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Improving the Optical Properties of Porphyrin Ring with Different Substitutions: As Candidate Using in Photosensitizer

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ABSTRACTS

In this research, different donor and acceptor substitutions were employed in attachment with porphyrin molecule and the optical properties improvement of it was studied. It was shown that the substituted porphyrin formation from hypothetical reagents was very exothermic. It was determined that all substituted porphyrin had lower value energy gap (E_g) in comparison to pristine porphyrin. The study of optical properties of substitutions showed that the substituents significantly improved the optical response of porphyrin. It was demonstrated that the superior optical properties obtained when highly electron donor substitutions such as NHLi and OLi was attached to the porphyrin molecule which corresponds to higher values of dipole moments. In addition, it was shown that the type of electron acceptor groups in the push-pull system had a slight effect on porphyrin's optical properties.

Keywords: Porphyrin, Photosensitizer, Push-Pull System, Optical Properties, donor and Acceptor Substituents.

1. INTRODUCTION

The main source of energy in our life is sunlight. Sunlight is transformed into chemical energy by green plants and other certain organisms via photosynthesis. Sunlight enables people to see everything during the day and the sun's energy can be captured through solar panels to generate electricity. Besides that, sunlight also can be used to perform photochemical reactions. In all cases of application of light, photosensitizers were employed to facilitate absorption and transformation of light's energy to a system. For instance, the chlorophyll was used to absorb light in photosynthesis. A dye-sensitized solar cell is the improved form of a solar cell. Photodynamic therapy is one of the most important uses of photosensitizers. An ideal photosensitizer for photodynamic therapy (PDT) must be non-toxic in the absence of light, have efficient at absorbing light energy and transferring it to the substrate, able to absorb light at longer wavelengths, increases light penetration into tissue, accumulated preferentially within tumours, and cleared rapidly from the normal surrounding tissue and organs at risk. The famous photosensitizers used in PDT and another optical research is porphyrin [1-2]. Highly conjugation system enables the porphyrin to have intense light adsorption in the visible region which plays an important role in the chemistry worlds and biology.

Donor-acceptor type of organic dyes (push-pull system) which comprised of three parts, electron donor (D) and acceptor (A) groups connected to the π-conjugated backbone. Such systems have an enormous possible implementation in optoelectronic and photonics [2–10]. These chromophores are a good choice in substances with high non-linear optical properties

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(NLO) [11–13] as well as dye-sensitized solar cells (DSSCs) [14–16]. In the previous published research, the annulene molecule as an aromatic π-conjugated system was sandwiched between two donor and acceptor substituents (push-pull system) and the optical properties improvement of it was studied [17]. The other research works studied the effect of C_{20} on optical properties of tetraphenyl porphyrin molecule [18]. The effects of some electron donating and electron withdrawing groups on the optical properties of porphyrin molecule are studied in this study.

2. COMPUTATIONAL DETAIL

All structures were optimized using B3LYP [19,20] method and exchange and correlation functional with 6-311 g(d,p) basis set. Vibrational frequencies were implemented at the same level of theory to confirm all structural are in global minimal. All calculation employed using Gaussian09 package [21]. The electronic density of state for all optimized structures was done using GaussSum03 [22]. Energy gap (Eg) was calculated based on the density of states (DOS) results:

$$Eg = E_{LUMO} - E_{HOMO} \quad (1)$$

where E_{HOMO} is the energy of the highest occupied molecular orbital (HOMO) and E_{LUMO} is the energy of the lowest unoccupied molecular orbital (LUMO). Electronic absorption spectra of all structures were calculated using time-dependent density functional theory (TDDFT) [23–25] employing the same basis set. In order to study the effect of donor and acceptor groups, different groups were chosen and the porphyrin molecule was sandwiched between them. For electron donor substitutions, the amine ($-NH_2$), lithium amide (-NHLi), N, N-dimethylamine ($-N(CH_3)_2$), methoxy ($-OCH_3$) and lithium oxide (-OLi) groups and for electron acceptor, the cyanide (-CN) and tri-fluorocarbon ($-CF_3$) groups were used.

