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Properties of two-photon fluorescence and superradiance of a new organic dye $C_{46}H_{51}N_2B$

G. Zhou[1,a], D. Wang[1], S. Yang[1], Y. Ren[1], X. Xu[1], Z. Shao[1,b], X. Zhao[1], M. Jiang[1], Y. Tian[2], F. Hao[2], S. Li, and P. Shi[2]

[1] State Key Laboratory of Crystal Materials, Institute of Crystal Materials, Shandong University, Jinan 250100, P.R. China
[2] Department of Chemistry, Anhui University, Hefei 230039, P.R. China

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Abstract. Linear and nonlinear optical properties of a new organic dye, trans-4-[*p*-(N-*n*-butyl-N-*n*-butylamino)-styryl]-N-methyl-pyridinium tetraphenylborate solution in dimethyl formamide (DMF) have been studied systematically. When excited with mode-locked picosecond 1 064 nm laser beam, intense upconversion fluorescence and superradiance can be obtained. The temporal behaviors of one-photon absorption and two-photon absorption (TPA) fluorescence and superradiance have been studied. The highest upconversion efficiency was found to be 4.1% at a pump energy of 4 mJ. By using an optical parameter amplifier (OPA) as the pump laser, the nonlinear transmittance and upconversion efficiencies of the dye solution at different wavelengths were measured. The strongest linear absorption was found at a wavelength of 930 nm whereas the highest upconversion efficiency was at 1 030 nm. The 100 nm red-shift for the highest upconversion efficiency wavelength compared with the strongest nonlinear absorption are caused by excited state absorption.

PACS. 42.65.-k Nonlinear optics – 78.20.Ci Optical constants (including refractive index, complex dielectric constant, absorption, reflection and transmission coefficients, emissivity) – 81.05.Lg Polymers and plastics; rubber; synthetic and natural fibers; organometallic and organic materials

1 Introduction

Organic chromophores with large two-photon absorption (TPA) cross-sections have been the subject of a great deal of attention due to their potential applications in many aspects, such as frequency upconversion lasing [1], optical power limiting [2–4] three-dimensional (3D) fluorescence imaging [5], 3D optical data storage [6], 3D lithographic microfabrication [7], and photodynamic therapy [8]. The large TPA cross-sections of organic dyes are closely connected with their extended π-conjugated electronic structures and charge transfer properties. A new generation of organic dyes with large TPA cross-sections and high upconversion efficiencies was first synthesized by the Prasad [1,9], and Mader groups [4]. Many efforts have been devoted to the synthesis and the determination of the nonlinear optical properties of the pyridinium series. Recently, a new organic dye, trans-4-[*p*-(N-*n*-butyl-N-*n*-butylamino)-styryl]-N-methyl-pyridinium tetraphenylborate, was synthesized by the Y. Tian's group. When excited with a near infrared laser beam, intense TPA fluorescence and superradiance can been observed. In this paper, we report the linear and nonlinear optical properties of the dye solution in dimethyl formamide (DMF).

[a] e-mail: gzhou@icm.sdu.edu.cn
[b] e-mail: zshao@icm.sdu.edu.cn

2 Linear optical properties

Figure 1 shows the linear absorption spectrum of a 1 cm-path dye solution in DMF with a concentration of 1×10^{-4} mol/l, which was measured by using a UV-VIS-IR recording spectrophotometer (Hitachi U3500) with a spectral resolution of 1 nm. In the upper-right corner of Figure 1 the chemical structure of the dye is shown. There are two strong linear absorption bands with peaks at 267 nm and 485 nm, respectively. The influence of the quartz and solvent has been excluded. No linear absorption can be observed in the entire range of 600–1 600 nm. Two-photon energy of 800–1 100 nm just falls into the stronger linear absorption band at 485 nm. So TPA would be expected in this wavelength range.

