

# Optical-limiting response of rare-earth metallo-phthalocyanine-doped copolymer matrix

B. Aneeshkumar, Pramod Gopinath, C. P. G. Vallabhan, V. P. N. Nampoore, and P. Radhakrishnan

*International School of Photonics, Cochin University of Science and Technology, Cochin 682 022, India*

Jayan Thomas

*Optical Science Center, The University of Arizona, Tucson, Arizona 85721*

Received August 19, 2002; revised manuscript received December 24, 2002

The nanosecond optical-limiting characteristics (at 532 nm) of some rare-earth metallo-phthalocyanines (Sm(Pc)<sub>2</sub>, Eu(Pc)<sub>2</sub>, and LaPc) doped in a copolymer matrix of poly(methyl methacrylate) and methyl-2-cyanoacrylate have been studied for the first time to our knowledge. The optical-limiting response is attributed to reverse saturable absorption due to excited-state absorption. The performance of LaPc in a copolymer host is studied at different linear transmissions. The laser damage thresholds of all the samples are also reported. © 2003 Optical Society of America

OCIS codes: 190.0190, 190.4710, 190.4400, 160.4330, 160.5470, 140.3440.

## 1. INTRODUCTION

Intense laser radiation from high-power lasers have become more prevalent in diverse areas of science and technology. However, the extreme optical density is equally hazardous to light-sensitive elements such as the human eye and light sensors because it can cause irreversible optical breakdown unless attenuated to a reasonably low intensity level. The light attenuation can be achieved by utilizing the optical-limiting behavior of different materials, and these optical limiters are indispensable devices in laboratory and field. A passive means of optical limiting is more appreciated, and in recent years, the need for passive optical limiters has motivated research efforts in the development of many optical-limiting materials and configurations. To achieve this goal, we have developed samples of rare-earth metallo-phthalocyanine (RePc) doped in a copolymer matrix of poly(methyl methacrylate) and methyl-2-cyanoacrylate. Rare earth is either Eu, Sm, or La. Here we report, to our knowledge, the first measurements of the optical-limiting response due to reverse saturable absorption of these RePc's in this particular copolymer host.

Among the various organometallic compounds studied, metallo-phthalocyanines are the most promising molecular materials<sup>1-6</sup> for use in the passive optical limiters because of their relatively low linear absorption and high ratios of excited-state to ground-state absorption cross section in the 450–600-nm region.<sup>7</sup> Rare-earth metallo-phthalocyanines are large planar molecules with  $D_{4h}$  symmetry, and the central metal atom is connected with the four ligands by nitrogen bridges. There are 18  $\pi$ -electrons surrounding the core metal atom with large delocalization to form a two-dimensional  $\pi$ -electron system. The large spin-orbit coupling for the rare-earth metal orbital of the conjugated ring results in the en-

hancement of the excited-state absorption by means of increased singlet to triplet intersystem crossing.<sup>8</sup>

## 2. EXPERIMENT

### A. Sample Preparation

All the RePc's were synthesized by the modification of the method by Kirin *et al.*<sup>9</sup> and were purified chemically and physically. Sm(Pc)<sub>2</sub> and Eu(Pc)<sub>2</sub> have a diphthalocyanine structure,<sup>10</sup> and LaPc has a planar structure. Diphthalocyanine is a sandwich compound with two phthalocyanine (Pc) rings coordinated to a central metal atom. The two Pc ligands are rotated 45° with respect to each other. Furthermore, one of the Pc rings is virtually planar, while the other is significantly distorted.<sup>11</sup> All the samples in this experiment have the typical features of metallo-phthalocyanines in their electronic absorption spectrum, such as a characteristic low-energy Q band, a high-energy S band, and an absorption valley around 532 nm in the visible region.<sup>6</sup> In order to fabricate copolymer samples impregnated with these molecules, a casting solution was first prepared by dissolving the RePc compound in a homogeneous mixture of 20% (by volume) of methyl-2-cyanoacrylate and 80% (by volume) of methyl methacrylate (MMA) monomer. All the RePc's show very good solubility in this monomer mixture. This uniform solution was filled in a clean glass mold made of optically flat glass plates. Large samples, completely free of air bubble, were obtained after the copolymerization reaction. Since the mold was fabricated from optically flat glass plates, the samples had extremely high surface quality, so that no polishing was required, and hence there was minimum scattering of the laser beam at large angles from the sample. Thus in the absence of scattering at large angles, the system measured change in trans-

mission due to a change in absorption. The main advantages are the ease of sample preparation and the rapid copolymerization process in the absence of elevated temperature.

