

Theoretical studies on metal porphyrin halides: geometrical parameters and nonlinear optical responses

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Abstract The geometrical parameters and static electric properties of several metal porphyrin halides, including Fe(III) porphine chloride (FePcCl), Fe(III) porphine bromide (FePBr), Fe(III) tetraphenylporphine chloride (FeTPPCl), aluminum phthalocyanine chloride (AlPcCl), gallium(III) phthalocyanine chloride (GaPcCl), and manganese(III) phthalocyanine chloride (MnPcCl), were investigated using density functional theory (DFT) methods. It was observed that FePBr and MnPcCl showed the highest total hyperpolarisabilities among the studied porphyrins. To investigate the effect of substituted phenyl groups on the nonlinear optical (NLO) responses of porphyrins, the optical properties of FeTPPCl and FePcCl were compared using UBLYP/cc-pVDZ+LanL2DZ level of theory. Moreover, the polarised continuum model (PCM) was employed to study the influence of solvation on the optical properties of FePcCl.

Keywords Density functional theory · Porphyrins · Geometrical parameters · Optical properties

Introduction

Nonlinear optical (NLO) compounds based on porphyrins are suitable for use in optoelectronics due to their high thermal stability and extended π -conjugated macrocyclic ring [1]. Despite considerable efforts to investigate the

NLO properties of these compounds [1, 2], insufficient information regarding the electric and optical properties of metal porphyrin halides is available.

In this paper, we study the geometrical parameters and the static electric properties (dipole moment, polarisability, and first hyperpolarisability) of several porphyrins including Fe(III) porphine chloride (FePcCl), Fe(III) porphine bromide (FePBr), Fe(III) tetraphenylporphine chloride (FeTPPCl), aluminum phthalocyanine chloride (AlPcCl), gallium(III) phthalocyanine chloride (GaPcCl), and manganese(III) phthalocyanine chloride (MnPcCl) using density functional theory (DFT) calculations. To investigate the effect of substituted phenyl groups on the NLO responses of the porphyrins, the optical properties of FeTPPCl and FePcCl were compared using UBLYP/cc-pVDZ+LanL2DZ level of theory. Moreover, the polarised continuum model (PCM) [3] was applied to study the influence of solvation on the optical properties of FePcCl.

Due to the inadequacy of the experimental data available, a complete comparison between the calculated and observed electric properties of the studied porphyrins was not possible. To examine the efficiency of the selected density functionals (BLYP and SVWN) in predicting the electric properties, *p*-nitroaniline (PNA) was considered as a case study since extensive theoretical and experimental data are available for this molecule [4–8].

Computational methods

Using Gaussian 03 [9], calculations were carried out at UBLYP/cc-pVDZ+LanL2DZ and USVWN/cc-pVDZ+LanL2DZ levels of theory for FePcCl, FePBr, and MnPcCl (in the case of FeTPPCl, UBLYP/cc-pVDZ+LanL2DZ calculations were performed to study the effect of

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substituted phenyl groups); LanL2DZ basis set was used for Fe and Mn and cc-pVDZ was considered for the other atoms. For AlPcCl and GaPcCl, the BLYP/cc-pVDZ and SVWN/cc-pVDZ procedures were applied. Figure 1 shows the molecular structures of the studied porphyrins. In all cases the molecules are neutral and the spin multiplicities are 1 (for AlPcCl and GaPcCl), 6 (for FePcCl, FePBr, and FeTPPCl) and 5 (for MnPcCl); see Table 1. Moreover, all the calculated frequencies are real indicating that the structures are stable.

The linear optical and NLO properties can be determined as follows:

The mean polarisability α can be written as [10]

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

For the first hyperpolarisability, the vector component along the dipole moment direction is

$$\beta_{\mu} = \frac{3}{5} \frac{\sum_i \mu_i \beta_i}{|\mu|} \quad i = x, y, z \quad (2)$$

Where

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad i, j = x, y, z \quad (3)$$

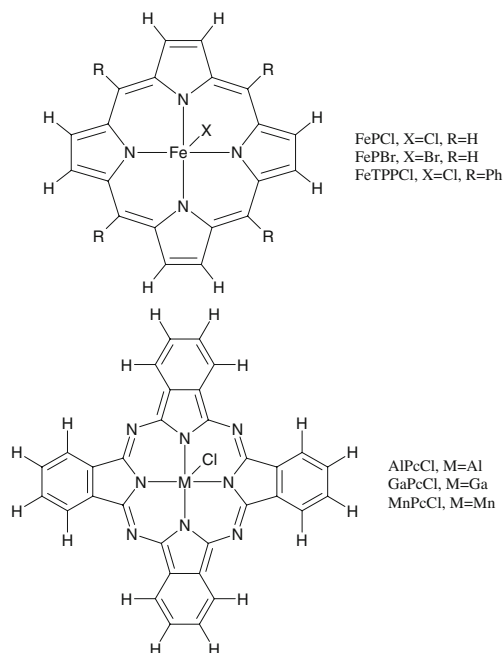


Fig. 1 Molecular structure of Fe(III) porphine chloride (FePcCl), Fe(III) porphine bromide (FePBr), Fe(III) tetraphenylporphine chloride (FeTPPCl), aluminum phthalocyanine chloride (AlPcCl), gallium(III) phthalocyanine chloride (GaPcCl), and manganese(III) phthalocyanine chloride (MnPcCl)

