Enhancement of Third-Order Nonlinear Response in Excited State of Metallophthalocyanines (PcM; M = H₂, Mg, Ni)

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In this paper we calculate the dynamic third-order nonlinear optical polarizabilities of three optical processes, third-harmonic generation, electric-field-induced second-harmonic generation, and degenerate four-wave mixing, for both ground and first excited singlet states in metal phthalocyanines in terms of the sum-over states formula. The transition moment elements and the transition energies in this formula are obtained using the INDO−SDCI method. The calculated second-order hypolarizabilities show a dispersion behavior with the difference from ground state and an enhancement of third-order nonlinear response in the first excited state. Among the PcM (M = H₂, Mg, Ni), there is a large enhancement of the first excited singlet state when there is a small third-order optical polarizability of the ground state. The calculated value of PcNi is compared with the observed one of the substituted PcNi in the order of magnitude. We also gain an understanding of enhancement mechanism for nonlinear processes in the excited state.

1. Introduction

The realization of all-optical switching, modulating, and computing devices is an important goal in modern optical technology. Nonlinear optical materials with a large third-order nonlinear susceptibility and a small signal attenuation arising from the linear optical absorption are indispensable for such devices, because the magnitudes of these quantities dominate the device performance. A strategy in the development of new materials with large nonlinear susceptibilities and extremely fast response times, in wavelength regimes where there is minimal background absorption, is the exploration of macrocycles. Metal phthalocyanines (here the hydrogen atom in the center of macrocycle is also regarded as a metal) are among the most attractive macrocyclic systems. Generally, phthalocyanines (Pc) are centrosymmetric planar organic molecules with a two-dimensional conjugated π-electron delocalization, and these macrocycle molecules can display a strong nonlinear optical response. Furthermore, the two-dimension π-conjugated system in Pc allows the tailoring of chemical and physical properties over a very wide range of chemical modifications by incorporating many different metal atoms into the ring and by substituting various functional groups at peripheral sites. Additionally, metal-phthalocyanines (PcM) are very stable organometallic materials, undergoing no noticeable degradation in air up to 400−500 °C. This exceptional thermal stability together with large chemical versatility makes it feasible to obtain high-quality thin films of a great variety of phthalocyanines by successive sublimation. These and the other unique properties have warranted the vast amount of basic and applied research concerning phthalocyanines.[1−11] The bulk third-order susceptibility measured in thin films and crystals, as well as the isotropically averaged molecular third-order polarizability measured in solution, have been obtained for a variety of free-base and metallo-substituted Pc compounds.[5−11] Nonresonant enhancement effects of third-order optical nonlinearities at the first excited state of macrocycle molecules were observed through population of the electronic

excited state for these molecule.[12,13] It will provide an alternative method for probing excited-state dynamics and a potential application for molecular switching.

In this study, we report third-order nonlinear polarizabilities of the first excited singlet state and ground state for PcM (M = H₂, Mg, Ni). The calculated results are based on a combination of the intermediate neglect of differential overlap (INDO) and configuration interaction (CI) methods coupled with the sum-over-states (SOS) method.[14,15] This approach is demonstrated to be successful in calculating the optical properties of organometallic compounds, inorganic solid materials, and polymers.[16−18] To our knowledge, however, experimental or theoretical investigations of nonlinear optical properties at excited states have not yet been reported for this class of macrocycle compounds. We also explain the origin of dramatic enhancement of excited state and search the relationship between the third-order nonlinear optical response and the photoinduced energy or electron-transfer processes in metal phthalocyanines.

2. Computational Procedures

The electronic structural calculations of PcM (M = H₂, Mg, Ni) molecules are based on an all-valence-electron, semiempirical INDO self-consistent field (SCF) molecular orbital (MO) procedure with configuration interaction (CI) modified by Zerner and co-workers.[19−22] The one-center core integral $U_{\mu\mu}$, resonance integral $\beta_{\mu\mu}$, two-electron integral $\gamma_{\mu\nu}$, overlap integral $S_{\mu\nu}$, and density matrix element $\mathbf{P}_{\mu\nu}$ are involved in the matrix element of the Fock operator under the INDO approximation. The INDO model as employed herein includes all one-center two-electron integrals, and two-center two-electron integrals $\gamma_{\mu\nu}$. The one-center two-electron integrals, $\gamma_{\mu\mu}$, are chosen from the approximation of Pariser, $\gamma_{\mu\mu} = F^0(\mu\mu) = IP_\mu - EA_\mu$, and the two-center two-electron integrals are calculated using the Mataga-Nishimoto formula, $\gamma_{\mu\nu} = 1.2/[R_{AB}+2.4/(\gamma_{\mu\mu} + \gamma_{\nu\nu})]$ in the spectroscopic version of the INDO method. Here, we only consider the valence orbitals of the constituent atoms of

