

SELF-FOCUSING IN NEW KERR MEDIA: LARGE THERMAL NONLINEARITY IN
METALLOTETRAPHENYLPORPHINS*

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A large optical nonlinearity of thermal origin has been observed in acetone solutions of a series of tetraphenylporphin, TPPH₂, MnTPP(CH₃CO₂⁻), FeTTPCl⁻, CoTPP, NiTPP, and CuTPP. The nonlinear Kerr coefficient is sensitively dependent on the nature of central metals in the compounds. The Mn compound exhibits the largest coefficient, $\approx 6 \times 10^{-5}$ esu, for 514 nm laser wavelength. The use of porphins offers increased flexibility in the preparation of different Kerr media.

INTRODUCTION

An optical nonlinearity in liquids can be induced by a refractive index change of thermal origin that is given by $\delta n = \alpha(dn/dT)$, where α is the linear absorption coefficient and T is the temperature [1]. This nonlinearity is nonlocal, relatively slow, and negative, i.e., defocusing occurs unless the thermal expansion coefficient is negative. Recently, Zhang and co-workers [2] reported that chlorophyll solutions possess a large nonlinear Kerr coefficient. They observed self-focusing and self-phase modulation at a power level of 5 mW using a He-Ne laser. The measured time constant and the Kerr coefficient were 100 ms and $2.8 \pm 0.8 \times 10^{-5}$ esu, respectively.

This finding of the large nonlinearity of chlorophyll and the importance of studying nonlinear effects with low-power lasers has prompted us to study substances similar to chlorophyll in their molecular structure. Synthetic tetraphenylporphin (abbreviated as TPPH₂) and its metal complexes (MTPP) are good model compounds for studying the family of porphyrins, which exist widely in nature, including the well-known chlorophyll a and b and heme of blood. These have been the subjects of numerous studies over the past decades. Investigations of the group of structural analogs of natural porphyrins which include porphins and its various metal derivatives have been productive on account of the work of Terenin [3], who proposed their use as convenient molecular models for the study of the behavior of chlorophyll in various photophysical and photochemical processes in photosyntheses. Other factors contributing to the successful study of these compounds are their great structural variety, their coordination capacity, their unusual structural properties, and their catalytic function.

The molecular structures of TPPH₂ (C₄₄H₃₀N₄) and chlorophyll are depicted in Fig. 1. Two central hydrogen atoms of TPPH₂ can be replaced by a metal atom, which is coordinated to four equivalent nitrogen atoms. The coordination field around the metal atom has a square planar symmetry. Chlorophyll involves magnesium as a central atom. Substitution by other metals is expected to exert a significant effect on the nonlinear optical properties due to the highly π -conjugated porphin ring. The results obtained indicate that all the tested compounds have coefficients greater or approximately equal to that of chlorophyll. Time constants are of the same order of magnitude. This has been confirmed by the Z-scan method [4] and a direct interferometric measurement of n_2 . The following metalloporphins were studied: TPPH₂ [Mn^{III}TTPP]⁺CH₃CO₂⁻, [Fe^{III}TTPP]⁺Cl⁻, [Co^{II}TTPP], [Ni^{II}TTPP], and [Cu^{II}TTPP].

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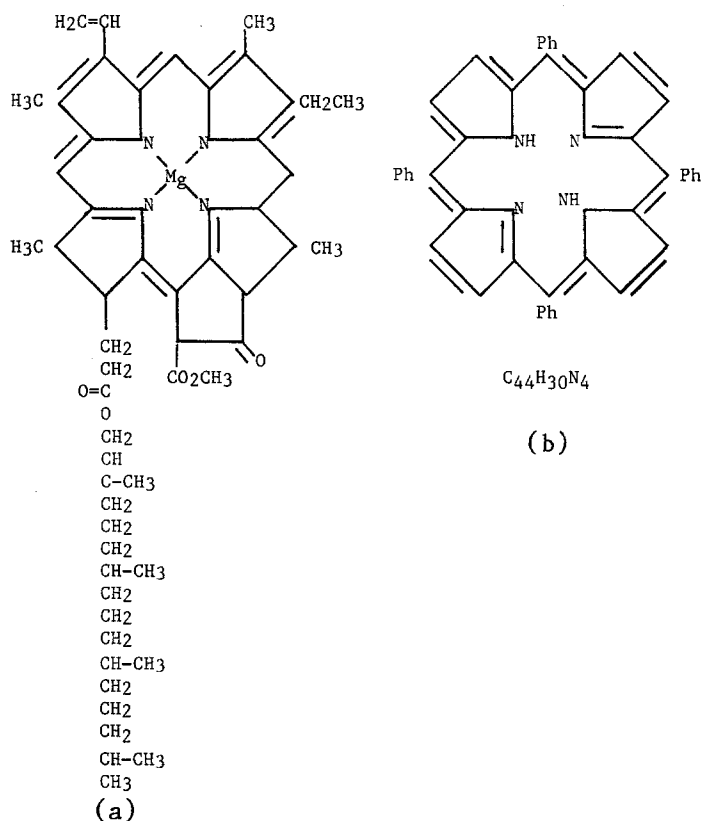


