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Abstract

The excessive use of fossil fuels has surged the need for alternative energy sources, such as solar energy. Organic photovoltaic (OPV) cells can potentially be an alternative to silicon solar cells. There is a large interest in OPV cells because they are strong absorbers and come at a low cost of synthesis. In this study, possible OPV compounds were designed, and theoretical computations were done to assess their efficiency. Density Functional Theory was used to calculate the HOMO-LUMO gap of the compounds designed. Semiconductors such as naphthalene, 1,1'-biphenyl, and α-septithiophene were used as the backbone with electron-withdrawing groups (EWG) attached. Seven of the 26 compounds demonstrated adequate results and four of them will be further pursued to synthesize. Lastly, results suggest there is most likely a correlation between the amount of EWGs attached to the semiconductor and its calculated efficiency.

Keywords: Organic photovoltaic compounds, Thiadiazole, HOMO-LUMO gap

Introduction

In an economy where the primary source of energy comes from fossil fuels, there is an urgent need for alternative energy sources. Solar energy has become increasingly popular due to its feasible transformation into electricity through photovoltaic cells.[1,2] A typical photovoltaic cell consists of two silicon semiconductor layers where one layer contains positively charged (p-type) holes and the other contains negatively charged (n-type) holes. When the sun hits the cell, photons push electrons out of their place and create more holes in the n-type layer. In the p-n junction—where the two layers touch—an electric field stops electrons and holes from moving between layers. However, the layers are connected in a circuit, thus the electric field pushes electrons through the circuit, and this creates a current.[1] For example, silicon-based photovoltaic cells are widely used because of their high efficiency and their low cost. Although silicon-based photovoltaic compounds have a favorable band gap of about 1.1 eV, they do not absorb visible light well due to the indirect nature of the gap.[1] Having a band gap of 1.1 eV would mean silicon cells can theoretically absorb 77% of incoming solar photons.[3] However, silicon cells are often difficult to recycle after they are retired and leave a large carbon footprint after production.[4] This is why there is a large interest in organic photovoltaic (OPV) compounds, as OPV cells are strong absorbers and come at a low cost of production (synthesizing).[3] Because OPV devices use a much smaller quantity of material, they should also have a smaller carbon footprint than traditional solar cells.

An OPV bilayer device is composed of an OPV compound (the active layer) that is sandwiched between a conductive electrode and a transparent conductive substrate.[3] Everything is then covered with glass or plastic. Although the architecture of an OPV device is critical, there is a focus on the active layer because it is the main OPV compound that absorbs sunlight.

In general, OPV compounds contain a conjugated polymer as the backbone.[3] Electron-withdrawing groups (EWG) and electron-donating groups (EDG) are then attached to the polymer to increase its efficiency. Some of the most efficient semiconductors used in OPV compounds include pentacene, perylene, buckminsterfullerene, sexithiophene, poly(triarylamine), phthalocyanine, poly(3-hexylthiophene), and poly(3-vinylthiophene).[3] Productive OPV compounds are mostly derived from the semiconductors listed above. It is why the focus of this project is to design possible OPV compounds to serve as the active layer in an OPV device.

In this study, compounds were designed as possible OPV compounds, and their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values were determined to calculate their HOMO-LUMO gap (analogous to the band gap). Finding the HOMO-LUMO (HL) gap is an important parameter that helps determine the electrical properties of a material.[3] For example, the HL gap determines which wavelengths of light are absorbed and emitted by the material.[5]

The compounds designed are based on, naphthalene, 1,1'-biphenyl, and α-septithiophene as the backbones because they are some of the most efficient semi-conductors in the field of organic electronics.[3,6] As shown on Figure 7, EWGs such as 1,2,5-thiadiazole, 1,3,4-thiadiazole, thieno[3,4-c][1,2,5]thiadiazole (TTDZ), and other thienothiadiazole derivatives were attached to the polymer backbones. This was done because thiadiazoles are known to correlate to ideal energy level alignments for high-performance OPV compounds as they lower the HOMO-LUMO gap (HL gap).[7] Therefore, by combining those factors, five sets of compounds were designed: sets **a**, **b**, **c**, **d**, and **e** with variations within each set, for a total of 26 compounds. In addition, the calculated energy conversion efficiency versus the HL gap and the LUMO level was explored for the compounds that showed promising results.

