NONLINEAR OPTICAL PROPERTIES OF NOVEL METALLOPHTHALOCYANINES

F. A. Alawainati [1], H. Manaa [1*], F. Z. Henari [2], Z. Biyiklioglu [3], T. Arslan [4], A. Jaafar [1]

[1] University of Bahrain, Department of Physics,
P.O. Box 32038, Bahrain; e-mail: hmanaa@uob.edu.bh
[2] Royal College of Surgeons in Ireland, Medical University of Bahrain,
Department of Medical Sciences, Bahrain
[3] Karadeniz Technical University, Department of Chemistry, Trabzon 61080, Turkey
[4] Giresun University, Department of Chemistry, Giresun 28200, Turkey

Detailed measurements of nonlinear optical properties and optical limiting for four phthalocyanine (Pc) derivatives (PcCo, PcCu, PcMn, and PcSi) are reported. The nonlinear optical properties were investigated using a Z-scan technique with a continuous-wave argon ion laser at 488 and 514.5 nm, and with a 532-nm pulsed Nd:YAG laser. All Pcs exhibited strong nonlinear properties and low optical-limiting thresholds. The nonlinear absorption coefficient, the sign and magnitude of the nonlinear refractive index, and the third-order nonlinear susceptibilities of each compound were calculated. Refractive nonlinear effects are the most dominant for continuous laser excitation and are mainly attributed to thermal effects, whereas the reverse saturation absorption coefficient may have an electronic origin. Threshold values indicated that the Pc derivatives are promising materials for optical-limiting applications.

Keywords: *optical limiting, phthalocyanine, nonlinear optical properties, Z-scan.*

НЕЛИНЕЙНЫЕ ОПТИЧЕСКИЕ СВОЙСТВА НОВЫХ МЕТАЛЛОФТАЛОЦИАНИНОВ

F. A. Alawainati [1], H. Manaa [1*], F. Z. Henari [2], Z. Biyiklioglu [3], T. Arslan [4], A. Jaafar [1]

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[1] Университет Бахрейна,
32038, Бахрейн; e-mail: hmanaa@uob.edu.bh
[2] Королевский хирургический колледж Ирландии Медицинского университета Бахрейна, Бахрейн
[3] Технический университет Карадениза, Трабзон, 61080, Турция
[4] Университет Гиресуна, Гиресун, 28200, Турция

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Для четырех производных фталоцианина (Pc) (PcCo, PcCu, PcMn и PcSi) исследованы нелинейно-оптические свойства с помощью метода Z-сканирования и излучения непрерывного лазера на ионах аргона на длинах волн λ = 488 и 514.5 нм и импульсного Nd:YAG-лазера на λ = 532 нм. Все Pc проявляли сильные нелинейные свойства и низкие пороги оптического ограничения. Рассчитаны коэффициент нелинейного поглощения, знак и величина нелинейного показателя преломления, а также нелинейная восприимчивость третьего порядка для каждого соединения. Рефракционные нелинейные эффекты преобладают для непрерывного лазерного возбуждения и в основном объясняются тепловыми эффектами, тогда как коэффициент поглощения обратного насыщения может иметь электронную природу. Пороги оптического ограничения указывают на то, что производные Pc являются перспективными материалами для приложений с ограничением оптики.

Ключевые слова: *оптическое ограничение, фталоцианин, нелинейно-оптические свойства, Z-сканирование.*

Introduction. Nonlinear optical materials, particularly organic materials with strong nonlinearities, have received considerable attention because of their importance in modern optical technologies. Many optical devices based on nonlinear optical properties have relied on π-electron conjugated organic materials such as porphyrins, phthalocyanines (Pcs), and phthalocyanines derivatives [1–3]. Pcs are aromatic systems with 18 π electrons. They can be modified either by incorporating up to 70 metal atoms in the cavity to form metallic Pcs (MPcs) or by attaching side groups at peripheral positions on the macrocycle to form Pc derivatives [4]. The nonlinear optical properties of Pcs and its derivatives have been extensively investigated with respect to the delocalized π-electron conjugated structures.