Figure 2a shows the one-photon absorption fluorescence of this dye in DMF with 1×10^{-6} mol/l concentration, which was measured by using a spectrofluorophotometer (Perkin-Elmer, LS50B). The excitation wavelength is 477 nm. The central wavelength and bandwidth of one-photon absorption fluorescence are 605 nm

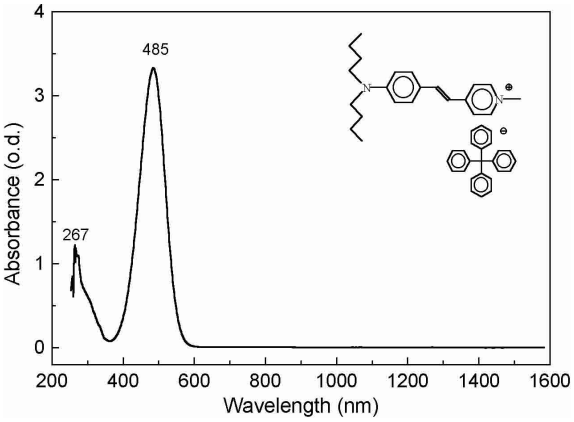

Fig. 1. Linear absorption spectrum of a 1 cm-path dye solution in DMF (1×10^4 mol/l). The chemical structure of the dye is shown in the upper-right hand corner.

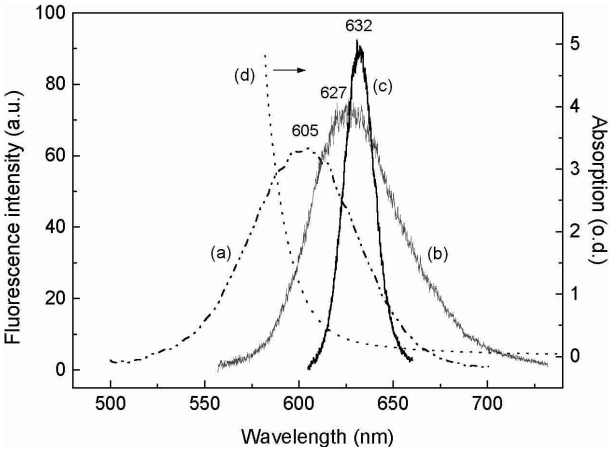

Fig. 2. One-photon absorption fluorescence (a) of the dye in DMF at 1×10^{-6} mol/l concentration. One-photon absorption fluorescence (b) and superradiance (c) at 0.01 mol/l concentration. Curve (d) is the linear absorption at 0.01 mol/l concentration.

and 100 nm, respectively. When the dye solution with a concentration of 0.01 mol/l is excited with a relatively weak 532 nm laser beam, intense one-photon absorption fluorescence can be observed. When the pump intensity is above a certain threshold (by focusing the laser beam or increasing the pump energy), intense one-photon absorption superradiance can be observed. The results are shown in Figures 2b and 2c. The pump beam was produced by a mode-locked Nd:YAG laser operating at 1 064 nm, with pulse duration, average energy per pulse, beam size, angular divergence and pulse repetition rate of 40 ps, 3.5 mJ, 3 mm diameter, 0.4 mrad and 10 Hz respectively. A KTP crystal was used to frequency double the laser output, from 1 064 nm to 532 nm in wavelength, with an efficiency of about 50%. A filter was used to cut the transmitted 1 064 nm laser. From Figures 2a and 2b, it can be seen that there is 22 nm red shift for the central wavelength of one-photon absorption fluorescence at high concentration (0.01 mol/l) than in the case of low concentration (1×10^{-6} mol/l). This is due to the re-absorption of the

