Computational investigation on non-linear optical properties of hexaphyrin and core modified hexaphyrins

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Abstract

Expanded porphyrin-based (Hexaphyrins) sensitizers are promising due to their excellent light harvesting feature in dye-sensitized solar cell (DSSC). We calculated the low-lying excitations of expanded porphyrins (EPs) as hexaphyrin and core modified hexaphyrin structures using Time-Dependent Density Functional Theory. Our calculation showed the EPs (both hexaphyrin and core modified hexaphyrin) have broad range of absorption band suitable for harvesting the visible and near infrared region of solar spectrum. All EPs studied here satisfy the energy condition of singlet fission (SF). SF is the process in which the theoretical limit of Shockley-Queisser (SQ) (33\%) can be overcome in single junction solar cell. The non-linear optical properties like first hyper polarizability $\beta$ and second order hyper polarizability $\gamma$ were calculated using coupled perturbed Hartree-Fock approach. From the second order NLO properties we carried out degenerate four wave mixing (DFWM) component ($\gamma^{(2)}(-\omega;\omega,\omega,-\omega)$) and finally quadratic non linear refractive indices of these EPs are calculated. Calculation showed EPs are promising as organic dye for the opto-electronic applications and useful for high efficiency DSSC and also useful for potential NLO materials as their hyper polarizabilities showed higher order non linearities.
1 INTRODUCTION

The organic conjugated molecules with diverse π electronic cloud delocalised all over are capable of showing various linear and non-linear optical (NLO) responses. Energy ordering of low-lying excited states of conjugated organic molecules show promise in the field of singlet fission (SF). SF is a multiexciton generation process in which from one excited singlet exciton two triplet excitons are generated. The generation of multiple excitons at a time overcomes the Shockley-Queisser (SQ) theoretical limit (∼33%) of photoconversion efficiency in single junction solar-cells. The energy criteria for SF is developed by Paci et al. in 2006 as:

\[ 2E(T_1 - S_0) \leq E(S_1 - S_0) \]  
and

\[ 2E(T_1 - S_0) < E(T_2 - S_0) \]

The first condition provides the essential energy condition for the formation of two triplet excitons out of one singlet exciton. The second condition nullify the triplet-triplet annihilation (TTA).

The non-linear optical response to applied electric fields is described in terms of the hyperpolarizabilities of the molecules. The effort was made earlier to calculate the first order hyperpolarizability in organic polar molecules due to their application in modulation of electro-optic effect, sensing, imaging, microfabrication and many more. The higher order nonlinearity was measured using Z scan method in crystals and also in molecules. Second and third order dynamic nonlinearity was theoretically observed recently in several acid derivatives.

In recent times porphyrin and metalloporphyrins are subject of immense interest due to their large non-linear responses such as third harmonic generation (THG) and two-photon absorption (TPA) cross sections. In this regard, expanded form of porphyrins (EPs) attract a considerable attention in recent times due to their interesting linear and nonlinear optical responses. Unlike porphyrin, EPs have more than four pyrrole rings or meso-links. It is also noted that number of pyrrole rings and meso-links in EPs guides their absorption spectra covering the entire visible range. EPs may have twisted geometry and possess 4n as well as 4n+2 π-electrons. Theoretical study based on correlated model shows EPs possessing 4n+2 electrons have large two-photon absorption than that of 4n electrons.

In this paper, hexaphyrin, core modified hexaphyrin such as Ni-hexaphyrin, Cu-hexaphyrin, and Au-hexaphyrin are considered to calculate linear and nonlinear optical properties. In modified hexaphyrin structures, the metals at the center in EPs provide a perturbation to the systems. The energy ordering the low-lying excited states in singlet and triplet subspaces are reported. Our calculation showed that all the EPs satisfy the first condition of SF however the second condition of SF is not satisfied. If one can tune the TTA cross section judicially then these material can be used as potential SF materials.

