The Carbazole Compounds Endowed with Phosphonic Anchoring Group for Sensitizer in Dye-Sensitized Solar Cells

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Abstract. The sensitizer dye contacts onto the TiO2 surface through an anchoring group in a Dye-Sensitized Solar Cells (DSSC). The thermal stability of the anchoring group and TiO2 binding contact is important to be considered in order to obtain the cell stability. Phosphonic acid is an anchoring group that has a good binding-contact thermal stability with TiO2 surface. In this research we investigated through the computational study the electronic properties of carbazole derivative compounds endowed with the phosphonic anchoring-groups (CP). A series of 10 CP derivatives was studied which has a different functional donor group. The electronic properties were investigated using the TD-DFT method with the CAM-B3LYP basis set. The substitution of carboxyl group with the phosphonic one showed the absorption spectrum to the blue shift (5-70 nm) which gave a less beneficial effect to the DSSC performance. The addition of donor functional group aniline into the CP (aniline-CP) could shift back the absorption spectrum to the red-shift. The DSSC parameter also has been calculated including the electron injection driving force $\Delta G_{\text{inject}}$ and the open circuit voltage ($eV_{\text{OC}}$). Overall the aniline-CP has the best performance among the observed compounds which showed the highest $\Delta G_{\text{inject}}$ (-0.84872 eV) and $eV_{\text{OC}}$ (2.763 V).

1. Introduction

According to the average solar radiation that is received every year, Indonesia is one of country that is promising to conduct the solar cell device development [1]. Among the solar cells devices, Dye-Sensitized Solar Cell has attracted many researches due to its economic value. The cell comprises of two electrodes, dye-sensitized semiconductor as a photoanode and platinized transparent conductive oxide (TCO) as a counter electrode that are sandwiched between liquid electrolytes [2,3].

They are many key parameters that influence the cell performance. One of the key parameters is the electron injection from the Lowest Unoccupied Molecular Orbital (LUMO) to the conduction band semiconductor [4–6]. To guarantee the highest injection efficiency, the good binding between dye and semiconductor surface become the most important thing. The commonly dye that is used as sensitizer in DSSC have carboxyl group as anchoring site to attach the dye on the semiconductor surface. Aside the carboxyl group there are also the others anchoring site that has been studied, for instance, phosphonic, pyridine, tetracyanate, hydroxyquinoline, catechol or salicylic acid [7–11]. Among these, phosphonic group is promising because it is has tridentate binding site that will make the dye attach strongly to the semiconductor surface [7,8]. Nilsing et. al have calculated that the phosphonic functional group was attached stronger to the TiO2 surface compare to the carboxylic group. The stronger interaction of anchoring site to the semiconductor will more facilitate the electron injection from the LUMO dye onto the conduction band semiconductor [9].
In this research we investigated the electronic properties of a series of carbazole dyes that has phosphonic group through a computational study. The carbazole dye is interesting to study because they have proven as a good candidate for sensitizer in DSSC application. The observed carbazole dyes have two anchoring site. The effect of carboxyl group substitution with the phosphonic to the electronic properties has been investigated. The addition of donating electron group to the carbazole compounds also has been simulated to improve their electronic properties. The cell parameters, including light harvesting efficiency, electron injection driving force and open circuit voltage also have been studied.

2. Computational Details

2.1. Molecule Model
The observed molecule were constructed from the carbazole dyes which has two anchoring site, namely CBC0 (Figure 1). The carboxylate functional group in the anchoring site position then were replaced by phosphonic functional group. The replacement one carboxylate group by phosphonic functional group created a compound namely CBP1 whereas the replacement two carboxylate functional groups with two phosphonic groups in the two positions of anchoring site created a compound namely CBP2. Then 10 donor functional groups were added into these carbazole compounds. The 10 donor functional groups are presented in Figure 2, whereas the resulted derivatives compounds are presented in Table 1.

![Figure 1](image)

**Figure 1.** Basic structure of observed carbazole dye. The basic compound, CBC0, is the compound with $X = H$ and the anchoring site = -COOH. The replacing one –COOH with the –PO$_3$H$_2$ result CBP1 and the replacing both of –COOH with the –PO$_3$H$_2$ result CBP2.