PcM compounds in the calculations. The valence orbitals are 1s for H; 2s, 2p for C, N, O; and 3s, 3p for Mg; 3d, 4s, 4p for Ni whose orbital exponents ζ and the other parameters used in calculations are listed in ref 23. The MO calculations are performed by the restricted Hartree-Fock method. The ground state, which is obtained from calculated results of the SCF, is taken as the reference state in the CI. In the context of treating electron−electron interactions (EEI) via CI, the SCF-MO formalism must include at least single- and double-excitation configuration interactions (SDCI) in order to properly calculate the energy order of the electron excited singlet states of PcM compounds. This treatment has been proved to be effect in the calculations of the linear conjugated polyenes.[24−27] Single- and double-substituted determinants relative to the ground state configuration are considered, and only singlet spin-adapted configurations need to be included in the CI calculations.[28] The determinant wave functions can be expressed as

$$\Phi_{CISD} = c_0\phi_0 + \Sigma_i\Sigma_a c_{i\to a}\phi_{i\to a} + \Sigma_{i>j}\Sigma_{a>b} c_{ij\to ab}\phi_{ij\to ab} \quad (1)$$

Here ϕ_0 is the reference state function, $\phi_{i\to a}$ represents a single-replacement state, and $\phi_{ij\to ab}$ a double-replacement state. Indices i, j, ... are used to denote orbitals occupied in ϕ_0 (internal orbitals), while a, b, ... are used for the remaining orbital space (external orbitals). The coefficients c are varied to minimize the expected value of the energy, leading to the equations

$$\Sigma(H_{st} - E_k\delta_{st})c_{sk} = 0; \quad t = 0, 1, 2, ... \quad (2)$$

where H_{st} are configurational matrix elements and E_k are energy elements. The excited states correspond to the configuration interaction wave functions Φ_{CISD} with higher energy roots E_k ($k > 0$). The energy difference between the excited state and ground state or between the two excited states is defined as the electron transition energy. The dipole and transition moment matrix elements are expressed as a sum of one-electron integrals. The oscillator strength is evaluated with the dipole length operator, maintaining all one-center charge and polarization terms in the CI calculations. Higher-order correlations are neglected since their influence is taken into account through the choice of semiempirical two-electron integrals γ and empirical resonance β.[29,30] The electron excited states of PcM compounds are obtained by configuration interactions of all single- and double-excited configurations from the six highest occupied molecular orbitals to the six lowest unoccupied orbitals. This leads to a total of more than 700 calculated states in the present study.

In the nonresonant region, the molecular third-order polarizability tensor γ can be described by the conventional sum-over-states (SOS) expression:[14−15]

$$\gamma_{abcd}(-\omega_p;\omega_1,\omega_2,\omega_3) = (2\pi/h)^3 K(-\omega_p;\omega_1,\omega_2,\omega_3)e^4$$
$$\{\Sigma_P[\Sigma'_{i,j,k}(<o|r_a^*|k><k|r_b^*|j><j|r_c^*|i><i|r_d^*|o>)/$$
$$((\omega_{ko} - \omega_p)(\omega_{jo} - \omega_1 - \omega_2)(\omega_{io} - \omega_p))] -$$
$$\Sigma_P[\Sigma'_{j,k}(<o|r_a^*|j><j|r_b^*|o><o|r_c^*|k><k|r_d^*|o>)/$$
$$((\omega_{jo} - \omega_p)(\omega_{jo} - \omega_1)(\omega_{ko} + \omega_2))]\} \quad (3)$$