3. RESULT AND DISCUSSION

3.1 Structural Optimization

The structures of all considered molecules were optimized at the B3LYP/6-311G(d,p) level of theory. In Figure 1 the optimized structure of all considered molecules is shown.

Porphyrin OLi-POR-CN N(CH$_3$)$_2$-POR-CN

NH$_2$-POR-CN NHLi-POR-CN OCH$_3$-POR-CN

OLi-POR-CF$_3$ N(CH$_3$)$_2$-POR-CF$_3$ NH$_2$-POR-CF$_3$

OCH$_3$-POR-CF$_3$ NHLi-POR-CF$_3$

Figure 1. The optimized structures of considered molecules.

To predict the feasibility of the formation reaction of these molecules, a hypothetical reaction was assumed in which the reaction was taken place between the doubly trans-chlorinated porphyrin molecules and other reagents. For instance, the reaction in Equation 2:

$$Annulene - Cl_2 + Na^+A^- + \ Na^+D^- \rightarrow D - Annulene - A + 2NaCl \qquad (2)$$

Where A and D show electron acceptor and electron donor groups, respectively. The enthalpies, Gibbs free energies and energies of the formation reactions were calculated. In Table 1, the results of Enthalpies and Gibbs free energies and energies of formation of these molecules are presented.

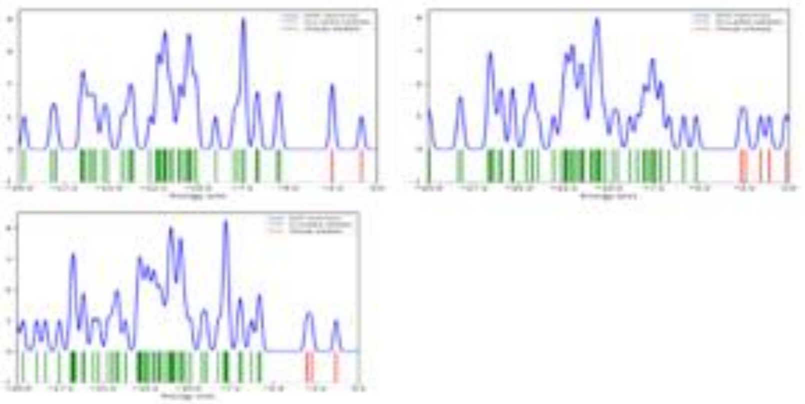
Table 1 The results of Enthalpies, Gibbs free energies for the formation reaction of considered molecules

Molecules	**ΔH (Kcal/mol)**	**ΔG (Kcal/mol)**	**ΔE (Kcal/mol)**
CN- POR-OLi	-125.72	-123.32	-127.07
CN- POR -$N(CH_3)_2$	-101.50	-97.55	-105.23
CN- POR -NH_2	-106.86	-104.65	-110.65
CN- POR -OCH_3	-85.092	-82.05	-88.092
CN-POR -NHLi	-142.17	-138.83	-145.33
CF_3- POR -OLi	-140.68	-135.08	-142.83
CF_3-POR -$N(CH_3)_2$	-116.98	-109.83	-121.57
CF_3-POR-NH_2	-122.27	-116.89	-124.66
CF_3-POR-OCH_3	-100.34	-94.16	-104.18
CF_3-POR-NHLi	-153.49	-147.01	-157.38