Fig. 1. Structure of chlorophyll (a) and tetraphenylporphin, TPPH₂ (b).

EXPERIMENTAL

All materials were supplied by Strem Chem. Inc. and used without further purification. In our experiments (see Fig. 2) the continuous wave (CW) output of an Ar laser was led to a cell containing a specimen made of a saturated acetone solution of the metalloporphin. A 200 mm focal length positive lens L₁ produced a 260- μ m-diameter waist at the entrance face of the cell. In this fashion, the strong defocusing caused a maximum spot size at an output plane. The index change was monitored with a Mach-Zehnder interferometer in a direction perpendicular to that of the argon laser beam. The nonlinear index change, which

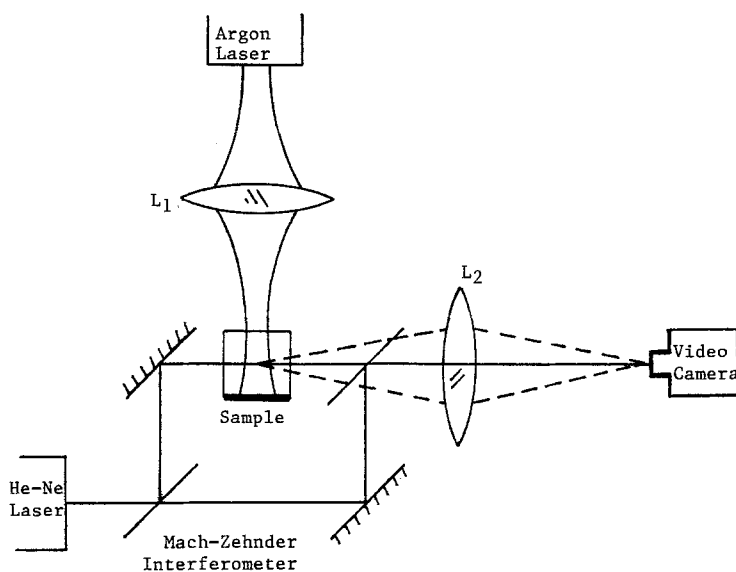


Fig. 2. Optical system employed.

was isotropic, was detected directly as a fringe motion with an unexpanded He-Ne laser beam at 633 nm. The power of this laser was kept low enough to avoid introduction of nonlinearities by its own. The sample plane was relayed to the observation plane with the aid of lens L_2 . The fringe motion, containing the transient response of the medium, was registered with a video camera.

RESULTS AND DISCUSSION

The response of the medium to CW radiation exhibited an initial stage (shown in Fig. 3a), in which an index change was induced in the medium at the onset of laser turn-on. At this stage the fringes showed a symmetrical index distribution. Then, the index pattern changed (Fig. 3b and c), due to a convection current. The pattern became stationary in approximately 0.4 sec (Fig. 3c). The resolution of a fringe shift was estimated to be 1/10 of a fringe. If we let E_0 , d , Δ , and λ be the electric field amplitude, interaction length, fringe shift, and wavelength of the argon laser, respectively, the nonlinear index is given by

$$n_2 = (\Delta \lambda) / (2d E_0^2)$$

As a reference, chlorophyll extracted from chards was used. (Chard juice was repeatedly filtered and subsequently dissolved in ethyl alcohol). Figure 4 shows the Mach-Zehnder stationary interferogram obtained for chlorophyll and the Mn compound at the same laser power for comparison. As is clearly seen in Fig. 4, the index change suffered by the Mn compound was significantly larger than that of chlorophyll. Another set of experiments was carried out by using a 7 mW He-Ne laser with a $1/e^2$ diameter of 1 mm, focused by a 280-mm

