Theoretical Study on Metalloporphyrins with Large Second-order Hyperpolarizabilities†

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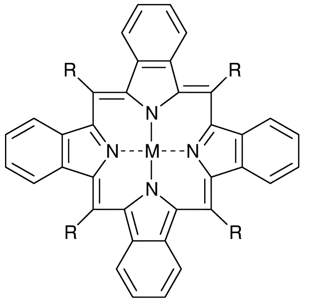
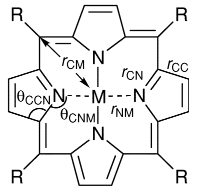
The effects of the conjugation system, the substituents and the central metals in a series of model compounds of benzoporphyrins, which have the largest experimental second-order hyperpolarizabilities (γ) to date, have been directly investigated by their structural features and charge-transfer (CT) nature.

Nowadays materials with unusual nonlinear optical (NLO) properties have influenced many research interests.[1–4] Although both theoretical and experimental research on materials with second-order NLO responses has been carried out for several years,[3–4] the relatively well-defined relationships of structure–property for the second-order NLO chromophores are more scarce than those for the first-order NLO compounds. In particular, theoretical studies on organometallic compounds for NLO properties have not kept up with the rapid experimental advances.[3–5] Several types of organometallic compounds with large conjugation systems have been reported with high second-order molecular hyperpolarizability.[3] The experimental γ values for some benzoporphyrins (see I) are surprisingly high to the order of 10^{-30} esu,[5] which rank as the highest ones to date. However, there is no theoretical research on this type of molecule. A better understanding of NLO properties and relations with their structures and charge-transfer nature is necessary for further research of these advanced materials. Therefore, the effects of different sized conjugation systems I and II, different central metals (M = Mg, Zn) and different substituents (R = H, Me, Ph, *m*-F-C_6H_4, *p*-Me-C_6H_4, *p*-MeO-C_6H_4) on γ were systematically investigated in this work.



I



II

M = Mg, Zn
1 R = H **4** *m*-F-C_6H_4
2 R = Me **5** *p*-Me-C_6H_4
3 R = Ph **6** *p*-MeO-C_6H_4

The nonlinear response of the molecular dipole polarizability p_i to the external electric field E can be written as follows [eqn. (1)],

$$p_i = \mu_i + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \ldots \quad (1)$$

where i, j, k and l are the indices for coordinates; μ_i is the permanent molecular dipole moment, and α_{ij}, β_{ijk} and γ_{ijkl} are the tensor elements of the molecular polarizability, first- and second-order hyperpolarizabilities, respectively. Employing the finite-field (FF) approach,[6] all components of the hyperpolarizabilities can be obtained by computing the dipole moment or energy with respect to the applied field direction and strength. In contrast to the experimental measurements, computational values are usually obtained in the case of a static applied electric field. Then, the second-order hyperpolarizability is given as [eqn. (2)].

$$\gamma = (4/6)\sum_{i,j}\gamma_{iijj}/5 \quad (2)$$

For large molecular systems like the title compounds, the semi-empirical PM3 method in the MOPAC software was used. The self-consistent field criterion was 10^{-8} au. Geometries were optimized with D_{4h} symmetry for the framework. The gradient norm of the optimized molecule is less than 0.01 au. The applied external static field value was 10^{-3} au by the program default. The reported γ values were obtained by energy expansion as usual.[2] Owing to the limit of computer resources, only the molecule zinc mesotetra-R-tetrabenzoporphyrin (R = H) of series I is calculated.

The experimentally determined γs for series I are 3.3, 0.9, 3.8, 4.0 and 4.8×10^{-30} esu with substituents **2**, **3**, **4**, **5** and **6**, respectively.[5] Obviously they are greater than the calculated static γ values of series II. In order to directly investigate the effect of the size of the conjugation system, γ and the structure and charge densities of series I (R = H) were computed. Structural parameters (see definitions in structures I and II of the compounds of series I are $r_{NM} = 2.032$, $r_{CM} = 3.510$, $r_{CN} = 1.401$, $r_{CC} = 1.422$ Å; $\theta_{CNM} = 126.12$, $\theta_{CCN} = 109.97°$. While those of its counterpart are $r_{NM} = 2.005$, $r_{CM} = 3.517$, $r_{CN} = 1.401$, $r_{CC} = 1.464$ Å; $\theta_{CNM} = 126.07$, $\theta_{CCN} = 108.08°$ (see Table 1). It can be seen

Table 1 Structural parameters and γ values of zinc-mesotetra-R-porphyrin

	1	**2**	**3**	**4**	**5**	**6**
r_{NM}/Å	2.005	1.983	1.928	1.928	1.928	1.928
r_{CM}/Å	3.517	3.599	3.825	3.825	3.826	3.827
r_{CN}/Å	1.401	1.406	1.445	1.445	1.445	1.445
r_{CC}/Å	1.464	1.466	1.439	1.440	1.439	1.438
θ_{CNM}(°)	126.07	125.54	123.19	123.19	123.20	123.20
θ_{CCN}(°)	108.08	106.93	101.15	101.16	101.16	101.16
q_M(e)	–0.1473	–0.2180	–0.3030	–0.2937	–0.3060	–0.3171
q_N(e)	0.2338	0.2735	0.2888	0.2855	0.2900	0.2958
$\gamma/10^{-36}$ esu	30.0	47.7	272.5	305.7	365.9	494.3

