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Third-Order Nonlinear Optical Susceptibilities of Solutions of Some Mesogenic Metallotetraphenylporphyrins by Nanosecond Degenerate Four-Wave Mixing Method

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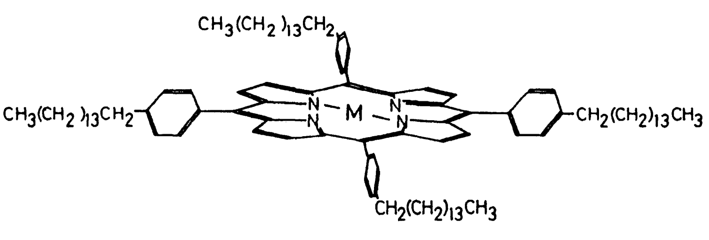
The benzene solutions of a mesogenic tetraphenylporphyrin, 5,10,15,20-Tetrakis(4-n-pentadecylphenyl)porphyrin, and its metal complexes(metal:Co,Ni,Cu,Zn, and V=O) were investigated to determine the 3rd-order nonlinear optical susceptibilities $\chi^{(3)}$ by nanosecond degenerate four-wave mixing (DFWM) at 532 nm. All solutions of approximately the same concentration($\approx 10^{-5}$ mol/l) showed $\chi^{(3)}$-values of the same order of magnitude, $\approx 10^{-11}$ esu.

Organic metal complexes are very attractive compounds for the design of novel advanced materials in the field of optoelectronics.$^{1)}$ Metal complexes possessing large extended π-conjugate systems, can be made to exhibit mesomorphic properties by attaching long aliphatic chains.$^{2)}$ In mesomorphic states, exciton migration among neighbouring molecules$^{3)}$ as well as molecular mobility could potentially influence the nonlinear optical processes. The effect by self-assembled systems are much more interesting than that in isotropic liquid and solid states, in respect to nonlinear optical phenomena. Furthermore, molecules in mesophases could easily be oriented by applied electric and magnetic fields. The nonlinear optical properties, such as $\chi^{(3)}$, of mesogenic metal complexes have not been studied extensively.

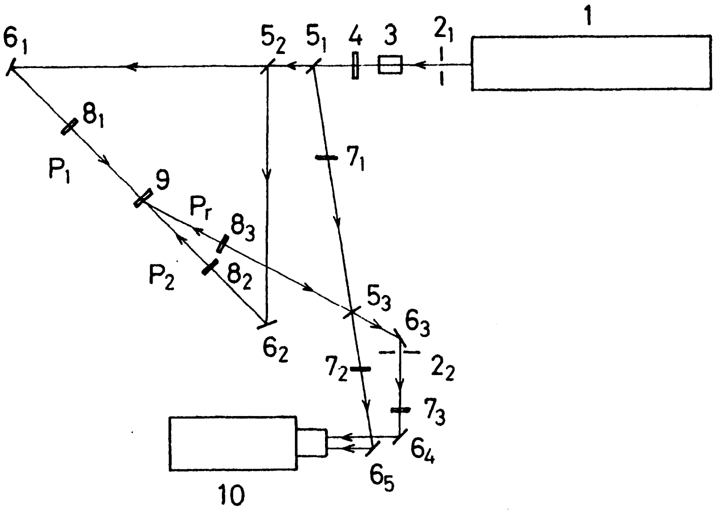


C_{15}TPPM M: H_2,V=O,Co,Ni,Cu,Zn

In this letter, $\chi^{(3)}$-values of mesogenic 5,10,15,20-Tetrakis(4-n-pentadecylphenyl)porphyrin ($C_{15}TPPH_2$) and its metal complexes (C_{15}TPPM;M:Co,Ni,Cu,Zn, and V=O) are reported. This is the first report that the

3rd-order nonlinear optical properties of mesogenic metal complexes were studied by DFWM method, as far as we know.

Standard methods of tetraphenylporphyrin and its metal complexes[4) were applied to synthesize the sample compounds. The mesomorphic properties were revealed by highly viscous states, observed between crystalline and isotropic liquid phase.[5,6)



1 : Nd:YAG laser
2_n: slit
3 : KD*P crystal
4 : $CuSO_4$ soln. and IR-cut filters
5_n: half mirror
6_n: mirror
7_n: ND filter
8_n: λ/4 plate
9 : sample
10 : streak camera
P_n: pump
P_r: probe

Fig. 1. Experimental setup for the DFWM measurements(n=1,2,...).

The experimental setup for nanosecond DFWM measurements is illustrated in Fig.1. The light source is a frequency doubled Q-switched Nd:YAG laser (Quantel YG571C), generating 532-nm-wavelength pulses of 7-ns (FWHM) and a streak camera(Hamamatsu C1587) was used as a photodetector.

