

Study of Substituent Effect on Properties of Platinum(II) Porphyrin Semiconductor Using Density Functional Theory

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ABSTRACT

Study of substituent effect on properties of platinum(II) porphyrin had been performed using the DFT method. The aim of the study is to investigate the effect of a substituent group on the electronic and optical properties of the platinum(II) porphyrin. Geometry optimization was conducted using DFT/B3LYP/LANL2DZ to obtain the molecular structure, electronic structure and energy profile. Band gap energy (E_g), the density of states (DOS), and UV-visible spectra are the semiconductor parameters to study. Computational results show that platinum(II) porphyrin and substituted platinum(II) porphyrin have properties of semiconductor based on E_g value, DOS, and UV-visible spectra. The results show that Mulliken partial charges of electron withdrawing substituents are higher than the electron donating substituents (CH_3 , OH, and NH_2). E_g values of the complexes with respect to the substituents follow this order: $\text{NH}_2 < \text{OH} < \text{NO}_2 < \text{COOH} < \text{I} < \text{CH}_3 < \text{Br} < \text{F} < \text{H}$, for DOS_{HOMO} values, the order is $\text{CH}_3 < \text{NO}_2 < \text{I} < \text{OH} < \text{F} < \text{NH}_2 < \text{COOH} < \text{Br} < \text{H}$ and the maximum wavelength (λ_{max}) for UV-visible adsorption spectra follows this order: $\text{NH}_2 > \text{OH} > \text{COOH} > \text{NO}_2 > \text{I} > \text{Br} > \text{CH}_3 > \text{F} > \text{H}$. Molecules with smaller E_g and DOS_{HOMO} values and higher λ_{max} are considered as the most appropriate semiconductor materials. Our results show that Pt(II)P- NH_2 has the smallest E_g and the highest λ_{max} among other substituted platinum(II) porphyrin molecules. Therefore, Pt(II)P- NH_2 are the most suitable semiconductor material based on the aforementioned criteria.

Keywords: platinum(II) porphyrin; semiconductor; substituent effect

ABSTRAK

Kajian pengaruh substituen terhadap sifat semikonduktor platina(II) porfirin dilakukan dengan metode DFT. Tujuan dari penelitian ini adalah untuk mempelajari pengaruh substituen terhadap sifat elektronik dan optik kompleks platina(II) porfirin. Optimasi geometri dilakukan dengan menggunakan metode DFT/B3LYP/LANL2DZ terhadap kompleks platina(II) porfirin sehingga diperoleh stuktur dan sifat elektronik kompleks. Celah pita (E_g), rapat keadaan (DOS) dan spektra serapan UV-Vis menjadi paramater sifat semikonduktor kompleks platina(II) porfirin. Hasil perhitungan menunjukkan bahwa muatan parsial Mulliken dari substituent penarik elektron lebih tinggi dibandingkan dengan substituen pendorong elektron. Harga E_g dari kompleks dengan substituent adalah: $\text{NH}_2 < \text{OH} < \text{NO}_2 < \text{COOH} < \text{I} < \text{CH}_3 < \text{Br} < \text{F} < \text{H}$, DOS_{HOMO} : $\text{CH}_3 < \text{NO}_2 < \text{I} < \text{OH} < \text{F} < \text{NH}_2 < \text{COOH} < \text{Br} < \text{H}$ dan spektra UV-Visible: $\text{NH}_2 > \text{OH} > \text{COOH} > \text{NO}_2 > \text{I} > \text{Br} > \text{CH}_3 > \text{F} > \text{H}$. Kita membutuhkan kompleks platina(II)porfirin yang memiliki nilai E_g dan DOS_{HOMO} yang paling kecil dan spectra UV-Visible yang paling panjang. Kita dapat menyimpulkan bahwa Pt(II)P- NH_2 memberikan performa terbaik dari paramater E_g , DOS dan spectra UV-Visible, oleh karena itu Pt(II)P- NH_2 dapat direkomendasikan sebagai material semikonduktor yang sangat potensial.

Kata Kunci: platina(II) porfirin; semikonduktor; pengaruh substituen

INTRODUCTION

Porphyrins are an organic-macrocyclic compound that is ubiquitous in the world, and they have been called the pigment of life [1]. It has identical conjugated-framework consisting of single bonds (C-C, C-N, C-H, N-H) and double bonds (C=C and C=N). The electroluminescence of porphyrin evidence that porphyrin is the composer of semiconductor materials. Porphyrin

can be modified by adding substituent, adding metal ion in the center, or enlarging macrocyclic system.