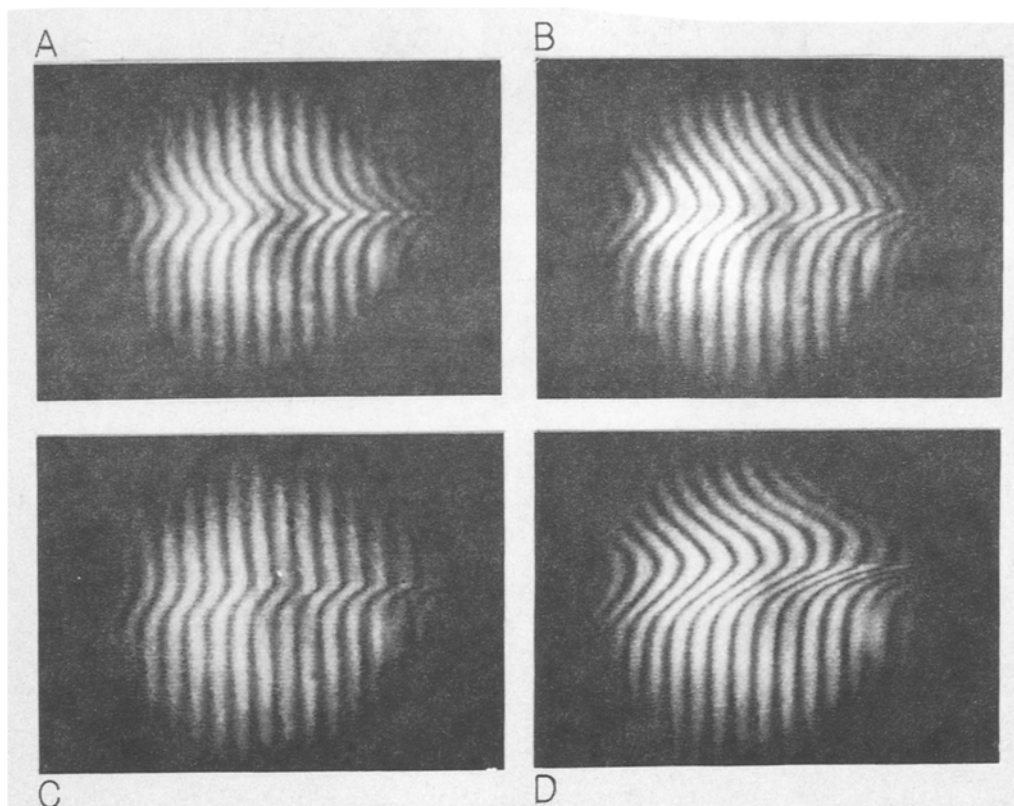


Fig. 3. Mach-Zehnder interferograms showing the response of $[\text{Mn}^{\text{III}}\text{TPP}]^+\text{CH}_3\text{CO}_2^-$ to a 50 mW, 514 nm laser beam; fringe motion toward the right-hand side indicates a decrease of the refractive index. An unperturbed medium shows straight parallel fringes whose separation is taken as the unit in fringe shift measurements. The time evolution of the refractive index appears at laser turn-on, and an equilibrium condition is observed approximately 0.4 sec from laser turn-on: a) near onset; b) convection current; c) stationary pattern. A larger convection yielded by TPPH_2 at the same illumination condition is shown in d). Light enters the medium from right to left.