Table 1 Metal oxidation states and spin multiplicities of the studied compounds. *FePcCl* Fe(III) porphine chloride, *FePBr* Fe(III) porphine bromide, *FeTPPCl* Fe(III) tetraphenylporphine chloride, *AlPcCl* aluminum phthalocyanine chloride, *GaPcCl* gallium(III) phthalocyanine chloride, *MnPcCl* manganese(III) phthalocyanine chloride

Molecule	Metal oxidation state	Spin multiplicity
FePcCl	+3	6
FePBr	+3	6
AlPcCl	+3	1
GaPcCl	+3	1
MnPcCl	+3	5
FeTPPCl	+3	6

Considering Kleinman symmetry in the static limit we have,

$$\beta_i = \sum_j \beta_{ijj} \quad i, j = x, y, z \quad (4)$$

Another quantity of interest is the total intrinsic quadratic hyperpolarisability (or simply the total hyperpolarisability) β_{tot} which has the form

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (5)$$

The conversion factors for energy, dipole moment (μ), polarisability (α), and first hyperpolarisability (β) are:

- 1 a.u. of energy = 27.2114 eV
- 1 a.u. of dipole moment = 2.541746 Debye
- 1 a.u. of polarisability = 0.148185 Å³
- 1 a.u. of first hyperpolarisability = 8.65710 × 10⁻³³ esu

Results and discussion

Geometrical parameters

Table 2 shows the structural parameters of the studied porphyrins: R_{M-X} (metal–halogen bond length); R_{M-N} (metal–nitrogen bond length); and R_{M-Ct} (distance between metal and the centre of the ring). (U)BLYP-calculated R_{M-X} values for FePcCl (I), FePBr (II), AlPcCl (III), GaPcCl (IV), MnPcCl (V), and FeTPPCl (VI) are, respectively, 2.267, 2.426, 2.206, 2.246, 2.361, and 2.274 Å. Using the same functional, R_{M-N} in compounds (I)–(VI) are found to be 2.119, 2.118, 2.012, 2.054, 1.997, and 2.12 Å, respectively. Furthermore, good agreement is found between the calculated results and the data available from the literature [11–15]; see Table 2.

Table 2 Structural parameters (in Å) of the studied porphyrins: R_{M-X} metal–halogen bond length, R_{M-N} metal–nitrogen bond length, R_{M-Ct} distance between metal and the centre of the ring

Molecule	Method	Reference	R_{M-X}	R_{M-N}	R_{M-Ct}
FePcCl	UBLYP	This work	2.267	2.119	0.557
	USVWN	This work	2.173	2.060	0.460
		11	2.449	2.049	0.414
		12	2.21		0.530
FePBr	UBLYP	This work	2.426	2.118	0.549
	USVWN	This work	2.319	2.058	0.446
AlPcCl	BLYP	This work	2.206	2.012	0.607
	SVWN	This work	2.159	1.974	0.525
		13	2.179	1.961–2.018	
GaPcCl	BLYP	This work	2.246	2.054	0.702
	SVWN	This work	2.181	2.003	0.586
		13	2.217	1.979–1.988	
MnPcCl	UBLYP	This work	2.361	1.997	0.411
	USVWN	This work	2.256	1.941	0.318
FeTPPCl	UBLYP	This work	2.274	2.12	0.552
		14	2.192	2.049	0.383
		15	2.211	2.06–2.078	

Electric properties: PNA

The static electric properties of PNA were determined using DFT methods. According to BLYP/cc-pVDZ (SVWN/cc-pVDZ) procedure the dipole moment is 7.01 (7.41) Debye, which is consistent with the values 7.37 Debye [4], 7.4 Debye [5], and 6.067 Debye [6]. The mean polarisability $\bar{\alpha}$ of PNA based on BLYP/cc-pVDZ (SVWN/cc-pVDZ) calculations is 93.05 (90.81) a.u., which is comparable with the values 83 a.u. [4], 104.70 a.u. [7], and 94.19 a.u. [6]. The magnitude of the static hyperpolarisability β_{μ} of PNA is evaluated to be 6.86×10^{-30} esu (using BLYP/cc-pVDZ level of theory); this is in reasonable agreement with the results 6.67×10^{-30} esu [5] and 10.54×10^{-30} esu [8].