Methods

Density Functional Theory (DFT) with the B3LYP functional and 6-311+G(d,p) basis set were used to calculate all the geometries at the ground state (S_0) level using the Gaussian 16 program on the Expanse supercomputer at the San Diego Supercomputer Center (SDSC).[8] The HOMO and LUMO values were then determined, and the HL gaps were calculated.

Results and Discussion

The compounds shown in Figure 1 are based on naphthalene as the semiconductor. In general, the HL gap decreases as more nitrogen atoms replace carbon atoms in the aromatic rings. Although the gap decreased significantly, it is still too high.

Set **b** compounds are shown in Figure 2, where 1,1'-biphenyl was used as the semiconductor backbone. Two biphenyl moieties were then attached at the 2 and 5 carbons of TTDZ. Nitrogen atoms then substituted several carbons in the biphenyl moieties to make 2,2-bipyrazine and other pyrazine and pyridine derivatives. Then, in compounds **b3**-**b6**, furan, and 1,3,4- oxadiazole were put in place of TTDZ. Replacing TTDZ with furan and 1,3,4-oxadiazole increased the HL gap significantly from 2.27 eV to 3.36 eV and 3.96 eV. Although it is uncertain, based on these results, it may be inferred that furan and its derivatives do not serve well in adjusting the HL gap in OPV compounds.

As seen in Figure 3, septithiophene was used as the semiconductor backbone. Benzene, pyrazine, and pyridine were conjugated to the thiophene rings of septithiophene. It was found that adding too many pyrazines to the semiconductor lowers the HL gap too much, whereas using pyridine lowers the HL gap to a favorable value. This can be seen in compound **c2** where pyrazine was used and the HL gap resulted in 0.98 eV, which is too low. Then, in **c3**, pyridine was used and resulted in a HL gap of 1.70 eV, which is a promising value. However, the LUMO value of **c3** was very low. Literature indicates a promising band gap is from 1.2 eV to 2.0 eV with a LUMO value of -3.6 eV to -4.0 eV.[9] Although, **c3** has a good HL gap, its LUMO value is insufficient with a value of -3.2 eV.

Set **d** compounds (Figure 4) were derived from compound **c3** because there are options for a lot of variabilities when using septithiophene as the semiconductor. Although pyrazine and pyridazine were also used in set **d** compounds, 3,4-dihydro-1,2,5-thiadiazole was conjugated to the thiophene rings of septithiophene to make a conjugated TTDZ system. It was found that having too many TTDZ's conjugated together lowers the HL gap too much. The average HL gap of the compounds in set **d** was 0.56 eV.

After evaluating the results of the HL gaps from set **a** compounds, where they were too high, and the HL gaps from set **d** were too low, set **e** compounds were designed strategically. As Figure 5 shows, septithiophene continued to be used as a semiconductor. However, less TTDZ was used, and a few benzene rings were placed with the intention to balance out the strong electron density pull from the TTDZ. It was found that two to four TTDZ moieties, conjugated with the semiconductor, resulted in proficient results. More specifically, compounds **e4**, **e5**, and **e6** came to have a HL gap of 1.1 eV to 1.5 eV and with a LUMO value of -3.7 eV to -3.9 eV. Both the HL gap and LUMO values were within ideal literature values.[9]

The compounds with HL gaps within acceptable parameters are plotted on the contour plot shown in Figure 6. This contour plot represents the bandgap (HL gap) on the x-axis and the LUMO value on the y-axis.[9] The contour lines demonstrate constant power conversion efficiencies. For example, compounds **e4** and **e6** would be about 8-9% efficient. Günes argues that a band gap (HL gap) of 1.1 eV can feasibly absorb 77% of solar photons, but do not mention the theoretical efficiency, whereas a band gap of 2 eV limits photon absorption to roughly 30%.[3] Regardless, these efficiencies are only theoretical, and there is a difference between efficiency and photon absorption.