Structures, properties and applications of metalloporphyrin complexes have been extensively studied both experimentally [2-6] and theoretically [7-13]. Metalloporphyrin has various structures starting from planar to concave depending on the central ions and substituent group due to the distortion effects [3]. The semiconducting properties of metalloporphyrin

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show that the small energy gap and the high electron density above the Fermi level can be used as the sensitizer on the dye-sensitized solar cell [4-10]. Metalloporphyrin complexes' electronic properties can be modified by changing the central ion and adding substituent group that can affect their electronic band gap and electronic absorption spectra [5-6,10].

Among all of the metalloporphyrins, the platinum(II) porphyrin seems to be a good candidate for a new semiconductor such as an organic light emitting diode (OLED) and photosensitizer [14-16]. Pt(II)-porphyrin is a low-spin diamagnetic complex as shown experimentally [16-18], however, the studies on the substituent effects on both structural and electronic properties of Pt(II)-porphyrin are the best insufficient. Because of that, we decided to conduct a theoretical study focusing on the substituent effects on the structural and electronic properties of Pt(II)-porphyrin. The properties of the substituted Pt(II)-porphyrin with CH₃, F, I, Br, COOH, NH₂, OH and NO₂ will be compared with the properties of pristine Pt (II) porphyrin. The effects of the different types of the substituents, i.e. electron donating or electron withdrawing will be further discussed. Several studies show that substituent can affect not only the UV-Visible spectra but also the geometry of metalloporphyrin [11-12].

COMPUTATIONAL METHODS

Materials

Platinum(II) porphyrin complex with electron donating (CH₃, OH, and NH₂) and withdrawing substituents (NO₂, COOH, I, Br, F) on meso position (R), as shown in Fig. 1(a).

Instrumentation

This research used a quad-core High Performance Computer (HPC) remotely accessed from Directorate of Systems and Information Resources, Universitas Gadjah Mada (UGM). All of the quantum mechanical calculations were performed using Gaussian 09 package [19]. Gauss Sum 2.2.5 [20] was used to calculate the density of states (DOS) of the complexes.

Procedure

Geometry optimization

Platinum(II) octa ethyl porphyrin (PtOEP) had been chosen as a parameter with XRD data result from Sheppard et al. [18]. The optimization was performed using DFT method with B3LYP hybrid functional and LANL2DZ basis set for all atoms. Charge and total spin multiplicity were set on either 0 or 1 depending on the electronic configuration of the molecules.

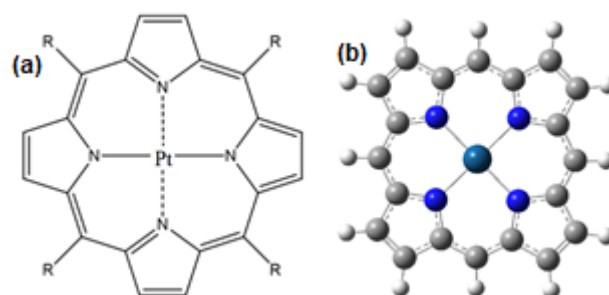


Fig 1. Structure of (a) Pt(II)-porphyrin substituted R and (b) the optimized geometry of Pt(II)-porphyrin

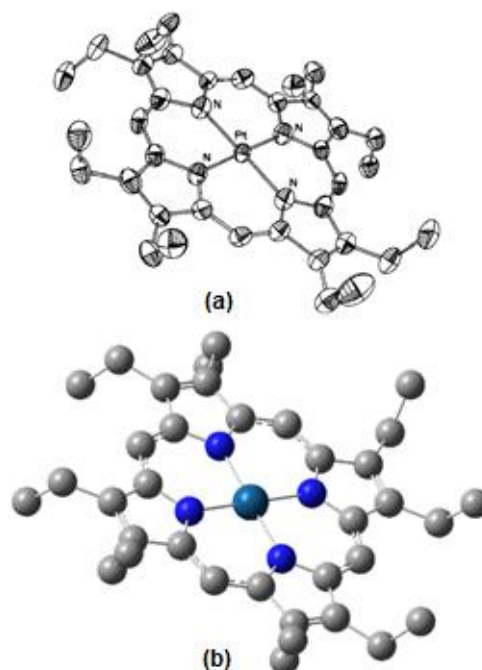


Fig 2. Platinum(II) octaethylporphyrin (PtOEP) from XRD (Sheppard,1988) (a) and the result geometry optimization with DFT/LANL2DZ/B3LYP (b)

