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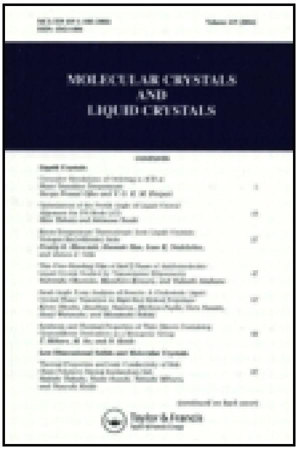

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Asymmetric Porphyrins and Metalloporphyrins for Nonlinear Optics

Jingui Qin [a] [b] , Tatsuo Wada [a] & Hiroyuki Sasabe [a]

[a] Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-01, Japan

[b] Department of Chemistry, Wuhan University, Wuhan. Hubei, 430072, People's Republic of China

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ASYMMETRIC PORPHYRINS AND METALLOPORPHYRINS FOR NONLINEAR OPTICS

JINGUI QIN*, TATSUO WADA and HIROYUKI SASABE
Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama, 351-01, Japan

Abstract A series of meso-monosubstituted porphyrins and metalloporphyrins, MOEP-X (M = 2H or Zn; OEP = octaethylporphyrin; X = NO_2, CN or CHO) and ZnTPP-NO_2 (TPP = tetraphenylporphyrin), were synthesized and characterized. The effect of the substituents and metals on the dipole moment is discussed. A preliminary investigation of the nonlinear optical property is presented.

INTRODUCTION

In the search for new nonlinear optical (NLO) materials, there has recently been increased attention in phthalocyanines and metallophthalocyanines[1-3]. The molecules studied so far are mainly of symmetric structure, and consequently, third order NLO properties are normally observed.

Porphyrins and metalloporphyrins are also two-dimensional conjugated π-electron macrocyclic systems with strong absorptions in the near-UV and visible region. Normally, they are very stable and melt at quite high temperature without decomposition. For example, the porphyrin nucleus is stable to concentrated sulfuric acid. Additionally, compared with phthalocyanines, porphyrins are more soluble, and their structure and properties are easier to modify. These features, therefore, make them attractive candidates for electro-photonic materials.

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* Permanent address: Department of Chemistry, Wuhan University, Wuhan, Hubei, 430072, People's Republic of China.

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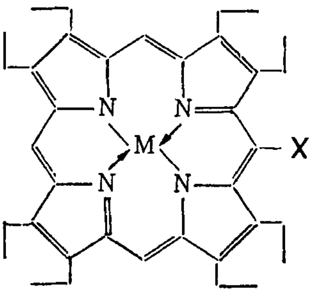
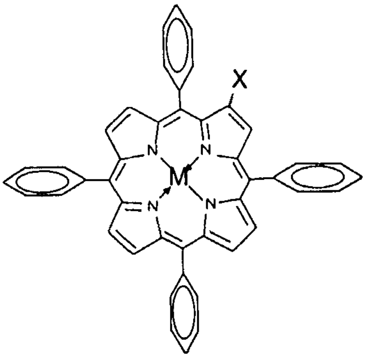
We are interested in the study of the second order NLO property of porphyrins. It is well established that an asymmetric molecular structure with intramolecular charge transfer is the first requirement in the molecular engineering of the organic second order NLO materials. This paper describes the synthesis, characterization, dielectric property and some preliminary results of the NLO properties of some asymmetric porphyrins and metalloporphyrins.

SYNTHESIS AND CHARACTERIZATION

Two types of porphyrins have been chosen as the parent molecules, namely OEP (octaethylporphyrin) and TPP (tetraphenylporphyrin). The electron-withdrawing substituents are attached directly to the periphery of the π-electron systems, which have the structure shown below.





1 M = 2H X = NO_2
2 Zn NO_2
3 2H CHO
4 2H CN
5 Zn CN

6 M = Zn X = NO_2

The reaction of OEP with the ice-cold mixture of fuming nitric acid and glacial acetic acid (1:1 in volume) for 80 seconds gave **1**. The Vilsmerer reaction of CuOEP gave **3**. The treatment of **3** with hydroxylamine hydrochloride followed by treatment with acetic anhydride yielded **4**. **6** was prepared by the nitration of ZnTPP with silver nitrate and iodine. The zinc complexes **2** and **5** were

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prepared by the reaction of the corresponding free base porphyrins with zinc acetate. All the compounds were purified by column chromatography and recrystallization.