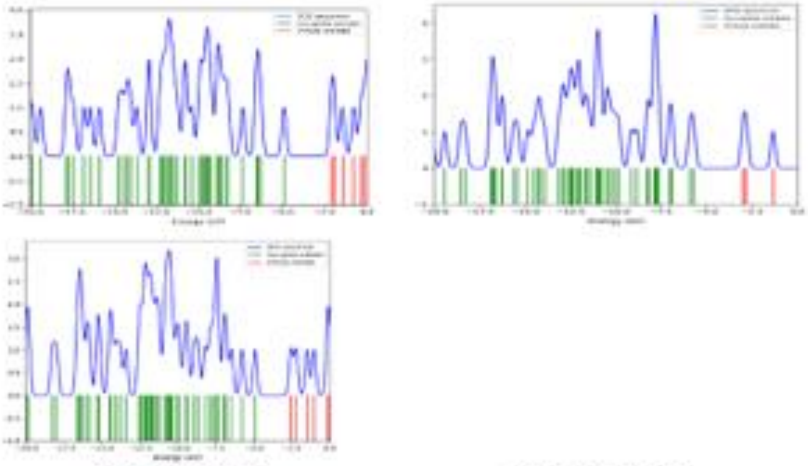
As presented in Table 1, the high negative values of enthalpies and Gibbs free energies and energies of formation show the possibility of their formation. Among them, the lower negative value of enthalpy, Gibbs free energy and energy belongs to CN- POR -OCH_3 molecule meanwhile the CF_3-POR-NHLi has higher negative values of enthalpy, Gibbs free energy and energy.

3.2 Electronic Properties

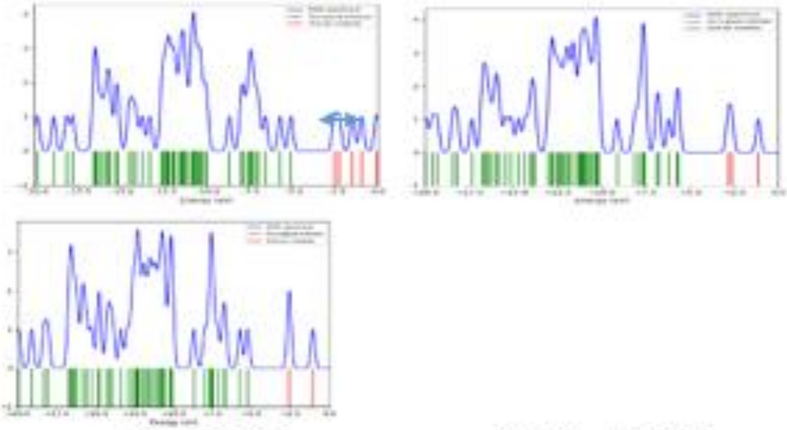
The density of state for all considered molecules was calculated as illustrated in Figure2.



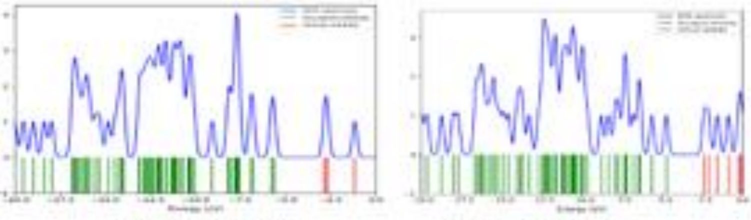
PORPHYRIN OLi-POR-CN N(CH$_3$)$_2$-POR-CN



NH$_2$-POR-CN OCH$_3$-POR-CN NHLi-POR-CN



OLi-POR-CF3 N(CH$_3$)$_2$-POR-CF$_3$ NH$_2$-POR-CF$_3$



OCH$_3$-POR-CF$_3$ NHLi-POR-CF$_3$

Figure 2. The DOS spectrum of all considered molecules.

Using the DOS spectrum results, the E_{HOMO}, E_{LUMO} and E_g are calculated as in Table 2.

Table 2 The results of the E_{HOMO}, E_{LUMO} and E_g for all considered molecules

Molecules	**HOMO**	**LUMO**	**E_g**	**μ(Depye)**
Porphyrin	-5.42	-2.5	2.92	0.0002
CN-POR-OLi	-5.15	-2.67	2.48	10.84
CN-POR-N(CH3)2	-5.75	-3.02	2.73	6.57
CN-POR-NH2	-5.34	-2.74	2.6	8.92
CN-POR-OCH3	-5.72	-3	2.72	6.32
CN-POR-NHLi	-4.91	-2.55	2.36	12.33
CF3-POR-OLi	-5.07	-2.54	2.53	8.69
CF3-POR-N(CH3)2	-5.67	-2.85	2.82	4.32
CF3-POR-NH2	-5.26	-2.59	2.67	6.64
CF3-POR-OCH3	-5.64	-2.83	2.81	4.15
CF3-POR-NHLi	-4.74	-2.38	2.36	10.47

