Phthalocyanines for photonic applications: a new perspective

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ABSTRACT

We present a comprehensive review of the nonlinear optical (NLO) properties of various phthalocyanines studied by our group over the last few years. The NLO coefficients obtained in the continuous wave (cw), nanosecond (ns), picosecond (ps), and femtosecond (fs) regimes are summarized and important conclusions drawn from these studies are highlighted. Wherever possible the figures of merit in different pulse domains are evaluated and discussed for possible applications in the field of photonics. Various schemes to identify and exploit the potential of these molecules are proposed. Necessary measures required for the realization of practical devices out of these molecules are delineated. The performance of these molecules vis-à-vis other phthalocyanines and related compounds is evaluated.

Key words: Nonlinear optical, Z-scan, Three-photon absorption, Phthalocyanines, Optical limiting.

1. INTRODUCTION

Phthalocyanines/metallophthalocyanines, Porphyrins, and their metallated derivatives are macromolecules with huge number of delocalized π electrons resulting in interesting third-order nonlinear optical (NLO) properties leading to extensive applications in optical limiting and all-optical switching [1-28]. Materials demonstrating strong reverse saturable absorption with nanosecond pulses find imminent applications in optical limiting while materials possessing strong multi-photon absorption with picosecond (or shorter pulse) excitation are promising for applications in biomedicine and imaging. Higher nonlinear refractive index combined with fast response time will be of assistance for applications in optical switching devices. Several hundreds of molecules, in various forms, have been investigated till date for identifying their potential in photonic applications. Once the molecular properties are understood and optimized they can be transformed into solids for device applications. Metallopolyynes [29] were demonstrated to be transparent and broadband optical limiters in the visible region with nanosecond pulses. GaAs nanocrystals [30] and variety of graphene structures and carbon nanotubes [31-34] have also been studied for applications in optical limiting. Metal nanoparticles-polymer nanocomposites [35] were recently shown to have low optical limiting threshold and broad spectral response. Semiconductor quantum dots [36, 37], bacteriorhodopsin films [38], waveguide arrays [39], gold nanoparticles synthesized using green methods [40] were some of the other materials which showed promise for optical limiting applications. Several novel techniques such as use of sub-wavelength coupled plasmonic waves [41] were also demonstrated to enhance the optical limiting properties. The ultimate aim of these studies is to find suitable materials which satisfy the conditions of (a) broad band spectral response, (b) low linear absorption, (c) high damage threshold, (d) large dynamic range, (e) cost effective, (f) practically feasible. Some of these materials were also tested with short pulses for optical switching applications which require low power (large nonlinearity) and fast response time (typically picosecond or less).

Phthalocyanines are versatile and ubiquitous class of molecules encompassing several benefits over similar organic and several other inorganic materials in nonlinear optics. Some of the significant characteristics these compounds exhibit include (i) planar structure, (ii) excellent chemical and thermal stability, (iii) large non-resonant optical nonlinearity, (iv) electronic response time in the picosecond (ps) and femtosecond (fs) time domain, and (v) ease of preparation/modification. The foremost advantage with these classes of molecules is the flexibility with which one can tailor their optical and nonlinear optical properties. The high stability and capability of phthalocyanines, especially, to accommodate different metal ions within their cavity result in diverse optical properties. Even though nonlinear optical properties of surplus of phthalocyanines and their derivatives [11-21, 42-56] have been investigated till date to assess their performance for NLO applications there remains further scope for investigation of novel structures with superior figures of merit. The best optical limiting performance till date has been achieved using a phthalocyanine in tandem

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with another nonlinear optical material justifies the potential of these molecules [56]. Many of the recent investigations of a variety of phthalocyanines were confined to only one time domain or two at the best. The efforts from material scientists, chemists, and physicists are to ensue and establish competent molecules with better figures of merit. It is, therefore, essential that any new molecule should be tested under rigorous conditions with laser pulses of various energies and durations to arrive at the exact figures of merit in each domain. Herein we present the results of our nonlinear optical studies in a new class of phthalocyanines using continuous wave, nanosecond, picosecond, and femtosecond pulses. A variety of techniques including Degenerate Four Wave Mixing (DFWM), Pump-probe, and Z-Scan were utilized to characterize these materials with cw, ns, ps, and fs pulse excitations. Our recent studies focused on several phthalocyanines which exhibited huge nonlinear coefficients in the cw, nsec (ns), picosecond (ps) and femtosecond (fs) time domains with potential applications in optical limiting, switching, and bio-imaging. We have also investigated the NLO properties of these molecules in thin film form and nanoparticles form. These studies suggest that it is possible to achieve large nonlinear coefficients combined with superior figures of merit with a systematic study.

