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Two-photon absorption in quantum dots based on a nonconjugated conductive polymer

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Two-photon absorption has been measured in a nano-optical material (quantum dots) based on the nonconjugated conductive polymer, iodine-doped poly(β-pinene). The measurement has been made using open-aperture z scan at 730–860 nm with 150 fs pulses. Exceptionally large two-photon absorption coefficient has been observed with a peak of magnitude $\sim$2.6 cm/MW that appeared at $\sim$1.53 eV which is close to half of the optical gap corresponding to the charge-transfer transition involving the isolated double bond. Saturation of absorption was observed at lower intensities and shorter wavelengths. The results have been attributed to the quantum dots (subnanometer size) formed upon doping. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2714995]

Nonlinear optics in quantum dots based on semiconductors and metals is a highly active area of research. Quantum dots of various metals and semiconductors have been fabricated and studied in detail.[1–7] While significant progress has been made in research of inorganic quantum dots, works on organic quantum dots are at the beginning stage. Conjugated polymers such as polydiacetylene are considered as one-dimensional systems (organic quantum wires) with electrons delocalized along the polymer backbone.[7–9] Exceptionally large and ultrafast off-resonant third order optical nonlinearities have been measured and studied in detail for these materials. Nonlinear optical measurements in iodine-doped conjugated polymers have been made and the nonlinearity $[\chi^{(3)}]$ was found to decrease with doping.[10] The decrease is due to the well known transition of the conjugated polymer to a metallic state upon doping.[11] Specific nonconjugated polymers having at least one double bond in the repeat have been shown to become electrically conductive upon doping.[12–15] In contrast to conjugated polymers, for nonconjugated conductive polymers such as doped polyisoprene the charge is localized close to the isolated double bond site. The structure of this system represents an ideal quantum dot (nanometallic) with a subnanometer dimension based on an organic material. The electrical conductivities of most doped nonconjugated conductive polymers are in the same range as that of nanometallics. In this letter, results of two-photon absorption measurements of such quantum dots based on a nonconjugated conductive polymer will be reported. Two-photon absorption has a number of photonic applications including optical limiting.

The polymer discussed in this letter is poly(β-pinene). The molecular structure is shown in Fig. 1. As recently reported,[15] the electrical conductivity of poly(β-pinene) increases more than 10×10^9 times upon doping with iodine. The final conductivity reaches a value of about $8 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at an iodine molar concentration of about 0.8. The quadratic electro-optic effect in doped poly (β-pinene) has been recently measured at a wavelength (633 nm) close to resonance and an exceptionally large Kerr coefficient has been observed. The magnitude of the Kerr coefficient at a higher doping level as measured is $1.2 \times 10^{-10}\ \mathrm{m/V^2}$ which is 50 times that of nitrobenzene. This large third order optical nonlinearity has been attributed to the special structure of the radical cations that are formed upon doping and the confinement of the system within a subnanometer dimension (Fig. 2). In this letter, the two-photon absorption coefficient (α_2) which is proportional to the imaginary part of $\chi^{(3)}$, measured at a specific range of wavelengths, is discussed. As it will be shown, the results are similar in some respects to that reported for inorganic metallic quantum dots.

Poly(β-pinene) pellets purchased from Aldrich Chemicals Corporation were dissolved in toluene. Using this solution, thin films (thickness $\sim$1.5 μm) of poly(β-pinene) were cast on quartz substrates. The samples initially colorless when exposed to iodine become darker as the doping level is increased.

The optical absorption spectra[13] of poly(β-pinene) as a function of iodine doping are shown in Fig. 3. The undoped film of poly(β-pinene) shows a weak peak at 280 nm. As the doping level increases, two peaks begin to be evident; one appearing at 310 nm (4 eV) and the other at 400 nm (3.1 eV). The peak at 4 eV has been attributed to the radical cation that is formed upon doping. The peak at 3.1 eV has been attributed to the charge transfer that occurs between the double bond and the dopant. The Fourier transform infrared spectroscopic studies for an undoped sample show peaks at 728 and 1610 cm^{-1} corresponding $=$C–H bending and C$=$C stretching modes, respectively. The intensities of these peaks are reduced as the polymer is doped with iodine indicating formation of the radical cations upon charge transfer from the double bond to iodine, as shown in Fig. 2. The production of radicals upon doping has been confirmed by electron paramagnetic resonance experiments.[16] The encircled regions involving the charge-transfer sites as shown in Fig. 2 represent the nano-optical domains or quantum dots.

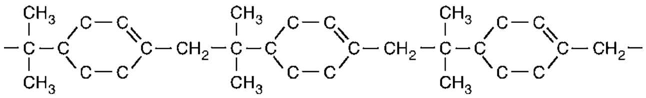

FIG. 1. Molecular structure of poly(β-pinene).

