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Nonlinear Absorption in Phthalocyanine Thin Films and Solutions Using a Continuous Wave Laser

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The nonlinear absorption of nanoscale thin films of iron phthalocyanine, zinc phthalocyanine, and metal-free phthalocyanine fabricated via thermal evaporation at various deposition temperatures was studied using the open-aperture z-scan method with a continuous wave laser. A solution of tetra-tert-butyl-phthalocyanine in chloroform was also studied via z-scan. The thin films exhibit pronounced saturable absorption, with the degree of nonlinearity highly dependent on the type of metal complex. No significant correlation was found between deposition temperature and nonlinear absorption. The liquid sample exhibits a transition from saturable absorption to reverse saturable absorption at high irradiance.

Keywords: phthalocyanine; nonlinear absorption; z-scan

1. Introduction

The proliferation of lasers in industrial, commercial, military, and scientific applications has heightened the need for improved laser safety lenses for optical sensors and the human eye. Optical limiters are promising candidates for next generation safety lenses, allowing for greater transparency under normal conditions while providing protection equivalent to current materials. The field of nonlinear optical properties in phthalocyanine-related molecules has been developed over the last three decades¹⁵. Phthalocyanine (Pc) and its derivatives have been widely studied as optical limiter candidates, and have shown considerable promise^{3,5,8,11,19,21,23,24,25,27,31}. This molecular family is particularly suitable towards nonlinear optical properties as it has many delocalized π -electrons⁸. Outstanding questions include the effect of crystal size^{10,20}. When exposed to a pulsed laser, Pc acts as a strong reverse saturable absorber (RSA), a material in which the excited state absorption cross section is greater than the ground state cross section. At high fluences, a greater portion of molecules become excited, increasing absorption - an optical limiter. In Pc, it is thought that this is primarily due to two-photon absorption^{3,5,27}, although other nonlinear processes such as three-photon absorption²² have also been suggested as contributors.

Beyond its high degree of optical nonlinearity, Pc has a host of other properties that make it an attractive candidate for practical limiters. The molecule itself can

be readily modified by bonding one of more than seventy metal ions to its center or adding peripheral and axial substituents⁵. Such alterations can have a significant effect on the behavior of the molecule, changing solubility¹⁴, heating response², optical absorbance¹², and other characteristics, potentially allowing manufacturers to create filters suited to many different situations with only relatively minor changes to the synthesis process. Phthalocyanine is frequently studied in liquid media^{3,5,19,22,24,31}, with many derivatives having good solubility in a wide range of solvents^{5,14}. Nanoscale thin films are another common medium, and more suited to practical filters. Films can be fabricated via a number of methods, including spin coating⁷, molecular beam epitaxy⁸, the Langmuir-Blodgett procedure⁷, monolayer self-assembly⁷, and thermal evaporation, the method used in this study. Thin films of Pc show remarkable flexibility due to weak intermolecular bonding¹⁸, a widening of absorption bands compared to solutions¹¹, and the ability to further tune the material’s properties by altering fabrication parameters^{12,16}.

Although the majority of optical studies of Pc use pulsed lasers^{3,5,8,11,19,21,22,25,26,27,31}, the relatively few that use continuous wave (CW) lasers have generally, though not universally, found strong saturable absorption (SA) behavior, the material growing more transparent in response to increased irradiance^{23,24}. While this would contraindicate Pc as material for laser safety lenses in situations where CW lasers are a risk, it raises the possibility of using Pc in a range of other applications in which SA is desirable, such as mode locking, pulse shaping, and light measuring techniques⁴.

Herein, we study the optical response of thin films of metal-free phthalocyanine (H₂Pc), iron phthalocyanine (FePc), and zinc phthalocyanine (ZnPc) when exposed to a CW laser using a simplified open-aperture z-scan procedure. We also vary the deposition temperature of our H₂Pc films, a parameter known to affect crystalline size and structure^{13,17}, to determine its effect on nonlinear absorption. In addition to films, a solution of tetra-tert-butyl-phthalocyanine (TTBPc) in chloroform was also measured using the z-scan method. We find evidence of strong saturable absorption in our thin films, with significant dependence on the metal complex used and no significant correlation between deposition temperature and nonlinear absorption. We observe a SA-to-RSA transition at high irradiances in our TTBPc-in-chloroform sample.

