Resonant and non-resonant third-order optical properties of metallophthalocyanines

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Non-resonant third-harmonic generation and resonant saturable absorption measurements of liquid solutions of silicon naphthalocyanine are discussed. The results provide further insight into the non-linear optical properties previously reported for random glassy polymers containing silicon naphthalocyanine.

(Keywords: non-linear optical properties; metallophthalocyanines)

INTRODUCTION

The macroscopic second-order, $\chi^{(2)}_{ijk}(-\omega_3;\omega_1,\omega_2)$, and third-order, $\chi^{(3)}_{ijkl}(-\omega_4;\omega_1,\omega_2,\omega_3)$, non-linear optical susceptibilities of conjugated π-electron organic and polymer structures are known to be unusually large, and their microscopic origin and virtual excitation processes can be successfully described by the many-electron theory of highly correlated quasi-one- (1D) and two-dimensional (2D) systems[1–3]. For 2D metallophthalocyanines[4–10], studies of the resonant third-order optical properties of disc-like silicon naphthalocyanine (SINC) (*Figure 1*), randomly dispersed in glassy polymer films, demonstrated that SINC behaves as an optical Bloch system, exhibiting absorption saturation of the large-oscillator-strength (α_0 of order $10^5\,\mathrm{cm}^{-1}$) Q band in the near-infra-red range and associated, large, intensity-dependent refractive index n_2 of order $1\times10^{-4}\,\mathrm{cm}^2\,\mathrm{kW}^{-1}$ (refs. 5–7). These properties allowed the first observation of absorptive optical bistability occurring through the non-linear electronic excitations of a random solid medium.

The development of random glassy polymers containing molecular units with large non-linear optical susceptibilities is a major approach towards realizing non-linear optical media that possess both important primary non-linear optical properties and secondary material properties such as thermal, mechanical, chemical and oxidative stabilities. Because of its large π-electron conjugation, the phthalocyanine structure intrinsically possesses one of the highest thermal and oxidative stabilities known for organic structures. Phthalocyanines incorporated into random glassy polymers by doping, or directly by covalent binding, provide an attractive approach to realizing highly stable non-linear optical media that can satisfy both primary and secondary property requirements. In this paper, we review experimental results recently obtained for the non-resonant and resonant third-order optical properties of a metallophthalocyanine.

LINEAR OPTICAL PROPERTIES OF SINC

The absorption spectrum of SINC dissolved in dimethylformamide (DMF) is shown in *Figure 2*. After a wide transparent region (850–2000 nm), SINC exhibits a characteristic, vibronically coupled, large-oscillator-strength Q band centred at 778 nm, followed by another

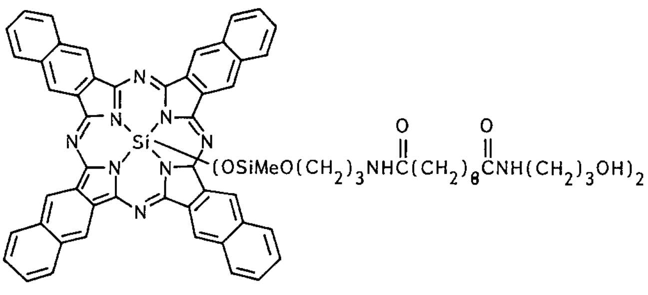

Figure 1 Schematic diagram for the molecular structure of SINC

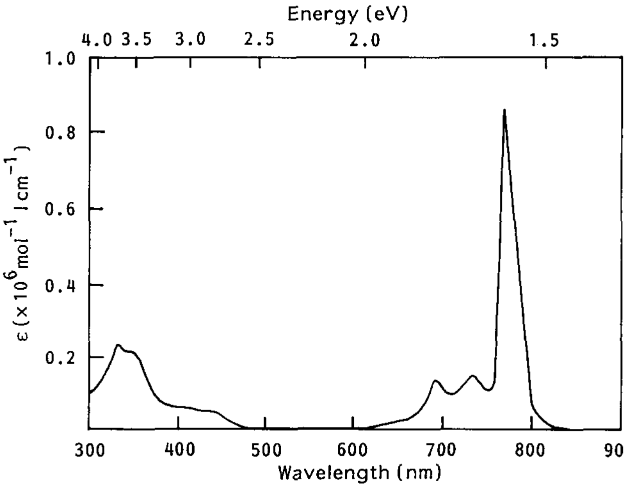

Figure 2 Linear absorption spectrum of SINC in DMF. The Q-band absorption peak occurs at 778 nm (1.59 eV) and the B-band peak is at 335 nm (3.70 eV). The solution is transparent at 850–2000 nm and at 500–600 nm