Calculation of the electronic properties

The UV/Vis absorption spectra calculation was conducted using time-dependent DFT method on the optimized ground state complex with 10 states ($N = 10$). The functional and the basis set were similar with the ground state energy optimization calculation. Calculation of DOS was performed on the optimized ground state complex with the energy range from -10.0 to 0.00 eV with the peak width of 0.30, based on the HOMO-LUMO energy range of the molecules.

RESULT AND DISCUSSION

Ground State Geometry

The computationally optimized structure for the unsubstituted Pt(II)-porphyrin complex was compared

with the XRD data (Fig. 2(a)). The mean standard deviation (MSD) of the bond length is approximately 1.22% and the MSD of the bond angle is approximately about 0.16% (Table 1 and 2). The optimized theoretical structure of Pt(II)-porphyrin (Fig. 1(b)) and experimental PtOEP (Fig. 2(b)) are both square planar. This shows that our employed method is sufficient to reproduce the experimental observation. However, in contrast with our hypothesis, the substituents do not give any significant effect on the structure of the complexes. The substituted complexes retain the square planar structure compared to the unsubstituted complexes, as displayed in Table 3. The table shows that both of bond angle and bond length of complexes have a similar structure. Theoretically, the structure is square planar, we can conclude that electron donating substituent (CH₃, OH, and NH₂) and electron withdrawing substituent (NO₂, COOH, I, Br, F) did not affect the structure of Pt(II)-porphyrin.

Mulliken Partial Charges

Population analysis is a mathematical way of partitioning a wave function or electron density into charges on the nuclei, bond orders and other related information. Atomic charges cannot be observed experimentally because they do not correspond to any unique physical property. In reality, atoms have a positive nucleus surrounded by negative electrons, not partial charge on each atom.

Condensing electron density and nuclear charges down to partial charges on the nucleus results in an understanding of the electron density distribution. The nucleophilic/electrophilic partial charges correspond well to the chemist's view of the ionic or covalent bond, polarity and others. Organometallics typically have charges on the order of ± 0.5 .

The fundamental assumption of Mulliken Population Analysis used by the Mulliken scheme for partitioning the wave function is that the overlap between two orbitals is shared equally. This method is often used for understanding chemistry rather than quantitatively predicting experimental results [21].

Substituent group will affect the charge density of organometallic compound. In this research, we modified platinum(II) porphyrin with electron donating and electron withdrawing group. Theoretically the electron-donating group is an activating group so that it gives atomic charge being negative. On the other hand, an electron-withdrawing group is a deactivating group. Hence, the atomic charge will be positive.

Based on theory, Table 4 shows that the electron donating substituent (CH₃, OH, and NH₂) gave the Mulliken partial charges lower than electron withdrawing substituent (NO₂, COOH, I, Br, F). It is caused by the

Table 1. Comparison of bond length XRD PtOEP and calculation DFT/LANL2DZ/B3LYP

Bond	XRD (Å)	Calculation (Å)	Deviation (%)
Pt-N1	2.012	2.044	1.592
Pt-N1a	2.012	2.044	1.586
N1-CA1	1.376	1.391	1.144
CA1-CB1	1.453	1.462	0.669
C7-C8	1.521	1.554	2.169
Pt-N2	2.013	2.044	1.540
Pt-N2A	2.014	2.044	1.487
N1-CA2	1.382	1.391	0.692
CA1-CM2A	1.377	1.394	1.265
CB1-C1	1.505	1.509	0.299
CB2-C3	1.509	1.509	0.033
CM1-CA3	1.365	1.394	2.152

Table 2. Comparison of bond angles XRD PtOEP and calculation DFT/LANL2DZ/B3LYP

Bond angles	XRD (°)	Calculation (°)	Deviation (%)
N1-PT-N2	90.001	89.997	0.004
N2-PT-N1A	90.010	89.997	0.014
N2-PT-N2A	180.000	179.890	0.061
PT-N1-CA1	126.920	126.649	0.214
CA1-N1-CA2	106.130	106.712	0.548
N1-CA1-CM2A	124.730	125.230	0.401
N1-PT-N1A	180.000	179.822	0.099
N1-PT-N2A	90.010	90.001	0.010
N1A-PT-N2A	90.010	90.004	0.007
PT-N1-CA2	127.030	126.638	0.309
N1-CA1-CB1	109.630	109.731	0.092