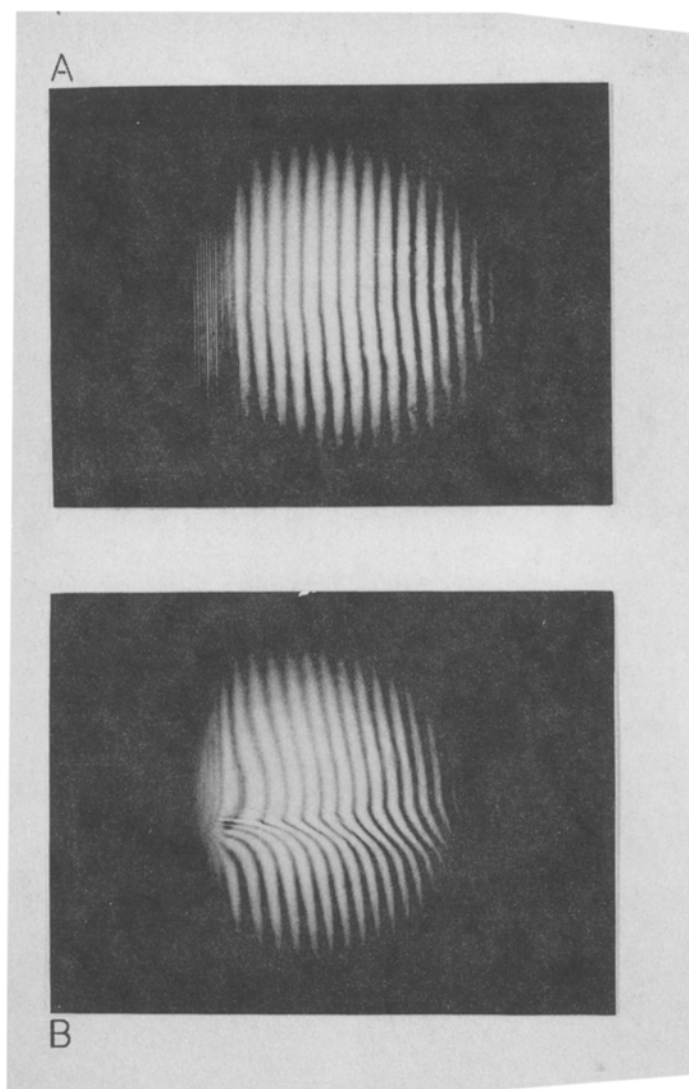


Fig. 4. Mach-Zehnder interferograms showing the response of a) chlorophyll and b) $[\text{Mn}^{\text{III}}\text{TPP}]^+\text{CH}_3\text{CO}_2^-$. Laser power is 30 mW at 488 nm. Here, light is incident from the left-hand side.

TABLE 1. Nonlinear Refractive Index n_2 for Meso-Tetraphenylporphin and Its Transition Metal Complexes at Ar-Laser Wavelengths of 488 and 514 nm

d electrons	Compound ^a	$n_2(\text{esu}) \times 10^5$		(n_2) rel. ^b	
		$\lambda 488$	$\lambda 514$	$\lambda 488$	$\lambda 514$
	Chlorophyll	1.18	1.01	1.00	1.00
0	TPPH ₂	1.91	5.98	1.62	5.92
d ⁴	$\text{Mn}^{\text{III}}\text{TPP}(\text{CH}_3\text{CO}_2^-)$	5.19	3.31	4.40	3.28
d ⁵	$\text{Fe}^{\text{III}}\text{TPP}(\text{Cl}^-)$	2.36	2.07	2.00	2.05
d ⁷	$\text{Ni}^{\text{II}}\text{TPP}$	1.18	0.84	1.00	0.83
d ⁸	$\text{Co}^{\text{II}}\text{TPP}$	1.18	0.82	1.00	0.81
d ⁹	$\text{Cu}^{\text{II}}\text{TPP}$	1.42	1.72	1.20	1.70

^aTPP: meso-tetraphenylporphin (2-) ligand.

^bRelative value referred to the n_2 of chlorophyll.

lens into a 10 × 10 mm cuvette filled with the sample solutions. Here the Z-scan method was used to measure n_2 .

Other metalloporphins also exhibited a large nonlinearity, as shown in Table 1. The n_2 value differs significantly from one compound to another. Obviously, this is due to the nature of the central metal atom, because the electronic state of the conjugated π -electron system in TPP compounds is strongly dependent on the nature of the central metal ions. A large nonlinear index was observed for the Mn^{III} compound, in which a Mn^{III} ion has vacant d orbitals that form $d\pi-p\pi$ bonding with the coordinated TPP molecule. In contrast, a relatively small n_2 was observed for the Co^{II} , Ni^{II} , and Cu^{II} compounds, in which the central atom ions have no vacant d orbital available for $d\pi-p\pi$ bond formation; a back donation from metal to ligand occurs in these compounds. These findings show evidence that the π -electron system of TPP is responsible for the large nonlinearity. The linear absorption coefficients, as measured with a spectrophotometer, ranged from 0.014 to 0.98 cm^{-1} .

In summary, solutions of metalloporphins provide sensitive Kerr media with response times of 0.2 sec. The saturated acetone solutions of $TPPH_2$ and $[Mn^{III}TPP]CH_3CO_2$ exhibit a nonlinear index of refraction 4 to 6 times larger than that of chlorophyll, for which the largest index has been reported thus far. Since the TPP complexes are highly soluble in common organic solvents, other solvents can be used to enhance the effect in rough proportion to their thermal expansion coefficient.

The electronic structure of porphins is changed over a wide range by replacing the central metal; the linear absorption coefficient at a given wavelength is sensitively dependent on the nature of the central metal. Therefore a sensitive Kerr medium that meets the user's needs with respect to laser wavelength and power level available can be readily obtained by judiciously choosing the central element. This added degree of freedom is the rationale in the use of metalloporphins as Kerr media.

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