The non-linear optical properties of these systems both in presence of frequency (ω) and absence of it. From second order hyperpolarizability the
quadratic nonlinear refractive index \( n_2 \) of these molecules are calculated which may help to modulate the frequency control over LASER emission\(^{13}\) The sign of \( n_2 \) helps to identify the one or two photon frequency dominance. If the sign of \( n_2 \) is positive, two photon frequency dominates over one photon frequency and vice versa.

2 COMPUTATIONAL APPROACH

These molecules hexaphyrin (a), core modified hexaphyrin such as Ni-hexaphyrin (b), Cu-hexaphyrin (c), and Au-hexaphyrin (e) shown in Fig. 1 are first optimized in Gaussian\(^{14} \) based on density functional theory (DFT) with B3LYP exchange correlation functional\(^{15,16} \) The basis set used in optimization for C, H, N and O atoms is 6-31G(d,p) while LANL2DZ basis set is used for metal atoms like Ni, Cu and Au. The low-lying excited states in singlet and triplet subspaces are calculated on these optimized molecular structures (a – d) through Time Dependent Density Functional Theory (TDDFT)\(^{17} \) The polarizabilities of a molecule is defined as a response to the applied electric field \( \vec{\varepsilon} \) which induces a dipole moment \( \vec{\mu} \). The perturbed Hamiltonian \( (H') \) due to electric field is defined as \( \vec{H'} = \vec{\mu} \cdot \vec{\varepsilon} \). The total energy modified due to such perturbation can be written in Taylor’s
series as:

\[
E(\vec{\epsilon}) = E(0) + \sum_i \left( \frac{\partial E}{\partial \epsilon_i} \right) \epsilon_i + \frac{1}{2} \sum_i \sum_j \left( \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \right) \epsilon_i \epsilon_j + 1 \frac{1}{6} \sum_i \sum_j \sum_k \left( \frac{\partial^3 E}{\partial \epsilon_i \partial \epsilon_j \partial \epsilon_k} \right) \epsilon_i \epsilon_j \epsilon_k + \frac{1}{24} \sum_i \sum_j \sum_k \sum_l \times \left( \frac{\partial^4 E}{\partial \epsilon_i \partial \epsilon_j \partial \epsilon_k \partial \epsilon_l} \right) \epsilon_i \epsilon_j \epsilon_k \epsilon_l + \ldots \tag{3}
\]

The second term in Eqn. 3 on the R.H.S determines the \(i^{th}\) component of dipole moment and defined as:

\[
\mu_i = - \left( \frac{\partial E}{\partial \epsilon_i} \right) \tag{4}
\]

The higher order terms in the R.H.S will give linear polarizability \(\alpha_{ij}\), first hyper polarizability \(\beta_{ijk}^{(1)}\) and second hyper polarizability \(\gamma_{ijkl}^{(2)}\) defined as:

\[
\alpha_{ij} = - \left( \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \right) \tag{5}
\]

\[
\beta_{ijk} = - \left( \frac{\partial^3 E}{\partial \epsilon_i \partial \epsilon_j \partial \epsilon_k} \right) \tag{6}
\]

and

\[
\gamma_{ijkl}^{(2)} = - \left( \frac{\partial^4 E}{\partial \epsilon_i \partial \epsilon_j \partial \epsilon_k \partial \epsilon_l} \right) \tag{7}
\]

The isotropic average of polarizability given by \(\alpha_{avg} = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ})\). First hyperpolarizability \(\beta\) and second hyperpolarizability \(\gamma\) calculated in static condition using finite electric field of 0.001 a.u.