As shown in Table 2, between all structures, the porphyrin has the highest value of E_g. The lowest value of E_g belongs to a structure that has NHLi substitution. Besides, high values of dipole moment were obtained for the NHLi-POR-CN and NHLi-POR-CF_3 molecules. The high values of dipole moments may be the result of higher charge transfer from electron donor group toward the porphyrin and electron withdrawing substituent.

3.3 Optical Properties

The time-dependent density functional theory (TDDFT) was used to calculate the UV spectrum for all these molecules. The -CN substituent, as an electron withdrawing substituent, was chosen, and attached to porphyrin molecule and different electron donating substituents was located on the other side. Figure3 illustrated the results of calculated UV spectra for porphyrin molecule substituted with -CN in one side and all other substituents in another side.

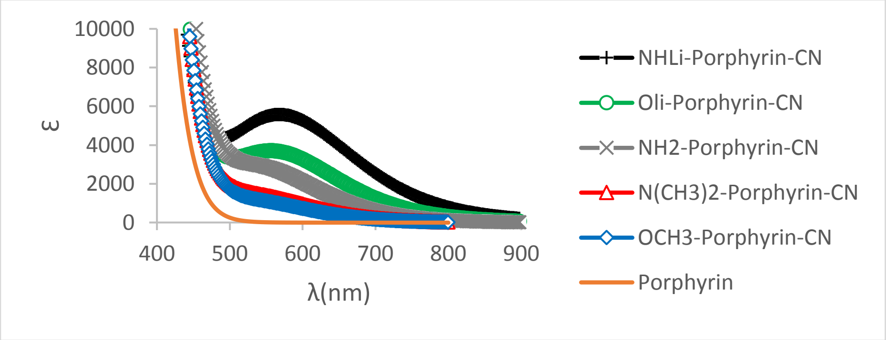


Figure 3. Results of UV spectra of porphyrin molecule substituted with CN and all other substitutions.

As shown in Figure3, the substitutions have a noble effect on optical properties of porphyrin. Between the 500 nm to 700 nm, the porphyrin has slight light adsorption. However, in donor and acceptor existence, light adsorption of it remarkably increased. Higher influenced was seen when the -CN and -NHLi substitution was employed. This may be due to higher electron donating characteristics of -NHLi substituent.

Besides that, the -CF_3 as other electron withdrawing substituent was located in one side of porphyrin and all other electron donating substitutions were located in another side of it and the UV spectra of all molecules were calculated. Figure4 shows the results of UV spectra for these molecules.

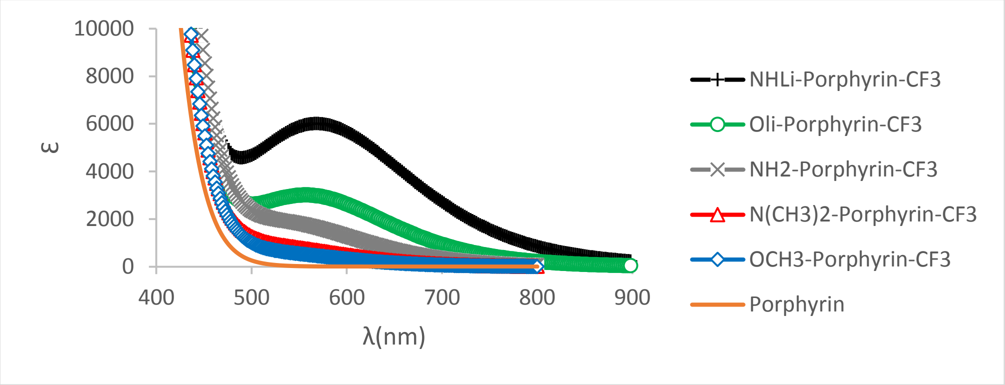


Figure 4. Results of UV spectra of porphyrin molecule substituted with CF3 and all other substitutions.