Electric properties: porphyrins

Based on the efficiency of BLYP and SVWN in predicting the electric properties of PNA, these functionals were used for the metal porphyrin halides in this paper. Using (U)BLYP functional, the dipole moments of the porphyrins (I)–(V) are calculated to be 3.00, 2.86, 3.51, 3.48, and 4.23 Debye, respectively; see Table 3. The dipole moment of AlPcCl, and GaPcCl from ref. [2] are 3.89 and 3.91 Debye, respectively, which are in close agreement with our results.

The mean polarisabilities α are included in Table 3. The (U)BLYP-calculated mean polarisabilities of (I)–(V) are 368.54, 375.97, 652.21, 655.05, and 669.21 a.u., respectively (it should be noted that the molecules were originally in the xy plane).

Table 3 Energies (a.u.), dipole moments (Debye), polarisabilities (a.u.), and first hyperpolarisabilities (10^{-33} esu) of the studied porphyrins

Molecule	Method	Energy	μ	$\bar{\alpha}$	β_{μ}	β_{tot}
FePcCl	UBLYP/cc-pVDZ+LanL2DZ	−1,571.77	3.00	368.54	−725.75	1,209.58
	USVWN/cc-pVDZ+LanL2DZ	−1,565.55	2.35	354.55	−1,713.00	2,854.99
FePBr	UBLYP/cc-pVDZ+LanL2DZ	−3,685.72	2.86	375.97	−1,019.14	1,698.56
	USVWN/cc-pVDZ+LanL2DZ	−3,677.81	2.20	360.98	−2,270.60	3,784.33
AlPcCl	BLYP/cc-pVDZ	−2,369.51	3.51	652.21	475.69	792.82
	SVWN/cc-pVDZ	−2,358.83	3.26	629.16	686.04	1143.41
GaPcCl	BLYP/cc-pVDZ	−4,051.91	3.48	655.05	−41.24	68.74
	SVWN/cc-pVDZ	−4,039.58	3.22	630.69	336.30	560.51
MnPcCl	UBLYP/cc-pVDZ+LanL2DZ	−2,230.9	4.23	669.21	−1,778.89	2,964.81
	USVWN/cc-pVDZ+LanL2DZ	−2,221.11	3.47	644.35	−1,917.80	3,196.33

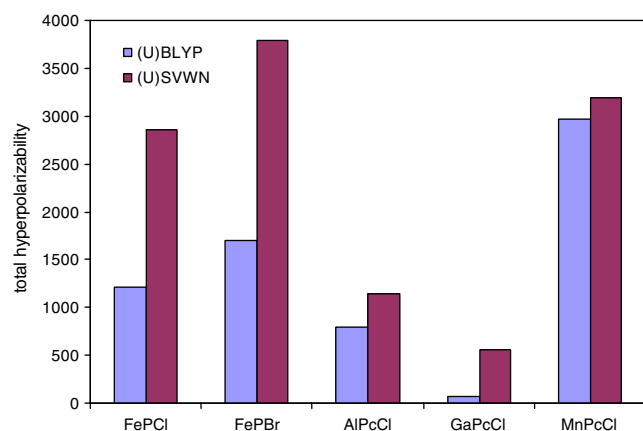


Fig. 2 Total hyperpolarisabilities (10^{-33} esu) of FePcCl, FePBr, AlPcCl, GaPcCl, and MnPcCl

The static hyperpolarisabilities have also been given in Table 3. As can be seen, FePBr and MnPcCl show the highest total hyperpolarisabilities among the studied porphyrins. The β_{tot} values are $1,698.56 \times 10^{-33}$ esu (UBLYP) and $3,784.33 \times 10^{-33}$ esu (USVWN) for FePBr and $2,964.81 \times 10^{-33}$ esu (UBLYP) and $3,196.33 \times 10^{-33}$ esu (USVWN) for MnPcCl. To help the interpretation, the total hyperpolarisabilities are also shown in Fig. 2.

The calculated energies of the studied porphyrins have also been represented in Table 3; it is observed that (U)BLYP method leads to more negative energy values in comparison with (U)SVWN.

