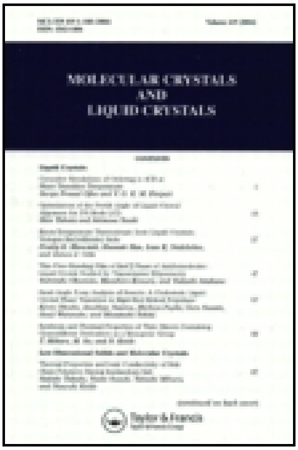

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Dependence of the Third Order Nonlinear Optical Susceptibility on Concentration and Peripheral Substituent of Metallophthalocyanines

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Third order nonlinear optical properties of metallophthalocyanines (MPcs) were investigated using degenerate four wave mixing (DFWM) method. We also studied how the replacement of peripheral substituent around the MPcs cores correlates with nonlinear optical properties. Therefore third order nonlinear optical susceptibilities ($\chi^{<3>}$) of MPcs with liquid crystal (MPcs-LC) were investigated. We found that the $\chi^{<3>}$ values of MPcs-LC increase in comparison with the corresponding values of MPcs. We supposed that this is caused by the increase of the charge transfer effects and change of the dipole moments of the molecule with the increase of molecules dimension.

Keywords: DFWM; liquid crystal (LC); metallophthalocyanines (MPcs); optical nonlinearity; third order nonlinear optical susceptibility

INTRODUCTION

Metallophthalocyanines (MPcs) have been extensively studied due to their potential applications in modern opto- and micro-electronic devices. The architectural flexibility of phthalocyanines (Pcs) facilitates the tuning of physical, chemical and optical properties over a very broad range by the change of the peripheral and axial substituents or by changing the central metal atom of the macrocycle.

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This possibility of incorporation of a variety of peripheral substituents around the phthalocyanine core as well as replacement of some of the isoindole units by other heterocyclic moieties, gives rise to different phthalocyanine analogs [1]. The physico-chemical parameters of the functional compounds can be significantly modified by intermolecular interaction and therefore can influence the nonlinear response. Delocalized two-dimensional π-electron conjugated system of substituted phthalocyanines gives rise to the large third order nonlinear optical susceptibility owing to the modified chemical and molecular structures [2–5]. Such nonlinear optical materials are very important because of their potential application in optical communications, optical storage, optical computing, harmonic generation, optical switching or optical limiting [6–8].

Liquid crystals (LCs) are known for their strong nonlinear optical properties [9]. A large contribution to the nonlinearity originates from molecular reorientation, an effect that was used to demonstrate many interesting optical phenomena, such as wave mixing, self-phase modulation, self-focusing, optical bistability, and optical Fréedericksz transitions [10].

It is well known that molecular arrangement of such systems has a strong influence on their nonlinear properties. In this work, we investigated the nonlinear optical properties of metallophthalocyanines (MPcs, where M = Co, Cu, Mg, Zn) with the liquid crystal (LC) for the original intention of exploring the possible influence of the molecule arrangement on the nonlinear optical properties of the systems. The formation of ordered aggregate in MPcs, which exerts specific effect on the electronic structure of the system, is expected to affect the nonlinear absorption properties. The interest in the bringing the phthalocyanine ring to the field of liquid crystals arises from the tendency of this macrocycle to stack up to give columnar structures, as well as its ability to form stable complexes with a wide variety of metal ions.

EXPERIMENTAL AND MATERIALS

The third order nonlinear optical susceptibilities ($\chi^{<3>}$) of metallophthalocyanines (MPcs) and host-guest systems (MPcs-LC) dissolved in tetrahydrofuran (THF) were measured by standard backward degenerate four wave mixing (DFWM) method using Nd:YAG laser (Quantel model YG472) working at 532 nm wavelength with 30 ps pulse duration and 1 Hz repetition rate [11].

Carbon disulfide (CS_2) was used as a reference material to calibrate the DFWM measurements. The third order nonlinear optical susceptibility of CS_2 was estimated to be $\chi^{<3>} = 1.65 \cdot 10^{-20}[m^2V^{-2}]$.

Purified MPcs powders, which were purchased from Sigma Aldrich Co., were dissolved in tetrahydrofuran (THF) and contained in 2 mm thick quartz cuvette. The host-guest systems (MPcs-LC) were prepared from liquid crystal (LC) (6CHBT: 1-(4-hexyl-cyclohexyl)-4-isothiocyanato-benzene), in which solutions of MPcs dissolved in THF (concentration $C = 1.0\,g/l$) were simply physically mixed and placed in 1 mm thick quartz cuvette.