In presence of a time-dependent electric field \(E = E_0 + E_\omega \cos(\omega t)\), the above
Eqn. 3 can be rewritten as:

\[ E(\vec{\epsilon}) = E(0) + \alpha_{ij}(0; 0)\epsilon_{0i} + \alpha_{ij}(-\omega; \omega)\epsilon_{0j} + \frac{1}{2}\beta_{ijk}(0; 0, 0)\epsilon_{0i}\epsilon_{0j}\epsilon_{0k} + \frac{1}{4}\beta_{ijk}(0; \omega, -\omega)\epsilon_{0i}\epsilon_{\omega j}\epsilon_{\omega k} + \beta_{ijk}(-\omega; 0, 0)\epsilon_{0j}\epsilon_{\omega k}\cos(\omega t) + \frac{1}{6}\gamma^{(2)}_{ijkl}(0; 0, 0)\epsilon_{0i}\epsilon_{0j}\epsilon_{0k}\epsilon_{0l} \]

\[ + \frac{1}{2}\gamma^{(2)}_{ijkl}(-\omega; \omega, 0, 0)\epsilon_{\omega j}\epsilon_{\omega k}\epsilon_{0l}\cos(\omega t) + \frac{1}{8}\gamma^{(2)}_{ijkl}(-\omega; \omega, -\omega, \omega)\epsilon_{\omega j}\epsilon_{\omega k}\epsilon_{\omega l}\cos(\omega t) + \frac{1}{4}\gamma^{(2)}_{ijkl}(-2\omega; \omega, 0, 0)\epsilon_{\omega j}\epsilon_{0l}\cos(2\omega t) + \frac{1}{4}\gamma^{(2)}_{ijkl}(0; \omega, -\omega, 0)\epsilon_{\omega j}\epsilon_{\omega l}\cos(2\omega t) + \frac{1}{24}\gamma^{(2)}_{ijkl}(-3\omega; \omega, \omega, \omega)\epsilon_{\omega j}\epsilon_{\omega l}\epsilon_{\omega \rho}\cos(3\omega t) + \frac{1}{4}\gamma^{(2)}_{ijkl}(-2\omega; \omega, 0, 0)\epsilon_{\omega j}\epsilon_{\omega l}\epsilon_{\omega \rho}\cos(3\omega t) \]

Coupled perturbed Hartree-Fock method implemented in Gaussian09 is used to calculate frequency independent and frequency dependent linear and non-linear coefficients. Static second order hyper polarizability \( \gamma^{(2)}(0; 0, 0, 0) \) and frequency dependent dc-Kerr coefficients \( \gamma^{(2)}(-\omega; \omega, 0, 0) \), the electric field induced second harmonic (EFISH) \( \gamma^{(2)}(-2\omega; \omega, 0, 0) \) and degenerate four wave mixing (DFWM), \( \gamma^{(2)}(-\omega; \omega, -\omega, \omega) \) are calculated. In case of De-Kerr one measures \( \gamma^{(2)}_{k} = \frac{3}{2}(\gamma_{\parallel} - \gamma_{\perp}) \) where

\[ \gamma_{\parallel} = \frac{1}{15}\sum_{\xi\eta}\{\gamma_{\xi\xi\eta\eta} + \gamma_{\xi\eta\eta\xi} + \gamma_{\xi\eta\xi\eta}\} \]

and

\[ \gamma_{\perp} = \frac{1}{15}\sum_{\xi\eta}\{2\gamma_{\xi\eta\eta\xi} - \gamma_{\xi\xi\eta\eta}\} \]

where \( \eta, \xi = x, y, z \) and \( \gamma_{\parallel} \) is the second hyper polarizability when the field is parallely polarized and \( \gamma_{\perp} \) is the second hyper polarizability when the field is perpendicularly polarized.

\[ \gamma^{(2)}_{DFWM}(-\omega; \omega, -\omega, \omega) = \frac{1}{3}\gamma^{(2)}_{k}(-2\omega; \omega, 0, 0) + \gamma^{(2)}_{k}(-\omega; \omega, 0, 0) - \frac{1}{3}\gamma^{(2)}_{k}(0, 0, 0, 0) \]

