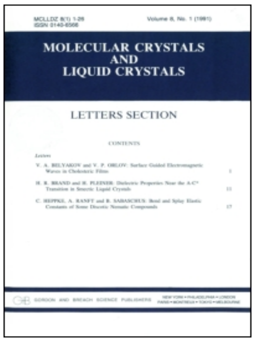

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The effect of solvent polarity on second order hyperpolarizability of selected phthalocyanines complexes

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ABSTRACT

The effect of the solvent polarity on nonlinear optical properties of selected phthalocyanines complexes of copper, cobalt, zinc and magnesium using degenerate four wave mixing (DFWM) method is presented. Ethanol and dimethyl sulfoxide were used as solvents for all studied complexes. The solvent effect is observed for the absorption spectra of metal phthalocyanines (MPcs) solutions. It was noticed that the solvent polarity as well as the central metal ion play a crucial role in determining the values of the second order hyperpolarizability (γ_{eff}) of studied macrocyclic compounds. In general, γ_{eff} values of MPcs solutions are changing with change of the solvent polarity in order of ZnPc > MgPc > CuPc > CoPc. And these values are higher for samples dissolved in polar aprotic solvent than in polar protic solvent.

KEYWORDS

Metal phthalocyanines (MPcs); Nonlinear optics; Second order hyperpolarizability; Solvent effect; DFWM

1. Introduction

Organometallic compounds such as metal phthalocyanines (MPcs) are very interesting because of their physicochemical properties, versatility, exceptionally high thermal stability, architectural flexibility, simplicity and low-cost production technology, which provide serious competition for traditional semiconductor materials currently used in micro- and optoelectronics. They can be used in organic light emitting diodes (OLED), organic field effect transistors (OFET), photovoltaic cells (PV), gas sensors and nonlinear optics [1–6].

MPcs represent a large family of π-conjugated materials, which are of interest in all optical devices (e.g. optical communication, optical storage, optical computing, optical switching, optical limiting, optical rectifying devices, optical recording) [7–10].

Metal phthalocyanines are called the macrocyclic compounds (ring structure), where the central atom or ion is bonded with ligands. They are characterized by high symmetry and extensively delocalized π-electron systems. Therefore, they possess the large values of nonlinearities, which can be changed by the manipulation of the electronic distribution of the macrocyclic core [6, 11].

The goal of this paper is to show how the solvent polarity affects on nonlinear optical properties of selected macrocyclic compounds. Therefore, the influence of the solvent polarity on the second order hyperpolarizability (γ) of selected metal phthalocyanines is presented. MPcs powders (where M = Co, Cu, Zn, Mg) were dissolved in polar protic and aprotic solvents:

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ethanol (EtOH) and dimethyl sulfoxide (DMSO), respectively. The second order hyperpolarizability (γ) of metal phthalocyanines were extracted from degenerate four wave mixing method.

2. Experimental

Nonlinear optics is the branch of optics, which describes the phenomena that occur as a consequence of the modification of the optical properties of a material by the presence of laser light. Therefore, in nonlinear optics regime, the electric polarization vector ($\vec{P}$) is assumed to be a power series of the electric field ($\vec{E}$):

$$\vec{P_i} = \chi_{ij}^{<1>}\vec{E_j} + \chi_{ijk}^{<2>}\vec{E}_{jk} + \chi_{ijkl}^{<3>}\vec{E}_{jkl} + \ldots \tag{1}$$

where $\chi^{<1>}$ is the linear susceptibility, $\chi^{<2>}$ and $\chi^{<3>}$ are the second and the third order nonlinear optical susceptibilities, respectively.

At the molecular level, a similar equation can be written for the light-induced molecular dipole moment:

$$\vec{p} = N\left(\alpha_{ij}\vec{E}_{loc} + \beta_{ijk}\vec{E}_{loc}^{2} + \gamma_{ijkl}\vec{E}_{loc}^{3} + \ldots\right) \tag{2}$$

where α_{ij} is the linear polarizability, β_{ijk} and γ_{ijkl} are the first order and the second order hyperpolarizabilities, respectively.

In the approximation of Lorentz-Lorentz local field model the $\vec{E}_{loc}$ can be expressed as follows:

$$\vec{E}_{loc} = F\,\vec{E} \tag{3}$$

where F is the local field correction factor ($F = \frac{(n^2+2)}{3}$), n is the refractive index of solution [12].

Therefore, the second order hyperpolarizability (γ) characterizing molecular optical nonlinearities can be estimated through the following equation:

$$\gamma = \frac{\chi^{<3>}}{F^4 N} = \frac{\chi^{<3>} M}{F^4 N_A C} \tag{4}$$

where N is the number of active species in the system per unit volume, N_A is Avogadro's number, C is the concentration of the solute, M is the molar mass.