RESULTS AND DISCUSSION

Figure 1 shows the comparison of absorption spectra of CoPc solution, liquid crystal (LC), and the host-guest system (CoPc-LC). We can notice that the optical absorption spectra show two major absorption regions. The single, sharp absorption peak in the visible region of CoPc solution (near 650 nm) and host-guest system of CoPc-LC (near 670 nm) spectra is associated with Q band. Small absorption peak, which we can notice in the Q band of CoPc solution, is assigned as vibrational components [12] and marked Q_{vib}. Strongly broadened peak near 320 nm in the same spectrum is called B (or Soret) band. Both the B and the Q bands are due to π-π^* transitions [11,13–17].

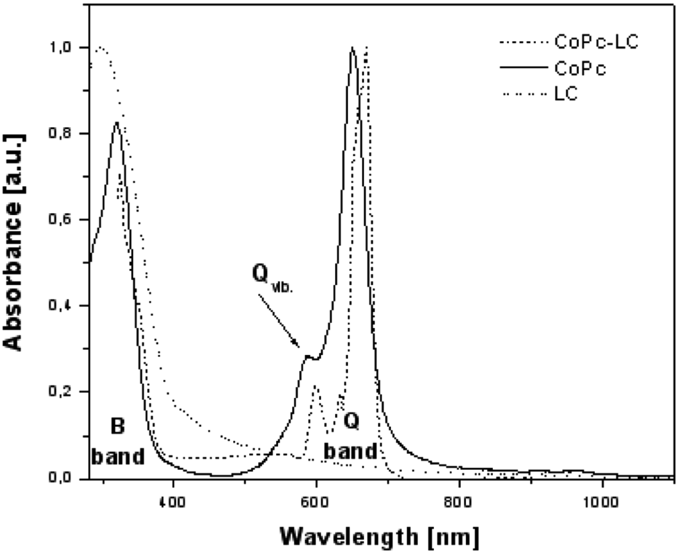

FIGURE 1 The comparison of absorption spectra of CoPc solution, liquid crystal (LC), and the host-guest system of CoPc-LC.

We can also see in Figure 1 that the LC has a small influence on the electronic structure of the CoPc molecule. This is probably caused by enhanced aggregation effect of CoPc-LC system. The aggregation phenomenon resulting in a red shift of the Q-band of CoPc-LC in comparison with CoPc is easily visible in optical absorption spectra. Similar behaviour was observed for all our metallophthalocyanines (MPcs) and host-guest systems (MPcs-LC). It is commonly known that the metal ion not only plays a crucial role in determining the shape and positions of particular bands, but also in the altering peripheral substitution in MPcs solutions [11,16].

Nonlinear optical properties of metallophthalocyanines (MPcs) and host-guest systems (MPcs-LC) solutions were investigated using nonlinear transmission and degenerate four wave mixing (DFWM) measurements at the excitation wavelength 532 nm. This is in the spectral range of the transmission window that extends from about 400 nm to about 550 nm and near the strongly absorbing Q band of MPcs (Fig. 1). Nonlinear transmission and DFWM measurements (near the Q band) of investigated solutions show strong resonant enhancement.

We used the nonlinear transmission measurement to check whether the LC and host-guest systems (MPcs-LC) possess the two-photon absorption coefficient $\beta = \frac{24\omega\pi^2\chi^{<3>\prime\prime}}{n^2c^2}$, that corresponds to the imaginary part of the third order nonlinear optical susceptibility at 532 nm in the picosecond regime. For host-guest systems (MPcs-LC) we obtained the straight lines (see Fig. 2) that intercept the ordinate axis and their values are less than unity. This allows us to consider only one-photon contribution to the absorption, and to conclude that these compounds exhibit only linear absorption at the excitation wavelength. Similar behaviour was observed for LC. Therefore, the third order nonlinear optical susceptibility is a real parameter at 532 nm, ($\chi^{<3>\prime\prime} = 0$) for LC and host-guest systems (MPcs-LC).

In the case of MPcs we noticed and recently published [16] that these compounds reveal the nonlinear absorption. The values of one-photon (α) and two-photon (β) absorption coefficients of studied compounds are presented in Table 1.