(11)
as $\gamma_k^{(2)} = \frac{3}{2}(\gamma_\parallel - \gamma_\perp)$ equation 8 can be written as:

$$
\begin{align*}
\gamma_{DFWM}^{(2)}(-\omega; \omega, -\omega, \omega) & \approx \frac{1}{2} \{ \gamma_\parallel^{(2)}(-2\omega; \omega, \omega, 0) - \gamma_\perp^{(2)}(-2\omega; \omega, \omega, 0) \} \\
+ & \frac{3}{2} \{ \gamma_\parallel^{(2)}(-\omega; \omega, 0, 0) - \gamma_\perp^{(2)}(-\omega; \omega, 0, 0) \} \\
- & \frac{1}{2} \{ \gamma_\parallel^{(2)}(0; 0, 0, 0) - \gamma_\perp^{(2)}(0; 0, 0, 0) \} \\
\end{align*}
$$

(12)

Finally from DFWM properties quadratic non-linear refractive index can be calculated using the formula:

$$
n_2 \left( \frac{cm^2}{W} \right) = 8.28 \times 10^{-23} \gamma_{DFWM}^{(2)}(-\omega; \omega, -\omega, \omega)(a.u.).
$$

(13)

3 RESULTS AND DISCUSSION:

3.1 TD-DFT results for expanded porphyrin systems

The optical properties of these systems are calculated theoretically (Fig.2) has an agreement with the experimental results [1]. Use of metal center increases the charge transfer process [20], thus the $\Delta_{ST}$ gap can be theoretically tune to exhibit various optical processes. Expanded monomer with carbazole as donor and -COOH as acceptor shows maximum absorption peak near 501 nm which matches the experimental value for normal porphyrin with same D-A [21]. Use of D-porphyrin-COOH network minimizes the recombination procedure and helps to transfer photo generated charge carriers [22]. TDDFT calculation shows broad absorption bands of these molecules which can be used to harvest solar energy in visible and infrared region. Small $\Delta_{ST}$ gap is useful for reverse intersystem crossing as it was found in our previous calculation [23] and it is useful to the fabrication of organic light emitting diodes (OLED) which demands RISC. As the energy gap $\Delta_{ST}$ computed between 0.7 eV to 0.91 eV the singlet state can be repopulated by the triplets thermally. Experimental values for maximum absorption as in case of hexaphyrin shows peaks at 568 nm, 720 nm, 900 nm and 1018 nm [24–26] where the experiment was done in dichloromethane (DCM) solution and the end group is substituted with fluorobenzene. For b and c the end group substitution and solution phase during UV/vis calculation are same. For b the absorption peaks are found at 362 nm, 454 nm, 521 nm, 577 nm and 684 nm [27] and for c the peaks are at 400 nm, 610 nm, 920 nm and 1080 nm [28]. For d the solution is still DCM but now the meso positions of the hexaphyrin system are substituted by fluorobenzene and the $\beta$ positions are substituted with phenyl group have absorption peaks at 390 nm, 500 nm, 680 nm, 810 nm and 1210 nm [29]. All these values are in good agreement with our computed values [1]. The one photon gap $S_0 - S_1$ for these molecules are higher in energy from 0.0-0.5 eV with respect to $2(S_0 - T_1)$. The TDDFT calculation shows few values of $S_0 - S_1$ below the values we report with zero oscillator strength, thus we neglected them. So, all the molecule studied here shows satisfactory energy condition which can validate SF, however the second condition is not
satisfied[2]. These materials can be used to improve the photo-conversion efficiency of single junction solar cell by producing multiple excitons at a time. Thus they are capable of both harvestation of solar spectrum in visible and infrared region as well as SF materials to improve the performance of single junction solar cell by crossing SQ limit.