2. Experiment

The liquid sample consists of 9.8×10^{-6} M TTBPc in chloroform. TTBPc powder of 97% purity was acquired from Sigma-Aldrich and dissolved in chloroform until the desired concentration was reached. The solution was placed in a 1 mm thick quartz cuvette for measurement.

Similarly, powders of H₂Pc, FePc, and ZnPc were acquired from Sigma Aldrich. The powders were outgassed in-situ for several hours before thermal evaporation in a high vacuum system with base pressure of around 10^{-6} mbar. For each deposition, a

Table 1. The deposition temperature T_{dep} refers to the 1 mm glass substrate temperature during deposition. The thickness l is obtained from an in-situ quartz crystal monitor. The linear absorption α_0 is measured at the laser's wavelength of 633 nm.

Material	T_{dep} (°C)	l (nm)	α_0 (10^6m^{-1})
H ₂ Pc	25	63	30
H ₂ Pc	100	57	34
H ₂ Pc	150	58	35
H ₂ Pc	200	59	27
H ₂ Pc	250	58	31
ZnPc	100	64	27
FePc	100	55	20

1 mm glass substrate was carefully cleaned for vacuum evaporation. Each substrate was heated to a constant deposition temperature T_{dep} . It is known that the deposition temperature from room temperature to 250 °C gradually increases the molecular crystal sizes in the thin film¹³. The film thickness l was monitored with an in-situ quartz crystal monitor (QCM) to cap at 60 nm. A summary of the deposition parameters of each film can be found in Table 1. The linear optical absorption coefficient α_0 of each thin film sample was measured in a photospectrometer¹², and extracted for $\lambda = 633$ nm, see Fig. 1.

A 633 nm CW HeNe laser (JDS Uniphase 1101) with maximum output power of 3.87 mW was focused to a spot with an experimentally observed radius of 10 μm to 17 μm , resulting in a maximum irradiance between 12 MW/m² and 4.3 MW/m². The sample was mounted on a track straddling the beam waist. In all figures, $z = 0$ mm is the location of the experimentally observed waist.

To quantify the nonlinear absorption of these samples, the nonlinear absorption (NLA) coefficient β is extracted from a fit of the data. In the absence of NLA, the irradiance I_T of light transmitted by a material with thickness l is governed by the Beer-Lambert law $I_T = I_0 e^{-\alpha_0 l}$, where I_0 is the irradiance of light incident on the sample and α_0 is the linear absorption coefficient. When third-order nonlinear processes such as two-photon absorption are significant, the linear absorption coefficient becomes dependent on the incident irradiance, such that it can be expanded to

$$I_T = I_0 e^{-(\alpha_0 + \beta I_0)l} \quad (2.1)$$

The NLA coefficient β is negative when describing SA behavior, and positive when describing RSA behavior.

To extract β , a simplified open-aperture z-scan procedure, adapted from that described by Sheik-Bahae et al.²⁹, was applied to the samples. Each sample was mounted on a horizontal track and shifted through the beam waist in 1 mm steps.

The optical power of the light transmitted by the sample was measured at each step. A separate measurement was performed with the sample removed to measure the power of light incident on the sample. The transmittance of the sample at each z -position was then computed by dividing incident power by transmitted power.

The transmittance was normalized by dividing transmittance at every z -position by the average far-field transmittance. As derived by Sheik-Bahae et al.²⁹, normalized transmittance as a function of z -position $T_N(z)$ for an open-aperture z -scan is given by

$$T_N(z) = \sum_{m=0}^{\infty} \left(\frac{-q_0}{1 + ((z - p_o)/z_0)^2} \right)^m \cdot \frac{1}{(m+1)^{3/2}} \quad (2.2)$$

Here, z_0 is the Rayleigh diffraction length, itself given by

$$z_0 = n\pi w_0^2/\lambda \quad (2.3)$$

Where n is the index of refraction of the propagation medium, approximated as 1, w_0 is the beam radius at the waist, and λ is the wavelength of the laser, 633 nm. The Rayleigh diffraction length z_0 is considered a free parameter, found via a numeric fit of the data. It is used to estimate the waist radius, which may slightly vary from sample-to-sample due to nonlinear refractive effects.

The peak position p_o is the z -position of the transmittance peak, and is another free parameter. The third free parameter is the q -factor q_0 , defined as

$$q_0 = \beta I_0 L_{\text{eff}}, \quad (2.4)$$

where $L_{\text{eff}} = (1 - e^{-\alpha_0 l})/\alpha_0$ is the effective length of the sample and l is the thickness of the sample.