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transparent region (500–600 nm) and a B (Soret) band located near 335 nm. The Q and B bands are due to widely separated $S_0(1^1A_g) \rightarrow S_1(1^1E_u)$ and $S_0(1^1A_g) \rightarrow S_2(2^1E_u)$ π-electron transitions, respectively, as is well established for metallophthalocyanines and related metalloporphyrins of D_{4h} symmetry[11–13]. In fluorescence measurements, a red emission from the S_1 state is observed in nearly mirror symmetry of the Q band. Strickler–Berg analysis[14] of the Q-band spectrum yields a radiative lifetime for the S_1 state of 8.8 ns, which is consistent with pump–probe measurements of transient absorption at 532 nm and transient bleaching at 770 nm. The transparent regions allow third-harmonic measurements with little or no absorption at the fundamental and harmonic frequencies.

NON-RESONANT THIRD-ORDER OPTICAL PROPERTIES OF SINC

Third-harmonic generation measurements of SINC dissolved in DMF were performed using the Maker fringe technique at the fundamental wavelengths 1907 and 1543 nm. The value of $\chi_L^{(3)}(-3\omega; \omega, \omega, \omega)$ of the solution is obtained through the relation[15]:

$$\frac{(A_m^L)_{corr}}{A_m^R} = \frac{\left(T_G \dfrac{l_c^G \chi_G^{(3)}}{n_{3\omega}^G + n_\omega^G} - T_L \dfrac{l_c^L \chi_L^{(3)}}{n_{3\omega}^L + n_\omega^L} (t_\omega^{(2)})^3 \right)^2}{\left(T_G \dfrac{l_c^G \chi_G^{(3)}}{n_{3\omega}^G + n_\omega^G} - T_R \dfrac{l_c^R \chi_R^{(3)}}{n_{3\omega}^R + n_\omega^R} (t_\omega^{(2)})^3 \right)^2} \qquad (1)$$

where

$$(A_m^L)_{corr} = 2(A_m^L)_{obs} / [\exp(-3\alpha_\omega l) + \exp(-\alpha_{3\omega} l)] \qquad (2)$$

is the mean value of the fringes of the liquid solution corrected for any absorption at ω and 3ω, and R refers to the reference liquid.

Determination of $\chi_L^{(3)}$ of the liquid solution from equation (1) requires the knowledge of $\chi^{(3)}$ of the glass window and the solvent. The following values[16] have been used in our calculations:

at 1907 nm $\chi_G^{(3)} = 0.584 \times 10^{-14}$ esu, $\chi_{DMF}^{(3)} = 0.631 \times 10^{-14}$ esu

at 1543 nm $\chi_G^{(3)} = 0.591 \times 10^{-14}$ esu, $\chi_{DMF}^{(3)} = 0.650 \times 10^{-14}$ esu

Figure 3 shows the concentration dependence of the solution $\chi_L^{(3)}$ at the fundamental wavelength of 1907 nm. The values of $\chi_L^{(3)}$ decrease linearly with increased concentration of SINC. Since the γ_2 value of DMF is known to be positive, the γ_1 value of SINC is thus observed to be negative in sign. In the infinite dilution limit where $w \rightarrow 0$, the microscopic third-order susceptibility γ_1 of the solute is obtained from the following expression[15]:

$$v_0 \frac{\partial \chi_L^{(3)}}{\partial w}\bigg|_0 + \chi_2^{(3)} \frac{\partial v}{\partial w}\bigg|_0 + v_0 \chi_2^{(3)} \left(1 - \frac{4}{n^2+2} \frac{\partial n^2}{\partial w}\bigg|_0 \right) = \frac{1}{M_1} \left(\frac{n^2+2}{3} \right)^4 N_A \gamma_1 \qquad (3)$$

where M_1 is the solute molecular weight, $\chi_2^{(3)}$ the macroscopic third-harmonic susceptibility of the solvent, N_A Avogadro's number and the subscript 0 denotes the infinite dilution limit. At 1907 nm, γ_1, which is the isotropically averaged value $\langle \gamma \rangle$ for SINC, is found to be $(-410 \pm 30) \times 10^{-36}$ esu. Third-harmonic generation measurements at 1543 nm show that $\chi_L^{(3)}$ is independent of the SINC concentration, and therefore $\langle \gamma \rangle$ is less than the experimental uncertainty of $\pm 30 \times 10^{-36}$ esu.