The emission spectra calculated in TDDFT method reveals that for molecule a and c there is high value of fluorescence intensity, but for molecule b and d the intensity is feeble (Fig 3). The Stoke’s shift for molecule a and c is minimal (5 and 16 nm respectively) which indicates that the excitation energy is almost completely emitted giving rise to the high fluorescence intensity(Table 1). For molecule b and the the shift is high (381 and 566 nm respectively) which implies loss of energy between excitation and emission(Table 1).

| Molecule | $S_1$ (eV) | $T_1$ (eV) | $f$   | Experimental $S_1$ (eV) | Stoke’s shift (nm) |
|----------|------------|------------|-------|-------------------------|-------------------|
| a        | 1.44       | 0.53       | 0.031 | 1.22                    |                   |
|          | 1.63       | 0.84       | 0.001 | 1.38                    |                   |
|          | 2.44       | 0.415      | 1.72  |                         | 5                 |
|          | 2.54       | 0.720      | 2.15  |                         |                   |
|          | 2.82       | 0.818      |       |                         |                   |
| b        | 1.32       | 0.41       | 0.031 | 1.81                    |                   |
|          | 2.09       | 0.57       | 0.075 | 2.15                    |                   |
|          | 2.13       | 0.105      | 2.38  |                         | 381               |
|          | 2.24       | 0.329      | 2.73  |                         |                   |
|          | 2.80       | 0.161      | 3.42  |                         |                   |
| c        | 1.44       | 0.72       | 0.040 | 1.15                    |                   |
|          | 1.58       | 0.82       | 0.030 | 1.35                    |                   |
|          | 1.66       | 0.006      | 2.03  |                         | 16                |
|          | 2.31       | 0.222      | 3.10  |                         |                   |
| d        | 1.18       | 0.48       | 0.040 | 1.02                    |                   |
|          | 2.07       | 0.58       | 0.263 | 1.53                    |                   |
|          | 2.20       | 0.337      | 1.82  |                         | 566               |
|          | 3.13       | 0.031      | 2.48  |                         |                   |

Table 1: TD-DFT results of expanded porphyrin monomer
3.2 Computed NLO properties

The NLO properties are calculated using coupled perturbed Hartree-Fock method. The frequency dependent calculation (done for the frequencies where the experimental absorption peaks are found to be maximum) shows extended nature of higher order non-linearities. The reason behind choosing the frequency where the maximum absorption takes place is due reason that at these frequency the phase matching occurs which is the essential criteria for any NLO phenomenon. It can be shown from our calculation that the $\alpha_{avg}$ values for a increased with frequency but the nonlinearity coming for the systems b, c and d (Fig. 3.2 and table 2, table 3). The $\beta$ and $\gamma$ values are increased due to the application of core modification2,3. The quadratic
non linear refractive index shows both positive and negative values (Fig 3.2 and table 4) which can be used to modulate LASER frequency for both one and two photon absorption.

Figure 4: Frequency dependent polarizability
Figure 5: Frequency dependent quadratic refractive index
Table 2: Frequency independent average polarizability $\alpha_{avg}$, first and second order hyper polarizability $\beta$ and $\gamma$

| Molecule | $\alpha_{avg}(0; 0; 0)$ (a.u.) | $\beta_{\parallel}(0; 0; 0)$ (a.u.) | $\beta_{\perp}(0; 0; 0)$ (a.u.) | $\gamma_{\parallel}(0; 0; 0; 0)$ (a.u.) | $\gamma_{\perp}(0; 0; 0; 0)$ (a.u.) |
|----------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|
| a        | $0.62 \times 10^3$            | $-0.12 \times 10^{-1}$        | $-0.40 \times 10^{-2}$        | $-0.45 \times 10^0$             | $-0.15 \times 10^0$             |
| b        | $0.64 \times 10^3$            | $0.18 \times 10^3$            | $0.61 \times 10^2$            | $-0.58 \times 10^0$             | $-0.19 \times 10^5$             |
| c        | $0.64 \times 10^3$            | $0.76 \times 10^{-2}$         | $0.25 \times 10^{-2}$         | $-0.19 \times 10^6$             | $-0.63 \times 10^5$             |
| d        | $0.63 \times 10^3$            | $-0.32 \times 10^0$           | $-0.11 \times 10^0$           | $-0.24 \times 10^3$             | $-0.81 \times 10^4$             |