2. EXPERIMENTAL DETAILS

Complete details of the experiments can be found in most of our earlier publications [11-21]. Briefly 6 ns pulses (10 Hz, 532 nm), ~2 ps pulses (1 kHz, 800 nm), and ~100 fs pulses (1 kHz, 800 nm), 632.8 nm cw He-Ne laser beam were used for the Z-scan and DFWM experiments. Thirteen different phthalocyanines (**P1 to P13**) were studied. All the samples were subject to purification prior to the NLO experiments. The absorbance changes were monitored before and after the NLO experiments to confirm the changes that occurred due to continuous exposure to the short pulses. Thin films were prepared by doping (dissolving) the phthalocyanines in PMMA and spin coating the obtained solution. Typically few tens of microns thick films were achieved and used for NLO studies. The complete nomenclatures of these compounds are presented in tables 1-3 and the procedures for synthesizing these molecules elsewhere.

3. RESULTS AND DISCUSSION

Femtosecond pulse domain

We have investigated eight new molecules with ~100 fs pulses using Z-scan, DFWM techniques. Table 1 presents a summary of the results from our studies and some representative molecules reported recently. It is evident that the nonlinear coefficients of our molecules are superior to many of the reported molecules. Most of our phthalocyanines exhibited strong three-photon absorption (3PA) coefficient/cross-sections even at moderate input intensities. Phthalocyanine nanoparticles **(P8)** exhibited enhanced 3PA compared to the actual phthalocyanine **(P4)**. **P8** proved to be a good optical limiter in the femtosecond domain with a limiting threshold of ~0.03 J/cm^2. **P4** and **P5** demonstrated excellent figures of merit **(W >>1 and V <0.68)**. We recorded large off-resonant second hyperpolarizability (**$\gamma \sim 10^{-31}$ esu**) for these molecules with ultrafast nonlinear optical response in the femtosecond domain [14]. These values are on par or better than the croconates, squaraine dyes, and other phthalocyanine analogues studied recently and extensively [59-61]. **P1-P3** and **P6-P7** illustrated a complicated nonlinear absorption behavior dependent on intensity of input pulses and the concentration of the solutions used. The n_2 values for these molecules varied in the range of $0.5\text{-}5\times10^{-15}$ cm^2/W. Subsequently we need to incorporate these molecules in a stable matrix (polymer or glass) and evaluate their NLO response for device applications. We expect the figures of merit in the doped material to be similar or improved. Some of these molecules (in PMMA) were tested for their response to the ultrashort pulses using a simple pump-probe technique (with ~50 fs pulses) we realized that these molecules had excited states whose dynamics/life times were in the 10-100 ps. DFWM experiments in solutions, with ~100 fs pulses, revealed response times in the femtosecond time domain. The nonlinear absorption in **P6** and **P7** switched from saturable type to reverse saturable type with increasing intensities suggesting a complicated behavior. Such switching mechanism can be utilized for optical signal processing applications provided one can achieve them with low peak powers. **P1-P3** nonlinear absorption data with fs pulses divulged the solvent contribution. The contribution from solvent(s) could be positive or negative thereby enhancing or diminishing the actual nonlinearity. A careful study is therefore essential to identify the exact contribution from the solute only. Our fs Z-scan and DFWM data suggests these are potential molecules for optical switching applications.

In recent times several materials including organic fluoropores like halogenated fluorine molecules, croconates, squaraines dyes, etc. have been investigated for their third order nonlinear optical (including 3PA) properties using femtosecond pulses in the NIR spectral regions [57-61]. However, we discovered that there are sporadic reports on organic molecules exhibiting 3PA in the significant wavelength region of 750–850 nm corresponding to the output of commercially available femtosecond Ti:sapphire source routinely used by the researchers for biological applications. We strongly feel that our materials might have a broad impact in biology and medicine through three-photon induced photodynamic therapy (PDT) in cancer treatment. In this regard we need to tag these molecules with some biomolecules for 3PA (or 2PA) based detection and the studies are in progress.