### B. Experimental Setup

The optical-limiting responses of the four RePc-doped copolymer composite were accomplished with a standard experimental configuration. A laser wavelength at 532 nm from a frequency-doubled, Q-switched Nd:YAG laser with a pulse width of 9 ns (FWHM) and a repetition rate of 10 Hz was used to excite the samples. All the samples have a thickness of 2.2 mm, which is comparable to the sample thickness used by different groups.<sup>12–14</sup> The laser pulses were focused with a 15-cm focal-length lens, and the sample was placed in such a way that it was slightly away from the focal plane of the lens. This was to prevent the rapid optical breakdown of the sample at the focal plane. The Rayleigh range inside the sample was 1.98 mm, which is comparable to the sample thickness. The incident and transmitted fluences were measured with energy detectors after averaging over ten pulses. The detector has a large collecting area to measure the total light output from the sample. This is important to avoid the effect of nonlinear refraction in the measurements. The optical-limiting response was studied by varying the input fluence with a laser beam attenuator arrangement and by monitoring the incident and transmitted fluence with a laser energy meter. The minimum input fluence was chosen to be  $\sim 0.1 \text{ J/cm}^2$  based on the signal-to-noise ratio of the detected signals. The maximum input energy was limited by the damage threshold of the RePc-doped copolymer host.

## 3. RESULTS AND DISCUSSIONS

The reverse saturable absorption<sup>15</sup> (RSA) of many chromophores can be described by a three-level model for the situation where the sample medium is excited by picosecond laser pulses. However, in this work we use nanosecond laser pulses, and therefore the intersystem crossing can be used to extend the optical limiting for longer laser pulses because of the added contribution to the absorption by the triplet states. Many authors<sup>7,16–18</sup> proposed a five-level model to describe the interaction of metallo-phthalocyanines with nanosecond laser pulses, which is depicted in Fig. 1. Here  $S_n$  and  $T_n$  are the singlet and triplet states, respectively, where  $n = 0, 1$  or  $2$  and every electronic energy level involves many vibronic sublevels. When interacting with a laser pulse at 532 nm, atoms from the  $S_0(\nu = 0)$  level get excited to the upper vibrational level of  $S_1$ . Through a nonradiative decay, within picoseconds, they can relax to the lowest vibrational level of  $S_1(\nu = 0)$ . Since Pc's have very low fluorescence,<sup>7</sup> the transition from  $S_1(\nu = 0)$  to  $S_0$  can be neglected. There for the main decay mechanism is the intersystem crossing from  $S_1(\nu = 0)$  to  $T_1(\nu = 0)$ . Here we assume that the intersystem crossing is fast<sup>17</sup> compared with the laser pulse width (9 ns), and virtually all the atoms excited from  $S_0$  reach first excited triplet state  $T_1$ . In fact, the intersystem crossing is higher for heavy-atom substituted Pc's due to large spin-orbit coupling of the metal orbital

and their mixing with the orbitals of the conjugated ring.<sup>19</sup> There for under-nanosecond pulse excitation, the main contribution to RSA comes from triplet states.

The ground-state absorption spectra at room temperature of the  $\text{Sm}(\text{Pc})_2$  in a copolymer matrix and in methyl methacrylate (MMA) monomer solution is shown in Fig. 2. All RePc's do have two absorption bands. The Q band at 600–800 nm in the visible region is due to the electronic transitions to the  $\pi-\pi^*$  states, and it strongly depends on the ligand; the different center metal causes only a small change. The Soret band or the B band is at the 300–400-nm region in the near-UV region. We observed a small difference in the linear absorption of the solution and the composite. This change can be attributed to aggregation of the  $\text{Sm}(\text{Pc})_2$  molecules in the matrix as well as the interaction between these molecules and the copolymer matrix. In solution,  $\text{Sm}(\text{Pc})_2$  has Q-band peaks at 670 nm, indicating the dominant contribution of monomer species. In the copolymer host, the stronger intermolecular interactions results in a higher degree of aggregation, and it replaces the Q-band structure by two broader peaks. The broadening arises as a result of the Davydov effect. The other two RePc's showed similar absorption behavior with a slight redshift of the Q band as the central metal atoms become heavier. For all the samples, the intensity of the B band is higher