Recently, Pc and its derivatives have been used in diverse applications such as optical data storage, photodynamic cancer therapy, photosensitizers for photodynamic therapy macrocycles, sensors, catalysis, and solar-energy conversion. Several experimental techniques have been developed to evaluate the various contributions of refractive dynamics in optoelectronic materials [4, 5]. In particular, the *Z*-scan technique, developed by Mansoor Sheik-Bahae et al. [6, 7], provides a straightforward and simple way to determine nonlinear refractive indices and absorption coefficients [5]. The simplicities of both the technique and the data analysis have enabled measurements of third-order nonlinear susceptibilities $\chi^{(3)}$ [8–12].

Materials with large nonlinear parameters are potential candidates for optical-limiting applications [13–15]. Optical power limiters have to be designed to protect human eyes and photodetectors from intense laser light from many sources over a broad spectrum, especially the 400–800 nm visible range. Intensive research has been performed to find ideal optical limiters with large spectral ranges and rapid response times ranging from picoseconds to microseconds [13–20].

Here, we investigate the nonlinear optical properties of cobalt(II), manganese(III), and copper(II) phthalocyanines bearing {2-[[4-((E)-{[4-(dimethylamino)phenyl]imino}methyl)phenyl](methyl)amino]ethoxy}groups at peripheral positions, as well as axially disubstituted silicon phthalocyanine. The chemical structures and a photophysical preliminary study have been reported previously [10]. Here, the linear and nonlinear optical properties of these Pc derivatives are studied in detail. Nonlinear optical properties in conjunction with optical limiting are extensively investigated with a continuous wave (CW) laser, tuned to 488 and 514.5 nm, and a 532-nm pulsed laser. The 532-nm wavelength occurs in a transparent band and produces either reverse saturation absorption (RSA) and/or two-photon absorption (TPA); saturation absorption occurs at other wavelengths where ground-state absorption is important [15]. The combination of CW and pulsed excitation modes reveal thermal versus electronic contributions to the nonlinear properties and the optical limiting.

Experimental. The *Z*-scan setup has been reported previously by Mansoor Sheik-Bahae et al. [6, 7]. A 30-mW argon-ion laser tuned to 514.5 or 488 nm was focused to a 20-μm beam waist in the sample via a 5-cm-focal-length convex lens. A 1-mm cuvette containing the sample was placed on a computer-controlled translation stage that can move over a ±10-cm range with a resolution of 1/50 mm. The change in laser light transmission through the sample was detected in the far-field with photodiodes. The nonlinear refractive index can be extracted by measuring the transmission through an aperture as the sample moved through the focus (closed case). When the transmission is measured in the same way without an aperture, the nonlinear absorption can be extracted (open case). The same apparatus was used with a 532-nm Nd:YAG laser that emitted 6-ns pulses at a repetition rate of 5–50 Hz. The optical limiting (OL) characterization was performed with the Nd-YAG laser, and the sample was placed in the trough (transmission minimum) position of the closed aperture case. The input intensity of the beam was varied via neutral density filters, and the corresponding output intensity was measured with a power meter.

PcCo, PcCu, PcMn, and PcSi were synthesized according to the procedure described previously [10]. All the Pc samples were dissolved in dimethylformamide at concentrations of 5×10^{-5} and 5×10^{-4} M.

Theory. In the *Z*-scan and optical-limiting experiments, the normalized transmittance is defined as the transmission of the sample $T(z)$ at position z, divided by the transmittance of the sample far from the laser focus (linear region). At low laser intensity (linear region), $T_{\text{low intensity}} = T_{\text{linear}}$. At a high laser intensity (linear and nonlinear), $T_{\text{large Intensity}} = T_{\text{linear}}.T_{\text{nonlinear}}$. Then, the normalized transmittance $T_{\text{norm}} = T_{\text{large Intensity}}/T_{\text{low intensity}} = T_{\text{nonlinear}}$. $T_{\text{nonlinear}}$ may be greater than 1 in the case of saturation absorption, or less than 1 in the cases of RSA or TPA. Nonlinear refractive effects can also modify the geometry of the laser and increase $T_{\text{nonlinear}}$.