Summary and Conclusions

An initial computational assessment was performed on possible OPV compounds. This initial computational assessment was based on comparing the HL gap to the LUMO gap. Various compounds were designed based on various semiconductors such as naphthalene, 1,1'-biphenyl, and α-septithiophene. The results discussed show that TTDZ is a highly effective EWG at lowering the HL gap. Based on the results, it can be concluded that compounds **b1**, **b2**, **c3**, **e1, e4**, **e5**, and **e6** showed the most efficient HL gap when compared to its LUMO value. However, of those seven compounds, only compounds **b2**, **e4**, **e5**, and **e6** will be pursued synthetically. Lastly, results indicate there is most likely a correlation between the amount of EWGs attached to a semiconductor and its calculated efficiency. This inference is stimulated by Figure 6, which has the seven most efficient compounds plotted. What can be analyzed from this plot is that compounds like **b1**, **c3**, and **e1,** that have minimal to no nitrogen atoms within the conjugated system and have few TTDZs attached, are the ones with the lowest efficiency. In comparison, the other four compounds that seem to have an appropriate ratio of TTDZ and nitrogen atoms are the ones with the highest efficiency. Further compounds ought to be designed and computed to further confirm this correlation.

Acknowledgments

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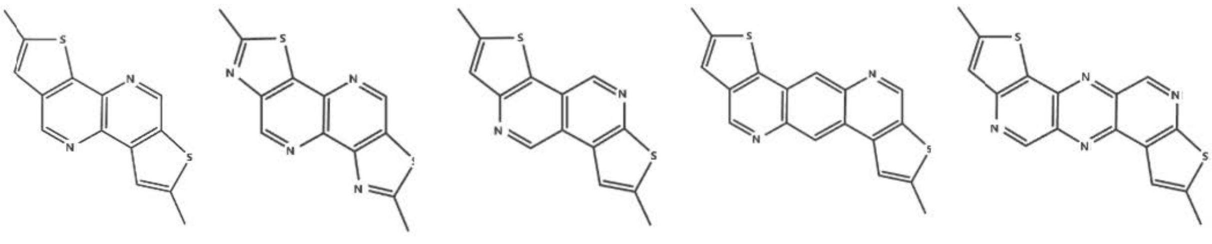