Figure 3 presents the examples of experimental and theoretical results of DFWM reflectivity (R) of host-guest systems (MPcs-LC) as a function of input pump intensity. The solid lines show the best fits to the experimental data, which were obtained from theoretical formula (1.1) taking into account only linear absorption coefficient (in the case of LC and host-guest systems) or from theoretical equation (1.2), where the linear and nonlinear absorption coefficients were took into account (in the case of MPcs dissolved in THF) [11,16,18]:

$$R = \frac{I_4(0)}{I_3(0)} = \begin{cases} \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \frac{\chi^{<3>^2} I_1(0) I_2(0)\exp(-\alpha L)}{\left[p\coth(pL) + \frac{\alpha}{2}\right]^2} & (1.1) \\ \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \frac{((\chi^{<3>\prime})^2 + (\chi^{<3>\prime\prime})^2) I_1(0) I_2(0)}{\left[q\coth(qL) - \frac{\phi}{2}\right]^2} & (1.2) \end{cases}$$

where $q^2 = \left(\frac{\phi}{2}\right)^2 - \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \left((\chi^{<3>\prime})^2 + (\chi^{<3>\prime\prime})^2\right) I_1 I_2$, $\phi = -\alpha - 2\beta(I_1 + I_2)$, and $p^2 = \frac{\alpha^2}{4} - \left(\frac{48\pi^3}{n^2 c\lambda}\chi^{<3>}\right)^2 I_1(0) I_2(0)$.

The parameters $\chi^{<3>\prime}$ and $\chi^{<3>\prime\prime}$ are the real and imaginary parts of third-order nonlinear optical susceptibility ($\chi^{<3>}$), respectively.

High instantaneous nonlinear optical susceptibilities in the resonant region have been attributed to optical pumping of the Q band. All estimated absolute values of the third order nonlinear optical susceptibility ($\chi^{<3>}$) are presented in Table 1. We observe that the values of the third order nonlinear optical susceptibility ($\chi^{<3>}$) of host-guest systems (MPcs-LC) are bigger than in the case of MPcs (see Fig. 4 and Table 1). We suppose that this is probably caused by increase of the charge-transfer effects and the change of the dipole moments of the molecules with the increase of the molecule dimension.

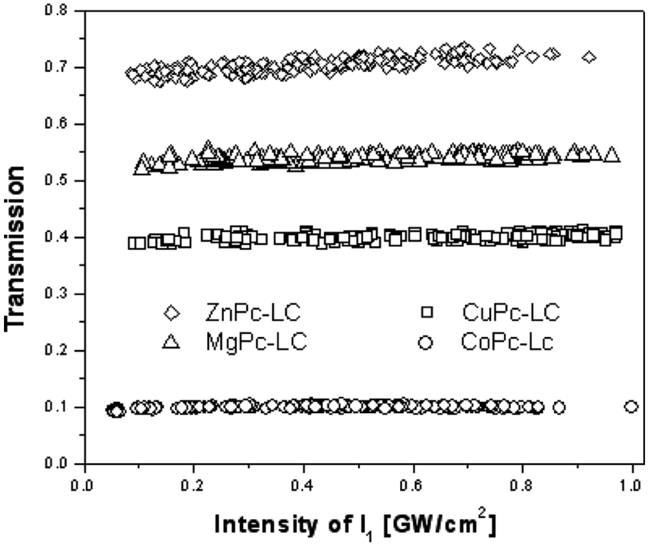

FIGURE 2 The transmission of host-guest systems (MPcs-LC) as a function of incident pump intensity.

TABLE 1 The Values of the Single (α) and Two-Photon (β) Absorption Coefficients, the Imaginary Parts ($\chi^{<3>''}$) of the Third Order Nonlinear Optical Susceptibility, and the Absolute Values of the Third Order Nonlinear Optical Susceptibility ($\chi^{<3>}$) of MPcs, LC and Host-Guest Systems (MPcs-LC) ($\lambda = 532\,\text{nm}$, $\tau = 30\,\text{ps}$)

Samples	α [cm^{-1}]	β [cmGW^{-1}]	$\chi^{<3>''} \cdot 10^{13}$ [esu]	$\lvert\chi^{<3>}\rvert \cdot 10^{19}$ [m$^2V^{-2}$]
ZnPc	5.02	2.04	7.33	1.12
MgPc	8.57	1.73	5.50	0.41
CoPc	9.23	1.45	5.22	0.23
CuPc	12.48	1.25	3.83	0.17
ZnPc-LC	3.57	–	–	1.29
MgPc-LC	6.54	–	–	1.42
CoPc-LC	22.8	–	–	1.04
CuPc-LC	9.16	–	–	0.19
LC	9.92	–	–	0.004

We can observe that the interaction between MPcs and LC molecules is very effective and causes the increase of optical nonlinearity. Effectively, we can observe in the host-guest systems (MPcs-LC)