Sample	**Wavelength, pulse-width**	**Third order nonlinearity (γ) $\times 10^{-31}$ esu**	**α_3 (cm^3/GW^2) $\times 10^{-5}$**	**Reference**
4,4'-bis(diphenylamino) stilbene (BDPAS) dendrimers	1100 nm, 150 fsec	-	0.51	[57]
Multi-branched chromophore	1300 nm, 160 fsec	-	0.385	[58]
Squaraine dyes	800 nm 50 fs	3-7.5	-	[59]
Croconate Dyes	800 nm ~100 fsec	0.24-0.53	-	[60]
Phthalocyanine analogues	800 nm 50 fs	1.11–2.26	-	[61]
(i) $(H_2)_2$SnPc (P1)	**800 nm ~100 fsec**		**4.0**	**[62]**
(ii) $Sn(OH)_2$Pc (P2)			**2.0**	**[62]**
(iii) $Sn(Cl)_2$Pc (P3)			**1.5**	**[62]**
(iv) 2(3), 9(10), 16(17), 23(24) tetra tert-butyl phthalocyanine (P4)		**4.27**	**9.1**	**[12]**
(v) 2(3), 9(10),16(17), 23(24) tetra tert-butyl Zinc phthalocyanine (P5)		**4.32**	**9.5**	**[12]**
(vi) 2,3,9,10,16,17,23,24-Octakis-(heptyloxy) Phthalocyanine (P6)			**0.8**	**[16]**
(vii) 2,3,9,10,16,17,23,24-Octakis-(heptyloxy) Phthalocyanine Zinc(II) (P7)			**3.6**	**[16]**
(viii) 2,3,9,10,16,17,23,24-tetra-(*tert*-butyl) Zinc phthalocyanine nanoparticles (Water) (P8)			**13.5**	**[17]**

Table 1 Comparison of femtosecond third order nonlinearity (γ) and three-photon absorption coefficients **(α_3)** of our phthalocyanines with other phthalocyanines and compounds reported in recent literature.

Picosecond pulse domain

Table 2 summarizes the results obtained with ps pulses. Five different phthalocyanines were investigated **(P9-P13)**. We recorded large, off-resonant second hyperpolarizabilities (γ) with estimated values of ~6.5×10^{-31} esu and ~8.9×10^{-31} esu for unsymmetrical alkyl **(P9)** and alkoxy phthalocyanines **(P10)**, respectively. Evaluated figures of merit (W ~93/88 for **P9**/**P10**) indicated these are potential molecules for photonic applications. Nonlinear absorption studies

indicated these were good saturable absorbers. In contrast to some of the reported molecules with similar pulse excitation our phthalocyanines are superior in terms of higher **γ**. **P11** and **P12** revealed strong 3PA (~10^{-22} cm^3/W^2) and strong, positive nonlinear refractive indices (~10^{-15} cm^2/W). Titanium phthalocyanine [66] demonstrated a higher **γ** value with picosecond excitation but the pulse duration was ~500 ps suggesting some thermal contribution to the overall nonlinearity obtained. Similarly, rare earth doped phthalocyanines exhibited larger nonlinearity but the excitation was at 532 nm and the confinement of the molecules in a polymer matrix could have contributed to higher nonlinearity. Our molecules when doped in a suitable polymer matrix are expected to demonstrate improved nonlinearities. ZnOcPc **(P13)** exhibited good nonlinear optical response in all the time domains. The structural changes in the phthalocyanines we investigated include (a) Alkyl and alkoxy (b) symmetric and unsymmetrical (c) metallated and free base versions. Even though we could arrive at some conclusions, based on our studies, on the dependence of NLO properties with respect to these structural changes more detailed studies are essential before we can identify the recipe to achieve device capable molecules. However, these studies definitely are indicative of the right path to choose for further studies.

Sample(s)	Details	γ (esu)	Reference
$ZnPc(OBu)_6(NCS)$	130 fs, 800 nm	2.35×10^{-31}	[63]
Fullerene Derivative 1 Fullerene Derivative 2	38 ps, 532 nm	0.237×10^{-31} 0.202×10^{-31}	[64]
Lead Phthalocyanines	90 ns, 532 nm	~10^{-34}	[65]
Titanium Phthalocynaine	~500 ps, 532 nm	~10^{-29}	[66]
Rare Earth Phthalocyanines in Polymer	~25 ps, 532 nm	~10^{-29}	[67]
2-(3-(Butane-1,4-dioic acid)-9(10),16,(17),23(24)-tri tert-butyl Phthalocyanine Zinc(II) (P9) **2-(3-(Butane-1,4-dioic acid)-8,11,15,18,22,25-hexakis-(butyloxy) Phthalocyanine Zinc(II) (P10)**	**~2 ps, 800 nm**	**6.5×10^{-31}** **8.9×10^{-31}**	**[68]**
$Cu(SO_3Na)$pc (P11) **$Ni(SO_3Na)$pc (P12)** **2(3),9(10),17(18),23(24)-((1,2-(dicarboxyethyl))-phthalocyanato zinc(II) (ZnOcPc) (P13)**	**~2 ps, 800 nm**	**n_2 ~1.5×10^{-15} cm^2/W** **n_2 ~1.4×10^{-15} cm^2/W** **n_2 ~0.13×10^{-16} cm^2/W**	**[18]** **[69]**