To investigate the effect of substituted (phenyl) groups on the NLO responses in porphyrins the electric properties of Fe(III) porphine chloride and Fe(III) tetraphenylporphine

Table 4 Comparison between the electric properties of FePcCl and FeTPPCl using UBLYP/cc-pVDZ+LanL2DZ procedure: energies and polarisabilities are in a.u. and dipole moments are in Debye

Molecule	Energy	μ	$\bar{\alpha}$	β_{μ} (a.u.)	β_{tot} (a.u.)	β_{μ} (10^{-33} esu)	β_{tot} (10^{-33} esu)
FePcCl	-1,571.77	3.00	368.54	-83.83	139.72	-725.75	1,209.58
FeTPPCl	-2,495.6	2.81	720.37	-87.97	146.96	-761.55	1,272.24

Table 5 Calculated energy (a.u.), dipole moment (Debye), polarisability (a.u.), and first hyperpolarisability (in both a.u. and 10^{-33} esu) of FePcCl based on UBLYP/cc-pVDZ+LanL2DZ level of theory and polarised continuum model (PCM) procedure

Medium	Energy	μ	$\bar{\alpha}$	β_{μ} (a.u.)	β_{tot} (a.u.)	β_{μ} (10^{-33} esu)	β_{tot} (10^{-33} esu)
Vacuum	-1,571.769	3.00	368.54	-83.83	139.72	-725.75	1,209.58
Argon	-1,571.773	3.35	391.26	17.89	29.81	154.83	258.06
Benzene	-1,571.777	3.77	442.75	271.89	453.15	2,353.80	3,923.00

Table 6 Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies (a.u.) of the studied porphyrins

Molecule	Method	HOMO	LUMO
FePcCl	UBLYP/cc-pVDZ+LanL2DZ	-0.175	-0.107
	USVWN/cc-pVDZ+LanL2DZ	-0.199	-0.136
FePBr	UBLYP/cc-pVDZ+LanL2DZ	-0.174	-0.107
	USVWN/cc-pVDZ+LanL2DZ	-0.197	-0.136
AlPcCl	BLYP/cc-pVDZ	-0.173	-0.124
	SVWN/cc-pVDZ	-0.208	-0.157
GaPcCl	BLYP/cc-pVDZ	-0.174	-0.124
	SVWN/cc-pVDZ	-0.209	-0.157
MnPcCl	UBLYP/cc-pVDZ+LanL2DZ	-0.174	-0.124
	USVWN/cc-pVDZ+LanL2DZ	-0.192	-0.155

chloride are compared in Table 4. We see that dipole moment decreases while mean polarisability and total hyperpolarisability increase from FePcI to FeTPPcI. These results confirm the influence of the substituted phenyl groups toward increasing the nonlinear optical properties of the porphyrin-based materials.

Moreover, in order to study the influence of solvation on the characteristics of the studied molecules, we considered the PCM; for this purpose the molecular parameters of FePcI were calculated in a couple of dielectric media including argon $\epsilon=1.43$ and benzene $\epsilon=2.247$ (see Table 5). Due to the polarisation of the molecule, it is expected that energy decreases and dipole moment increases with the reaction field. The DFT-calculated energy of the molecule decreases from $-1,571.769$ a.u. in vacuum to $-1,571.777$ a.u. in benzene, and the molecular dipole moment increases from 3.00 Debye for the isolated molecule to 3.77 Debye in dielectric medium $\epsilon=2.247$. Additionally, in the context of the PCM procedure, the mean polarisability and the total hyperpolarisability of FePcI are found to be ~ 1.2 and 3.2 times higher in benzene, respectively, compared with the corresponding values in the gas phase. These results demonstrate a considerable dependency on solvent polarity of linear optical and NLO responses.

Frontier orbitals

The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are represented in Table 6 (it should be noted that the data in Table 6 refer to alpha orbitals). According to (U)BLYP functional, the HOMO energies of the molecules (I)–(V) are evaluated to be -0.175 , -0.174 , -0.173 , -0.174 , and -0.174 a.u., respectively. Using the same procedure, the LUMO energies are -0.107 a.u. for FePcI and FePBr and -0.124 a.u. for AlPcCl, GaPcCl, and MnPcCl. Furthermore, it was observed that in all cases the HOMO and LUMO energies based on (U)SVWN are more negative than the results determined by (U)BLYP.

Summary

Dipole moments, polarisabilities, and first-order hyperpolarisabilities of several metal porphyrin halides, including FePcI, FePBr, FeTPPcI, AlPcCl, GaPcCl, and MnPcCl, were investigated using DFT calculations. It was found that FePBr and MnPcCl show the highest total hyperpolarisabilities among the studied porphyrins.

A comparison between the electric properties of FePcI and FeTPPcI indicates that the substituted phenyl groups

increase the linear optical and NLO responses. The $\bar{\alpha}$ values are evaluated to be 368.54 a.u. for FePcI and 720.37 a.u. for FeTPPcI and β_{tot} values are found to be 1209.58×10^{-33} esu and 1272.24×10^{-33} esu for FePcI and FeTPPcI, respectively.

Moreover, the PCM was employed to study the influence of solvation on the optical properties of FePcI. Results indicate that the NLO characteristics of the molecules depend considerably on solvent polarity.

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