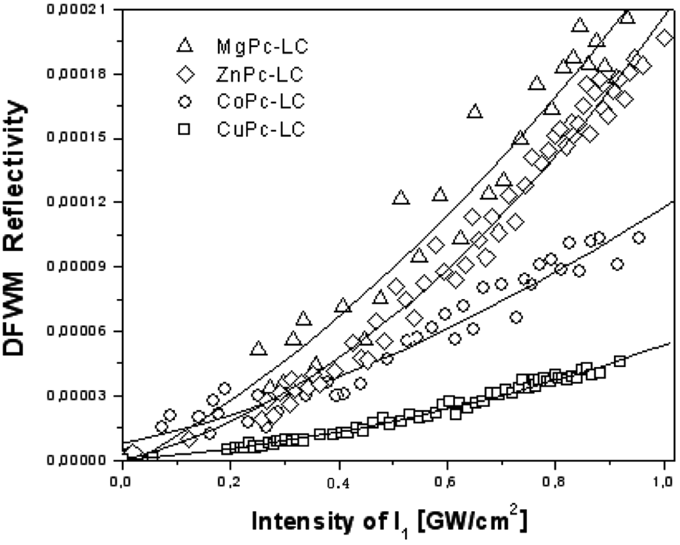

FIGURE 3 DFWM reflectivity (R) of host-guest systems (MPcs-LC) as a function of input pump intensity.

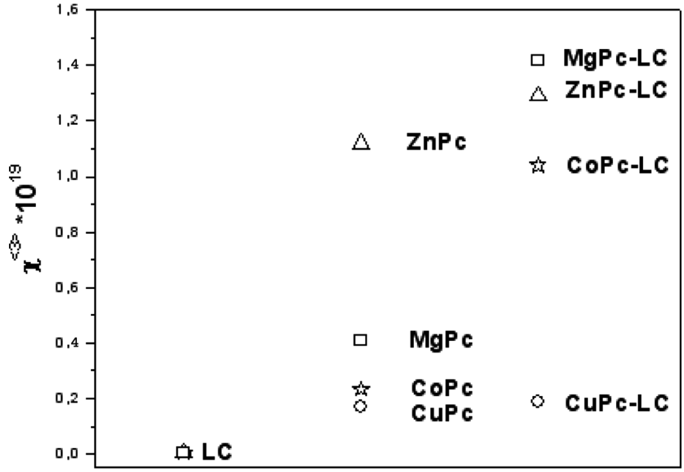

FIGURE 4 Changes of the third order nonlinear optical susceptibilities ($\chi^{<3>}$).

increase of efficiency in the degenerate four wave mixing experiment in comparison with MPcs.

The dramatic enhancement in $\chi^{<3>}$ that we observed in the host-guest systems (MPcs-LC) classifies them as a new potential class of materials for nonlinear optical devices.

CONCLUSIONS

In this work, we present the results of the measurements of third order nonlinear optical susceptibility ($\chi^{<3>}$) of metallophthalocyanines (MPcs, where M = Co, Cu, Mg, Zn), liquid crystal (LC), and host-guest systems (MPcs-LC). The $\chi^{<3>}$ values of studied compounds were measured using standard backward degenerate four wave mixing (DFWM) method. The DFWM experiment was conducted at 532 nm, so the larger $\chi^{<3>}$ value of studied materials could arise from the one- and two-photon resonant contributions at the Q and B-band regions, respectively.

We studied how the substituting of peripheral substituent around the metallophthalocyanines (MPcs) cores correlates with nonlinear optical properties. We investigated the nonlinear optical properties of host-guest systems (MPcs-LC) with the original intention of exploring the possible influence of the molecule arrangement on the nonlinear optical properties of the systems. The formation of ordered aggregates in MPcs, which exerts specific effects on the electronic structure of the system, is expected to affect the nonlinear absorption properties. We observed that the value of third order nonlinear optical susceptibilities ($\chi^{<3>}$) of host-guest systems (MPcs-LC) increase in comparison with the corresponding values of MPcs. We suppose that this is due to the increase of the charge-transfer effects and the change of the dipole moments of the molecules with the increase of the molecules dimension. Effectively, we can observe in the host-guest systems (MPcs-LC) high diffraction efficiency in the degenerate four wave mixing experiment. In this connection we can see how the substituting of the peripheral substituent around the metallophthalocyanines cores correlate with nonlinear optical properties. The dramatic enhancement in $\chi^{<3>}$ that we have observed in host-guest systems (MPcs-LC) classifies them as a new potential class of materials for nonlinear optical devices.

We also found that the third order nonlinear optical susceptibility ($\chi^{<3>}$) values of the ZnPc and MgPc are larger than CuPc and CoPc. We supposed that the attenuation of third order nonlinear optical susceptibility ($\chi^{<3>}$) of CuPc and CoPc comes from the d valence orbital contribution of central metal atom. Moreover, the question of planarity or non-planarity of MPc molecules is still controversial especially for ZnPc and MgPc [19,20]. That is why we cannot exclude that enhancement of ($\chi^{<3>}$) in these cases is connected with molecular deformation.

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