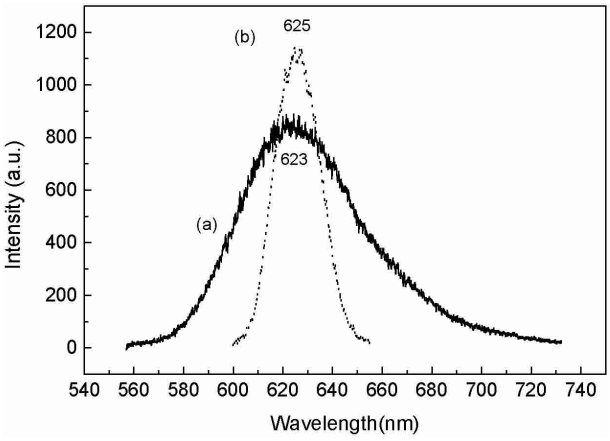

Fig. 3. TPA fluorescence (a) and superradiance (b) of the dye solution in DMF (0.01 mol/l).

dye solution at high concentrations. Figure 2d shows the linear absorption spectrum of the dye at a concentration of 0.01 mol/l. It can be seen that there is a partial overlap between the red-side of linear absorption and the blue-side of one-photon absorption fluorescence. The fluorescence at short wavelength cannot emit from the dye solution at high concentrations due to re-absorption. There is a slight red shift for the central wavelength of one-photon absorption superradiance (632 nm) compared with that of one-photon absorption fluorescence (627 nm).

3 Nonlinear optical properties

3.1 Spectral properties of TPA fluorescence and superradiance

When a 1 cm-path dye solution in DMF at 0.01 mol/l concentration was pumped by focused (f = 15 cm) picosecond 1 064 nm laser beam, intense TPA fluorescence and superradiance can be observed, as shown in Figures 3a and 3b. In the measurement of TPA fluorescence, the focal plane of the lens was outside the cuvette; in the measurement of TPA superradiance however, the focal plane was at the center of the cuvette. The threshold of the superradiance is 0.5 mJ under the condition that the focal plane is at the center of the cuvette. The central wavelength and bandwidth (FWHM) are 623 nm and 60 nm, and 625 nm and 18 nm for TPA fluorescence and superradiance, respectively. There is a slight blue shift when compared with the case of one-photon.

3.2 Lifetime of one-photon absorption fluorescence and TPA fluorescence

Figures 4a and 4b show the temporal behavior of one-photon absorption and TPA fluorescence, which were measured by using a streak camera (Hamamatsu, model: C5680-01) in conjunction with an imaging spectrographer (Hamamatsu, model: C5094). The scatter points are the

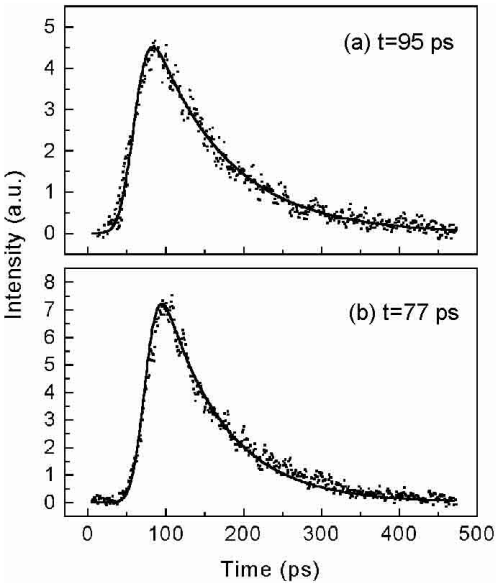

Fig. 4. Temporal profile of one-photon absorption (a) and TPA fluorescence (b) of the dye solution in DMF (0.01 mol/l).

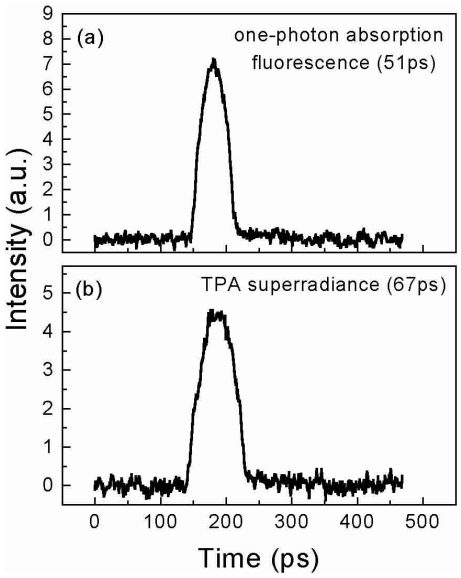

Fig. 5. Temporal profile of one-photon absorption (a) and TPA (b) superradiance of the dye solution in DMF (0.01 mol/l).