a1: 4.211376 eV

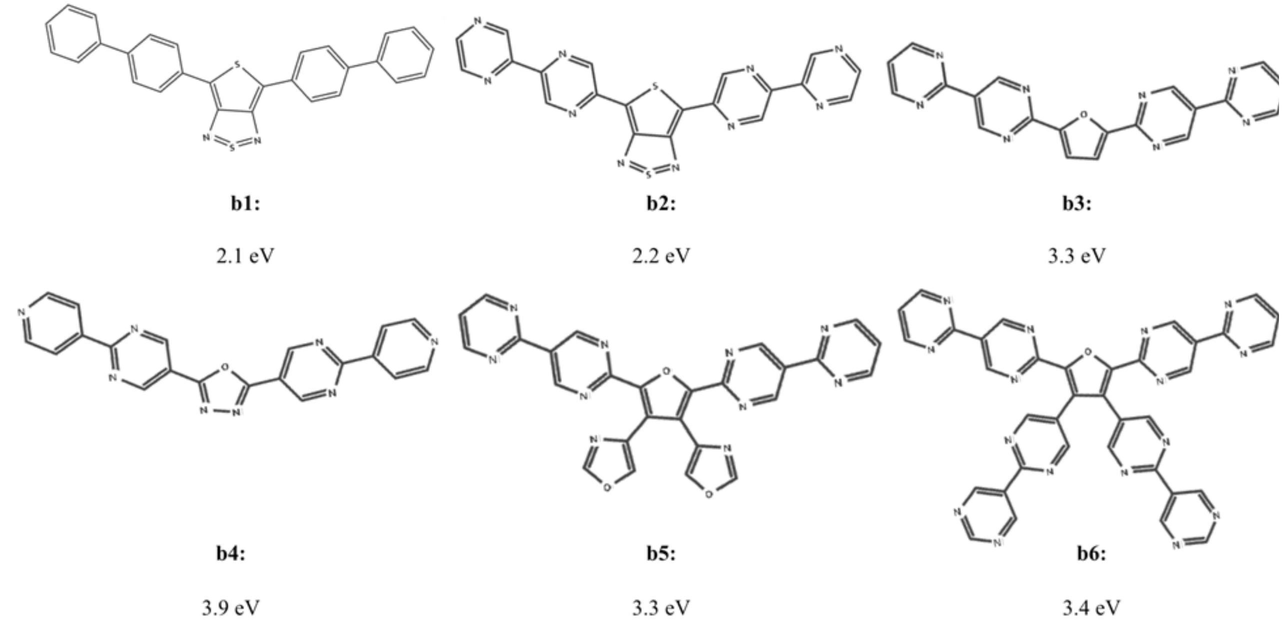
a2: 4.460800 eV

a3: 3.963856 eV

a4: 3.572720 eV

a5: 3.065168 eV

Figure 1. Set a compounds and their HOMO-LUMO gap computed at B3LYP/6-311+G(d,p).



b1:

2.1 eV

b2:

2.2 eV

b3:

3.3 eV

b4:

3.9 eV

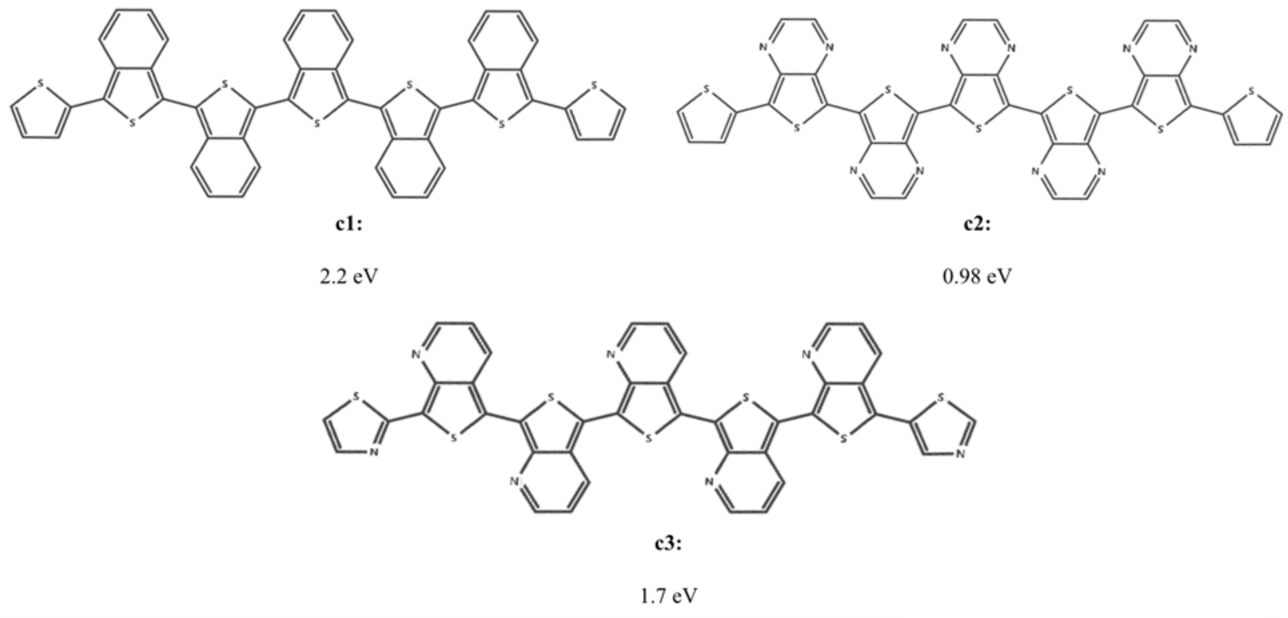
b5:

3.3 eV

b6:

3.4 eV

Figure 2. Set b compounds and their HOMO-LUMO gap computed at B3LYP/6-311+G(d,p).



c1:

2.2 eV

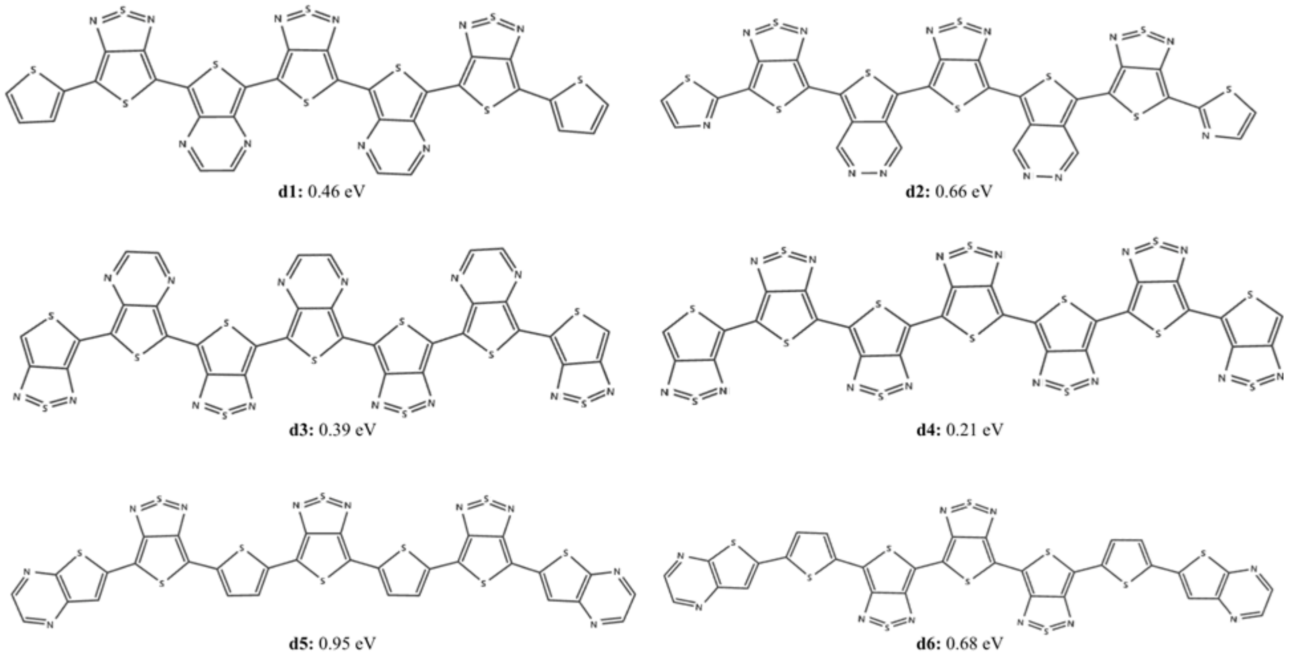
c2:

0.98 eV

c3:

1.7 eV

Figure 3. Set c compounds and their HOMO-LUMO gap computed at B3LYP/6-311+G(d,p).