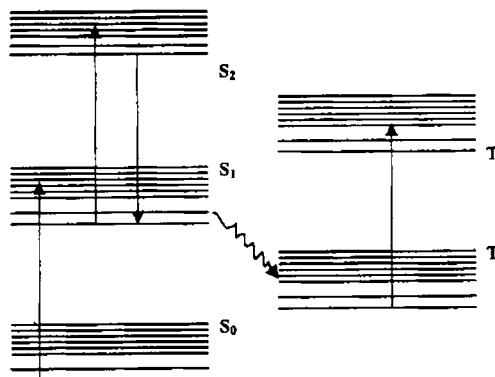


Fig. 1. Five-level energy-level model for the reverse saturable absorption for RePc in copolymer host.

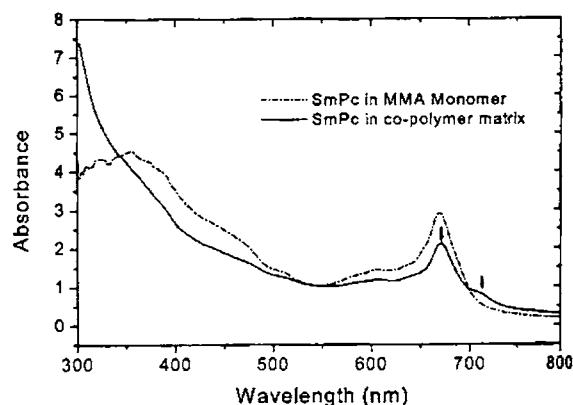


Fig. 2. Room-temperature ground-state linear absorption spectra of  $\text{Sm}(\text{Pc})_2$  in MMA monomer solution and in a copolymer host.

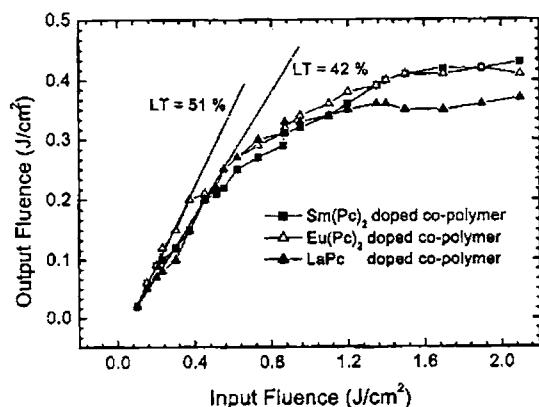


Fig. 3. Optical-limiting behavior of the RePc-doped copolymer samples for excitation at 532 nm. The linear transmission (LT) at 532 nm for the Sm(Pc)<sub>2</sub>-doped sample is 51% and for the Eu(Pc)<sub>2</sub>- and LaPc-doped samples is 42%.

than that of the *Q* band, which is explained elsewhere.<sup>20</sup> At the valley of the linear absorption spectrum, reverse saturable absorption could occur, because in this wavelength region the absorption cross section of the excited state is larger than that of the ground state.<sup>7</sup>

We have also measured the laser damage thresholds for the three RePc-doped copolymer samples. The laser damage threshold is defined here to be the fluence necessary to cause a permanent measurable change in the sample transmission measurements. The damage threshold of the sample is large if the sample is translated laterally after every few shots during testing. The damage threshold of the samples ranged between 1.8 and 2 J/cm<sup>2</sup>. The damage threshold for the undoped copolymer host was 2 J/cm<sup>2</sup>. For the Eu(Pc)<sub>2</sub>- and Sm(Pc)<sub>2</sub>-doped samples, the damage threshold was 1.8 J/cm<sup>2</sup>, and for the LaPc-doped sample it was 1.9 J/cm<sup>2</sup>. It is found that the presence of RePc in the copolymer matrix reduces its damage threshold. We suggest that the decrease of the laser damage threshold in the doped copolymer hosts may be related to defects in the microstructure of the copolymer as well as foreign-body microinclusions.