Hereafter the symbols $\gamma(3\omega)$, $\gamma(2\omega)$, and $\gamma(\omega)$ represent the third-order polarizability of third-harmonic generation (THG) of $\gamma(-3\omega;\omega,\omega,\omega)$, electric-field-induced second-harmonic generation (EFISHG) of $\gamma(-2\omega;\omega,\omega,0)$, and degenerate four-wave mixing (DFWM) of $\gamma(-\omega;\omega,\omega,-\omega)$, individually. The prefactor $K(-\omega_p;\omega_1,\omega_2,\omega_3)$ must be taken as the same value for the THG, EFISHG, and DFWM at the static case of an input photon
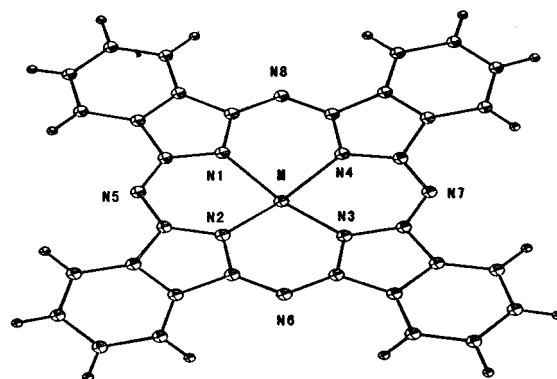

Figure 1. PcM molecular structure (M = H$_2$, Mg, Ni).

energy of zero, and it is the relative magnitudes of the ground and excited-state nonlinear polarizabilities for each optical process at nonzero frequency.[29] In the following calculations, we use the same prefactor K in order to make the remark to justify plotting curves for the three types of nonlinear polarizability against common axes. In eq 3, the first summation involves the two-photon allowed states, referred to as type II terms, and the second summation involves four photon volleys between the reference state that is the ground or first excited state in these calculations and one-photon allowed states, referred to as type I terms. To obtain a reliable value of γ_{abcd}, accurate values of transition energies and dipole moments must be used in eq 3. Here, it is noted that eq 3 does not include line width (or damping) terms in the frequency denominators. If these line width terms are used, the calculated γ value will be a small shift at low frequent region and not show an unlimited value at the input frequency equaling to transition frequency.

The calculations of the third-order polarizabilities of PcM compounds are based on the experimental structural data. The crystal PcH$_2$ belongs to the monoclinic space group $P2_1/c$ with unit-cell parameters $a = 19.85$, $b = 4.72$, $c = 14.8$ Å, $\beta = 122.25°$.[31] The PcMg belongs to the monoclinic space group $P2_1/n$ with unit-cell parameters $a = 17.098$, $b = 16.951$, $c = 12.449$ Å, $\beta = 105.88°$.[32] The crystal PcNi belongs to the monoclinic space group $P2_1/a$ with unit-cell parameters $a = 19.9$, $b = 4.71$, $c = 14.9$ Å, $\beta = 121.9°$.[33] The common feature of these macrocycles is a basis structure consisting of four pyrrole units, which are linked in a circular manner by an azamethine bridge. The molecular structure of PcM is shown in Figure 1, and the plane made by the four isoindole nitrogens of phthalocyanine ligand is called the N4-plane, hereafter. The Mg atom of the PcMg molecule is 0.496 Å out of the N4-plane, and H$_2$ and Ni are in the N4-plane for the PcH$_2$ and PcNi molecules, respectively. The standard geometry of C−H is selected to be 1.08 Å in all the calculations. The coordinate systems are defined in the calculations. The coordinate origin is located in the center of the N4-plane, and the x and y axes are lain down the N4-plane. The z axis is defined by the right-hand rule of coordinate systems. In this way we can obtain the atomic coordinates from the atomic position parameters of PcM (M = H$_2$, Mg, Ni) experimental structural data.[31−33]