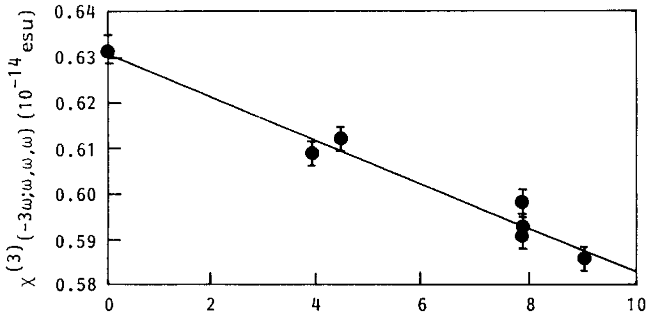

Figure 3 Concentration dependence of $\chi_L^{(3)}$ $(-3\omega;\ \omega,\ \omega,\ \omega)$ for solutions of SINC in DMF at 1907 nm fundamental wavelength

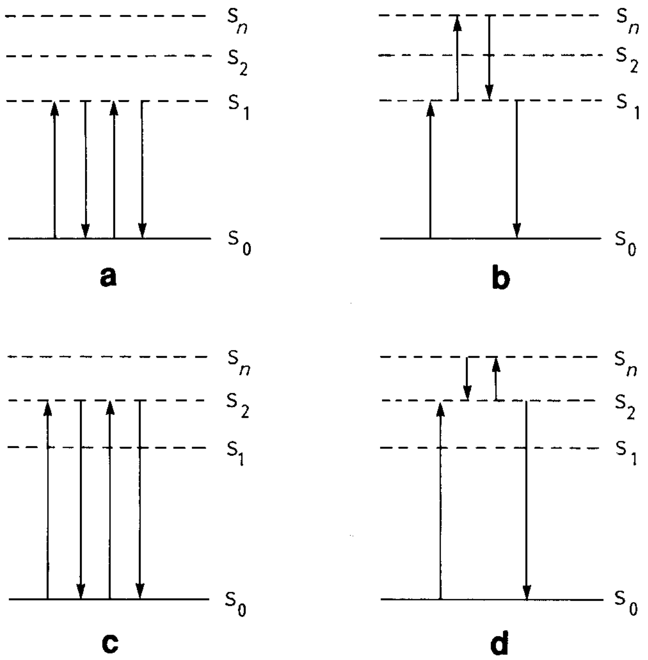

Figure 4 Key examples of third-order virtual excitation processes contributing to γ_{ijkl} $(-3\omega;\ \omega,\ \omega,\ \omega,\ \omega)$ of SINC. The (a) type I and (b) type II virtual excitation processes that involve the $S_0 \rightarrow S_1$ virtual transition dominate the (c) type I and (d) type II processes that involve the $S_0 \rightarrow S_2$ tranisition

The $\langle \gamma \rangle$ of SINC can be understood in terms of the key examples of type I and type II third-order virtual excitation processes schematically illustrated in *Figure 4*. The state S_n is a postulated large-cross-section singlet state accessible through S_1 and S_2. The $S_0 \rightarrow S_1 \rightarrow S_0 \rightarrow S_1 \rightarrow S_0$ virtual excitation process shown in (a) is a type I term deriving from the large-oscillator-strength $S_0 \rightarrow S_1$ Q-band excitation. A dominant type II term is shown in (b) where the $S_0 \rightarrow S_1 \rightarrow S_n \rightarrow S_1 \rightarrow S_0$ virtual excitation process involves both the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_n$ virtual transitions. Correspondingly, less important type I and type II virtual processes are illustrated in (c) and (d), respectively, where each involves the $S_0 \rightarrow S_2$ transition. Since the $S_0 \rightarrow S_1$ transition is much stronger than the $S_0 \rightarrow S_2$ transition, the virtual excitation processes shown in (a) and (b) dominate those shown in (c) and (d). Further, as a general rule, 2D conjugated structures have smaller non-resonant $\langle \gamma \rangle$ values than their 1D analogues[6].

For the fundamental laser frequencies used in the present experiment of SINC, the third harmonic frequencies are larger than the Q-band excitation energy at 1.59 eV. The 3ω resonance of the Q band occurs for a fundamental frequency that is one-third of the Q-band excitation energy or 0.53 eV (2334 nm), and the 3ω resonance of the 3.70 eV B band occurs for a fundamental frequency of 1.23 eV (1005 nm). Since 1907 nm is above the 3ω resonance at 2334 nm, the experimentally measured value of $\langle\gamma\rangle$ is negative for that fundamental wavelength. The close proximity of 1907 to 2334 nm also implies that $\langle\gamma\rangle$ is near-resonantly enhanced and, therefore, large in magnitude. The fundamental wavelength of 1543 nm, however, is well between the 3ω resonances of the Q and B bands, and the experimental value is very small since it lies in the cross-over region between these resonances.