This normalization procedure has the advantage of separating nonlinear effects from linear ones. Hence, very weak variations due to nonlinear effects can be measured.

Normalized transmittance as a function of the sample's position z is related to the nonlinear absorption coefficient (open case) and is given by [7]

$$T(z) = 1 - \frac{q_0}{2\sqrt{2}} \quad \text{for } q_0 < 1, \tag{1}$$

$$q_0 = \frac{\beta I_0 \left(1 - e^{-\alpha l}\right)}{\left(1 + z^2 / z_0^2\right)\alpha}. \tag{2}$$

Here, β is the nonlinear absorption coefficient, α is the linear absorption coefficient, l is the thickness of the sample, I_0 is the intensity of the laser beam at the focus ($z = 0$), and z_0 is the Rayleigh radius. In the Gaussian approximation, z_0 is related to the beam waist through the relation $z_0 = \pi w_0^2/\lambda$, where λ is the wavelength.

The normalized transmittance through an aperture as a function of the sample position z is related to the nonlinear refractive index coefficient (closed case), as given by [7]:

$$T(z) = 1 - \frac{4\Delta\varphi x}{\left(x^2 + 9\right)\left(x^2 + 1\right)}, \tag{3}$$

where $x = z/z_0$, and Δφ is the laser-induced phase shift, which is related to the nonlinear refractive index given by

$$n_2 = \frac{\Delta\varphi\lambda\alpha}{2\pi I_0 \left(1 - e^{-\alpha l}\right)}. \tag{4}$$

The third-order nonlinear susceptibility is a complex quantity that is related to the nonlinear absorptive and refractive coefficients, as given by [7]:

$$\mathrm{Im}\chi^{(3)} = \frac{n^2 \varepsilon_0 c\lambda\beta}{2\pi}, \qquad \mathrm{Re}\chi^{(3)} = 2n^2\varepsilon_0 c n_2, \tag{5}$$

where n is the linear index of refraction, c is the speed of light, and ε_0 is the free-space permittivity. The absolute value of $\chi^{(3)}$ is calculated from

$$\chi^{(3)} = [(\mathrm{Im}\chi^{(3)})^2 + (\mathrm{Re}\chi^{(3)})^2]^{1/2}. \tag{6}$$

Results and discussion. The nonlinear optical properties of Pc derivatives, including the nonlinear refractive effect, the nonlinear absorption effect, and the nonlinear third-order susceptibility, were investigated with the *Z*-scan technique. As discussed above, the emphasis of this work is on the transparency regions of the materials. Therefore, the 488- and 514-nm CW source was used, whereas in the pulsed-laser excitation regime the 532-nm second-harmonic of the Nd:YAG laser was used.

Nonlinear absorptive effects in the CW regime. Figure 1a shows the 514.5-nm normalized transmission without an aperture (open case) for PcCo as a function of the z position. It is characterized by a decrease in the transmittance with a minimum at the focal point ($z = 0$), indicating intensity-dependent absorption or RSA. To exhibit RSA in a compound, the excited-state absorption must be greater than the ground-state absorption [15–17]. The nonlinear absorption coefficient β calculated by fitting Eq. (1) to the experimental data for PcCo at 514.5 nm was 0.82×10^{-3} cm/V. Similar calculations were performed for the other compounds. *Z*-scan measurements were performed for all the compounds at various 488 and 514.5-nm power levels. Table 1 lists the calculated β values at different powers for the PcCo, PcMn, PcCu, and PcSi compounds. For all the investigated wavelengths, β increased with power until reaching the saturation level. Therefore, the optimal power to obtain the nonlinear optical absorptive parameters was around 5 mW, which was the best compromise between saturation and a good signal-to-noise ratio.

