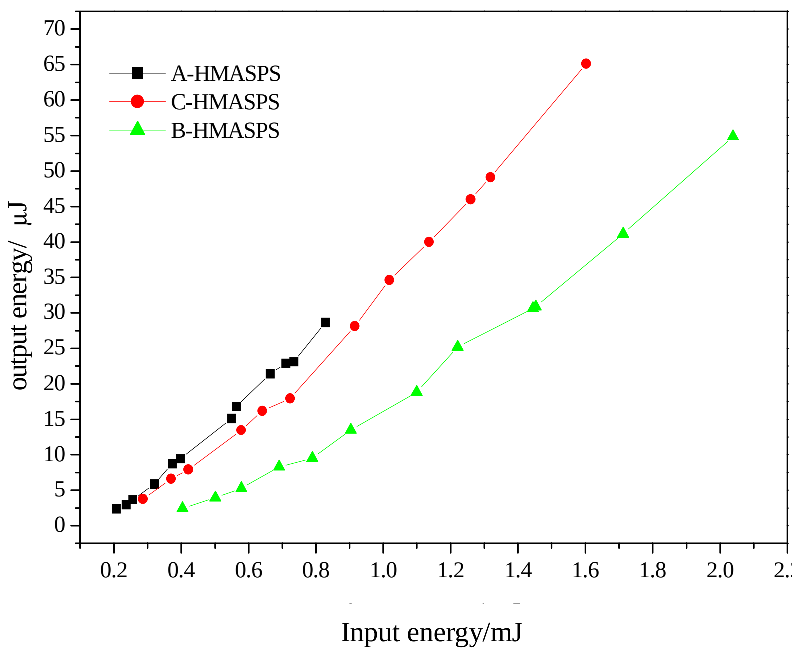
	Linear homogeneous copolymer nm	Linear copolymer nm	Cross-linked copolymer nm
HMASPS	~ 617 (597)	~ 617 (598)	~ 613 (593)
HEASPS	~ 618 (603)	~ 618 (601)	~ 605 (593)

Figure 2 is the output-input curves of HMASPS in three different matrices. Some characteristics can be generalized as follows: 1. Dye-doped linear homogeneous polymer and linear copolymer have much lower output threshold of 0.2 mJ than that of dye

cross-linked copolymer. 2. A much higher damage threshold can be obtained in dye-doped linear copolymer than in linear homogeneous polymer. 3. At the same pump condition, HMASPS in cross-linked copolymer gives the lowest two-photon upconversion lasing efficiency. Due to the similar molecular component, HMASPS and HEASPS in three polymer matrices exhibit same properties as listed above.

We believe that the deep cross-link in matrix B caused the low transmission ratio which led to the low two-photon up-conversion lasing efficiency. And the covalent bond may be the other reason for the low lasing efficiency of dye in matrix B. The strong hydrogen bond presented in linear copolymer caused high thermal stability of matrix which contributed to a high optical damage threshold.

Figure 2 The output-input curves of HMASPS in three different matrices.



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References

1. Y. Ren, Q. Fang, W. T. Yu, H. Lei, Y. P. Tian, M. H. Jiang, Q. C. Yang, Thomas C. W. Mak., *J. Mater. Chem*., **2000**, *10*, 2025.
2. G. S. He, R. Signorini, P. N. Prasad, *Appl. Optics*, **1998**, *37* (24), 5720.
3. X. M. Wang, Y. F. Zhou, W. T. Yu, C. Wang, Q. Fang, M. H. Jiang, H. Lei, H. Z. Wang, *J. Mater. Chem.*, **2000**, *10*, 2698.

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