Table 3: Frequency dependent average polarizability $\alpha_{avg}$ and first order hyper polarizability $\beta$

| Molecule | $\omega$ (a.u.) | $\alpha_{avg}(-\omega; \omega)$ (a.u.) | $\beta_{\parallel}(-2\omega; \omega, \omega)$ (a.u.) | $\beta_{\perp}(-2\omega; \omega, \omega)$ (a.u.) | $\beta_{\parallel}(-\omega; \omega, 0)$ (a.u.) | $\beta_{\perp}(-\omega; \omega, 0)$ (a.u.) |
|----------|-----------------|----------------------------------------|-------------------------------------------------|-------------------------------------------------|----------------------------------------|----------------------------------------|
| a        | 0.045           | $0.73 \times 10^4$                      | $0.10 \times 10^4$                               | $-0.44 \times 10^0$                              | $-0.42 \times 10^9$                   | $-0.42 \times 10^9$                   |
|          | 0.050           | $0.85 \times 10^3$                      | $-0.16 \times 10^1$                              | $0.93 \times 10^1$                               | $-0.20 \times 10^4$                   | $0.48 \times 10^9$                    |
|          | 0.063           | $0.81 \times 10^3$                      | $0.47 \times 10^1$                               | $-0.64 \times 10^0$                              | $0.13 \times 10^1$                    | $0.12 \times 10^1$                    |
|          | 0.080           | $0.13 \times 10^4$                      | $0.10 \times 10^2$                               | $-0.39 \times 10^3$                              | $0.10 \times 10^6$                   | $-0.12 \times 10^1$                   |
| b        | 0.066           | $0.92 \times 10^4$                      | $0.36 \times 10^4$                               | $-0.46 \times 10^5$                              | $0.20 \times 10^5$                   | $0.31 \times 10^5$                    |
|          | 0.079           | $0.58 \times 10^3$                      | $0.26 \times 10^6$                               | $0.18 \times 10^7$                              | $0.38 \times 10^5$                   | $0.78 \times 10^2$                    |
|          | 0.087           | $-0.10 \times 10^4$                     | $0.25 \times 10^5$                               | $-0.18 \times 10^5$                              | $0.38 \times 10^5$                   | $0.78 \times 10^2$                    |
|          | 0.100           | $0.55 \times 10^3$                      | $0.12 \times 10^6$                               | $0.22 \times 10^6$                              | $0.10 \times 10^6$                   | $0.10 \times 10^6$                    |
|          | 0.126           | $-0.13 \times 10^3$                     | $-0.65 \times 10^6$                              | $-0.65 \times 10^6$                              | $-0.12 \times 10^6$                  | $-0.12 \times 10^6$                   |
| c        | 0.042           | $0.72 \times 10^4$                      | $0.66 \times 10^4$                               | $0.38 \times 10^0$                               | $0.12 \times 10^2$                   | $0.10 \times 10^2$                    |
|          | 0.049           | $0.83 \times 10^3$                      | $0.27 \times 10^9$                               | $-0.86 \times 10^{-2}$                          | $0.84 \times 10^{-1}$                | $-0.11 \times 10^{-1}$                |
|          | 0.075           | $0.98 \times 10^3$                      | $0.16 \times 10^1$                               | $0.70 \times 10^0$                               | $-0.12 \times 10^6$                  | $-0.10 \times 10^6$                   |
|          | 0.114           | $0.75 \times 10^3$                      | $0.49 \times 10^0$                               | $0.31 \times 10^1$                               | $0.13 \times 10^2$                   | $-0.42 \times 10^1$                   |
| d        | 0.037           | $0.75 \times 10^4$                      | $0.13 \times 10^4$                               | $0.19 \times 10^1$                               | $-0.17 \times 10^1$                  | $-0.18 \times 10^1$                   |
|          | 0.056           | $0.72 \times 10^3$                      | $0.73 \times 10^1$                               | $0.10 \times 10^2$                               | $0.95 \times 10^0$                   | $0.75 \times 10^0$                    |
|          | 0.067           | $0.94 \times 10^3$                      | $0.18 \times 10^0$                               | $0.60 \times 10^0$                               | $0.12 \times 10^1$                   | $0.12 \times 10^1$                    |
|          | 0.091           | $0.48 \times 10^3$                      | $-0.70 \times 10^2$                              | $-0.16 \times 10^3$                              | $-0.22 \times 10^1$                  | $-0.33 \times 10^1$                   |
|          | 0.116           | $0.72 \times 10^2$                      | $-0.93 \times 10^2$                              | $0.74 \times 10^2$                               | $0.82 \times 10^1$                   | $-0.23 \times 10^2$                   |
Table 4: Frequency dependent average second order hyper polarizability $\gamma$