The values of l and α_0 depend upon the sample and are listed in Table 1. The waist radius w_0 was extracted from the fit value of z_0 , and the maximum irradiance was found by dividing the output power of 3.87 mW by the cross-sectional area of the beam assuming a radius of w_0 . The first seven terms of the sum in Eq. 2.2 are sufficient to obtain results with more than three significant digits.

3. Results

The linear absorption coefficient as a function of irradiation wavelength for the thin films under study are shown in Fig. 1. The normalized transmittance as a function of z -position for samples of H₂Pc, ZnPc, and FePc deposited at 100 °C with approximately equal thickness is compared in Fig. 2. Their respective fit parameters and extracted values can be found in Table 2. The significantly lower linear absorption in FePc and ZnPc results from the addition of metal complexes,

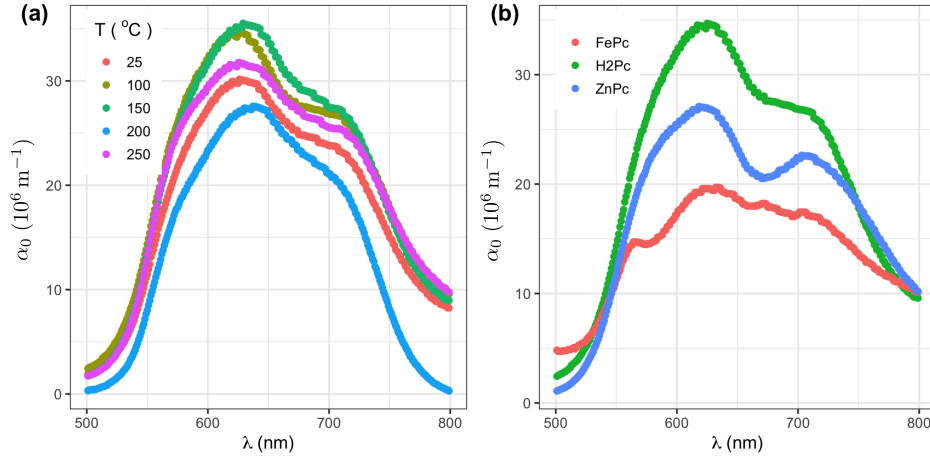


Figure 1. Absorption spectra (a) for H_2Pc thin films deposited from room temperature to 250 °C, and (b) for FePc , H_2Pc , and ZnPc deposited at 100 °C. Data from T. Fry¹².

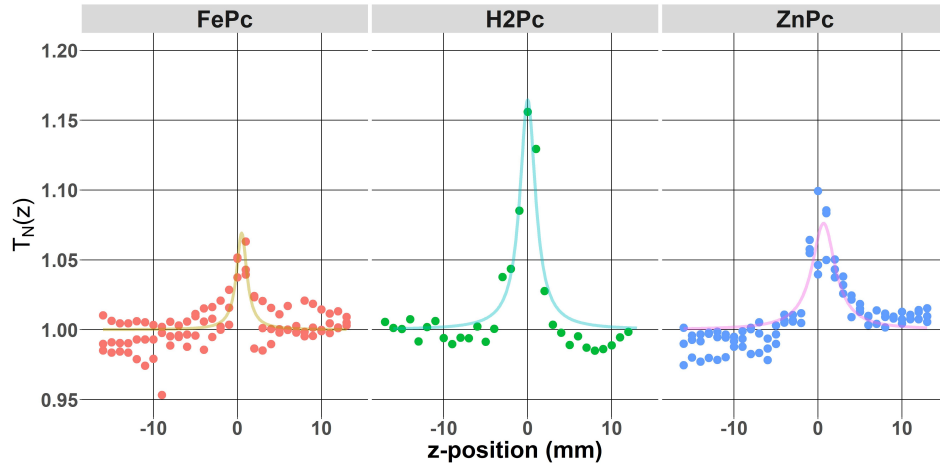


Figure 2. Normalized transmittance T_N vs z -position of H_2Pc , FePc , and ZnPc thin films. Lines are fits to data.

which generally decreases the extinction coefficient of the phthalocyanine molecule by altering molecular energy levels⁸.