Similar to the -CN substitutions, the -CF_3 group in accompany with other donor substitutions have a great influence on the optical properties of porphyrin. As illustrated in -CN case, higher effects were observed when -NHLi and -OLi present. The higher optical activity of porphyrin molecule in the existence of -NHLi and -OLi substituents may be the results of their electron releasing characteristics.

Observing the effect of single substituents on optical properties of porphyrin, the considered substituents were attached to porphyrin molecule and the optical properties of them were calculated. In Figure5, the calculated light absorption for pristine and substituted porphyrin with different substituents are compared.

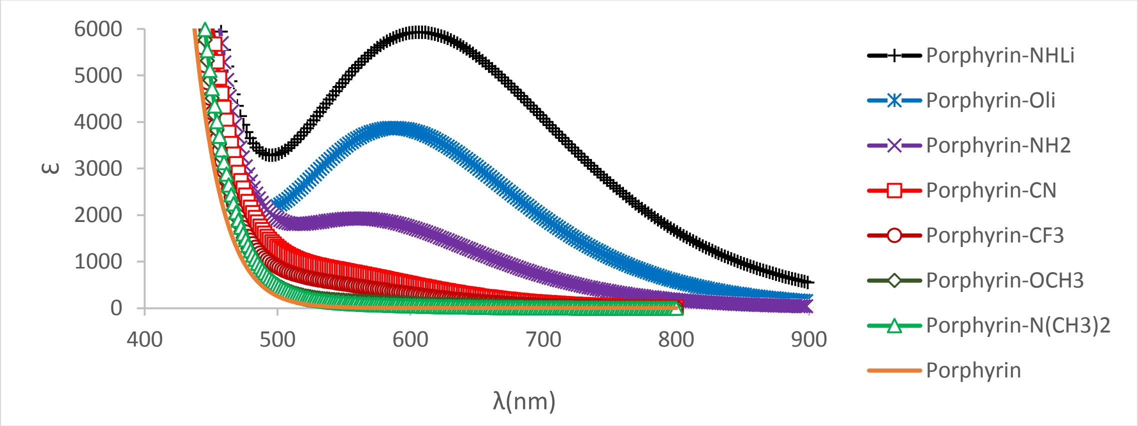


Figure 5. Calculated light absorption for pristine and substituted porphyrin.

As shown in Figure5, all substituents improve the optical properties of porphyrin while the -NHLi and -OLi substitutions have greater effects than the other substitutions. Results in Figure 3-5 indicate that the -CN and -CF_3 (electron withdrawing substitutions) have a slight effect in the push-pull system and the optical properties of porphyrin mainly affected by -NHLi and -OLi substitutions.

In our previously published article [18], the fullerene C_{20} was attached to porphyrin molecule to improve its optical properties of it. In comparison to that research, it is shown that the donor and acceptor groups have higher effects than fullerene C_{20}. The donors and acceptors simultaneously increase the absorption intensity and make the transitions red-shifted. Additionally, the effect of donor and acceptor groups on the optical properties of porphyrin molecule was studied [26]. They showed that the donor and acceptor groups improve the optical properties of porphyrin. Compared to other related works [ref], this study employed simpler donor and acceptor groups and make higher improvements in optical properties of porphyrin.

CONCLUSION

The influences of different donor and acceptor substitutions are studied in this research. The energy analysis demonstrates that the formation of these molecules from hypothetical reagents is very exothermic. The E_g calculation shows that substituted porphyrin has a lower value of E_g in comparison to pristine porphyrin. The dipole moment of the porphyrin molecule is drastically affected by these substituents. The higher values of dipole moments obtained for NHLi-POR-CN and NHLi-POR-CF_3 molecules. The optical properties study of these molecules shows that all substitutions increase the optical response of porphyrin. It has shown that the higher optical properties obtained when the high electron donor substitution such as -NHLi substitution attached to porphyrin molecule which corresponds to higher value of dipole moments (higher charge transfer).

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