2.2. Computation Methods
The calculations in this research have been conducted using the Gaussian 16 code [12]. The optimization geometries using the CAM-B3LYP functional [13]. This functional is the best choice for such a huge molecule because contain a good long range-corrected [14,15]. After obtaining the optimized geometry, the TD-DFT calculation was performed to investigate the electronic properties [16]. The AVOGADRO [17] and GAUSSUM [18] were used to help the calculation result visualization including HOMO-LUMO localization and UV-VIS absorption spectrum.

3. Result and Discussions

3.1. The effect of phosphonic group substitution in the anchoring site
The spectrum UV-VIS of the CBC0, CBP1 and CBP2 which was obtained from the TDDFT calculation is shown in Table 1. Table 1 shows that the substitution of carboxyl groups with the phosphonic groups gives the wavelength maximum shift to the high energy. This condition is avoided
in the Dye-Sensitized Solar Cells (DSSCs). This result guides us to substitute the carboxyl groups with phosphonic ones only in one site.

| No | Compound Name | Replacing X |
|----|---------------|-------------|
| 1  | Methoxy-CBP1  | -OCH₃       |
| 2  | Amine-CBP1    | -NH₃        |
| 3  | Hexoxy-CBP1 (OC₆H₁₃) | -OC₆H₁₃ |
| 4  | Aminhexyl-CBP1 | -NHC₆H₁₃ |
| 5  | Aniline-CBP1  | Aniline     |
| 6  | Phenothiazine-CBP1 | Phenothiazine |
| 7  | Fluorene-CBP1 | Fluorene    |
| 8  | Silole-CBP1   | Silole      |
| 9  | Pyrrole-CBP1  | Pyrrole     |
| 10 | Methoxy-CBP1  | Triazine    |

Table 1. The derivatives compounds of CBP1 investigated in this research.
3.2. The effect of donating electron groups to the electronic properties

The calculated spectrum UV-VIS for the CBP1 derivatives is shown in Figure 3. Figure 3 shows that most of the observed compounds has three peaks on their UV-VIS absorption spectrum at about 270 nm, 350 nm and 400 nm.

The electronic transition characteristic obtained from the calculation is presented in Table 2. The observed dyes show the electron transition from HOMO to LUMO except fluorine-CBP1, silole-CBP1 and pyrrole-CBP1. They show the electron transition from HOMO-2 to LUMO for fluorine-CBP1 and HOMO to LUMO+2 for silole-CBP1 and pyrrole-CBP1. Table 2 also informs that the maximum wavelength of anililine-CBP1 show a red shift compare to the CBP1 one.

To further understand the electronic transition character, the visualization of orbital molecules that involve in the electronic transition the HOMO-LUMO profile has been visualized. The visualization shows that all the substituted phosphonic group compounds have the LUMO that close to the carboxylic groups (for example the LUMO of CBP1 is presented in Figure 4.a), except the phenothiazine-CBP1 which has the LUMO near to the phosphonic group (Figure 4.b). This fact indicates that only phenotizine-CBP1 which will show a good electronic injection when the phosphonic group is attached to the semiconductor surface. Although that, the others still have a good candidate to be applied as sensitizer in DSSC because their LUMO position is located on the other side of the anchoring site, the carboxyl group. For the last case, the phosphonic group only has a role as the anchoring site but the electron injection will occur through the carboxyl side.
Figure 3. Calculated spectrum UV-VIS of the CBP1 derivatives, A: (a) methoxy-CBP1, (b) hexoxy-CBP1, (c) amine-CBP1, (d) hexyl-amine CBP1. B: (e) aniline-CBP1, (f) phenothiazine-CBP1, (g) fluorine-CBP1. C: (h) silole-CBP1, (i) pyrrole-CBP1, (j) triazine-CBP1.
Table 2. The electronic transition characteristic of the observed compound

| No | Compound name        | λ (nm) | f   | Electronic transition character |
|----|----------------------|--------|-----|---------------------------------|
| 1  | CBC0                 | 401.68 | 1.213 | HOMO -> LUMO 72%               |
| 2  | CBP1                 | 401.50 | 1.1301 | HOMO -> LUMO 73%              |
| 3  | Methoxy-CBP1         | 397.61 | 1.1282 | HOMO -> LUMO 71%              |
| 4  | Amine-CBP1           | 399.44 | 1.0463 | HOMO -> LUMO 68%              |
| 5  | Hexosi-CBP1 (-OC$_6$H$_{13}$) | 398.33 | 1.1411 | HOMO -> LUMO 72%              |
| 6  | Aminhexyl-CBP1       | 397.83 | 1.0882 | HOMO -> LUMO 75%              |
| 7  | Aniline-CBP1         | 400.76 | 1.1171 | H-2 -> LUMO 61%               |
| 8  | Phenothiazine-CBP1   | 337.90 | 1.0331 | HOMO -> LUMO+2 33%            |
| 9  | Fluorene-CBP1        | 337.47 | 1.1635 | HOMO -> LUMO +2 37%           |
| 10 | Silole-CBP1          | 395.92 | 1.0692 | HOMO -> LUMO 60%              |
| 11 | Pyrrole-CBP1         | 397.52 | 1.5324 | HOMO -> LUMO 41%              |
| 12 | Triazine-CBP1        | 395.33 | 1.0764 | HOMO -> LUMO 68 %             |