3. Results and Discussions

3.1. Third-Order Nonlinear Optical Polarizabilities of Ground States. The electron excited states of PcM (M = H$_2$, Mg, Ni) are obtained by configuration interactions of all single- and double-excited configurations from the six highest occupied molecular orbitals to the six lowest unoccupied orbitals. This leads to a total of more than 700 calculated states. For the
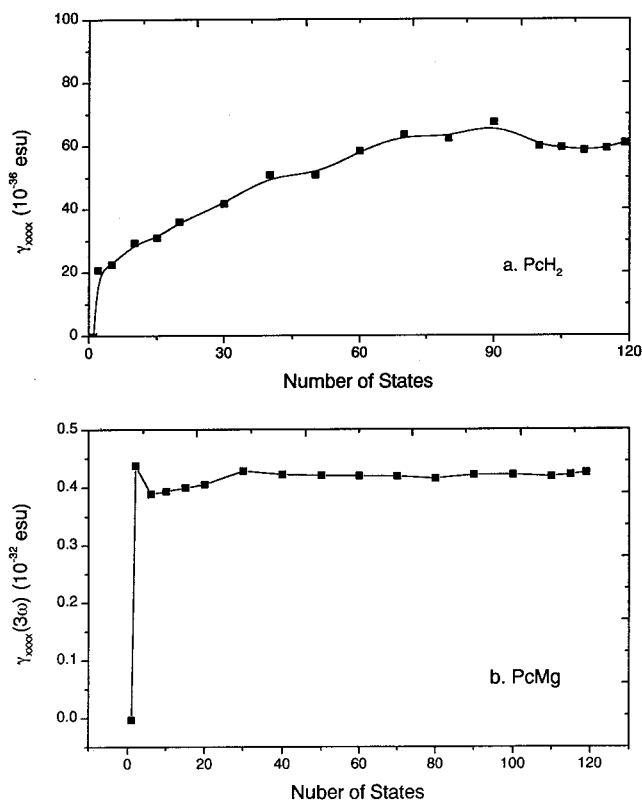
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Figure 2. Convergence behavior of $\gamma_{xxxx}(3\omega)$ with number of states considered in SOS calculations at $\hbar\omega = 0.650$ eV.
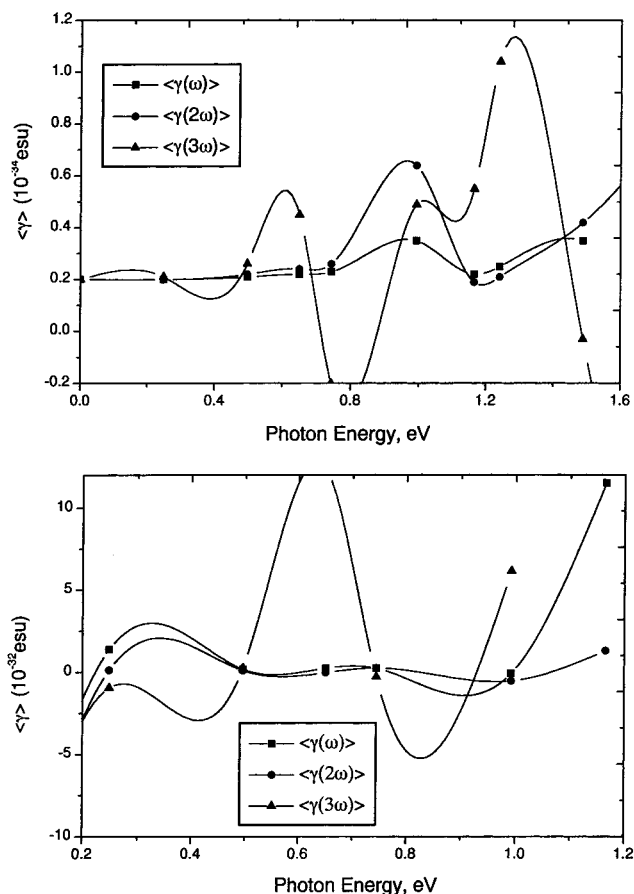

Figure 3. (a) Calculated dispersion of $\langle\gamma\rangle$ of PcH$_2$ for three different processes at the ground state. (b) Calculated dispersion of $\langle\gamma\rangle$ of PcH$_2$ for three different processes at the first excited state.

calculation of γ, we generally truncate the infinite SOS expansion to a finite one over about 120 states after apparent convergence of γ has been reached. Figure 2 shows the plots of the calculated third-order polarizability $\gamma(3\omega)$ components γ_{xxxx} having the largest contribution to the average third-order polarizability of $\langle\gamma\rangle$, versus the number of states for PcM at $\hbar\omega = 0.650$ eV. It is found that the convergence of γ_{xxxx} for PcMg is reached after summation over about 35 states, and the γ_{xxxx} obtained from summation over about 35 states is about 85% of the γ_{xxxx} obtained from summation over about 120 states for PcH$_2$.

