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SHORT COMMUNICATION

Third-order Nonlinear Optical Properties of Octa-substituted Metal-free Phthalocyanine Thin Films

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Third-order nonlinear optical susceptibility, $\chi^{(3)}$ of symmetrically octa-substituted metal-free phthalocyanine thin films measured by the third-harmonic generation technique are reported. The metal-free phthalocyanine has been found to show a $\chi^{(3)}$ $(-3\omega;\ \omega,\omega,\ \omega)$ value as large as 7.73×10^{-12} esu at 1.80 μm. The figure of merit, $\chi^{(3)}/\alpha$, was estimated to be 4.17×10^{-17} esu cm at 1.05 μm and 6.97×10^{-16} esu cm at 1.65 μm. Both linear and third-order optical properties of liquid-crystalline metal-free phthalocyanines are discussed.

Keywords: third-order optical nonlinear properties; optical susceptibility; phthalocyanine; third-harmonic generation

INTRODUCTION

Organic molecular and polymeric materials such as π-conjugated polymers, charge-transfer complexes, dyes, liquid-crystalline materials, dye-grafted polymers and organometallic compounds have attracted much attention for applications in third-order nonlinear optics.[1-3] one of the important factors that contributes to large third-order optical nonlinearity is the extended π-electron conjugation. One-dimensional π-conjugated polymers such as polyacetylene, polydiacetylene and polyheterocycles show the largest third-order nonlinear optical susceptibilities $\chi^{(3)}$. In addition large $\chi^{(3)}$ values have also been observed for π-conjugated organometallic compounds.[4] Of significant interest are the metallophthalocyanines because their third-order nonlinear optical susceptibility $\chi^{(3)}$ can be tailored by modifying their chemical structures and large $\chi^{(3)}$ values could be observed from resonance contributions.[4-22] The octa-substituted phthalocyanines with long peripheral alkyl chains show liquid-crystalline phases;[23-27] however, their solid-state structures depend upon the nature of the substituted alkyl side-chains.[28] Interesting conductive properties of discotic liquid-crystalline phthalocyanines have been reported by several research groups,[29-33] though very little is known about their nonlinear optical properties in the solid state. In this communication, we report third-order nonlinear optical properties of a liquid-crystalline metal-free octa[(2-ethyl)hexyloxy]phthalocyanine, abbreviation H_2Pc[-(2-ethyl)hexyl]$_8$, and compare its properties with previously reported results on other metal-free phthalocyanine derivatives.

EXPERIMENTAL

Figure 1 shows the chemical structure of 2,3,9,10,16,17,23,24-octa({2-ethyl}hexyloxy)-phthalocyanine. The H_2Pc[O-(2[ethyl)hexyl]$_8$ was prepared using the method of Lelievre *et al.*[34] The product was spectroscopically characterized by NMR, UV/visible, IR and thermal methods and these data were found to be in good agreement with those reported in the literature.[35] A spin-coated film, 134 nm thick, was used for

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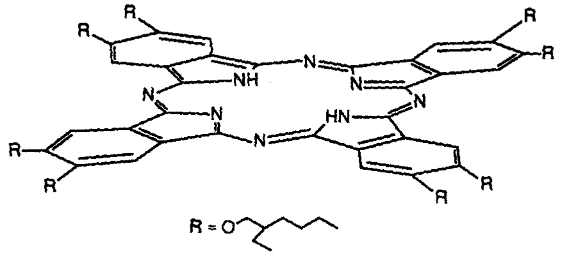

Figure 1 Chemical structure of octa-substituted metal-free phthalocyanine $H_2Pc[O\text{-}(2\text{-}ethyl)hexyl]_8$.

recording the optical spectrum as well as for third-harmonic generation measurements. Optical absorption spectra of spin-coated thin films were recorded from a UV–Vis spectrophotometer (Shimadzu UV-240) at room temperature. The third-order nonlinear optical susceptibility $\chi^{(3)}$ was measured by third-harmonic generation (THG) from the 1.0 μm to the 2.10 μm region.

RESULTS AND DISCUSSION

Figure 2 shows the optical absorption spectrum and wavelength-dependent $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ of a $H_2Pc[O\text{-}(2\text{-}ethyl)hexyl]_8$ thin film. The thin film shows two absorption bands, at 630 and 754 nm in the Q-band region, arising from the transition from the ground state to two excited states. The $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ values were determined using the known procedure reported in the literature.[22] The $\chi^{(3)}$ value of 3.0×10^{-14} esu for fused silica was used as a reference at 2.1 μm, and the refractive indices of both reference and sample was assumed to be the same. The $\chi^{(3)}$ of thin films varies with wavelength and follows the absorption spectrum. The $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ values of 2.20×10^{-12} esu at 1.05 μm and 7.73×10^{-12} esu at 1.80 μm were determined. The magnitude of $\chi^{(3)}$ values is largely governed by the absorption, which increases with increasing absorption coefficient. The larger $\chi^{(3)}$ value at 1.80 μm appears to be