Figure 3 shows the optical-limiting response of the three rare-earth metallo-phthalocyanine-doped copolymer samples. All the samples have comparable linear transmission at 532 nm. At very low input fluence, the transmission obeys Beer-Lambert law. At high input fluence, the output fluence decreases with an increase in input fluence, and we observe an optical-limiting response with a saturated output fluence. Of the three RePc's studied, the LaPc-doped copolymer host shows a better optical-limiting property. The Eu(Pc)<sub>2</sub>- and Sm(Pc)<sub>2</sub>-doped samples have an almost similar optical-limiting response but less than that of the LaPc-doped sample.

Reverse saturable absorption due to excited-state absorption is the main mechanism for metallo-phthalocyanine molecules to produce an optical-limiting effect. The ratio of effective excited-state to ground-state absorption cross section  $\sigma_{\text{eff}}/\sigma_0$  can be used as a figure of

merit for optical limiting based on reverse saturable absorption.<sup>19</sup> This can be defined as

$$\sigma_{\text{eff}}/\sigma_0 = \ln T_{\text{sat}}/\ln T_{\text{lin}}, \quad (1)$$

with

$$T_{\text{sat}} = \exp(-\sigma_{\text{eff}}N_0l), \quad (2)$$

where  $T_{\text{lin}}$  is the linear transmittance at very low excitation power,  $T_{\text{sat}}$  is the saturated transmittance for a high degree of excitation, and both parameters are measured experimentally from the variation of transmittance with input fluence.  $N_0$  is the total molecular population, and  $l$  is the length of the laser pass through the doped copolymer sample. As shown in Fig. 3, the linear transmittance is 0.42 for Sm(Pc)<sub>2</sub>- and LaPc-doped samples with a saturated transmittance of 0.2 and 0.17, respectively. For the Eu(Pc)<sub>2</sub>-doped sample, the linear transmittance is 0.51 with a saturated transmittance of 0.19. The estimated figures of merit are 2, 1.83, and 1.86 for LaPc, Sm(Pc)<sub>2</sub>, and Eu(Pc)<sub>2</sub>, respectively, from Eq. (1). Compared with the reported value of  $\sim 3$  for C<sub>60</sub> and  $>10$  for phthalocyanine complexes,<sup>8,19</sup> the figures of merit for the rare-earth metallo-phthalocyanine-doped copolymer samples are not large enough. However, a wide range of structural modifications at the molecular level is possible in these materials by substituting various functional groups at peripheral sites, which can dramatically improve the optical-limiting performance of metallo-phthalocyanines.<sup>5,6,21,22</sup> Further study of this influence on the optical-limiting properties is deserved.

The optical-limiting responses of LaPc-doped samples with linear transmission (LT) of 42% and 21% are shown in Fig. 4. Both samples have a path length of 2.2 mm. The sample with 21% LT has more LaPc concentration than the sample with 42% LT. We do not have the exact value of the LaPc concentration in the copolymer matrix, which is difficult to measure due to the small size reduction of the copolymer matrix after polymerization. From Fig. 4, one can see that a sample with a larger concentration of LaPc has a better optical-limiting response, for example, the output fluence saturates at 0.19 J/cm<sup>2</sup> for the sample with 21% LT, but for the sample with 42% LT, the saturation value of the output fluence increases to 0.36

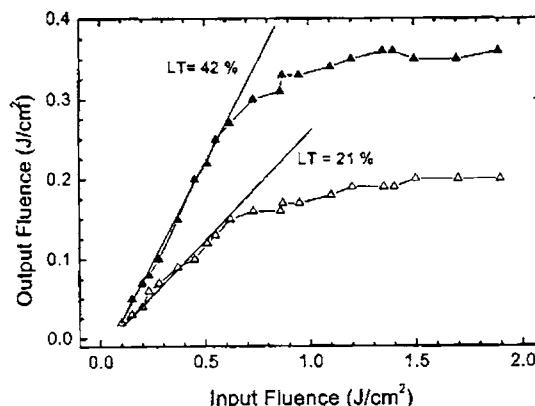


Fig. 4. Variation of output fluence with respect to input fluence for LaPc-doped copolymer sample for an optical path length of 2.2 mm for a linear transmission (LT) of 42% and 21%.