The molecular structure of all the compounds was confirmed by elemental analysis, NMR, IR, mass and UV-visible spectroscopies. As an example, the following are the characterization data for the compound **5**,

Elemental analysis (%) :

Found: C 70.80, H 6.96, N 11.03;

Calcd. for $C_{37}H_{43}N_5Zn$:

C 71.30, H 6.95, N 11.24.

^{1}H NMR data in $CDCl_3$, (δ_{ppm}) :

9.92 (s, 2H): β, δ-meso-H ;

9.88 (s, 1H): γ-meso-H ;

4.33(q, 4H), 4.03(q, 4H), 3.97(q, 4H), 3.96(q, 4H): CH_2 ;

1.90 (t, 6H), 1.82-1.87 (m, 18H): CH_3 .

Mass spectrum (SIMS): m/z 621 (M^+)

IR (KBr): $\nu_{C\equiv N}$ 2211 cm^{-1}

UV-visible spectrum (in benzene) ;

λ_{max}: 414.0, 551.4, 591.4 .

DIPOLE MOMENT

The dipole moments of all the compounds were calculated, using the Guggenheim-Palit equation[4], from the dielectric constants which were measured in benzene. Table 1 shows the results:

TABLE 1 Dipole moment of the compounds

Compound	μ (D)
1	4.6
2	6.0
4	6.2
5	8.0
6	5.9

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It is well known that the electron-withdrawing ability of a nitro (NO_2) group is stronger than that of a cyano (CN) group. However, the cyano compounds (**4** and **5**) showed higher values of the dipole moment than the corresponding nitro compounds (**1** and **2**). Here, steric hindrance between the meso- and β-pyrrole substituents (ethyl) appears to play an important role (see Fig.1). The nitro group is not coplanar with the porphyrin ring, resulting in a less effective conjugation and charge-transfer. On the other hand, the linear cyano group is coplanar with the macrocyclic ring, giving rise to the effective charge-transfer.

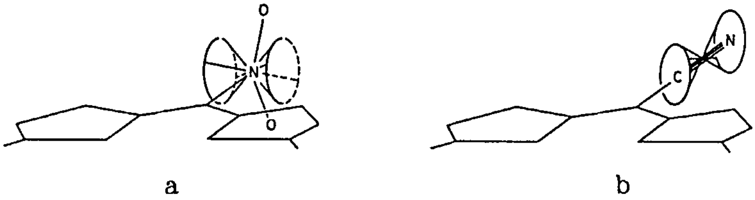

FIGURE 1. Schematic representation of the steric hindrance of meso-substituted OEP: (a) NO_2; (b) CN.

The dipole moments of the zinc complexes (**2** and **5**) are obviously higher than those of the corresponding metal-free porphyrins (1 and **4**). It was well established that insertion of the electronegative metals (e.g. Mg, Zn, Cu, etc.) renders the porphyrins more reactive for reactions with oxidants and electrophiles[5] due to the metal-to-ligand-charge-transfer (MLCT). In these monosubstituted metalloporphyrins, metal atoms behave as the electron donors, while the nitro and cyano groups are the electron acceptors.

Comparing the dipole moments of **2** with **6**, it seems that there is no big difference between the two types of porphyrins. This is not suprising since both compounds contain the same metal as well as the same substituents which are attached directly to the periphery of the macrocyclic π-electron cores which are essentially the same.

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NONLINEAR OPTICAL PROPERTY

Currently, electric-field-induced second harmonic generation (EFISH) measurements are being performed in order to evaluate the second-order molecular polarizabilities (β) of the compounds.

Thin films of the compound **1** in a glassy polymer matrix were prepared by spin coating onto indium-tin-oxide (ITO) coated glass. Corona-poling was performed to achieve the alignment of the porphyrin molecules. In situ spectroscopic absorption measurement was carried out during poling and depoling. Optical second harmonic generation (SHG) of the poled films was measured. All the measurements have confirmed the second order nonlinear optical response. Further studies are in progress.

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