measured data points and the solid lines are the best fitting lines. The lifetimes of one-photon absorption and TPA fluorescence of this dye are 95 ps and 77 ps, respectively. This difference in lifetimes is caused by the different pump conditions for the measurement of one-photon absorption and TPA fluorescence. The dye solution has a strong linear absorption at 532 nm. The pump energy is very weak to avoid the generation of superradiance. In the case of TPA fluorescence, the pump laser beam of wavelength of 1 064 nm was focused on the center of the sample. It is the high pump energy that leads to the relatively short lifetime of two-photon fluorescence.

3.3 Temporal behavior of the one-photon absorption superradiance and TPA superradiance

The temporal profiles of the one-photon absorption superradiance and TPA superradiance were measured by using the previously mentioned streak camera. The results are shown in Figures 5a and 5b. The duration of one-photon absorption superradiance and TPA superradiance are 51 ps and 67 ps respectively, which are shorter than the lifetime of fluorescence. The temporal duration of TPA superradiance is longer than that of one-photon absorption superradiance, but the reason for this is not clear at the present time.

3.4 Upconversion efficiencies and optical power limiting at 1 064 nm

In the measurement of upconversion efficiencies and the optical power limiting, the amplifier of the Nd:YAG laser was used and the maximum pump energy was 10 mJ. A two-channel energymeter (EPM 2000, Molectron) was

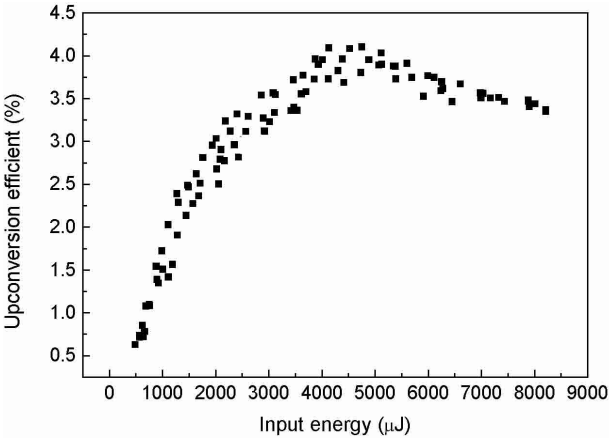

Fig. 6. Upconversion superradiance efficiencies at different pump energies at 1 064 nm. The pump laser beam was produced by a mode-locked Nd:YAG laser.

used to measure the input and output energy. An IR-filter was used to cut the transmitted pump laser in the measurement of upconversion efficiencies and a VIS-filter was used to cut the upconverted superradiance in the measurement of optical power limiting. Two Glan-Taylor polarizers were used to change the pump energy continuously. For both experiments, a 1 cm-path dye solution sample in DMF at 0.01 mol/l concentration was used. Figure 6 shows the upconversion efficiency at different pump energies. Each data point is an average of 10 pulses. The highest upconversion efficiency was 4.1% when the pump energy was about 4 mJ. At lower pump energies, the efficiency was lower. However, at higher pump energies, the efficiency was not found to increase. This was caused by the saturation absorption of the pump energy. Figure 7 shows the optical power limiting property of this dye