Figure 1b shows the normalized transmission with an aperture (closed case) for PcMn at 514.5 nm as a function of the z position. It is characterized by a peak followed by a trough, which is an indication of a negative refractive nonlinearity. In a focusing effect, the sample behaves like a thin lens. As the sample moves toward the laser focus along the z-axis, the beam intensity increases, forming a self-lensing nonlinear action in the medium. Negative self-lensing that occurs before the focal point tends to collimate the beam, which narrows it at the aperture. Hence, the diffraction is reduced, leading to increased transmittance that appears as a peak in Fig. 1b. As the sample continues to move until it passes the focus, the self-defocusing action increases the beam divergence, resulting in a broader beam at the aperture and a reduced transmittance. Hence the z-scan signal becomes a trough. This peak-trough signature indicates a self-defocusing behavior that acts like negative lensing, with a negative nonlinear refractive index n_2. The calculated value for n_2 derived from fitting Eq. (1) to the experimental data for PcMn at 514.5 nm is -10.85×10^{-8} cm^2/W. Table 1 lists the calculated n_2 values for PcCo, PcMn, PcCu, and PcSi at different laser powers.

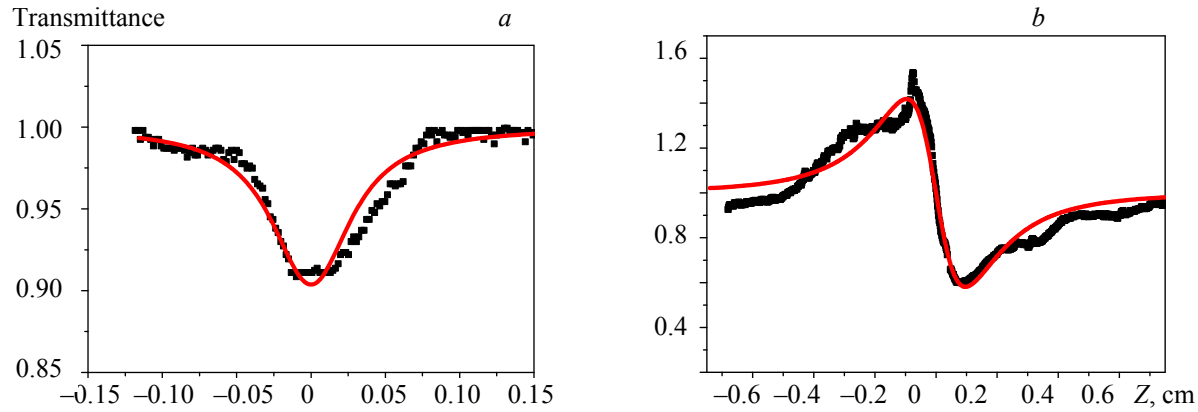

Fig. 1. Normalized transmission of PcCo at 514.5 nm: a) open aperture, b) closed aperture. The solid line is a fit of the data to Eq. (1).

The third-order susceptibility for each compound was also calculated and listed in Table 1. It varies from 0.3×10^{-16} to 7.75×10^{-16} m/V^2 at the two wavelengths. The large nonlinear susceptibilities of the Pc derivatives mostly originate from the strong nonlinear absorption along with a strong thermo-optic coefficient. The strong nonlinear susceptibility confirms the potential of the Pcs derivatives, relative to other organic compounds, because of the extensive two-dimensional π-electron conjugation. Nevertheless, these values are weaker than those obtained at 632 nm for the same samples [10]. The percentage of the imaginary part in the total nonlinear susceptibility was calculated and is shown in Table 1. It did not exceed 15%, which indicates that the refractive nonlinear effects dominate with this type of excitation. PcSi has lower values at both wavelengths, which may be due to a different chemical structure relative to the other three Pcs [10]. As discussed below, its OL threshold was also lower than those of the other compounds.

TABLE 1. Nonlinear Optical Parameters of Pcs Using a CW Laser

λ, nm	P, mw	I, 10^3 W/cm^2	β, 10^{-3} cm/W	n_2, 10^{-8} cm^2/W	χ_{im}, 10^{-17} m^2/V^2	χ_r, 10^{-16} m^2/V^2	χ_{tot}, 10^{-16} m^2/V^2	χ_{im}/χ_{tot}, %	OL I_{th}, 10^3 W/cm^2
PcCo									
488	4.9	2.23	1.84	−9.85	5.53	7.03	7.05	7.87	2
514.5	7	3.40	0.82	−10.85	2.61	7.75	7.75	3.36	2.8
PcMn									
488	1.61	1.54	0.42	−3.32	1.27	2.37	2.37	5.37	2
514.5	1.61	0.78	0.26	−8.05	0.81	5.75	5.75	1.41	2.8
PcCu									
488	7.70	2.47	0.32	−8.38	0.97	5.98	5.98	1.62	2.1
514.5	3.50	1.13	1.99	−8.19	6.29	5.85	5.88	10.75	2.8
PcSi									
488	15.40	9.79	0.14	−0.41	0.43	0.29	0.30	14.71	> 4
514.5	17.50	9.66	0.02	−0.50	1.80	4.50	4.50	1.39	> 4