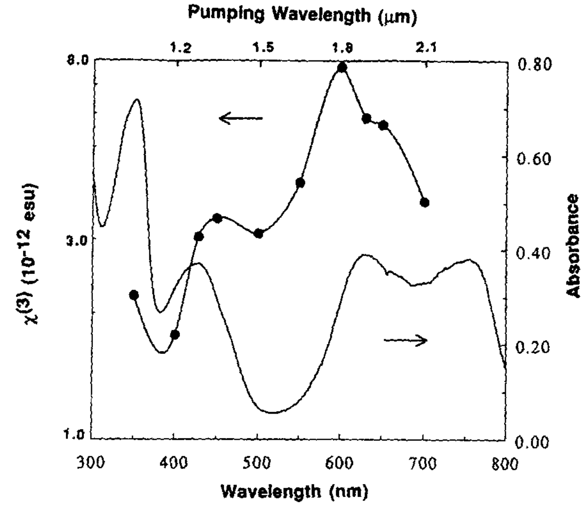

Figure 2 Optical absorption spectrum and wavelength-dependent third-order nonlinear optical susceptibility $\chi^{(3)}$ of $H_2Pc\{O\text{-}(2\text{-}ethyl)hexyl\}_8$ films, 136 nm thick, in the 1.05–2.1 μm region.

Table 1 Comparison of the $\chi^{(3)}$ values of metal-free phthalocyanines

H_2Pcs	$\chi^{(3)}$ (10^{-12} esu)	Wavelength (μm)	Measurement technique	Ref.
$H_2Pc[O\text{-}(2\text{-}ethyl)hexyl]_8$	2.20	1.05	THG	This work
	7.73	1.80	THG	This work
H_2Pc	3.0	1.907	THG	11
	4.0	1.064	DWFM	8
$H_2Pc(CP)_4$[a]	5000	1.064	DWFM	36
$H_2Pc(SC_8H_{17})_4$	1.7	1.50	THG	37
(Phase I)	1.9	1.80	THG	37
(Phase II)	0.87	1.50	THG	37
	6.8	1.80	THG	37
$H_2Pc(SC_{12}H_{25})_4$	2.1	2.01	THG	37
$H_2Pc(t\text{-}Bu)_4$	1.9	1.907	THG	38
H_2PcR_8	0.62	1.064	THG	40
	0.84	1.904	THG	40

[a] CP, cumylphenoxy; $R = OCH_2 - CON(C_8H_{17})_2$

due to a three-photon resonance corresponding to 600 nm in the absorption spectrum. Another three-photon resonance-enhanced $\chi^{(3)}$ peak appears at 1.35 μm corresponding to 450 nm in the Soret band region. The $\chi^{(3)}$ value at 1.80 μm was found to be larger by a factor of 3.50 than at 1.05 μm. The calculated figures of merit ($\chi^{(3)}/\alpha$) were 4.17×10^{-17} esu cm at 1.05 μm and 3.67×10^{-16} esu cm at 1.80 μm. An interesting observation is the large figures of merit of 6.97×10^{-16} esu cm at 1.65 μm and 6.11×10^{-16} esu cm at 1.5 μm estimated in the transparency window between the Soret and Q-band regions.

Table 1 compares the $\chi^{(3)}$ values of various metal-free phthalocyanines which change significantly depending upon the chemical structure. In addition, measurement techniques as well as measurement wavelengths also influence $\chi^{(3)}$ values, as is apparent from the data measured by THG and degenerate four-wave mixing (DFWM) technique. THG-measured $\chi^{(3)}$ values of $H_2Pc[O\text{-}(2\text{-ethyl})hexyl]_8$ are of the same order as those of $H_2Pc(SC_8H_{17})_4$ thin films at 1.80 μm.[37] On the other hand, the $\chi^{(3)}$ value measured by DFWM for $H_2Pc(cumylphenoxy)_4$ in the Soret band region is at least three orders of magnitude larger than those of the THG $\chi^{(3)}$.[36] The large differences in $\chi^{(3)}$ arise from resonance contributions; a one-photon resonance in DFWM dominates the three-photon resonance seen in THG. Diaz-Garcia *et al.*[39, 40] measured $\chi^{(3)}$ values seven times larger than that of a fused silica reference at 1.907 μm for $H_2Pc[OCH_2CON(C_8H_{17})_2]_8$ spin-coated thin films and an order of magnitude larger; i.e. 20-fold, at 1.064 μm and 30-fold that of fused silica at 1.907 μm for Langmuir–Blodgett films, the latter arising from ordered structures. The $\chi^{(3)}(-3\omega;\ \omega,\ \omega,\ \omega)$ values of 6.2×10^{-13} esu at 1.064 μm and 8.4×10^{-13} esu at 1.904 μm were evaluated.[40] Third-order optical nonlinearities of phthalocyanines are governed by various factors such as metal atoms, peripheral substituents, axial ligands, length of π-conjugation, crystal structure and fabrication methods.[41] Studies on the effects of metal atoms and peripheral groups on third-order optical nonlinearities of liquid-crystalline phthalocyanines are under way and will be discussed in a future publication. In summary, we have demonstrated that a liquid-crystalline metal-free phthalocyanine shows large $\chi^{(3)}$ values in the Q-band region due to a three-photon resonance enhancement and a large figure of merit ($\chi^{(3)}/\alpha$) in the transparency window existing between the Soret band and the Q-band region.

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