| Molecule   | $\omega$ (a.u.) | $\gamma_{\parallel}(-2\omega; \omega, \omega, 0)$ (a.u.) | $\gamma_{\perp}(-2\omega; \omega, \omega, 0)$ (a.u.) | $\gamma_{\parallel}(-\omega; \omega, 0, 0)$ (a.u.) | $\gamma_{\perp}(-\omega; \omega, 0, 0)$ (a.u.) |
|------------|------------------|------------------------------------------------------|------------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| Hexaphyrin | 0.045            | -5.26x10^6                                           | 7.51x10^7                                            | 0.18x10^6                                       | 7.41x10^5                                       |
|            | 0.050            | 7.71x10^6                                            | 4.41x10^7                                            | 0.22x10^7                                       | 7.51x10^6                                       |
|            | 0.063            | 1.11x10^7                                            | -8.26x10^6                                          | -0.38x10^6                                     | -0.63x10^5                                     |
|            | 0.080            | -1.36x10^8                                           | -8.51x10^7                                          | -0.15x10^7                                     | -0.61x10^5                                     |
| Ni Hexaphyrin | 0.066        | 0.36x10^6                                            | -4.46x10^6                                          | -0.66x10^6                                     | -0.22x10^6                                     |
|            | 0.079            | -1.36x10^11                                           | -8.28x10^9                                          | -0.45x10^7                                     | -0.13x10^8                                     |
|            | 0.087            | -2.41x10^9                                            | 8.71x10^9                                           | 0.35x10^9                                      | 0.92x10^8                                      |
|            | 0.100            | -1.11x10^10                                           | -2.56x10^8                                          | -0.44x10^8                                     | 0.16x10^9                                      |
|            | 0.126            | 0.34x10^9                                            | -4.56x10^9                                          | 0.15x10^10                                     | 0.48x10^9                                      |
| Cu Hexaphyrin | 0.042        | -5.81x10^6                                            | 1.11x10^7                                           | 0.22x10^6                                      | 0.16x10^6                                      |
|            | 0.049            | -4.71x10^6                                            | -3.21x10^6                                          | 0.11x10^7                                      | 0.32x10^6                                      |
|            | 0.075            | 0.34x10^6                                            | 1.31x10^6                                           | -0.38x10^7                                     | -0.12x10^7                                     |
|            | 0.114            | -1.11x10^9                                           | -2.41x10^8                                          | 0.42x10^9                                      | 0.70x10^8                                      |
| Au Hexaphyrin | 0.037        | -5.91x10^6                                            | 3.31x10^7                                           | 0.65x10^6                                      | 0.21x10^6                                      |
|            | 0.056            | 0.11x10^8                                            | 0.57x10^7                                           | -0.20x10^6                                     | -0.23x10^5                                     |
|            | 0.067            | 0.40x10^6                                            | -0.40x10^7                                          | -0.48x10^6                                     | -0.81x10^5                                     |
|            | 0.091            | 0.18x10^9                                            | 0.74x10^8                                           | -0.26x10^7                                     | -0.74x10^6                                     |
|            | 0.116            | 0.30x10^9                                            | 0.12x10^9                                           | 0.36x10^8                                      | 0.13x10^8                                      |
Table 5: Values for $\gamma_{DFWM}$ and $n_2 \left( \frac{cm^2}{W} \right)$

