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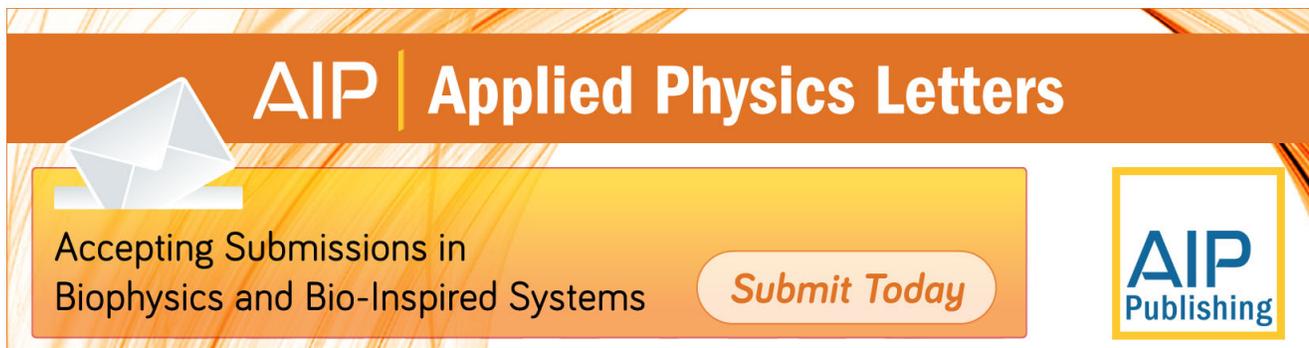
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# Dynamic studies of charge-separated-state enhancement of the optical nonlinearity of a porphyrin heterodimer

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Light-induced enhancement of the third-order nonlinear optical susceptibility of a heterodimer consisting of two different porphyrin monomers, a zinctetra(4-sulfonatophenyl)porphyrin and a zinctetra(4-*N*-methyl-pyridyl)porphyrin, was observed when the sample was optically pumped by a 30 ps, 532 nm pump pulse. The temporal behavior of the enhancement was studied. It was found that the enhancement was due predominantly to the population of the charge-separated state with a large electronic third-order nonlinear optical susceptibility © 1996 American Institute of Physics. [S0003-6951(96)03439-0]

Nonlinear optics is expected to play a major role in the technology of photonics. Recent progress in the field of high-speed optoelectronics and information technology has encouraged the search for materials with a large, fast nonlinear optical (NLO) response and for new ways to enhance the NLO response. Studies on light-induced enhancement of the third-order nonlinear optical susceptibility  $\chi^{(3)}$  of materials have been attracting much attention. Rogovin reported a stark-enhanced phase conjugation in shaped-microparticle suspensions.<sup>1</sup> Garito and colleagues found a new way to achieve large  $\chi^{(3)}$  through excited-state population,<sup>2</sup> and the enhanced NLO process related to optically pumped electronic excited states was observed in some conjugated organic materials.<sup>3,4</sup>

It has been shown that the stacked and bridged porphyrin<sup>5</sup> or phthalocyanine<sup>6</sup> assemblies can exhibit unusual optical, electron-transfer and conductivity properties owing to the strong  $\pi$ - $\pi$  interactions between the two macrocycles and the formation of exciton coupling in the sandwich complexes. Depending on the nature of the central metal and peripheral substituents in porphyrins and phthalocyanines, a wide range of redox properties and photophysical properties can be obtained. Thus, their association should lead to a peculiarly wide range of donor-accepted complexes. Noncovalently bound heterodimers consisting of two different porphyrin monomers, one of which is equipped with four positively charged sidegroups and the other with four negatively charged sidegroups, are attractive assembly models because an effective charge transfer can occur in these molecules through photoexcitation of the sensitizer component.<sup>7</sup> Subpicosecond time-resolved photoinduced absorption measurements for porphyrin dimers show that charge transfer occurs within 300 fs after photoexciton, and the charge-recombination time is 50–500 ps.<sup>8</sup> Therefore, we believe that it is more meaningful to study the charge-separated-state NLO process of supramolecules such as porphyrin dimers. Enhanced nonlinear absorption related to the absorption of charge-separated state in a polymer/methanofullerene film was reported recently,<sup>9</sup> but to our knowledge, study on the

dynamic behavior of charge-separated-state NLO process has not been done before.