Now, we discuss the third-order optical properties based on the calculated results at the ground state to distinguish the excited-state enhancement of optical nonlinearities in PcM. An average $\langle\gamma\rangle$ of phthalocyanine with a different metal is obtained from the expression $\langle\gamma\rangle = 1/5(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + \gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyxx} + \gamma_{yyzz} + \gamma_{zzxx} + \gamma_{zzyy})$. Figures 3a−5a depict the frequent dependence of $\langle\gamma\rangle$ with different optical physical processes at the ground state for PcM (M = H$_2$, Mg, Ni), respectively. In Figure 3a, in the static case where the input photon energy is zero, the values of the THG, EFISHG, and DFWM processes have a same number of 0.20×10^{-34} esu; however, in the dynamic case when an input energy of $\hbar\omega$ is 0.650, 0.992, 0.992 eV, the $\langle\gamma(3\omega)\rangle$, $\langle\gamma(2\omega)\rangle$, and $\langle\gamma(\omega)\rangle$ is individually 0.44×10^{-34}, 0.64×10^{-34}, 0.35×10^{-34} esu. It is also shown that the energy of 3×0.650 eV or 2×0.992 eV approaches the transition energy of about 2.0 eV, which is about 16540 cm^{-1} obtained from the calculated results between ground and first excited singlet states. Note that different resonance enhancements take place in different optical processes. For instance, in the THG process, we can have ω, 2ω, 3ω resonances. In the EFISHG and DFWM processes, there are possible one-photon (ω) and two-photon (2ω) enhancements of $\langle\gamma\rangle$. These are evidenced from Figure 3a that the first near resonant enhancement appears at 3ω ($\hbar\omega = 0.650$ eV) for the

THG process and at 2ω ($\hbar\omega = 0.992$ eV) for the EFISHG or DFWM process. Therefore, we can choose an input wavelength to obtain the nonresonant third-order polarizability among the measuring techniques of the THG, EFISHG, and DFWM processes from a known transition energy or absorption spectrum of the considering material.

To gain a better understanding of the origin of the large third-order nonlinear optical response from the calculated results in PcM (M = H$_2$, Mg, Ni) compounds, we consider the two types of competing third-order virtual excitation processes in determining γ. The type-I processes are of the form S$_g \rightarrow$ S$_m \rightarrow$ S$_g$ $\rightarrow$ S$_m \rightarrow$ S$_g$, where S$_g$ is the ground state and S$_m$ is a one-photon allowed excited state. The intermediate state is S$_g$ itself, and this process makes a negative contribution to γ at a low-frequency region. For example, the calculated $\langle\gamma(0)\rangle_I$ is -0.032×10^{-34} esu in the static case, and the calculated dynamic $\langle\gamma(3\omega)\rangle_I$, $\langle\gamma(2\omega)\rangle_I$, and $\langle\gamma(\omega)\rangle_I$ are -0.078×10^{-34}, -0.039×10^{-34}, and -0.035×10^{-34} esu at an input photon energy of 0.650 eV for PcH$_2$, respectively. For the type-II processes, S$_g \rightarrow$ S$_m \rightarrow$ S$_n \rightarrow$ S$_m \rightarrow$ S$_g$, the intermediate state S$_n$ is a two-photon allowed excited state. The obtained results illustrate the electron density redistribution for the virtual transitions S$_g \rightarrow$ S$_m$ and S$_m \rightarrow$ S$_n$, which are important to the type-I and type-II terms, respectively. The transition S$_g \rightarrow$ S$_2$ yields a transition moment of 2.085 D for PcH$_2$. In contrast, the transition S$_2 \rightarrow$ S$_1$ produces a large transition moment of 6.259 D, which dominates the positive type-II contributing term in γ. The type-II process makes a larger, positive contribution to γ and therefore determines the overall sign of γ to be positive, a result that is corroborated by theoretical values. For instances, the calculated

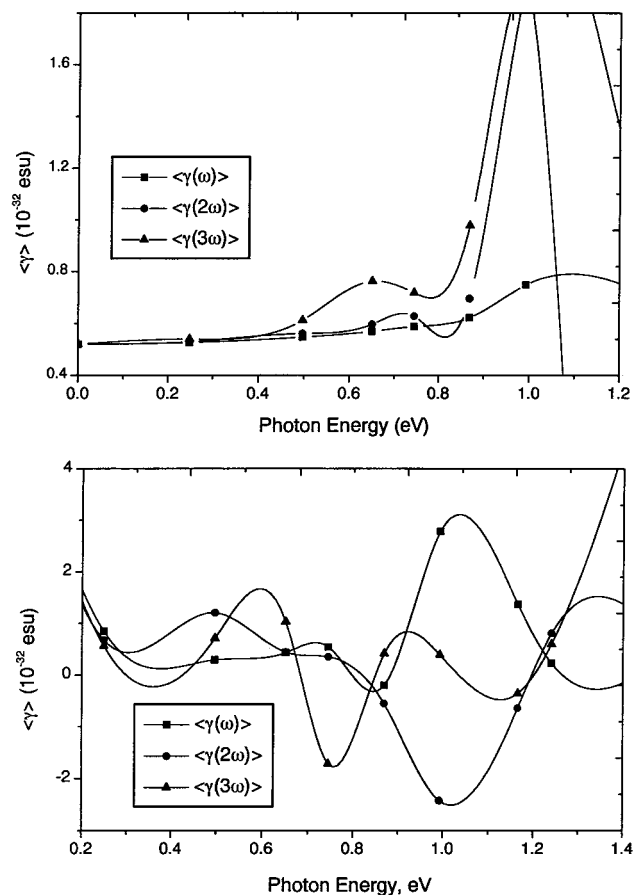**11224** *J. Phys. Chem. B, Vol. 105, No. 45, 2001*