| Molecule      | $\omega$  | $\gamma_{DFWM}$ (a.u.) | $n_2$ (a.u.) |
|---------------|-----------|-------------------------|--------------|
| Hexaphyrin    | 0.045     | -3.83x10^6              | -3.17x10^{-16} |
|               | 0.050     | 1.87x10^7               | 1.55x10^{-15} |
|               | 0.063     | 4.99x10^5               | 4.13x10^{-17} |
|               | 0.080     | -4.39x10^6              | -3.63x10^{-16} |
| Ni Hexaphyrin | 0.066     | -2.40x10^6              | -1.98x10^{-16} |
|               | 0.079     | -6.07x10^9              | -5.02x10^{-13} |
|               | 0.087     | -1.68x10^8              | -1.39x10^{-14} |
|               | 0.100     | -8.43x10^8              | -6.98x10^{-14} |
|               | 0.126     | 1.90x10^9               | 1.57x10^{-13} |
| Cu Hexaphyrin | 0.042     | -3.29x10^6              | -2.72x10^{-16} |
|               | 0.049     | 1.16x10^6               | 9.60x10^{-17} |
|               | 0.075     | -3.73x10^6              | -3.09x10^{-16} |
|               | 0.114     | 4.85x10^8               | 4.01x10^{-14} |
| Au Hexaphyrin | 0.037     | -3.93x10^6              | -3.25x10^{-16} |
|               | 0.056     | 2.35x10^6               | 1.94x10^{-16} |
|               | 0.067     | 1.61x10^6               | 1.33x10^{-16} |
|               | 0.091     | 5.02x10^7               | 4.15x10^{-15} |
|               | 0.116     | -5.57x10^7              | -4.61x10^{-15} |

The sign of DFWM and $n_2$ depends on the contribution from one photon and two photon. If the two photon contribution is dominating in the non-resonant regime then the sign of DFWM and $n_2$ will be positive and vice-versa.

4 CONCLUSION

We concluded that the range of the absorption band of EPs are diverse in nature. Thus solar energy can be harvested in visible as well as near infrared region of the solar spectrum. Here we got the values for singlet to triplet gap ($\Delta E_{ST}$) are ranging from 0.70 to 0.91 which is quite small than the normal porphyrin dimer, for normal porphyrin these values ranges from 1.52-1.69. Thus EPs are showing better results for $\Delta E_{ST}$ compared to porphyrin. When we use metal center the absorption peaks are quite similar to the experimental result of EPs whose core modified with metal center. All the systems studied satisfy the first condition for SF, which can be applicable to design potential SF material to overcome theoretical SQ limit. Small $\Delta_{ST}$ gap helps the triplet excitons to populate themselves to singlet exciton states through RISC and made possible for the fabrication of OLED. The emission spectra shows for molecule a and c the Stoke’s
shift is minimum giving rise to higher fluorescence intensity compared to molecule b and d with large Stoke’s shift. The NLO properties studied shows higher order nonlinearity in hyperpolarizability. These properties have many applications in the field of electro-optic measurements, sensing, LASERS and many more. The quadratic non linear refractive index $n_2$ shows both positive and negative values which indicates that for both two photon and one photon frequency the modulation of LASER intensity can be done. So we can choose the porphyrin systems for our opto-electronic and NLO calculations as these systems shows diverse application. Successful tuning of the $\Delta_{ST}$ gap and frequency lead these materials to fabricate electro-optic miniaturizer.

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