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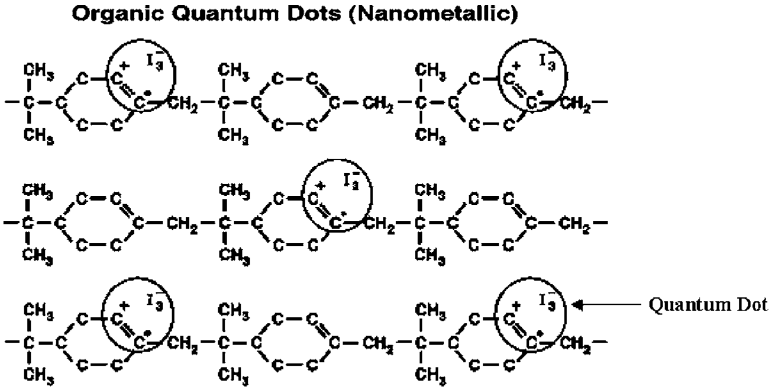

FIG. 2. Quantum dots in poly(β-pinene) created upon doping with iodine and consequent charge transfer from the double bond to the dopant. The encircled regions represent the quantum dots with a subnanometer dimension.

In order to measure the two-photon absorption coefficient of doped poly(β-pinene), the z-scan technique[17] without an aperture was used. The measurement was made using 150 fs pulses from a Ti:sapphire laser over the wavelength range of 730–860 nm. The laser beam was passed through an attenuator to control the input power of the beam. The beam was then focused using an objective lens (5×). The sample mounted on a motorized X-Y stage, with a precision of 0.1 μm, was moved through the focus along the beam propagation direction (z axis). The output power was measured as a function of the sample position (z). Data were recorded for continuous wave (cw) and in mode locked (pulsing) conditions to separate any effect of scattering.

A set of z-scan data obtained with the mode locked condition (pulse width of 150 fs) is shown in Fig. 4 for the wavelengths of 750, 810, and 850 nm. In the cw condition only noise signal was observed indicating no two-photon absorption. As Fig. 4 indicates, partial saturation of absorption was detected at lower intensities. At higher intensities (near the focus) only two-photon absorption is significant. Two-photon absorption is given by $\Delta\alpha=\alpha_2 I$, where $\Delta\alpha$ is the change in the linear absorption coefficient, α_2 is the two-photon absorption coefficient, and I is the peak intensity. From the z-scan data, the magnitude of the two-photon absorption coefficient was determined over the wavelength range of 730–860 nm (Fig. 5). The maximum two-photon absorption coefficient (α_2) was obtained at about 1.53 eV (810 nm) with a magnitude of about 2.6 cm/MW. The maximum is near half of the optical gap (3.1 eV) corresponding to charge transfer in doped poly(β-pinene). An additional peak was observed at about 1.46 eV (850 nm). The peak at 1.46 eV may be due to electron-phonon interaction involving a phonon band of the charge-transfer complex. The magnitude of α_2 as obtained is comparable to or higher than that of semiconductor and metallic quantum dots.[1–6] Saturation of absorption at lower intensities was observed in specific metallic quantum dots.[4] In the present case, the saturation decreases at longer wavelengths as would be expected based on the fact that linear absorption decreases at longer wavelengths (Fig. 6). The magnitude of α_2 depends on the dopant concentration since the linear absorption spectrum changes with dopant concentration (Fig. 2). In this letter, results for medium-doped poly(β-pinene) are discussed. As the results indicate, the linear absorption due to charge transfer between the double bond and the dopant has the dominant contribution to the two-photon effect. The large α_2 in this polymer has been attributed to the special structure of this electronic system confined within a subnanometer dimension. As shown in Fig. 2, the charge-transfer sites have a subnanometer dimension based on calculations using the known chemical bond distances. As it is well known, the size of the quantum dots is the major factor that determines the magnitude and response time of the nonlinearities.[1–6,18–20] The ultrashort laser pulses (150 fs) used in the measurements reported here probe only the electronic or the fast effect. The observed effect is predominantly due to two-photon absorption since the linear absorption at wavelengths above about 750 nm is low (Fig. 3). In addition, the peak appears at

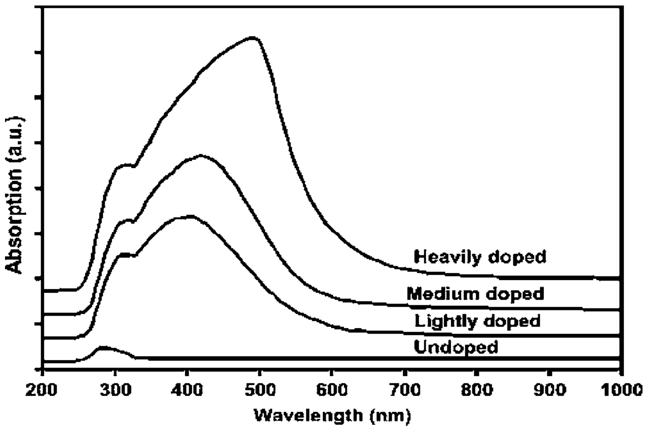

FIG. 3. Optical absorption spectra of poly(β-pinene) for different of molar concentrations (y) of dopant. Lightly doped ($y\sim0.20$), medium doped ($y\sim0.45$), and heavily doped ($y\sim0.75$).