The sample cell was 1 mm thick and spectroscopic grade benzene was used as solvent without further purification. CS_2 was selected as a standard material to determine the $\chi^{(3)}$ values of the samples($\chi^{(3)}_{CS_2} = 1.7 \times 10^{-12}$ esu).[7) The intensity of the phase-conjugated (pc) signal could be detected with negligible intensity generated by the solvent, at the low concentration(< 0.1 g/l), however, the solvent signal had been substracted. The details of measurement are described elsewhere.[8)

The $\chi^{(3)}$ values can be estimated by applying the following equation:

$$\chi^{(3)} = \frac{n^2 c \lambda}{24\pi^3 L} \cdot \sqrt{R} \cdot \sqrt{I_1 I_2} \times B \qquad (1)$$

$$= \chi^{(3)}_{CS_2} \left(\frac{n_s}{n_{CS_2}}\right)^2 \cdot \sqrt{R_s/R_{CS_2}} \times B \qquad (1a)$$

where n, c, L, R, I_1, and I_2 are the refractive index at wavelength λ, the velocity of light in vacuum, the sample thickness, the pc reflectivity of the sample, and back and forward pump intensities, respectively. B is a

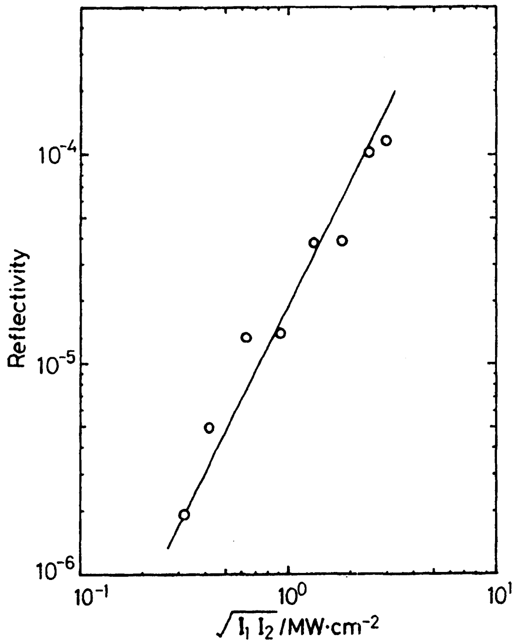


Fig.2. Plots of R vs. $\sqrt{I_1I_2}$ for C_{15}TPPCo at 0.05 g/l.

correction factor for the light absorption by the sample, given by $B = \ln(1/T)/\sqrt{T'}(1-T)$, where T and T' are the transmittance for pump and probe beam, respectively, with T=T' in the present work. Equation 1a can be used in the case that the susceptibility of the standard sample is known, with R_s and R_{CS_2} being the reflectivities, and n_s and n_{CS_2} the refractive indices of sample and CS2, respectively.

These equations can be applied, when reflectivity R is proportion to pump intensity $\sqrt{I_1I_2}$. A typical plot of R vs. $\sqrt{I_1I_2}$ is shown in Fig.2. All $\chi^{(3)}$-values determined in this work are derived from data obtained under the above proportional relation.

Table 1 shows the resulting $\chi^{(3)}$-values of benzene solutions of $C_{15}TPPH_2$ and C_{15}TPPM, obtained by applying equations 1 and 1a, denoted by $\chi_a^{(3)}$ and $\chi_r^{(3)}$, respectively.

The difference between the $\chi^{(3)}$-values obtained by both methods are very small and the $\chi^{(3)}$ of all samples are of the same order of magnitude, $\approx 10^{-11}$ esu, and comparable to those reported by C.Maloney et al. for metallotetraphenylporphyrins without substituents.[9]

Table 1. Third-order nonlinear susceptibilities of benzene solutions of $C_{15}TPPH_2$ and C_{15}TPPM (0.5 g/l) at 532 nm[a]

Compound	Susceptibility/esu	
	$\chi_r^{(3)} \times 10^{11}$	$\chi_a^{(3)} \times 10^{11}$
$C_{15}TPPH_2$	4.0	5.2
C_{15}TPPCo	5.6	7.4
C_{15}TPPNi	6.9	10.
C_{15}TPPCu	5.0	6.4
C_{15}TPPZn	1.5	——
C_{15}TPPV=O	3.2	3.5

a) $\chi_a^{(3)}$- and $\chi_r^{(3)}$- values are those obtained by applying equations 1 and 1a, respectively.

Figure 3 shows the concentration dependence of the relative pc intensity, in which the uncorrected signal shows a maximum due to the absorption of incident light. The corrected values linearly increase with concentration.

Comparative DFWM studies of the crystalline, isotropic liquid, and mesomorphic states of these compounds are in progress.

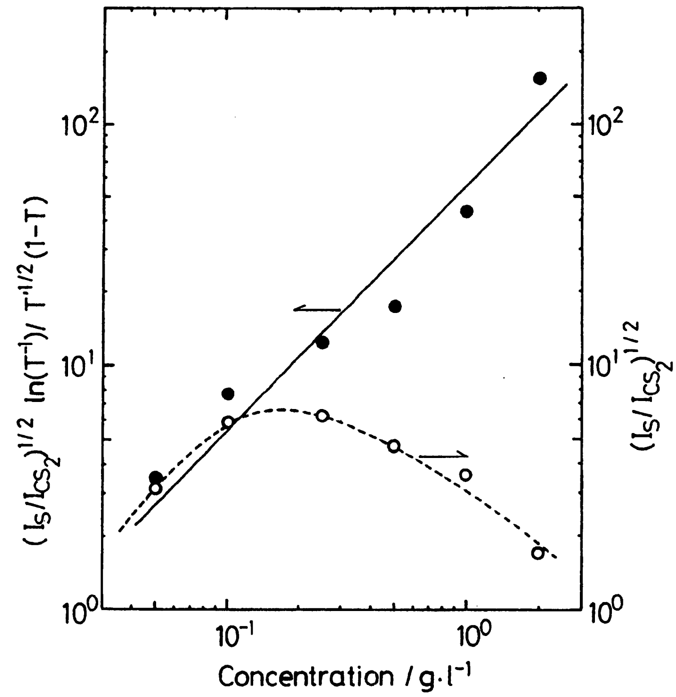


Fig.3. Concentration dependence of the relative pc intensity for C_{15}TPPCu solution.

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