Degenerate four wave mixing method is used to determine the effective value of the third order nonlinear optical susceptibility ($\chi_{eff}^{<3>}$). In general, DFWM is the third order nonlinear optical process, in which two pump and one probe laser beams interact within material to generate a phase-conjugated beam [1, 4, 13–15]. The formation of the fourth beam can also be explained by a diffraction grating model, in which two beams interfere inside the sample to form the diffraction grating of nonlinear refractive index and/or the diffraction grating of absorption. The third beam diffracts on this grating to form a phase-conjugated signal that retraces the probe path [14]. Therefore, the effective value of the third order nonlinear optical susceptibility ($\chi_{eff}^{<3>}$) can be determine from the DFWM experimental data and below formula [16]:

$$\chi_{eff}^{<3>} = \left(\frac{n}{n_{ref}}\right)^2 \left(\frac{L_{ref}}{L}\right) \left(\frac{a}{a_{ref}}\right)^{1/2} \frac{\alpha L e^{\alpha L/2}}{1 - e^{-\alpha L}} \chi_{ref}^{<3>} \tag{5}$$

where n is the refractive index, L is the thickness, a is the coefficients calculated from the experimental data using the following expression $I_4 = aI_1^3$ (the subscript *ref* refers to reference material).

In the present work DFWM measurements were performed using a Nd:YAG laser (Quantel Model YG472) working at 532 nm (30 ps, 1 Hz). The experimental set-up of DFWM is described elsewhere [1–5, 17–18]. The absorption spectra of solution were performed using a double beam Perkin-Elmer UV-VIS Lambda 2 spectrophotometer.

Selected phthalocyanines complexes coordinated with transition metal ions such as copper (Cu^{2+}), cobalt (Co^{2+}), zinc (Zn^{2+}) and magnesium (Mg^{2+}) were purchased from Sigma Aldrich Co. These compounds differ in the degree fill of *3d* subshell: the magnesium phthalocyanine (MgPc) is devoid of *3d* electrons (closed shell structure), zinc phthalocyanine (ZnPc) has completely filled *d*-shell (closed shell structure), while cobalt phthalocyanine (CoPc) and copper phthalocyanine (CuPc) have the unfilled *3d* orbital (open shell structures).

Metal phthalocyanines (MPcs) were dissolved in ethanol (EtOH) and dimethyl sulfoxide (DMSO), and their concentration was 1 g/L. The solvents, which were used during the DFWM experiment, possess different polarity. DMSO is polar aprotic solvent whereas ethanol is polar protic solvent (see Table 1) [19]. The quartz cuvette at 1 mm thickness were used for all DFWM measurements. Carbon disulfide (CS_2) was used as the reference material to calibrate the DFWM measurements. The value of the second order hyperpolarizability of CS_2 was experimentally obtained and is $\gamma = 4.70 \cdot 10^{-49}$ m^5/V^2.

Table 1. Some parameters of solvents: n_D - refractive index of pure solvent at the average *D*-line of sodium at 20°C, *SA* - empirical parameter of solvent hydrogen-bond donor acidity, *SB* - empirical parameter of solvent hydrogen-bond acceptor basicity, μ - dipole moment $1D \approx 3.33564 \cdot 10^{-30}$ *Cm*, ε_r - dielectric constant of the pure liquid at 25°C [19].

Solvent	Nature	n_D	*SA*	*SB*	μ [D]	ε_r
DMSO	Polar aprotic	1.4793	0.072	0.647	3.9	46.45
EtOH	Polar protic	1.3614	0.400	0.658	1.7	24.55

3. Results and discussion

The molecular structure of metal phthalocyanines is shown in Fig. 1. Ligand phthalocyanine ($Pc = C_{32}H_{16}N_8{}^{-2}$), which consists of four isoindole rings (pyrrole ring + benzene) connected

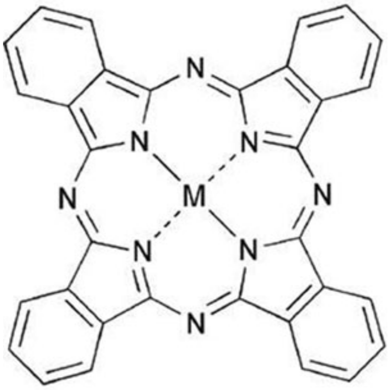

Figure 1. Molecular structure of metal phthalocyanines ($C_{32}H_{16}N_8M$).

by azomethane bridge, is able to bind in its centre a metal cation (= forming MPcs). Coordination bonds are formed between the central atom and four nitrogen atoms of isoindole rings. The number of electrons associated with the metal in the complex (both from metal and from the ligand) is 18. Therefore, this system of 18 electrons surrounding metal is highly delocalized forming so-called two-dimensional coupled system of 18π [1, 4, 20].