All samples exhibit strong saturable absorption. The nonlinear coefficient of the H_2Pc sample was calculated to be $4.5\times$ larger than that of FePc , and $1.7\times$ that of ZnPc (see Table 2). Given the similar thicknesses and deposition temperatures - and thus crystallite sizes - of the samples, it is suggested this difference in nonlinearity is due to the metal complexes themselves. The difference in Rayleigh diffraction length - and associated beam waist radius - between the samples is surmised to be

Table 2. Fit parameters (q_0 and z_0) and extracted values for each thin film deposited at 100 °C. See Table 1 for the thickness and absorption coefficient of the samples, used to compute L_{eff} .

Material	q_0	z_0 (mm)	w_0 (μm)	I_0 (MW/m ²)	L_{eff} (nm)	β (m/W)
H ₂ Pc	-0.368	1.27	16.0	4.80	25.0	-3.06
FePc	-0.177	0.78	12.5	7.83	33.6	-0.67
ZnPc	-0.193	1.78	19.2	3.43	30.9	-1.82

due to uncertainty in the fit. It is also possible that this is due in part to nonlinear refractive effects such as thermal lensing causing the beam focus to change. Since SA effects are frequently attributed to depopulation of the ground state when pumping time is long compared to relaxation times³³ - as is the case for CW irradiation - this is likely related to differences in linear absorption, with H₂Pc having the highest α_0 and FePc the lowest.

The normalized transmittances as a function of z -position for samples of H₂Pc deposited at 25 °C, 100 °C, 150 °C, 200 °C, and 250 °C are compared in Fig. 3. The fit parameters and extracted values can be found in Table 3.

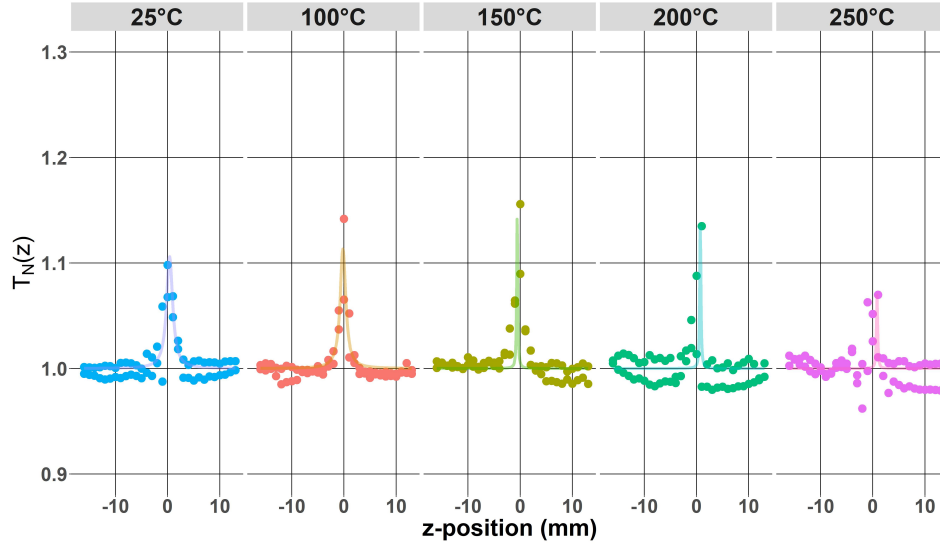


Figure 3. Normalized transmittance T_N vs z -position of H₂Pc thin films deposited at 25 °C, 100 °C, 150 °C, 200 °C, and 250 °C. Lines are fits to data.

The magnitude of β appears to generally decline with increasing deposition temperature, with a large decrease between the sample fabricated at 100 °C and the sample fabricated at 150 °C. However, this may be caused in part by the large increase in apparent waist irradiance between these two samples. This increase is

Table 3. Fit parameters (q_0 and z_0) for H₂Pc thin films with different deposition temperatures T_{dep} . See Table 1 for the thickness and absorption coefficient of the same samples, used to compute L_{eff} .

T_{dep} (°C)	q_0	z_0 (mm)	w_0 (μm)	I_0 (MW/m ²)	L_{eff} (nm)	β (m/W)
25	-0.257	0.759	12.4	8.06	28.4	-1.12
100	-0.272	0.700	11.9	8.73	25.0	-1.24
150	-0.331	0.124	5.0	49.3	24.7	-0.29
200	-0.331	0.134	5.2	45.7	29.3	-0.25
250	-0.177	0.134	5.2	45.6	26.7	-0.15

thought to be due to uncertainty in the fit because of low scan resolution about the beam waist rather than an actual increase in irradiance. Additionally, damage and imperfection in the samples might result in local thickness variations that introduce additional uncertainty in the values of the extracted parameters. The relatively small variation in β among the first two samples and among the last three indicates that if a relationship does exist between deposition temperature and nonlinear absorption, it is only weak.