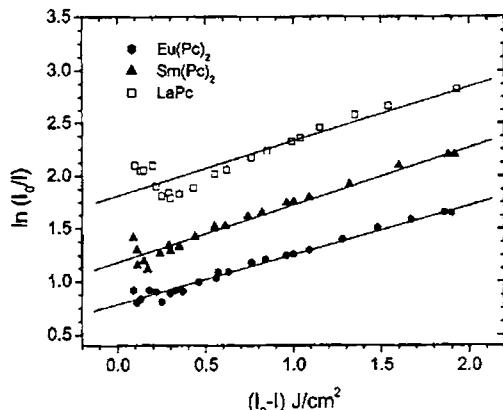


Fig. 5. Plot of  $\ln(I_0/I)$  versus  $(I_0 - I)$  for the RePc-doped copolymer samples. The plot for  $\text{Sm}(\text{Pc})_2$  and  $\text{LaPc}$  are upshifted by 0.5 and 1 unit, respectively, for presentation. The straight line is the best linear fit to the data points.

$\text{J}/\text{cm}^2$ . This indicates that the number density of  $\text{LaPc}$  in the laser beam is a main factor affecting the clamping level.

Kojima *et al.*,<sup>23</sup> while explaining the optical-limiting property of a polyacene-based oligomer using a five-level energy diagram, have shown that, in the case of reverse saturable absorption due to excited-state absorption, the incident laser intensity  $I_0$  and the transmitted laser intensity  $I$  obeys the relation

$$\ln(I_0/I) = k(I_0 - I) + A_g, \quad (3)$$

where  $k$  is a constant that depends on the absorption cross sections and lifetimes of the ground, excited-singlet, and excited-triplet states, and  $A_g$  is the ground-state absorbance. Equation (3) says that the plot of  $\ln(I_0/I)$  versus  $(I_0 - I)$  should be a straight line with slope  $k$  and intercept  $A_g$ . Figure 5 shows the plot of  $\ln(I_0/I)$  versus  $(I_0 - I)$  for the three doped samples. The straight-line nature of the graph is a clear indication that RSA is the main mechanism causing optical limiting in these samples. The RSA in metallo-phthalocyanines is due to the excited-state absorption.<sup>7</sup> In Fig. 5, at low  $(I_0 - I)$ , the plot shows a rolling-off nature. This is because Eq. (3) has an approximate linear relation<sup>23</sup> between  $\ln(I_0/I)$  and  $(I_0 - I)$ .

#### 4. CONCLUSIONS

In conclusion, the optical-limiting response for  $\text{Sm}(\text{Pc})_2$ ,  $\text{Eu}(\text{Pc})_2$ , and  $\text{LaPc}$  doped in a copolymer matrix of poly(methyl methacrylate) and methyl-2-cyanoacrylate were investigated at 532 nm, with nanosecond pulses. The observed limiting response is mainly due to the reverse saturable absorption, which is caused by the excited-state absorption in these samples. Laser damage thresholds were also measured for the doped and undoped copolymer samples.

#### ACKNOWLEDGMENTS

The authors are grateful to Netherlands Universities Funding for International Collaboration for partial fi-

ancing of this project. B. Aneeshkumar expresses his gratitude to the Cochin University of Science and Technology for financial support.

The e-mail address of B. Aneeshkumar is aneesh@cusat.ac.in.