Table 2 Comparison of picosecond third order nonlinearity (**γ**) of our phthalocyanines with other phthalocyanines and compounds reported in recent literature.

Nanosecond pulse domain

P4-P7 and **P11-P13** were studied for the NLO properties in the nanosecond time domain. The results of our studies and the nonlinear coefficients estimated are presented in table 3. Some of these possess n_2 in the 10^{-11} cm^2/W range, which is one of the highest reported till date. The nonlinear coefficient **β** also represents one of the highest reported for any of the phthalocyanines or other molecules. The limiting thresholds evaluated for these molecules have been found to be **~0.5 J/cm²**. The value of γ was also superior to many recently reported molecules. Further studies

such as spectral dependence of the observed nonlinear coefficient will establish these molecules credentials for optical limiting. Even thought the comparisons presented in table 3 are not exhaustive our experience and knowledge suggests these are one of the best performing molecules in the nanosecond time domain. That the best performance by any optical limiter (in terms of threshold and dynamic range) has been with a phthalocyanine indicts hope that a practical optical limiter will be achieved soon. We are in the process of making free-standing thin films of these materials to study their limiting properties in different spectral regions.

Sample	Wavelength	α_2 (cm/GW)	n_2 (cm^2/W) $\times 10^{-11}$	$\chi^{(3)}$ (esu) $\times 10^{-10}$	Reference
Zn Phthalocyanine	532 nm	47.74	-	-	[70]
$Sm(Pc)_2$ $Eu(Pc)_2$	596 nm 604 nm	31 50	-	-	[71]
Alkynyl phthalocyanines	532 nm	12 – 56	-	-	[72]
$Nd(Pc)_2$	532 nm	42	-	-	[73]
GaPc dimers	532 nm	32 - 35	-	-	[74]
Octaalkylphthalocyanines and their 15 metallated derivatives	532 nm	15 - 96	-	-	[75]
P4 **P5**	**532 nm** **6 ns**	**~310 (pc1)** **~420 (pc2)**	**1.13** **0.86**	**6.02** **4.64**	**[12,13]**
P6 **P7**	**532 nm** **6 nm**	**~1650** **~1850**	**1.61** **1.56**	**10.0** **9.98**	**[15]**
P11 **P12** **P13**	**532 nm** **6 ns**	**~25** **~1.1** **~43**	**0.0120** **0.0047** **0.0094**	**0.04** **<0.04** **0.06**	**[18]** **[69]**

Table 3: Comparison of two-photon absorption coefficient **(α_2)** with reported values in literature obtained using ns pulses.

cw domain

The third-order nonlinear optical and optical limiting properties of **P4, P5, P6, P7, and P9** were investigated using a continuous wave laser at 633 nm. We have employed the Z-scan technique to evaluate the sign and magnitude of nonlinear refractive index and the nonlinear absorption coefficient. Optical limiting based on nonlinear refraction was performed and limiting thresholds were estimated for all the samples. The magnitude of the third order nonlinearity measured were one of the highest reported in the cw regime till date. The nonlinearities in our molecules are at least two orders of magnitude higher than any of the reported molecules [76-86].

Table 4 summarizes the NLO data obtained from our studies and comparison with some of the potential molecules reported recently. Unsymmetrical Phthalocyanine **(P9)** had better limiting characteristics and its nonlinear coefficients were comparatively high. We expect the comparatively higher values of the NLO coefficients for **P9** due to the lack of symmetry in its structure, resulting from the uneven peripheral substitution. The lack of symmetry generally, increases the magnitude of third-order susceptibility. It has been suggested that they could posses high negative third-order susceptibility if the transition moment between all the excited state are small and asymmetry is small, or, when the transition moment between excited states are large. We have also demonstrated that these phthalocyanines possess low optical limiting thresholds in the range of ~1.8 mW – 8.0 mW. These could be efficiently used as optical limiters by utilizing their high refractive nonlinearity and judicious aperture based design in low power cw regime.