The presence of strong SA contrasts with the RSA behavior has been previously observed in pulsed laser studies of metal phthalocyanines^{3,25,27,31,11,19}. Since the laser wavelength falls near a linear absorption maximum, it is expected that the material is more likely to exhibit SA^{30,9}. The duration of pumping is also expected to play a role in the direction of nonlinearity. RSA in phthalocyanine is reported to be governed by excited state absorption (ESA) and two photon absorption (TPA)³⁴. When phthalocyanine is exposed to pulsed radiation, ESA is a primarily fluence-dependent process with little dependence upon pulse width. TPA, however, is strongly dependent upon pulse width, with increased width resulting in decreased RSA behavior both theoretically and experimentally.³⁴ In the limit of infinite width, e.g. a CW laser, the RSA behavior is expected to be much weaker than under nanosecond pulsed irradiation, allowing SA processes to dominate.

Normalized transmittance as a function of z -position for the TTBPc-in-chloroform sample is shown in Fig. 4. A range of 41 z -positions is presented to demonstrate the presence of SA at all sample positions, even far from the beam waist. The “far-field” was taken to be $z = -20, -19, 19$, and 20 mm in these plots. A fit of measurements in the RSA region, between $z = -5$ and $z = 5$ mm, using Eq. 2.2 is also shown in Fig. 4. Data from each of the three runs were renormalized with a scale factor taken to be the average of the normalized transmittances at $z = -5, -4, 4$, and 5 mm for the purposes of this fit. A single fit was then created using renormalized data from all three runs and then multiplied by the scale factor before plotting.

The TTBPc sample exhibits a very broad peak about the waist, with a sudden and dramatic dip within a few millimeters of the actual waist position.

A sample of pure chloroform in the same cuvette was measured, and the response was found to be highly linear. Similar SA to RSA transitions have been reported previously; for example, Rao et al. reported such a transition during a study of alkyl-phthalocyanine nanoparticles in chloroform solution²⁶. Vivas et al. similarly observed a transition in a z-scan study of lutetium bisphthalocyanine in chloroform³³. SA to RSA transitions in phthalocyanines are typically identified with pump wavelengths around the Q-band of the absorption spectrum³². In bisphthalocyanine, this has been explained through a dramatic decrease in the ground state absorption cross section and a simultaneous increase in the excited state cross section at the edges of the Q-band using a three-level model³³.

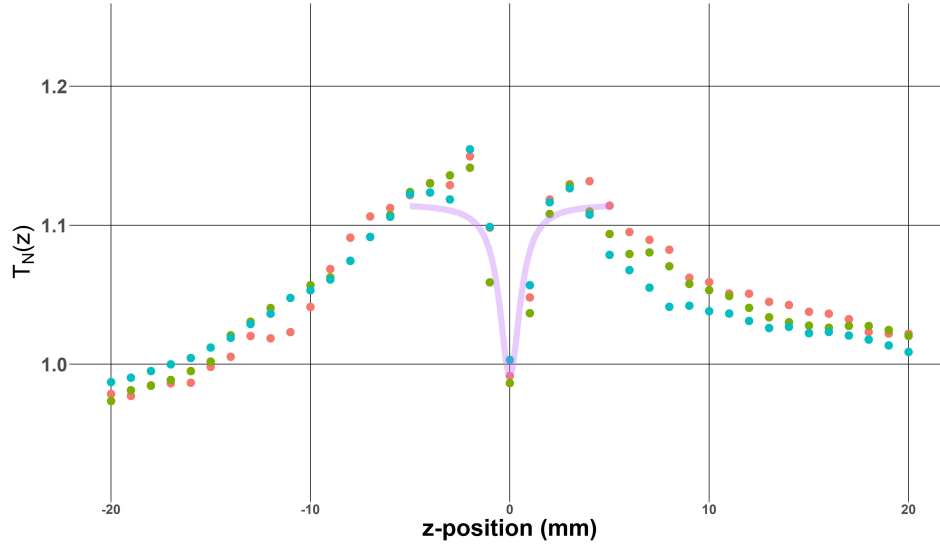


Figure 4. Normalized transmittance T_N vs z -position of TTBPc in chloroform. The three runs, marked in different colors, were performed in sequence over a period of several hours.