Table 3. The structure parameters of Pt(II)-P-R complexes

Substituent Group	Bond Length (Å)				Bond Angle (°)					
	Pt-N1	Pt-N2	Pt-N3	Pt-N4	N1-Pt-N3	N1-Pt-N2	N1-Pt-N4	N2-Pt-N4	N2-Pt-N3	N3-Pt-N4
H	2.043	2.043	2.043	2.043	180.000	90.000	90.000	180.000	90.000	90.000
CH ₃	2.043	2.043	2.043	2.043	179.980	90.009	89.989	179.938	90.002	90.000
F	2.042	2.042	2.042	2.042	179.999	89.999	89.999	179.997	90.002	89.999
I	2.048	2.048	2.048	2.048	179.997	90.005	89.993	179.990	89.996	90.006
Br	2.046	2.046	2.046	2.046	179.993	89.993	89.983	179.964	90.004	90.020
NH ₂	2.045	2.044	2.044	2.045	179.935	90.022	89.989	179.886	89.978	90.010
NO ₂	2.042	2.042	2.042	2.042	179.945	90.016	89.998	179.977	89.985	90.001
OH	2.042	2.042	2.042	2.042	179.975	90.000	90.000	179.977	89.999	90.000
COOH	2.041	2.041	2.039	2.041	179.932	90.108	90.097	179.766	89.899	90.097

ability of the substituent to donate electron through the resonance of the porphyrin ring. Electron donating substituent has a high ability so that its increased electron density in porphyrin ring and decreased Mulliken partial charge Pt(II). On the other hand, electron-withdrawing substituent can withdraw electron from porphyrin ring through the resonance. Therefore, the Mulliken partial charges increase.

Band Gap

The electronic structure of metals, semiconductors and many other solids may be described in terms of band or zone theory. The chemical approach to band theory is to take molecular orbital theory. One of the molecular orbitals is bonding and has lower energy than that of the atomic orbitals. The other is antibonding and is of higher energy

For a semiconductor, the band gap is the difference in energy between removing and adding an electron to the neutral solid; for a finite system this corresponds to the difference between the energies of the highest occupied Kohn-Sham orbitals of the neutral and anionic system [23]. The valence electron-electron interactions were modeled using a density functional theory (DFT) that the

Table 4. Mulliken charges and value of orbital level energy on complexes Pt(II)P-R

Substituent Group	Pt(II) charge (Mulliken)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
H	0.848	-5.65	-2.47	3.18
F	0.857	-6.01	-3.09	3.01
Br	0.857	-6.05	-3.10	2.94
CH ₃	0.820	-5.16	-2.23	2.93
I	0.860	-5.93	-3.03	2.90
COOH	0.862	-6.20	-3.37	2.83
NO ₂	0.880	-7.22	-4.48	2.75
OH	0.817	-4.97	-2.39	2.57
NH ₂	0.784	-3.76	-1.65	2.11

Table 5. The DOS abundance on HOMO and LUMO orbital complexes Pt(II)P-R

Complexes	E_{HOMO} (eV)	E_{LUMO} (eV)
Pt(II)P-CH ₃	0.984	1.992
Pt(II)P-NO ₂	0.988	1.994
Pt(II)P-I	0.995	1.975
Pt(II)P-OH	0.996	1.919
Pt(II)P-F	0.997	1.956
Pt(II)P-NH ₂	0.999	1.986
Pt(II)P-COOH	1.000	1.992
Pt(II)P-Br	1.000	1.947
Pt(II)P-H	1.982	1.992