In this letter, we report our studies on light-induced enhancement of the optical nonlinearity of a heterodimer (here we refer to it as ZnTSPP-ZnTMPyP) consisting of two different porphyrin monomers, a zinctetra(4-sulfonatophenyl)porphyrin (ZnTSPP) and a zinctetra(4-*N*-methyl-pyridyl)porphyrin (ZnTMPyP). The temporal behavior of the enhancement of  $\chi^{(3)}$  for the porphyrin dimer was measured by using degenerate-four-wave-mixing (DFWM) with an additional pump beam. For comparison, the measurement was performed also on the two porphyrin monomers. It was verified by comparing the time evolution of the enhanced NLO process that the enhancement for ZnTSPP-ZnTMPyP is due predominantly to the population of the charge-separated state, whereas the enhancements for ZnTSPP and ZnTMPyP are due to the population of their first excited singlet state.

ZnTSPP-ZnTMPyP was formed in the liquid phase by pairing electrostatically ZnTSPP with ZnTMPyP bearing oppositely charged substituents. It was prepared by mixing ZnTSPP with ZnTMPyP in a molar ratio of 1:1 in H<sub>2</sub>O/CH<sub>3</sub>OH 4:1 *v/v*, in which more than 90% of the porphyrin monomers were dimerized. The concentration of the sample has  $1.18 \times 10^{-4}$  M. The porphyrin dimer has a slipped “face-to-face” structure with a plane-to-plane distance of 30–35 nm, and two pyrroles rings of each monomer are mutually overlapping. The Soret band (410–430 nm) of ZnTSPP exhibits a blue shift on addition of ZnTMPyP, whereas the *Q* band (500–650 nm) shifts to the red.<sup>7</sup> The two monomers fluoresce strongly, while in the dimer the fluorescence is quenched, indicating the existence of a very efficient charge transfer from the electron-donating ZnTSPP to the electron-accepting ZnTMPyP. The *Q* band (500–650 nm) of the dimer is attributed to the transition involving delocalized molecular orbital due to the strong  $\pi$ - $\pi$  coupling between the two macrocycles, to give a new singlet excited state  $^1(\pi, \pi^*)$ . Excitation of the dimer with a 532 nm pump pulse, lead to the population of the  $^1(\pi, \pi^*)$  excited state. They deactivate rapidly within a few hundred fs to the low-

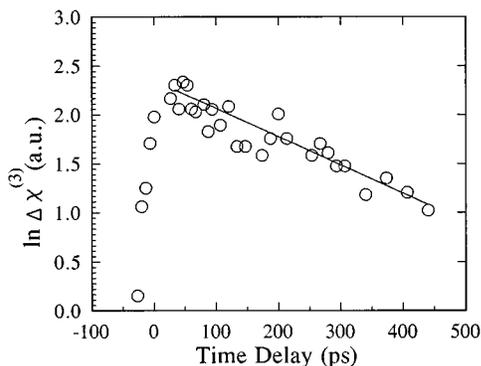


FIG. 1. Time evolution of  $\Delta\chi^{(3)}$  of ZnTSPP-ZnTMPyP on the action of the 532 nm pump pulse of energy of 0.6 mJ. The solid curve is a fit with an exponent of 340 ps.

lying charge-separated state through the charge transfer from ZnTSPP to ZnTMPyP.