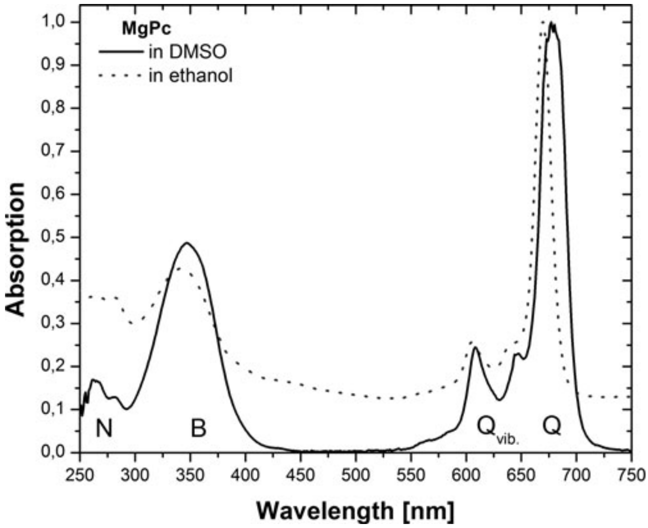

Figure 2. Absorption spectra of MgPc dissolved in different solvents.

For clarity, Figure 2 shows only the example of the absorption spectra of magnesium phthalocyanine (MgPc) dissolved in ethanol (EtOH) and dimethyl sulfoxide (DMSO). It should be noted that the absorption spectra of the studied metal phthalocyanines are very similar. However, in the dependence of the substituted metal into MPcs core one can observe some changes in the energy structure [1–4].

From Figure 2, one can notice that there are two main absorption bands centred on the phthalocyanine ligand (conventionally labelled as Q and B bands). The narrow Q-band (at about 670 nm) and a relatively wide B-band (at about 345 nm) arise due to $\pi \rightarrow \pi^*$ transitions on the phthalocyanine macrocycle. Much wider B-band is associated with shorter molecules lifetime in this state and the contribution of several overlapping resonances lines. One can notice that there are at least two electronic transitions overlapping in the B region. In Q-band, one can see two additional absorption peaks (at about 605 nm and 640 nm), which are assigned as vibrational components ($Q_{vib.}$-bands). In Figure 2, one can also see the N-band (at about 282 nm), which is strongly related to the variations of electron density on the pyrrole nitrogen atoms. These atoms are responsible for the coordination of the central atom in the MPcs complex formation. Therefore, this band is the most sensitive to substitutions of the central metal atom. In N-band region, one can observe clear doublet structure, which is not due to Davydov splitting. In contrast, Davydov splitting is observed both for the Q and B (Soret) bands [1, 4, 20].

From Figure 2, one can also see the shift of absorption spectra in dependence on the different solvent polarity. Moreover, the solvent effect leads to changes in the widths and shapes of absorption bands. Comparing the absorption spectra of various MPcs described elsewhere [1–5, 7–10], one can conclude that the solvent polarity as well as the central metal ion play a crucial role in determining the shape and position of each band. The differences related to the position and intensity of the absorption bands of all studied metal phthalocyanines are due to varying degrees of interaction a metal ion [1, 20] and solvent with π-electron system of the macrocycle.

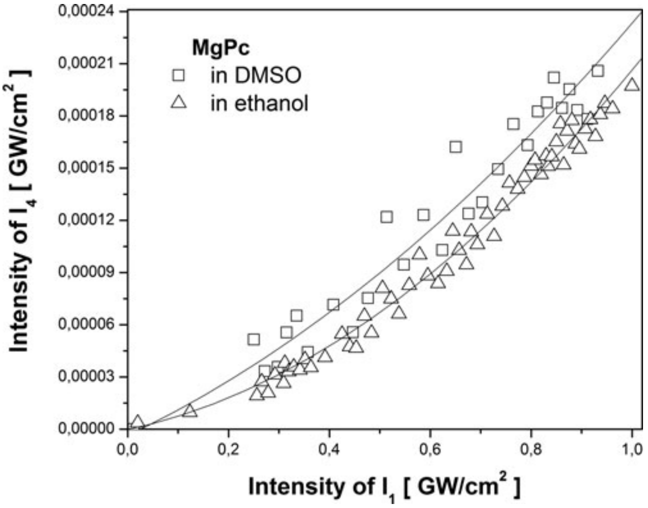

Figure 3. Phase-conjugated signal (I_4) as a function of the pump signal (I_1).

Typical plots of the a phase-conjugated signal (I_4) as a function of the pump signal (I_1) is presented in Figure 3 [1–5, 17–18]. From the DFWM experimental data as well equations (5) and (4) one can calculate the effective values of the second order hyperpolarizability (γ_{eff}) for MPcs dissolved in different solvent polarity (see Table 2). It should be mention that the used solvents possess the value of third order nonlinear optical susceptibility. These values are weak but they cannot be neglected. Therefore, these values were taken into account during calculation the values of the second order hyperpolarizability.