Figure 4. The LUMO profile of (a) CBP1 and (b) phenothiazine CBP-1.

3.3. The effect of donating electron groups to the DSSC parameter

The calculated DSSC parameter is presented in Table 3. Table 3 displays the DSSC parameters including the oscillator strength (f), electron injection driving force ($\Delta G_{\text{injection}}$) and open circuit voltage ($V_{\text{oc}}$). The oscillator strength influences the light harvesting efficiency (LHE). The molecules which have a higher oscillator strength will have a higher light harvesting efficiency [19]. Table 3 also informs that all the CBP1 derivatives show the $\Delta G_{\text{injection}}$ decrease except for aniline-CBP1 which show an almost the same value with the basic compound CBC0. We assume that the replacing of carboxyl moiety with the phosphonic one decreases the withdrawn of electron, but the present of three methoxy phenyl with the nitrogen atom in the centre of aniline moiety support the good electron donating that induce a $\Delta G_{\text{injection}}$ increasing. The other DSSC parameters of aniline-CBP1, oscillator strength and $V_{\text{DC}}$, also show a good value that makes this compound as a good candidate to be used as sensitizer in DSSC. The aniline also can be further studied as an electron donating moiety for the other basic compounds.
Table 3. The calculated DSSC parameters of the investigated compounds

| Compound name                  | f   | $E_{ox}^{dye}$ (eV) | $E_{max}$ (eV) | $E_{ox}^{dye*}$ (eV) | $\Delta G_{inj}$ (eV) | Voc (V) |
|--------------------------------|-----|---------------------|----------------|---------------------|----------------------|---------|
| CBC0                           | 1,213 | 6,674               | 3,54602       | 3,12798            | -0,87202             | 2,741   |
| CBP1                           | 1,1301 | 6,659               | 3,08802       | 3,57098            | -0,42902             | 2,763   |
| Methoxy-CBP1                   | 1,1282 | 6,726               | 3,11822       | 3,60778            | -0,39222             | 2,734   |
| Amine-CBP1                     | 1,0463 | 6,686               | 3,10392       | 3,58208            | -0,41792             | 2,766   |
| Hexoxy-CBP1 (-OC$_6$H$_{13}$) | 1,1411 | 6,713               | 3,11262       | 3,60038            | -0,39962             | 2,737   |
| Aminhexyl-CBP1                 | 1,0882 | 6,703               | 3,11652       | 3,58648            | -0,41352             | 2,761   |
| Aniline-CBP1                   | 1,1171 | 6,245               | 3,15128       | 3,15128            | -0,84872             | 2,763   |
| Phenothiazine-CBP1             | 1,0331 | 6,586               | 3,12662       | 3,45938            | -0,54062             | 2,755   |
| Fluorene-CBP1                  | 1,1635 | 6,669               | 3,11012       | 3,55888            | -0,44112             | 2,754   |
| Silole-CBP1                    | 1,0692 | 6,636               | 3,13152       | 3,50448            | -0,49552             | 2,759   |
| Pyrrole-CBP1                   | 1,5324 | 6,616               | 3,11892       | 3,49708            | -0,50292             | 2,743   |
| Triazine-CBP1                  | 1,0764 | 6,732               | 3,13622       | 3,59578            | -0,40422             | 2,746   |

4. Conclusions
The phosphonic moiety in the anchoring site position of the investigated carbazole compound gave a blue shift of the UV-VIS spectrum maximum wavelength which is avoided for the DSSC application.

The insertion of aniline moiety gave the red shift back of the UV-VIS spectrum maximum wavelength.

This research also revealed that the insertion of aniline as an electron donating showed a good value of oscillator strength, $\Delta G_{inj}$ and Voc that makes this compound as an interesting compound to be studied further.

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