In our experiments, a forward DFWM geometry with an additional variable-time-delay pump beam was used,<sup>4</sup> where the light source was a Nd:YAG laser system with a 30 ps, 1064 nm single pulse output. The 1064 nm pulse from the laser was doubled by a KDP crystal to produce the second-harmonic pulse at 532 nm. The 532 nm beam then served as the pump beam. The remaining 1064 nm beam was split into two beams which served as the DFWM probes. To eliminate thermal grating contribution the polarizations of the two probe beams were chosen to be orthogonal. The two probe beams with wave-vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$  were focused in coincidence on the sample at a small angle of 1.5 degree. The pump beam was also focused on the interaction region in the sample cell whose thickness was 2 mm. The diameter of the pump beam was  $\sim 0.6$  mm, whereas those of the probe beams were  $\sim 0.4$  mm to ensure their overlap. The excited-state DFWM experiment began with the arrival of the pump pulse which excited sample's molecules to the excited states. After excitation, and before relaxation to the ground state, the two probe pulses arrived, producing a diffracted signal in the  $2\mathbf{k}_2 - \mathbf{k}_2$  direction which was proportional to the square of  $\chi^{(3)}$  of the sample, and detected by a photomultiplier.

In an optically pumped third-order NLO process the material exhibits an effective third-order nonlinear optical susceptibility,  $\chi_{\text{eff}}^{(3)}$ , that is related to populations of all the populated states:

$$\chi_{\text{eff}}^{(3)} = \chi_{\text{solvent}}^{(3)} + F \sum_{S_n} N_{S_n} \gamma^{S_n},$$

where  $\chi_{\text{solvent}}^{(3)}$  is the third-order NLO susceptibility of the solvent, and  $F$  is the local field factor.  $N_{S_n}$  and  $\gamma^{S_n}$  are the number density and the molecular hyperpolarizability of the state  $S_n$ , respectively.

When the ZnTSPP-ZnTMPyP solution was pumped by the 532 nm pump beam, enhancement of the DFWM signal was observed. No evident absorption of ZnTSPP-ZnTMPyP at 1064 nm was observed either the pump beam existed or not, indicating that the nonlinearities of the ground state and the excited states at this wavelength are nonresonant. Varying the delay time of the pump pulse while two probe pulses arrived simultaneously, we measured the corresponding

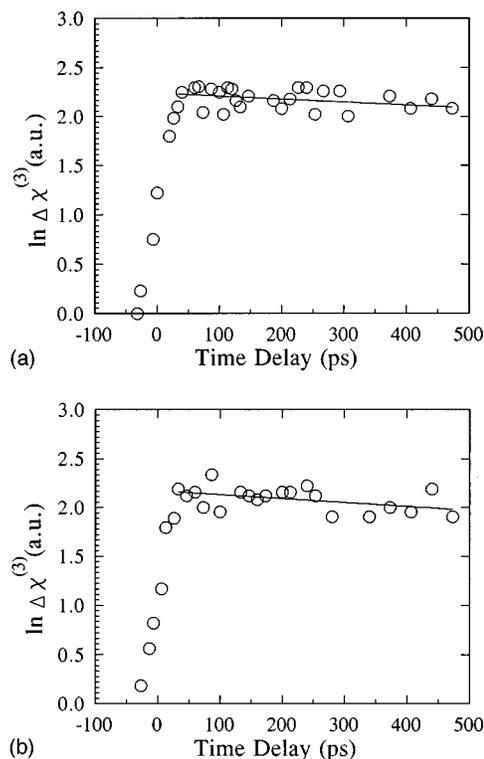


FIG. 2. Time evolution of  $\Delta\chi^{(3)}$  of ZnTSPP (a) and ZnTMPyP (b) on the action of the 532 nm pump pulse of energy of 0.6 mJ. The solid curves are a fit with an exponent.