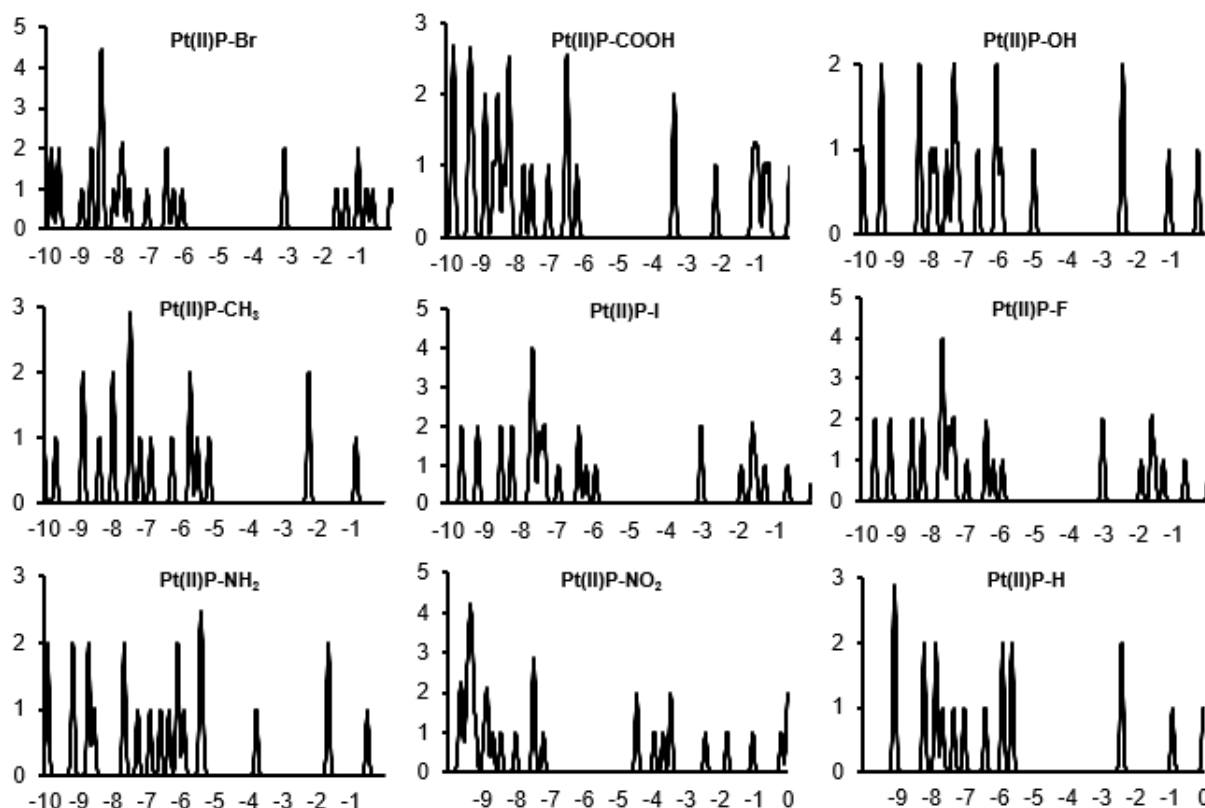


Fig 3. DOS spectra Pt(II)P-R with Gaussum 2.2.5 calculation

approximations allow the development of an electron-electron potential using the electronic charge density [24].

The calculation of the structural properties of semiconductor is a good test of the accuracy of the Local Density Approximation (LDA) of the density functional theory [23]. In this research, we used B3LYP hybrid functional, which include LDA and GGA functionals. Based on previous study, B3LYP hybrid functional is the most accurate method compare with the other DFT functionals [25-26].

Mitchell defined that an E_g value of material semiconductor is between 1.5–4.0 eV [27]. We can conclude that it will be easier for electron to be excited from orbital HOMO to orbital LUMO if the band gap energy is small. On the other hand, we have to keep track of the probability of recombination (further discussion in DOS section).

Table 4 shows the profile of band gap energy (E_g) the complexes. We can conclude from the table that substituent group decreased the E_g value. Electron donating substituents (CH_3 , OH, and NH_2) tend to decrease the stability of orbital (HOMO and LUMO), which cause the increase of the level of orbital energy, in contrast, with the electron withdrawing substituents (NO_2 , COOH, I, Br, F). This result related to Barbee's results [11] that Pt(II)-P- NH_2 has the smallest E_g value (2.11 eV).

Density of State (DOS)

The density of states (DOS) is defined as the number of the states that can be occupied by electron on a given energy level. DOS can be used as a parameter to measure the probability of recombination to occur for any given initial and final energy states.