Optical limiting in the CW regime. With CW excitation, the origin of the large optical nonlinearities of the Pc derivatives is probably attributed to either thermal or electronic (population) effects, or a combination of both. The thermal effects, which are generally unwanted, are limited and minimized by working at the lowest possible excitation power.

As noted above, the nonlinear optical parameters of these compounds are large; thus, the compounds may be considered promising candidates for OL applications. OL is a nonlinear effect of materials in which their transmittance decreases under high irradiance. At low irradiance, the transmittance is almost constant and obeys the Lambert–Beer law. OL is based either on RSA or TPA. When the irradiance increases, photons involved in optical transitions are absorbed instead of being transmitted; this is absorption-based OL. The second common mechanism for OL in nonlinear optical materials is related to the change in molecular

polarization by laser effects. This leads to refractive-based OL that increases the solid angle of the transmitted laser beam at large irradiances.

Figure 2 shows the OL behaviors of the Pc compounds at 488 and 514.5 nm. The OL threshold can be defined as that input irradiance (I_{th}) when the transmittance of the material falls to half of its low-irradiance value.

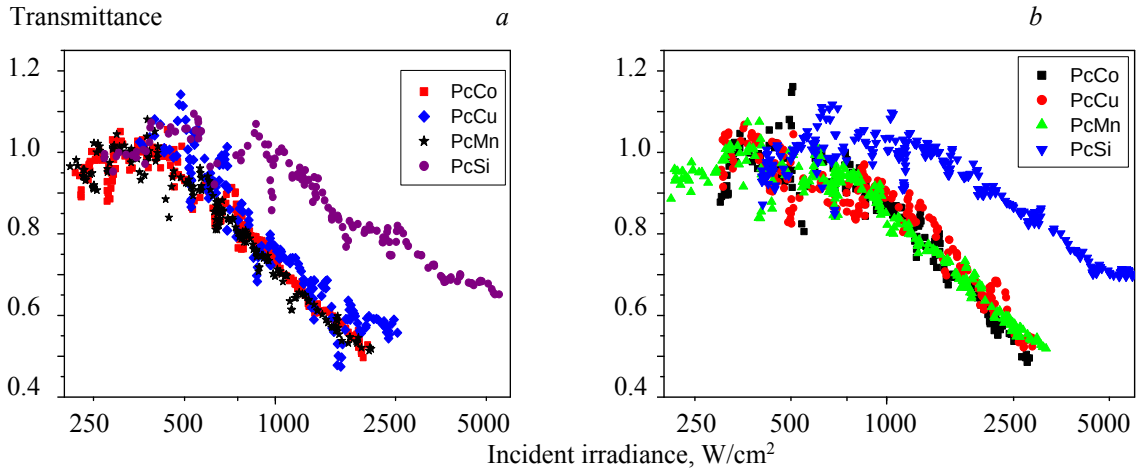

Fig. 2. Optical limiting of phthalocyanine derivatives in the continuous excitation regime at 514.5 (a) and 488 nm (b).

The I_{th} values of PcCo, PcMn, PcCu, and PcSi at different wavelengths are listed in Table 1. In previous work [10], the I_{th} value for PcCu at 632.8 nm was the lowest (560 W/cm^2), whereas that for PcCo was 640 W/cm^2, and those for PcMn and PcSi were still larger.