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Figure 4. (a) Calculated dispersion of $\langle\gamma\rangle$ of PcMg for three different processes at the ground state. (b) Calculated dispersion of $\langle\gamma\rangle$ of PcMg for three different processes at the first excited state.
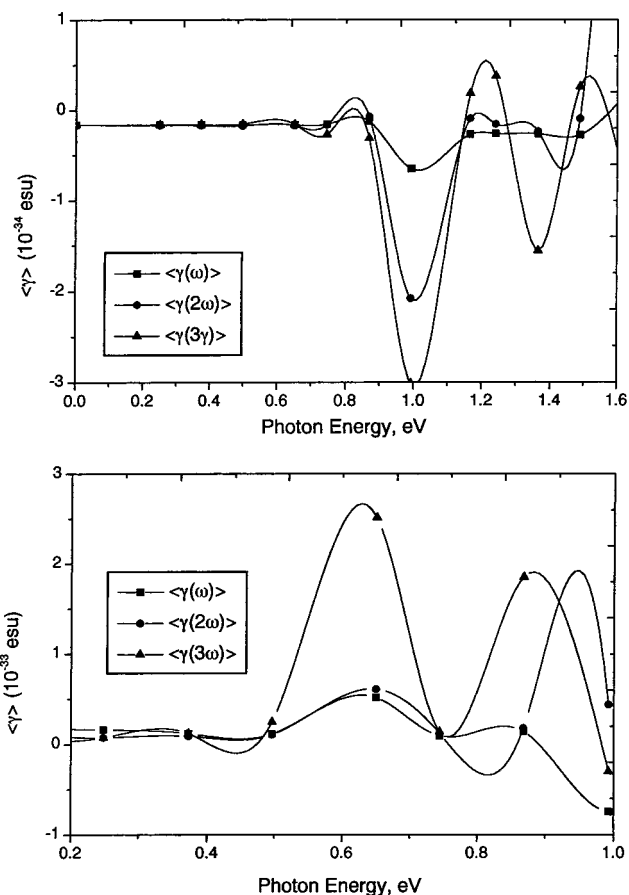
Figure 5. (a) Calculated dispersion of $\langle\gamma\rangle$ of PcNi for three different processes at the ground state. (b) Calculated dispersion of $\langle\gamma\rangle$ of PcNi for three different processes at the first excited state.

$\langle\gamma(0)\rangle_{II}$ is 0.228×10^{-34} esu in the static case, and the calculated $\langle\gamma(3\omega)\rangle_{II}$, $\langle\gamma(2\omega)\rangle_{II}$, $\langle\gamma(\omega)\rangle_{II}$ are 0.523×10^{-34}, 0.276×10^{-34}, and 0.252×10^{-34} esu at an input photon energy of 0.650 eV in PcH$_2$, respectively. In the THG process, the calculated value of 0.20×10^{-34} esu at the ground state of the PcNi can be compared as the observed third-order polarizability of 0.84×10^{-34} esu in an octasubstituted PcNi at an input energy of 0.650 eV (wavelength of 1907 nm).[34] Here, the S$_2$ state is the lowest energy, one-photon allowed excited state. It is principally defined by the configuration consisting of the excitation of a single electron from the π HOMO to the π^* LUMO + 1 orbital, and it has the doubly excited configurational character of about 9%. The S$_1$ state is the lowest energy, two-photon allowed excited state. This state has the contributions of 80% from the configuration forming by an electron from the π HOMO to the π^* LUMO, and has the doubly excited configuration character of about 8%. However, the S$_3$ state, which is the high energy, strongly correlated, two-photon allowed excited state, has the doubly excited configuration character of about 57% and the singly excited configuration character of about 40%. These results show that the doubly excited configurations have a substantial contribution to type-II processes in determining γ.