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Table 2 Structural parameters and γ values of magnesium mesotetra-R-porphyrin

	1	**2**	**3**	**4**	**5**	**6**
r_{NM}/Å	1.918	1.901	1.860	1.860	1.860	1.860
r_{CM}/Å	3.494	3.567	3.785	3.784	3.785	3.786
r_{CN}/Å	1.407	1.410	1.439	1.439	1.439	1.439
r_{CC}/Å	1.462	1.464	1.438	1.439	1.438	1.437
θ_{CNM}(°)	127.68	127.05	124.30	124.30	124.30	124.31
θ_{CCN}(°)	110.34	109.11	103.05	103.06	103.06	103.05
q_M(e)	0.2184	0.1752	0.1366	0.1457	0.1334	0.1229
q_N(e)	0.1229	0.1502	0.1531	0.1502	0.1543	0.1592
$\gamma/10^{-36}$ esu	25.0	44.1	287.9	316.4	383.0	538.8

that changing the size of the conjugation system influences r_{CC} most among all these geometric parameters. it is shorter in the benzoporphyrin than in the porphyrin, which brings more intensive interaction for the large conjugation system. Such strong interaction is probably responsible for its large nonlinearity. In fact, γ of the benzoporphyrin derivative (case **1**) is 240.8×10^{-36} esu, which is 8 times larger than that of its counterpart. Formal charges at the metal centre (q_M) are –0.1222 and –0.1473 e, and those at the nitrogen atom (q_N) are 0.2857 and 0.2338 e for the former and latter molecules, respectively. This suggests that when the conjugation system is enlarged to be benzoporphyrin, the metal centre receives more electrons from the donor part—nitrogen atoms. This kind of intensified charge-transfer is certain to be beneficial for the notable NLO properties. Based on the comparisons it may be concluded that the larger conjugation system will result in the stronger electronic interaction and more intensified charge-transfer between the donor and acceptor portions, which elevates the nonlinearities. This phenomenon is similar to organic systems, where nonlinearities increase with the system size.[2]

Usually the electron-donating capabilities of the studied substituents are in following order: H < Me < Ph < m-FC_6H_4 < p-Me-C_6H_4 < p-MeO-C_6H_4. Because NLO properties mainly depend on the electronic interaction of the system, it is generally believed that the nonlinearities increase as the electron-donating capabilities the substituent becomes more intensive. Our previous molecular design study on first-order nonlinearities confirms this idea. Just as expected, calculations of metalloporphyrins are consistent with it. In all M-mesotetra-R-porphyrins (M = Zn, Mg), the metal centre receives more electrons and the nitrogen atom releases more electrons as the substituent changes from **1** to **6**. This phenomenon shows that more intensive electron-donating groups can result in stronger CT effects between donor and acceptor portions. Such classification of donor and acceptor can be evidenced by their formal charge changes (see Tables 1 and 2). The experimental data for benzoporphyrin derivatives also follow this order except for the phenyl substituent.[5]

The structural parameters do not vary much when the substituent contains the phenyl part. In this situation, the conjugation system is enlarged, so the intensified electronic interaction can be expected as exemplified by the shortened r_{NM}, r_{CC}, θ_{CNM} and θ_{CCN}. This fact is similar to the previous discussion about the effect of the size of the conjugation system. r_{CN} is enlarged so as to make the nitrogen atom closer to the metal centre, which contributes to the strong electronic interaction between the donor part—nitrogen atom and the acceptor part—metal atom. However, there is the strange case of **3**. As shown in Tables 1 and 2 q_M and q_N do not follow the order of the substituent electron-donating capability no matter what type of metal atom is involved. This singularity is consistent with the experimental γ of zinc mesotetraphenylbenzoporphyrin. The unusual γ may be understood by its distinctive CT nature.

Here, both the main group metal Mg and transition metal Zn were considered. As we know, when the metal atom changes, the interaction between the metal centre and the nearby nitrogen atom will also change. Therefore, r_{NM}, r_{CM} and r_{CN} which are easily affected by the metal centre are expected to be enlarged with the increased size of the metal atom, *i.e.*, Mg < Zn. As a consequence, θ_{CNM} and θ_{CCN} become small with the increased size of the metal atom, *i.e.*, Mg < Zn. These have been verified by our calculations. Both metal atoms have similar electronic properties; for example, they do not contain the singly occupied orbitals. Thus, it is no wonder that their experimentally measured nonlinear responses are similar.[5] This fact has been reproduced by the present study of the title compounds; our calculations show that metal atoms do not introduce remarkable effects on NLO properties. In fact, the experimental study[5] also shows that benzoporphyrins with and without the metal centre possess similar γ values. However, the signs of q_M and q_N are different. The zinc atom gains some extra electrons, while magnesium loses electrons. This may be due to the fact that Zn has the vacant 4p orbitals, which can accept electrons more easily than Mg.

Based on the above discussions, it may be concluded that: (i) a large nonlinear optical response accompanies a large conjugation system; (ii) substituents with more powerful charge transfer capabilities enhance the nonlinearities; (iii) the effect of the metal centre on the nonlinear optical interactions is less significant for porphyrin derivatives. As a result, the focus of the molecular design of the NLO organometallic materials is to seek a proper large conjugation system with a powerful electron-donating or electron-withdrawing substituent and a selected metal centre.

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