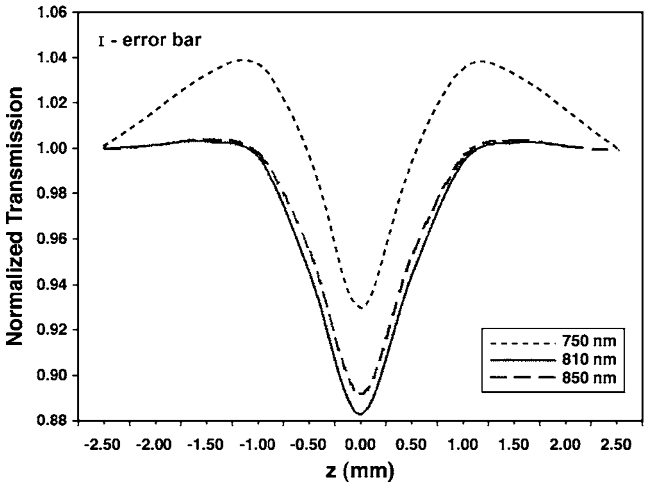

FIG. 4. Open-aperture z-scan data of organic of doped poly(β-pinene) at 750, 810, and 850 nm. The measurement has been made using 150 fs pulses from a Ti:sapphire laser.

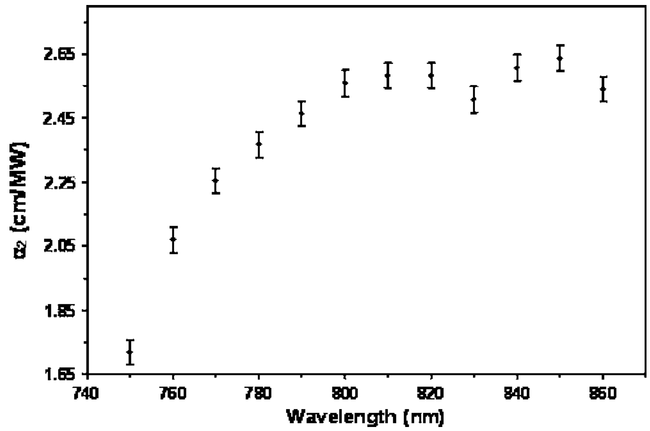

FIG. 5. Two-photon absorption coefficient in doped poly(β-pinene) as a function of wavelength. Two peaks at 810 nm (1.53 eV) and 850 nm (1.46 eV) have been observed.

810 nm (Fig. 5) which is about half of the optical gap corresponding to the charge transfer in doped poly(β-pinene). These results can be understood only by considering two-photon absorption. Some contribution due to excited-state absorption may also be present.

Two-photon absorption in a nano-optical material (quantum dots) based on the nonconjugated conductive polymer, doped poly(β-pinene) has been measured over the wavelength range of 730–860 nm with 150 fs pulses. A peak in two-photon absorption was observed at about 1.53 eV with a large magnitude of α_2 ($\sim$2.6 cm/MW). An additional peak at 1.46 eV was observed that may correspond to a phonon band. More detailed measurements of two-photon absorption along with nonlinear refractive index are in progress. The large magnitude of α_2 has been attributed to the special structure of the radical cation and charge-transfer sites confined within a subnanometer dimension. While a conjugated polymer transforms into a metallic state upon doping, a nonconjugated conductive polymer upon doping has a quantum dot structure leading to a greatly enhanced third order optical susceptibility.

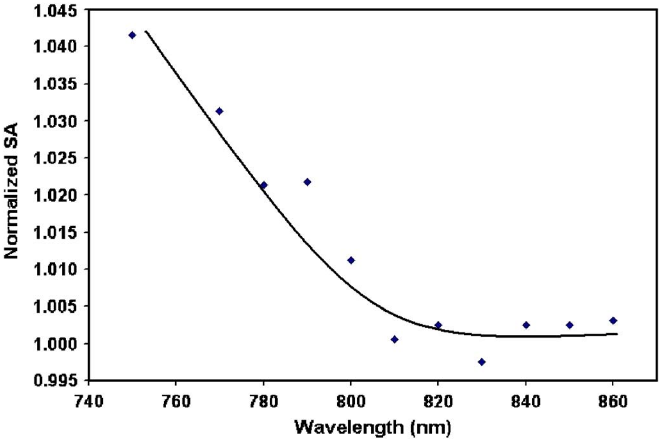

FIG. 6. Saturation of absorption in doped poly(β-pinene) measured at different wavelengths. The saturation decreases at longer wavelengths since linear absorption decreases at longer wavelengths (the solid line is a guide to the eye).

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