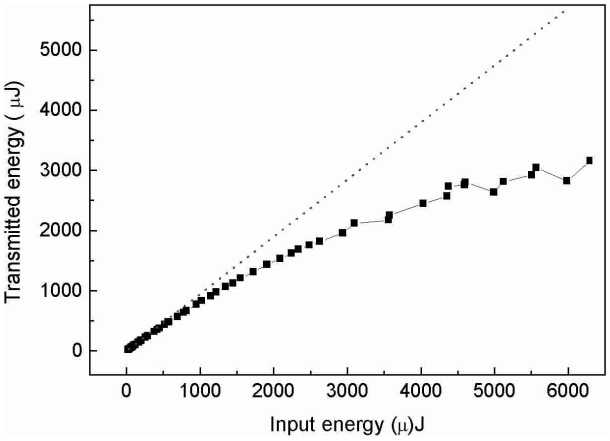

Fig. 7. Optical power limiting properties of the dye solution in DMF (0.01 mol/l) at 1 064 nm.

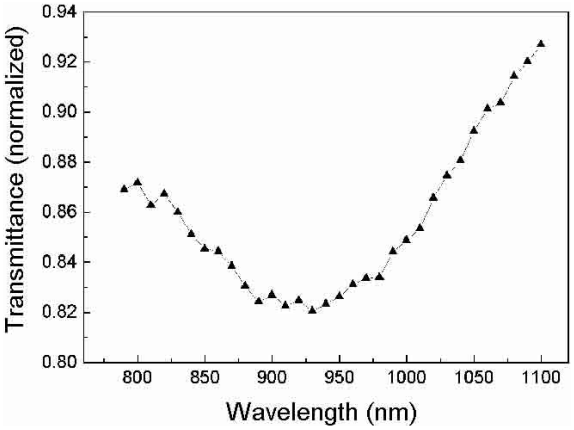

Fig. 8. Nonlinear transmittance of the dye solution in DMF (0.01 mol/l) at different wavelengths.

solution in DMF. The dotted line is the linear transmittance of the sample at 1 064 nm, whereas the scatter line of squares is the measured transmitted pump energy. From Figure 7, it can be seen that this dye solution in DMF has an obvious optical power limiting effect at 1 064 nm.

3.5 Upconversion efficiencies and nonlinear transmittance at different wavelengths

In order to study the nonlinear optical properties systemically, we measured the nonlinear transmittance and upconversion efficiencies at different wavelengths. An optical parametric amplifier (OPA) was used as a tunable source to provide the optical pump beam at different wavelengths. The average output energy, beam size, angular divergence, pulse duration and repetition rate were 0.8 mJ, 2.5 mm diameter, 5 mrad, 40 ps and 10 Hz respectively. The experimental setup is similar to that used in the measurement of upconversion efficiencies and optical power limiting at 1 064 nm, except that the two Glan-Taylor polarizers were not used and the source of the pump laser beam was the OPA. Figure 8 shows the nonlinear transmittance of a 1 cm-path solution of this dye. The influence

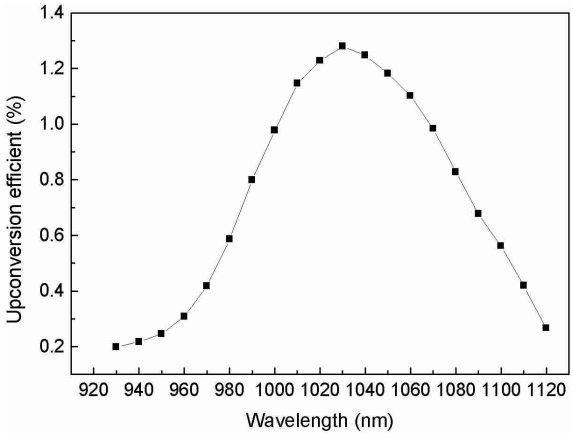

Fig. 9. Upconversion superradiance efficiencies of the dye solution in DMF (0.01 mol/l) at different wavelengths.

of the solvent and cuvette has been excluded. There was intense nonlinear absorption in the entire range of 800–1 100 nm, with the strongest absorption at about 930 nm. Figure 9 shows the upconversion efficiencies at different wavelengths. It can be seen that the highest upconversion efficiency is 1.3% at about 1 030 nm. The upconversion efficiency at 1 064 nm is 1.1%, which is much smaller than that in Figure 5. This is due to the difference of the optical pumping conditions. The energy of the pump beam from the OPA is only about 0.8 mJ, which is much smaller than that produced by the mode-locked Nd:YAG laser. Also, the angular divergence of the OPA is much larger than that of the mode-locked Nd:YAG and the intensity of the focused laser beam from the OPA would have been much smaller than that from the Nd:YAG laser. Hence, the measured upconversion efficiencies are much smaller when the OPA was used.