Nonlinear absorptive effects in the pulsed regime. To better understand the physical mechanisms of the optical nonlinearities, we performed *Z*-scan and OL measurements in the pulsed-laser regime. The CW and pulsed lasers enable a precise comparison of the nonlinear parameters and the OL potentials. Figure 3 shows the normalized 532-nm transmission without an aperture (open case) as a function of z position for all the compounds. The transmission is symmetric with respect to the focal point ($z = 0$), where there is minimum transmission. Thus, intensity-dependent absorption was observed, which is often referred to as RSA. This is more likely to occur because all the samples probed at this wavelength were off-resonance.

TABLE 2. Nonlinear Optical Parameters and OL Performance in the Pulsed Regime at 532 nm

Pc	β, 10^{-9} cm/W	χ_{im}, 10^{-14} m^2/V^2	OL I_{th}, 10^2 J/cm^2
PcCo	0.31	8.69	1.6
PcCu	0.54	15.42	0.6
PcMn	0.19	5.47	2.5
PcSi	0.31	8.70	1.0

The RSA may be attributed to an optical transition between the excited singlet state S_1 and a higher excited singlet state S_2, and/or transitions between excited triplet states T_1 and T_2. The relative contribution of each type could be determined with time-resolved techniques. The β values were calculated for all the compounds by fitting Eq. (1) to experimental data and are given in Table 2.

Refractive nonlinear effects are either absent in the pulsed regime or lower than the experimental sensitivity limits. This indicates that the refractive nonlinear effects measured in the CW regime are purely thermal. However, the absorptive effects in the pulsed regime most likely have electronic origins with an imaginary part of the third-order susceptibility $\chi_{im}^{(3)}$ varying between 5×10^{-14} to 15×10^{-5} m^2/V^2. Consequently, it is expected that the OL properties have the same origin.