DFWM signal intensities from which the corresponding  $\chi_{\text{eff}}^{(3)}$  could be obtained. When the probe pulses preceded the pump pulse, it encountered only molecules in the ground state and, therefore, the measured  $\chi_{\text{eff}}^{(3)}$  was contributed only from the solvent and the ground-state molecules. When the probe followed the pump, it encountered a mixture of molecules in the excited and ground states; and the  $\chi_{\text{eff}}^{(3)}$  was contributed from the solvent, excited-state molecules, and the ground-state molecules. From the data of  $\chi_{\text{eff}}^{(3)}$  such measured, we can get the corresponding susceptibility difference  $\Delta\chi^{(3)} = \chi_{\text{eff}}^{(3)} - (\chi_{\text{solvent}}^{(3)} + \chi_g^{(3)})$ , where  $\chi_g^{(3)}$  is the susceptibility of ZnTSPP-ZnTMPyP when all molecules are in the ground state. Then, we obtained the delay-time dependence of  $\Delta\chi^{(3)}$  as shown in Fig. 1. One can see that  $\Delta\chi^{(3)}$ , which represents the NLO enhancement, exhibits a rise time that is longer than the pulse width, and then followed by a single exponential decay whose decay time is  $\sim 340$  ps, consistent with the time of the charge recombination of porphyrin heterodimers.<sup>8</sup> Therefore, this enhanced NLO process can be explained as following: the optical pumping initially populates the  $^1(\pi, \pi^*)$  excited state with a very short lifetime (a few hundreds fs), then an efficient charge transfer from the  $^1(\pi, \pi^*)$  state to the low-lying charge-separated state with a very fast rate, and finally the population of the charge-

TABLE I. Measured values of  $\chi^{(3)}$  with and without the pump beam and the charge-recombination time of ZnTSPP-ZnTMPyP.

$\chi^{(3)}$ (without pump)	$\chi^{(3)}$ (with pump)	Charge-recombination time
$1.6 \times 10^{-15}$ esu	$1.3 \times 10^{-14}$ esu	340 ps

separated state recovers to the ground state through the charge recombination with a much slower rate. Since the charge-transfer rate is more than 1000 times faster than any competing process, the quantum efficiency for charge transfer approaches unity. It is the population of the charge-separated state that produces the enhancement of  $\chi^{(3)}$  because the population of the  $^1(\pi, \pi^*)$  state with a very short lifetime is much less than that of the charge-separated state.

In order to confirm our explanation, we measured also the time evolution of the enhancement of  $\chi^{(3)}$  for the two monomers, ZnTSPP and ZnTMPyP, which are shown in Fig. 2(a) and 2(b), respectively. From Fig. 2, one can find that they exhibit a similar temporal behavior to that of ZnTSPP-ZnTMPyP, but the decay times are much longer than that of ZnTSPP-ZnTMPyP, and determined to be 2.5 and 3.2 ns, respectively. These times are consistent with the lifetimes of the first excited singlet state of  $S_1$  of ZnTSPP and ZnTMPyP.<sup>10</sup> Therefore, the enhancement of  $\chi^{(3)}$  for the two monomers are attributed to the population of the excited state  $S_1$ .

When the pump pulse was set to precede the probe pulses by 40 ps, we measured the value of  $\chi^{(3)}$  of ZnTSPP-ZnTMPyP under an unsaturated pumping condition (energy of the pump pulse was  $\sim 0.6$  mJ), which was enhanced by nearly 10 times. In the measurement, the value of  $\chi^{(3)}$  of the sample was determined in comparison with the measurements on a reference sample of  $CS_2$ .<sup>11</sup> Table I gives the values of  $\chi^{(3)}$  with and without the pump beam and the

charge-recombination time of ZnTSPP-ZnTMPyP.

In summary, we investigated dynamic behavior of light-induced enhancement of the third-order NLO susceptibility of a heterodimer, ZnTSPP-ZnTMPyP. By measuring the time evolution of the enhanced NLO process, it was verified that the enhancement is due predominantly to the population of the charge-separated state with a large electronic third-order nonlinear optical susceptibility.

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