3.2. Third-Order Nonlinear Optical Polarizabilities of Excited States. An enhancement mechanism for nonlinear processes originating from real population of electronic excited states is analyzed based on the theoretical results in PcM (M = H$_2$, Mg, Ni). In experiments, an electron excited state can be generated to use laser pulse at certain wavelength and then populated for times long enough to permit nonresonant measurements.[13,35−38] Therefore, when an excited state is popu-

TABLE 1: Calculated $\langle\gamma\rangle$ in the DFWM Process for the Ground and Excited Reference States at Different Photon Energies[a]

energy		0.0	0.248	0.496	0.650	0.744	0.992	1.161	1.240
PcH$_2$	G	0.20	0.20	0.21	0.22	0.23	0.35	0.22	0.25
	S$_1$	−25.38	139.71	18.11	23.80	23.64	−6.96	1151.52	17853.52
PcMg	G	52.10	52.74	54.80	57.01	58.86	74.89	85.38	72.42
	S$_1$	728.03	84.70	29.53	43.44	54.45	278.85	137.38	23.87
PcNi	G	−0.16	−0.16	−0.16	−0.16	−0.15	−0.65	−0.27	−0.26
	S$_1$	2.25	1.64	1.17	5.19	0.94	−7.45	3.80	2.58

[a] The unit of $\langle\gamma\rangle$ is 10^{-34} esu and energy is eV.

lated prior to a nonresonant measurement, this state becomes a reference state. In the calculation of the SOS of eq 3, we select this excited state, usually, the first excited singlet state as the reference state, and the beginning of summation is from this reference state. Figures 3b−5b show the frequent dependence of $\langle\gamma\rangle$ with different optical physical processes at the first excited singlet state for PcM (M = H$_2$, Mg, Ni), respectively. Comparing with the obtained results of the ground state shown in figures 3a−5a, we can see that the calculated third-order optical polarizabilities $\langle\gamma\rangle$ at the first (S$_1$) excited singlet state of PcM (M = H$_2$, Mg, Ni) are enhanced throughout the considered frequency region. For example, the calculated $\langle\gamma(3\omega)\rangle$, $\langle\gamma(2\omega)\rangle$, and $\langle\gamma(\omega)\rangle$ at the S$_1$ excited state are 12.33×10^{-32}, -0.03×10^{-32}, and 0.24×10^{-32} esu for PcH$_2$ at an input energy of 0.650 eV, respectively. The absolute value $|\langle\gamma\rangle|$ of the S$_1$ excited state is compared with the $|\langle\gamma\rangle|$ of the S$_0$ ground state. Throughout the entire calculated frequency range, for the DFWM process as shown in figures 3−5 and Table 1, the |-$\langle\gamma(\omega)\rangle|$ of S$_1$ is significantly larger than that of S$_0$, reaching

enhancements as high as a factor of more than 100 for PcH$_2$ and more than 10 for PcNi. There is a small enhancement of the first excited singlet state if there is a large third-order optical polarizability at the ground state, such as in the PcMg; however, there is a large enhancement of excited state if there is a small third-order optical polarizability at the ground state, such as in the PcH$_2$. These findings are also obtained from the measurement of third-order optical nonlinearities in ground and excited states for squarylium cyanine dyes.[37] The dispersion behavior of $\langle \gamma \rangle$ at the S$_1$ is a difference from that at the S$_0$, and the nonresonant frequent region is smaller at the S$_1$ than at the S$_0$ in the THG, EFISHG, and DFWM processes. In fact, when we consider the applications of nonlinear optical materials, such as optical switching, modulating, and computing devices, a nonlinear susceptibility in a nonresonant region is most important. For the S$_0$ state of PcMg, one-photon absorption takes place at photon energy of more than 0.85 eV, and for the S$_1$ state of PcNi, one-photon absorption takes place at photon energy of more than 0.55 eV. The absorptivities of PcM compounds will result in the thermooptic effect and signal attenuation in nonlinear optical materials. When the transition energy from the S$_1$ state to higher excited states is close to an input photon energy of 1.165 eV, the phase-conjugated signal significantly increases in the DFWM process, that is, the resonance enhances in the dynamic $\langle \gamma(\omega) \rangle$ of S$_1$ as shown in Figures 3b-5b. This obtained result indicates a potential application in light-controlled molecular devices. Enhancements of excited states of optical nonlinearity in linear conjugate molecules[35] and bacteriochlorophylls[13,38] have been observed, and the third-order optical susceptibilities $\chi^{(3)}$ can be enhanced by more than 2 orders of magnitude. In terms of an analysis from the obtained results, we can introduce the three principal origins in the enhanced magnitude of nonlinear optical polarizibility $\langle \gamma \rangle$ of the S$_1$ excited state. First, the transition energies of $\hbar\omega_{mS1}$ between the S$_1$ and the intermediate virtual m ($m <$ 120 in this study) states are all smaller than the transition energies of the S$_0$ ground-state excitation processes. Second, many new excited states with large transition dipole moments are accessible through the populated S$_1$ state and the S$_m$ excited state. As can be seen in eq 3, the smaller transition energies of $\hbar\omega_{mn}$ and larger transition dipole moments of μ_{mn} cause the individual virtual excitation processes that makeup the γ at S$_1$ state to be larger than those of the γ at S$_0$ state. Third, in contrast to the γ at S$_0$, which is primarily determined by only two competing terms that nearly cancel one another, the γ at S$_1$ is composed of a great number of terms that are not only individually larger than those of the γ at S$_0$ but also have a reduced degree of cancellation, or even the same sign between the type-II and type-I terms.