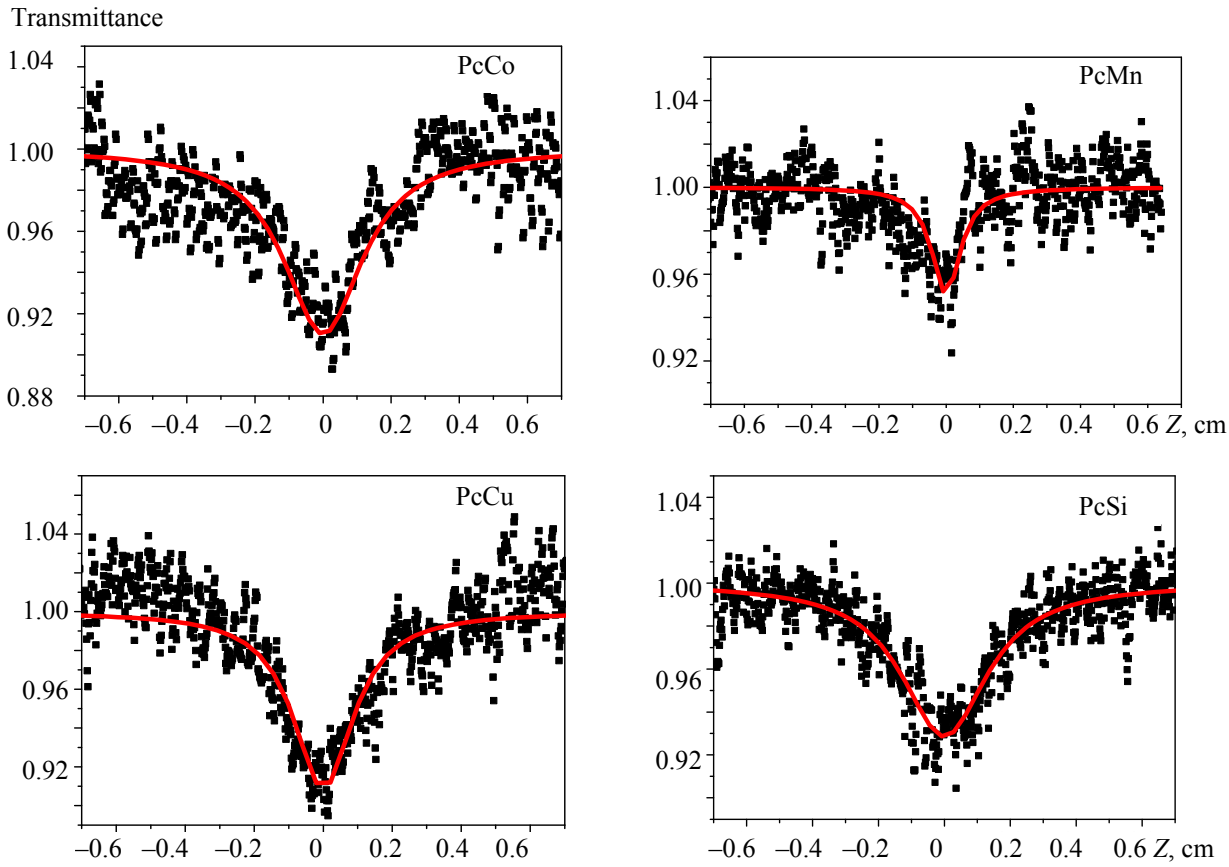

Fig. 3. Normalized transmission (open aperture) of phthalocyanine compounds at 532 nm. The solid line is a fit of Eq. (1) to the data.

Optical limiting in the pulsed regime. The OL performance in all the Pc compounds was directly measured via fluence-dependent transmittance in the off-resonance region at 532 nm. The experimental method used to investigate the optical limiting is the same as that described for the CW regime. The measurements show a clear OL behavior where the transmittance is constant at low fluence (linear absorption that obeys the Lambert–Beer law) and then decreases at large fluence. The OL thresholds, ranging over 60–250 J/cm^2, were obtained when the transmittance fell to 50% of its low-fluence value (Table 2).

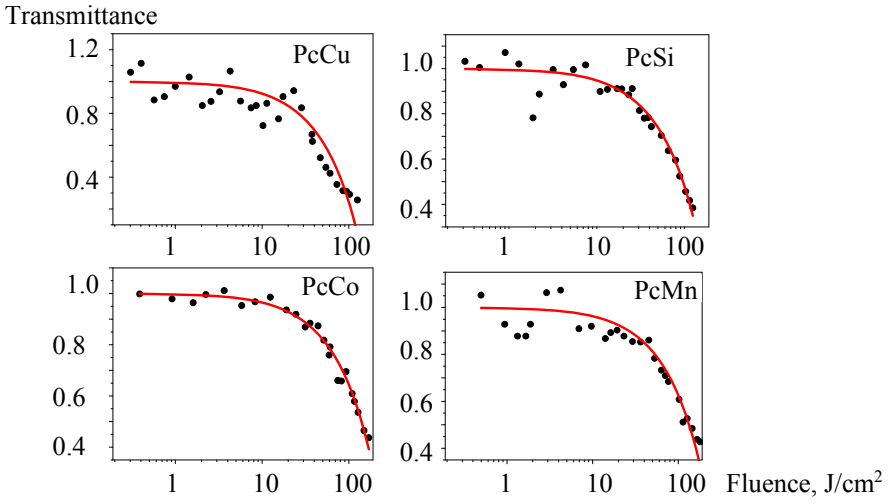

Fig. 4. Optical limiting with the fitted data of phthalocyanine derivatives PcCo, PcCu, PcMn, and PcSi at 532 nm in the pulsed-laser regime.

Figure 4 shows the OL data fitted with the equation $T = 1 - \beta_0 F_0$, where F_0 is the incident laser fluence and β_0 is the fitting parameter. This equation was derived from Eq. (1), where $z = 0$ and the incident intensity I_0 is replaced by F_0.

Conclusions. Nonlinear optical properties of the phthalocyanine derivatives PcCo, PcCu, PcMn, and PcSi have been investigated using 488-nm and 514.5-nm emission from a CW laser, and 532-nm emission from a pulsed laser. The signs and magnitudes of the nonlinear coefficients have been evaluated for both absorptive and refractive cases, along with the third-order nonlinear susceptibilities. The OL behavior was also was investigated in the CW and pulsed excitation regimes. The contributions of thermal and electronic effects in the nonlinear and OL properties were discussed. All four Pc compounds had strong nonlinear parameters, which were confirmed by low OL thresholds in the CW and pulsed excitation regimes.

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