From Table 2, one can see that the effective value of the second order hyperpolarizability (γ_{eff}) is changed with changing the solvent polarity (compare Tables 1 and 2). This singularity is often observed for π-conjugated compounds possessing an intense electron transition (usually $\pi \rightarrow \pi^*$) in the UV–Vis region, which is assigned to the intramolecular charge-transfer (CT) occurring along the molecular axis. Generally, origins of solvent effect are well understood and directly connected with the intermolecular interactions between the solute and solvent in the ground and excited states [19]. On the other hand, in polar protic solvent, the aggregation tendency of MPcs becomes stronger. This can be related with the enhancement to aggregation by hydrogen bonding formation by the active hydrogen atom in polar protic solvent. Polar aprotic solvent has no active hydrogen atoms to form hydrogen bonding with phthalocyanine. Thus the relations of aggregation of MPcs

Table 2. Effective values of the second order hyperpolarizability (γ_{eff}) for studied materials dissolved in different solvents.

	$\gamma_{eff} \times 10^{45}$ [m^5/V^2]			
	CoPc	CuPc	MgPc	ZnPc
DMSO	3.07	4.09	4.10	4.14
EtOH	2.89	3.95	4.00	4.04

are not obvious [21]. Thus, one can observed that the values of the second order hyperpolarizability are higher for MPcs dissolved in polar aprotic solvent than in polar protic solvent.

From Table 2 it can be also noted that the values of the second order hyperpolarizability are changing with changing the central metal ion into the phthalocyanines ring. This behavior is not surprise because it depends on the degree of interaction of the metal ion with π-electron system of the macrocycle. The degree of influence depends on the number of electrons on the outer shell *3d* of the central cation [1,4]. The changes of γ_{eff} of metal phthalocyanines can be also explained from the electronic structures of the upper occupied and lower vacant molecular orbitals for the ground states of MPcs. The lowest energy molecular orbitals of CuPc and CoPc are different from those of ZnPc and MgPc. The valence electronic structures of ZnPc and MgPc are very similar and they exhibit a large gap between the HOMO and LUMO. Therefore in the energy structure of metal phthalocyanines with the central metal ion, which is devoid of *d* electrons (MgPc) or is in configuration of d^{10} (ZnPc) mutual mixing of metal and ligand orbitals is neglected. As a result, all the observed transitions occur between centring orbitals on the ligand phthalocyanine (Pc). Whereas, phthalocyanines containing certain transition metals (such as CuPc, CoPc) have a more complex energy structure because *3d* metal orbital lies between HOMO (π) and LUMO (π^*) levels of Pc ring. Therefore, that can cause decrease in the value of the second order hyperpolarizability of CuPc and CoPc in comparison with ZnPc and MgPc. This suggests that the different electronic transport behaviour observed in the different MPcs can be directly related to the properties of molecular orbitals [1,4,22].

Differences in the nonlinear optical properties of studied MPc can also be related to the size of the phthalocyanine cavity ring and its deflection as well as the symmetry of the molecule. Co^{2+} and Cu^{2+} ions have a similar size to the size of the phthalocyanine cavity ring (approx. 3.82Å – 3.86Å) and at room temperature they represent the macrocycle in the equilibrium geometry. As a result, their structures are planar and have D_{4h} symmetry. Contrary to this, the Zn^{2+} ion is larger than the equilibrium cavity ring but not so large that it cannot be placed in it. This results in tension of the ring and as a consequence the cavity dimensions of ZnPc is the greatest (approx. 3.96Å) and can cause increase in the value of the second order hyperpolarizability. On the other hand, the Co has the smallest atomic radius from the other metal atoms (Cu, Zn and Mg). Therefore, one can say that the smaller the atomic radius the stronger the chemical action. Thus it can be deduced that CoPc has greater chemical stability and relatively small tendency for dimerization in solvents among the other MPcs.

4. Conclusions

In this paper, the effect of the solvent polarity on the second order hyperpolarizability (γ_{eff}) of metal phthalocyanines (MPcs, where M = Co, Cu, Zn and Mg) is presented. The γ_{eff} values of MPcs dissolved in polar protic (ethanol) and polar aprotic (dimethyl sulfoxide) solvents have been determined from standard backward degenerate four wave mixing method at 532 nm.

It was found that the studied compounds exhibit large values of the second order hyperpolarizability, which depend on the solvents polarity as well as on the central metal ion. Therefore, the γ_{eff} values are higher for MPcs dissolved in polar aprotic solvent than in polar protic solvent.

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