4. Summary

In this work, we have presented the calculated third-order optical polarizabilities γ in the three optical processes at the both ground state and first excited singlet state for the PcM (M = H$_2$, Mg, Ni). It is found that the γ at the excited state is larger than that at ground state and the dispersion behavior of the γ at excited state is different from that at the ground state. The nonresonant frequent regions of the γ at the excited state are all smaller than those at ground state in the THG, EFISHG, and DFWM optical processes. There is a large enhancement of excited state if there has a small third-order optical polarizability at the ground state; however, there is a small enhancement of the first excited singlet state if there is a large third-order optical polarizability at the ground state. We also introduced the

principal origins that are a large transition dipole moment and small transition energy, and a reduced degree of cancellation of individual terms in the enhancements of nonlinear optical response at the excited state.

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(23) The input parameters are as follows: Slater exponents H, ζ_{1s} = 1.200 Å^{-1}; C, $\zeta_{2s,2p}$ = 1.625 Å^{-1}; N, $\zeta_{2s,2p}$ = 1.950 Å^{-1}; O, $\zeta_{2s,2p}$ = 2.275 Å^{-1}; Mg, $\zeta_{3s,3p}$ = 1.103 Å^{-1}; Ni, $\zeta_{4s,4p}$ = 1.473 Å^{-1}, ζ_{3d} = [6.706(0.4212) + 2.874(0.7066)] Å^{-1}. Valuence state ionization energies: H, I_{1s} = -13.06 eV; C, I_{2s} = -19.42 eV, I_{2p} = -10.70 eV.; N, I_{2s} = -25.58 eV, I_{2p} = -13.25 eV.; O, I_{2s} = -32.49 eV, I_{2p} = -15.88 eV.; Mg, I_{3s} = -7.64 eV, I_{3p} = -4.52 eV; Ni, I_{4s} = -9.94 eV, I_{4p} = -5.41 eV, I_{3d} = -14.46 eV. Coulomb repulsion integrals: H, γ = 12.85 eV.; C, γ = 11.11 eV.; N, γ = 12.01 eV.; O, γ = 13.00 eV.; Mg, $\gamma_{3s,3p}$ = 4.79 eV.; Ni, $\gamma_{4s,4p}$ = 7.34 eV, γ_{3d} = 13.10 eV, γ_{3d4s} = 8.61 eV. Resonance integrals: H, β = -11.8 eV.; C, β = -22.4 eV.; N, β = -27.6 eV.; O, β = -34.2 eV.; Mg, β = -9.45 eV.; Ni, $\beta_{4s,4p}$ = -1.0 eV, β_{3d} = -32.0 eV.

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(28) The INDO$-$SDCI (Mataga-Nishimoto) calculation of $\gamma_\pi(-3\omega;\omega,\omega,\omega)$ at $\omega = 0.66$ eV for benzene was 1.133×10^{-36} esu on page 798 of ref 29 and 1.14×10^{-36} esu by ours. Any one of them is added to γ_σ of 1.38×10^{-36} esu to be about 2.50×10^{-36} esu. This value is nearer than the INDO$-$SDCI (Ohno-Klopman) calculated value of 2.19×10^{-36} esu to the experimental value of 2.4×10^{-36} esu.[29] Accordingly, we select the Mataga-Nishimoto method in the treating electron repulsion integrals, and the obtained γ values are only used to make systematic comparisons in PcM compounds.

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