RESONANT THIRD-ORDER OPTICAL PROPERTIES OF SINC

A saturable absorber exhibits the important resonant properties of non-linear absorption and non-linear refraction with increased incident light intensity. Absorption saturation has long been known for metallophthalocyanine liquid solutions[13] and only recently has it been reported for polymer films in the case of SINC[6]. Picosecond single-beam and pump–probe measurements of SINC liquid solutions have been carried out. *Figure 5* shows the saturation behaviour typically observed in the single-beam measurements of the intensity dependence of the absorption coefficient αL for 30 ps pulses at 770 nm within the Q band. SINC was dissolved in transparent cyclohexanone. The data were analysed as described previously[6]. The full curve in *Figure 5* is the least-squares fit to a Bloch-type saturable absorber of the form:

$$\alpha(I)L=\frac{\alpha_0 L}{1+I/I_S}+\alpha_B L \qquad (4)$$

where I_S is the threshold power for the saturation, $\alpha_0 L$ gives the low-intensity linear absorption, and $\alpha_B L$ is the unsaturable background absorption. The behaviour is qualitatively the same as that observed earlier for SINC films. For 30 ps pulses, the threshold intensities for saturation in the liquid samples were in the range of 30–100 MW cm^{-2}. The range in I_S values reflects sample-to-sample variations. In the presence of impurities and aggregation, both I_S and $\alpha_B L$ increase significantly.

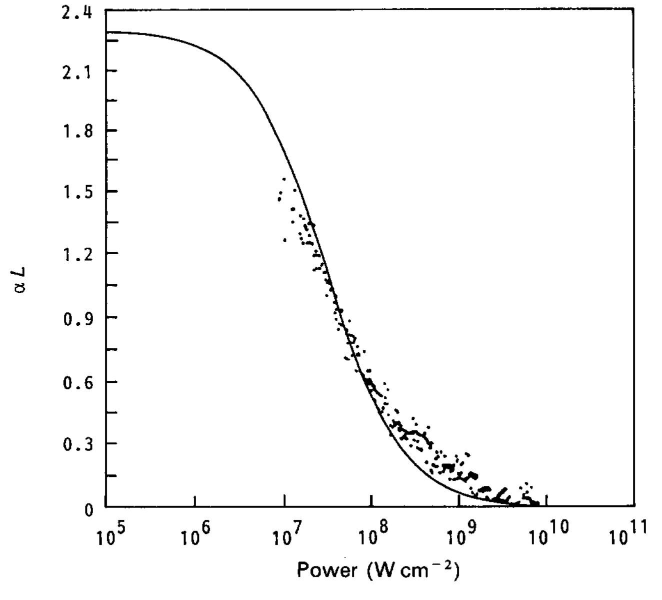

Figure 5 Saturable absorption measured at pulse width $\tau_P = 30$ ps and wavelength $\lambda = 770$ nm. The full curve is the least-squares fit to equation (4)

From the saturable absorption measurements as a function of pulse duration, one can estimate the non-linear refractive index n_2 as described earlier for SINC films[6]. From the optical susceptibility $\chi(\omega)$ for a Bloch-type system, one obtains:

$$n_2=\frac{1}{3}\left(\frac{4\pi}{n_0}\right)^2\chi^{(3)}=-\left(\frac{\alpha_0\lambda}{4\pi I_S}\right)\left(\frac{\Delta}{(1+\Delta^2)^2}\right) \qquad (5)$$

where α_0 is the linear absorption coefficient, Δ is the detuning $(\omega-\omega_0)/\Gamma$, and I_S is the saturation power. The similar saturation behaviour seen for the liquid and films is important because the value of n_2 for a SINC film is of order 10^{-4} cm^2 kW^{-1}, which is the largest n_2 value obtained for a conjugated structure[6].

CONCLUSIONS

The non-resonant and resonant optical properties of SINC liquid solutions were studied by third-harmonic generation and saturable absorption measurements. At a fundamental wavelength of 1907 nm, the isotropically averaged third-harmonic susceptibilty $\langle\gamma\rangle$ was measured to be $(-410\pm30)\times10^{-36}$ esu, while at 1543 nm, $\langle\gamma\rangle$ was less than the experimental sensitivity of $\pm30\times10^{-36}$ esu. Liquid SINC solutions can be described as easily saturable, optical Bloch systems that exhibit absorption saturation behaviour similar to SINC films, which have unusually large values for the linear absorptivity coefficient α_0 of order 10^5 cm^{-1} and intensity-dependent refractive index n_2 of order 10^{-4} cm^2 kW^{-1}. The n_2 value is the largest obtained so far for a conjugated structure and is the basis for the electronic absorptive optical bistable behaviour.

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