#### REFERENCES

1. D. Dini, M. Barthel, and M. Hanack, "Phthalocyanines as active materials for optical limiting," *Eur. J. Org. Chem.* **20**, 3759–3769 (2001), and references therein.
2. G. de la Torre, P. Vazquez, F. Agullo-Lopez, and T. Torres, "Phthalocyanines and related compounds: organic targets for nonlinear optical applications," *J. Mater. Chem.* **8**, 1671–1683 (1998), and reference therein.
3. F. E. Hernandez, S. Yang, E. W. Van Stryland, and D. J. Hagan, "High-dynamic-range cascaded-focus optical limiter," *Opt. Lett.* **25**, 1180–1182 (2000).
4. K. P. Unnikrishnan, J. Thomas, B. Paul, A. Kurian, P. Gopinath, V. P. N. Nampoori, and C. P. G. Vallabhan, "Nonlinear absorption and optical limiting in solutions of some rare earth substituted phthalocyanines," *J. Nonlinear Opt. Phys. Mater.* **10**, 113–121 (2001).
5. Peiwang Zhu, Peng Wang, Wenfeng Qiu, Yunqi Liu, Cheng Ye, Guangyu Fang, and Yinglin Song, "Optical limiting properties of phthalocyanines-fullerene derivatives," *Appl. Phys. Lett.* **78**, 1319–1321 (2001).
6. J. S. Shirk, R. G. S. Pong, S. R. Flom, H. Heckmann, and M. Hanack, "Effect of axial substitution on the optical limiting properties of indium phthalocyanines," *J. Phys. Chem. A* **104**, 1438 (2000).
7. Chunfei Li, Lei Zhang, Miao Yang, Hui Wang, and Yuxiao Wang, "Dynamic and steady-state behaviors of reverse saturable absorption in metallophthalocyanine," *Phys. Rev. A* **49**, 1149–1157 (1994).
8. J. W. Perry, K. Mansour, I.-Y. S. Lee, X.-L. Wu, P. V. Bedworth, C.-T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian, and H. Sasabe, "Organic optical limiter with a strong nonlinear absorptive response," *Science* **273**, 1533–1536 (1996).
9. I. S. Kirin, P. N. Moskalev, and Yu. A. Moskashev, "New complex compounds of phthalocyanine with rare earth elements," *Russ. J. Inorg. Chem.* **12**, 707–712 (1967).
10. C. C. Leznoff and A. B. P. Lever, eds., *Phthalocyanines: Properties and Applications* (VCH, Deerfield Beach, Fla., 1989).
11. K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. van Opdenbosch, G. Pepe, and J. E. F. Meyer, "Structure of bis(phthalocyaninato)neodymium(III)," *J. Am. Chem. Soc.* **102**, 4835–4836 (1980).
12. Haiping Xia and M. Nogami, "Copper phthalocyanine bonding with gel and their optical limiting properties," *Opt. Mater.* **15**, 93–98 (2000).
13. A. Kost, L. Tutt, M. B. Klein, T. Kirk Dougherty, and W. E. Elias, "Optical limiting with  $\text{C}_{60}$  in polymethylmethacrylate," *Opt. Lett.* **18**, 334–336 (1993).
14. M. Meneghetti, R. Signorini, M. Zerbetto, R. Bozio, M. Maggini, G. Scorrano, M. Prato, G. Brusatin, E. Menegazzo, and M. Guglielmi, *Synth. Met.* **86**, 2353–2354 (1997).
15. C. R. Giuliano and L. D. Hess, "Nonlinear absorption of light: optical saturation of electronic transitions in organic molecules with high intensity laser radiation," *IEEE J. Quantum Electron.* **QE-3**, 358–367 (1967).
16. M. Sanghadasa, In-Seok Shin, R. D. Clark, Huaisong Guo, and B. G. Penn, "Optical limiting behavior of octa-decyloxy metallo-phthalocyanines," *J. Appl. Phys.* **90**, 31–37 (2001).
17. Tiejun Xia, D. J. Hagan, A. Dogariu, A. A. Said, and E. W. Van Stryland, "Optimization of optical limiting devices based on excited-state absorption," *Appl. Opt.* **36**, 4110–4122 (1997).
18. T. C. Wen and I. D. Lian, "Nanosecond measurements of

- nonlinear absorption and refraction in solutions of bis-phthalocyanines at 532 nm," *Synth. Met.* **83**, 111–116 (1996).
19. J. W. Perry, K. Mansour, S. R. Marder, K. J. Perry, D. Alvarez, Jr., and I. Choong, "Enhanced reverse saturable absorption and optical limiting in heavy-atom-substituted phthalocyanines," *Opt. Lett.* **19**, 625–627 (1994).
  20. G. A. Kumar, J. Thomas, N. V. Unnikrishnan, V. P. N. Nampoori, and C. P. G. Vallabhan, "Optical properties of phthalocyanine molecules in cyano acrylate polymer host," *Mater. Res. Bull.* **36**, 1–8 (2001).
  21. Xin Wang, Chunling Liu, Qihuang Gong, Yanyi Huang, and Chunhui Huang, "Anomalous heavy atom effect on optical limiting property of homoleptic double decked sandwich-type lanthanide diphthalocyanines," *Opt. Commun.* **197**, 83–87 (2001).
  22. Pen Wang, Shuang Zhang, Peiji Wu, Cheng Ye, Hong Wei Liu, and Fu Xi, "Optical limiting property of optically active phthalocyanine derivatives," *Chem. Phys. Lett.* **340**, 261–266 (2001).
  23. Y. Kojima, T. Matsuoka, N. Sato, and H. Takahashi, "Optical limiting property of a polyacene-based oligomer synthesized under high pressure," *Macromolecules* **28**, 2893–2896 (1995).