To permit a rough estimate of the NLA coefficient about the beam waist, we use an approximated linear absorption coefficient α_0^* for a related phthalocyanine derivative, 1,8,15,22-tetraalkoxy-phthalocyanine (hereafter referred to as TAPc). The molar attenuation coefficient ϵ for TAPc was measured by Apostol et al.² using a 5×10^{-6} M solution of TAPc in chloroform. From their absorption spectrum plot, we estimate ϵ to be $31\,500\text{ M}^{-1}\text{cm}^{-1}$ at 633 nm, and thus α_0^* for the TTBPc sample was estimated to be 31 m^{-1} . With this value we approximate the effective length L_{eff}^* of our sample to be 0.985 mm.

The fit of the three runs using Eq. 2.2 and assuming a waist at $z = 0$ returned a value of 0.38 ± 0.06 for q_0 and 0.56 ± 0.16 for z_0 . The apparent waist irradiance across the three runs is thus $11 \pm 4\text{ MW/m}^2$, and the approximated NLA coefficient β^* is $3.6 \pm 1.4 \times 10^{-5}\text{ m/W}$. Apparent waist irradiance could be higher than that estimated

Table 4. Two photon absorption coefficient β and experimental parameters for selected studies (Ref.) of saturable absorbers as thin films (TF) with thickness l under continuous wave (CW) laser pumping.

Material	Medium	Pulse Length (ns)	l (μm)	β (m/W)	Ref.
OHPc	1% in PMMA TF	CW	10	-6.1×10^{-4}	23
ZnOHPc	1% in PMMA TF	CW	10	-6.8×10^{-4}	23
ZnTriTBPc	1% in PMMA TF	CW	10	-9.1×10^{-3}	23
TTBPc	1% in PMMA TF	CW	9	-4.9×10^{-3}	24
ZnTTBPc	1% in PMMA TF	CW	12	-1.1×10^{-2}	24
Mn-Doped ZnO	Doped with 1% Mn	CW	0	-1.2×10^{-1}	1
CuPc nanoparticles	TF	8.0×10^{-5}	1	-5.3×10^{-3}	35
Amido Black 10B	4×10^{-4} M in PVA TF	CW	85	-3.5×10^{-4}	30
ZnPc	TF	2.5×10^{-4}	0.2	-3.5×10^{-9}	20
BG dye	0.05 mM in water	CW	10^3	2.1×10^{-5}	6
CeO ₂ -CoPc	0.1% in water	CW	-	6.9×10^{-5}	28
TTBPc	5×10^{-4} M in CHCl ₃	6	10^3	3.1×10^{-9}	19

for our thin films due to greater fit uncertainty related to the use of significantly fewer data points. Our estimates for β^* indicate weak RSA behavior about the beam waist, although our values are greater by four to five orders of magnitude than those reported in pulsed-laser studies of TTBPc-in-chloroform solution¹⁹ and related phthalocyanines in other solvents^{25,3}. It should be noted however that, due to the use of the linear absorption of TAPc rather than TTBPc, β^* is only an approximation of the actual NLA coefficient β .

The two-photon coefficients and relevant experimental parameters of other SA and RSA materials are listed in Tab. 4. The measured β values from Tab. 3 are much larger, sometimes exceeding these coefficients by two orders of magnitude or more. This may be due to the relatively high molecular density in thin films compared to the low-concentration solutions and doped thin films. Moreover, the relatively large beam cross-section impinging on the detector exaggerates the effects of refraction in the present measurements. It should be noted that there have been few studies of the archetype phthalocyanine thin films using CW irradiation to date, limiting a comparison.

4. Conclusion

All thin film samples of H₂Pc, FePc, and ZnPc were observed to act as strong SAs, with H₂Pc exhibiting the greatest nonlinearity, followed by ZnPc and FePc. No significant correlation was observed between deposition temperature and nonlinear absorption, although noise and low scan resolution introduce significant uncertainty into our measurements of β . This appears to contraindicate H₂Pc, FePc, and ZnPc thin films for use as practical optical limiters in situations where CW lasers might be encountered, but their strong SA behavior recommends them for applications in which SA is desirable. TTBPc dissolved in chloroform appears to act as a SA at irradiances as low as 4 kW/m², but acts as an RSA at irradiances around 4 MW/m²

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to 12 MW/m².

5. Acknowledgements

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