From Figures 1, 8 and 9, it can be seen that:

(1) there is 40 nm blue-shift for the strongest nonlinear absorption wavelength (930 nm) compared with twice of the wavelength of linear absorption peak at 485 nm;

(2) there is 100 nm red-shift for the highest upconversion efficiency wavelength (1 030 nm) compared with the strongest nonlinear absorption wavelength.

These phenomena may be caused by an excited state absorption. From Figure 1 it can be seen that there is a small linear absorption peak located at around 267 nm. This corresponds to the second singlet excited state S_2. At wavelengths longer than 1 000 nm, the electrons at ground state S_0 are excited to the first singlet excited state S_1 by TPA. The electrons in an S_1 state cannot be excited to S_2 state by excited state absorption (ESA) because the energy gap between S_1 and S_2 is too large at this wavelength range. At wavelengths shorter than 950 nm, the electrons in the S_0 state are initially excited to the S_1 state by TPA, then some of the electrons in the S_1 state can absorb a photon and be excited to the S_2 state. So at wavelengths shorter than 950 nm, TPA and ESA take place simultaneously. It is the ESA that leads to the blue shift

of the strongest nonlinear absorption wavelength. When electrons are excited to the S_2 state, a large number of the electrons may not participate in the emission process, and hence at short wavelengths the upconversion efficiencies are found to be small. It is the excited state absorption that leads to the red shift for the highest upconversion efficiency wavelength.

4 Conclusions

In this paper we report the linear and nonlinear optical properties of a new organic dye $C_{46}H_{51}N_2B$ in DMF. The central wavelength and bandwidth (FWHM) of TPA fluorescence and superradiance were found to be similar with those of one-photon absorption fluorescence and superradiance. The lifetimes of one- and two-photon fluorescence were measured to be 95 ps and 77 ps respectively. The nonlinear transmittance and upconversion efficiencies at different wavelengths were also measured. There was 100 nm red shift for the highest upconversion efficiencies compared with the strongest nonlinear absorption wavelength. This phenomenon may be explained by ESA, but need to be substantiated by further experiments. For example, a tunable femtosecond laser could be used to study the upconversion efficiencies at different wavelengths. This is because excited state absorption cannot take place when pumped by a femtosecond laser beam. Further experiments are to be undertaken using this property.

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References

1. G.S. He, L. Yuan, Y. Cui, M. Li, P.N. Prasad, J. Appl. Phys. **81**, 2529 (1997).
2. W. Tutt, T.F. Boggess, Prog. Quant. Electron. **17**, 299 (1993).
3. C.W. Spangler, J. Mater. Chem. **9**, 2013 (1999).
4. J.E. Ehrlich, X.L. Wu, I.-Y.S. Lee, Z.-Y. Hu, H. Rockel, S.R. Marder, J.W. Perry, Opt. Lett. **22**, 1843 (1997).
5. W. Denk, J.H. Strickler, W.W. Webb, Science **248**, 73 (1990).
6. D.A. Parthenopoulos, P.M. Rentzepis, Science **245**, 843 (1989).
7. S. Maruo, O. Nakamura, S. Kawata, Opt. Lett. **22**, 132 (1997).
8. A.M.R. Fisher, A.L. Murphree, C.J. Gomer, Laser Surg. Med. **17**, 2 (1995).
9. G.S. He, G.C. Xu, P.N. Prasad, B.A. Reinhardt, J.C. Bhatt, A.G. Dillard, Opt. Lett. **20**, 435 (1995).