Table 5 and Fig. 3 show that the DOS abundance is affected differently by the substituents. DOS abundance in the LUMO has a similar value, disregard with the type of the substituents. It means that the type of the substituent group has no significant effects, LUMO is the empty orbital that can be occupied by excited electron. On the other hand, the type of the substituent affects DOS abundance in orbital HOMO. Electron donating substituents (CH_3 , OH, and NH_2) tend to have smaller

DOS abundance than electron withdrawing (NO_2 , COOH, I, Br, and F). Orbital HOMO is occupied orbital so that substituent group affects the electron density in orbital.

Electron donating substituents increase the electron density on the molecule so that DOS_{HOMO} abundance decreased. Table 5 showed the DOS_{LUMO} abundance is higher than DOS_{HOMO} . We can define that LUMO orbital has the number of states which can be occupied much more than HOMO orbital so that electron will easily excite to orbital LUMO. Otherwise, orbital HOMO has a variation of DOS abundance so that orbital HOMO has a variation of probability to be recombination. The higher DOS_{HOMO} implies higher probability of recombination, which is an undesired property for a semiconductor material. We can conclude from Fig. 3 that electron-donating groups shift the HOMO orbital, while electron withdrawing groups shift the LUMO orbital to Fermi level.

UV-Visible Spectra

Sensitizer on the material semiconductor, which is applied in photocatalyst, should be designed to absorb light in visible range. Based on that fact, we calculated the UV-visible spectra of the complexes. Table 6 and Fig. 4 show that the substituent groups increase the maximum wavelength of the complexes (Bathochromic shift) following the Woodward-Fieser rules.

Electron donating substituents (CH_3 , OH, and NH_2)

Table 6. Absorption length of UV-Vis spectra Pt(II)P-R

Complexes	λ_{max} (nm)
Pt(II)P- NH_2	622.35
Pt(II)P-OH	534.68
Pt(II)P-COOH	457.38
Pt(II)P- NO_2	440.44
Pt(II)P-I	384.39
Pt(II)P-Br	376.13
Pt(II)P- CH_3	369.15
Pt(II)P-F	355.31
Pt(II)P-H	350.92

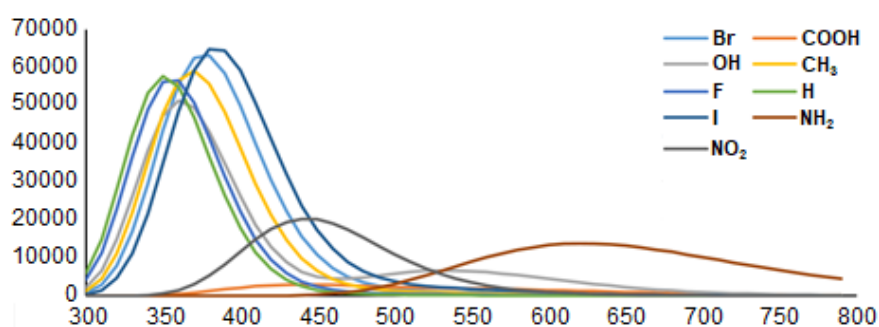


Fig 4. UV-Vis absorption spectra of Pt(II)P-R

tend to have a longer maximum wavelength than electron withdrawing (NO_2 , COOH , I , Br , and F). If we compare the E_g values of the complexes, we can conclude that electron donating substituent tend to have lower band gap energy and higher maximum wavelength. It is related with Planck equation that $E \sim 1/\lambda$ so that there is a correlation between the energy and wavelength. From this study we can agree that platinum(II) porphyrin that is substituted by electron donating group have semiconductor properties better than electron withdrawing group based on the band gap energy (E_g), DOS abundance, and UV-visible spectra. Electron donating groups have a lower E_g , lower DOS_{HOMO} abundance, and higher maximum wavelength of UV-Visible spectra where in particular, Pt(II)-P-NH₂ can be recommended as a highly potential semiconductor material. Woodward-Fieser rule suggests that the substituent on the organic molecule shifted the spectra to the longer wavelength for this compound.

CONCLUSION

The substituent groups affect the semiconductor properties of platinum(II) porphyrin such as the band gap energy (E_g), DOS abundance, and UV-Visible spectra. Pt(II)-porphyrin substituted with electron donating groups (CH_3 , OH , and NH_2) tend to have the semiconductor properties better than substituted electron withdrawing (NO_2 , COOH , I , Br , and F). Based on the mentioned semiconductor properties, Pt(II)-P-NH₂ can be recommended as a highly potential semiconductor material.

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