Table 4 Comparison of cw third order nonlinearity of our phthalocyanines with other compounds reported in recent literature.

Form of sample	Sample	n_2 (cm^2/W)	β (cm/W)	$\lvert \chi^{(3)} \rvert$ (esu)
Solution conc. : 5 x 10^{-5} M Solvent : $CHCl_3$ *Ethanol	**P6 [10, 11]**	**− 1.6 x 10^{-6}**	**− 0.004**	**0.9 ± 0.18 x 10^{-4}**
	P7 [10, 11]	**− 0.8 x 10^{-6}**	**−0.0029**	**0.46 ± 0.09 x 10^{-4}**
	P9 [10, 11]	**− 2.6 x 10^{-6}**	**− 0.009**	**1.48 ± 0.3 x 10^{-4}**
	P4 [10, 11]	**− 2.0 x 10^{-6}**	**− 0.015**	**1.0 ± 0.2 x 10^{-4}**
	P5 [10, 11]	**−0.25 x10^{-6}**	**− 0.00325**	**0.14 ± 0.03 x 10^{-4}**
Thin Film 1 % by wt. (doped in PMMA) Solvent : $CHCl_3$	**P6 [10, 11]**	**− 7.1 x 10^{-6}**	**− 0.061**	**4.0 ± 0.8 x 10^{-4}**
	P7 [10, 11]	**− 6.4 x 10^{-6}**	**− 0.068**	**3.6 ± 0.7 x 10^{-4}**
	P9 [10, 11]	**− 16.0 x 10^{-6}**	**− 0.91**	**10.0 ± 2.0 x 10^{-4}**
	P4 [10, 11]	**− 12.0 x 10^{-6}**	**− 0.49**	**7.0 ± 1.4 x 10^{-4}**
	P5 [10, 11]	**− 14.2 x 10^{-6}**	**− 1.1**	**8.6 ± 1.7 x 10^{-4}**
Fast green FCF dye (Acid blue 3) @ *632.8 nm* [76]		− 0.032 x 10^{-6}	− 0.000065	-
Triphenylmethane dye (Acid blue 7) @ *632.8 nm* [77]		− 0.188 x 10^{-6}	− 0.00308	0.0835 x 10^{-4}
Castor Oil @ *514 nm* [78]		− 0.032 x 10^{-6}	-	-
Zinc Tetraphenyl Porphyrin @ *632.8 nm* [79]		− 0.14 x 10^{-6}	-	-
Night Blue dye doped PMMA films @ *632.8 nm* [80]		− 0.1474 x 10^{-6}	-	-
Basic green 1 dye @ *632.8 nm* [81]		− 0.16 x 10^{-6}	− 0.0017	0.0724 x 10^{-4}
Dispersed red 13 Doped PMMA films @ *633 nm* [82]		− 1856.0 x 10^{-6}	-	-
CdS Nanocrystals Silica Matrix @ *514.5 nm* [83]		− 1.85 x 10^{-6}	− 0.087	-
Poly (3-dodecylthiophene) @ *633 nm* [84]		-	-	Im $\lvert \chi^{(3)} \rvert$ = − 2.0 x 10^{-4}
PbS Nanoparticle @ *632.8 nm* [85]		− 0.434x 10^{-6}	-	-
In_2O_3 Nanoparticle @ *632.8 nm* [86]		− 0.389 x 10^{-6}	-	-

Future directions for our studies include (1) performing the NLO studies at different wavelengths to categorize the spectral response, (2) repeating the studies in solution and in a polymer/glass matrix, (3) executing the time-resolved studies of all these molecules to ascertain the response times, (4) model the nonlinear absorption behavior based on a five level model including all the possible absorption mechanisms such as excited state absorption, 2PA, 3PA etc. [87] (5) fabricating the actual devices (e.g. free-standing thin films for limiting applications, doped polymer waveguides for switching applications etc.), (6) testing the actual device performance.

4. CONCLUSIONS

Our studies revealed large nonlinear coefficients for most of thirteen new phthalocyanine molecules studied in all the cw, ns, ps, and fs time domains. Nonlinear coefficient evaluated are summarized and compared with some of the recently reported and relevant molecules (in each time domain). Some of the molecules were studied for their excited state dynamics while some of these were studied for optical limiting in the nanosecond domain. Further studies are in progress to arrive at the complete understanding of optical nonlinearities in all the time domains so as to achieve their figures of merit and evaluate their potential.

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