d1: 0.46 eV

d2: 0.66 eV

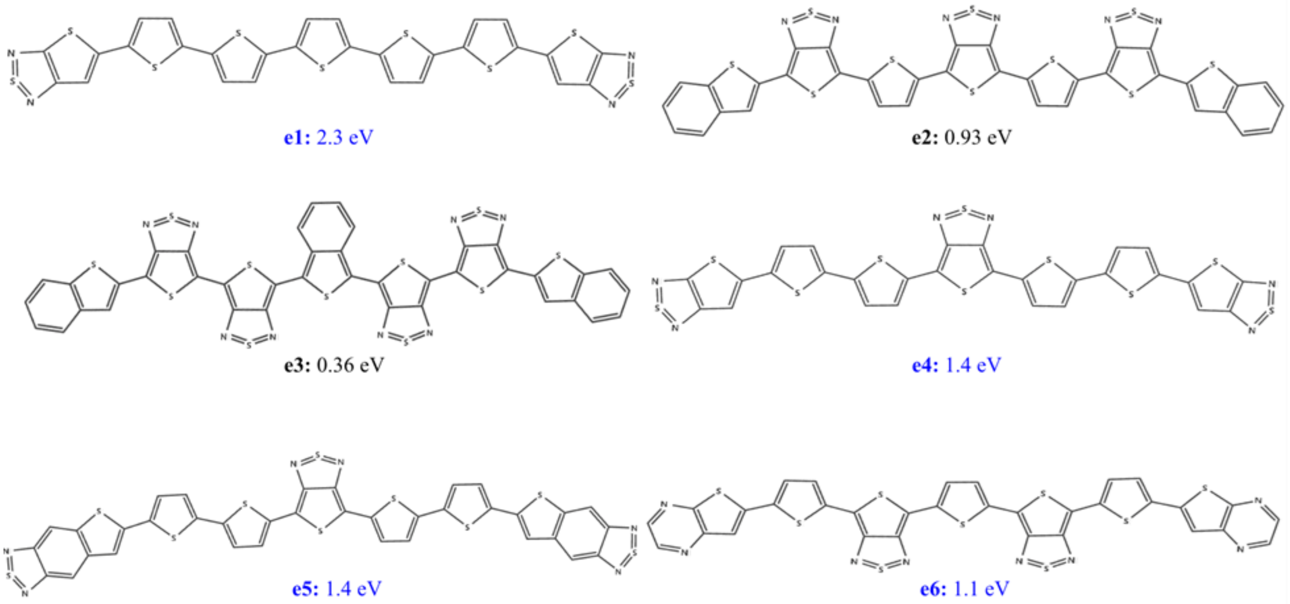
d3: 0.39 eV

d4: 0.21 eV

d5: 0.95 eV

d6: 0.68 eV

Figure 4. Set d compounds and their HOMO-LUMO gap computed at B3LYP/6-311+G(d,p).



e1: 2.3 eV

e2: 0.93 eV

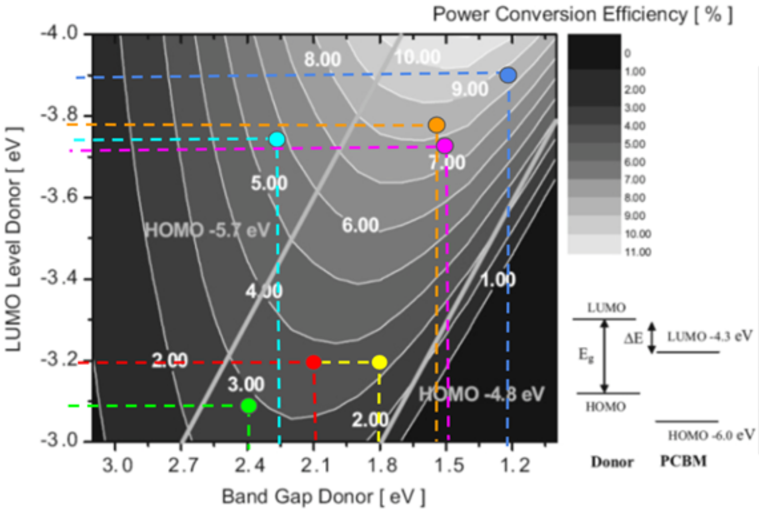
e3: 0.36 eV

e4: 1.4 eV

e5: 1.4 eV

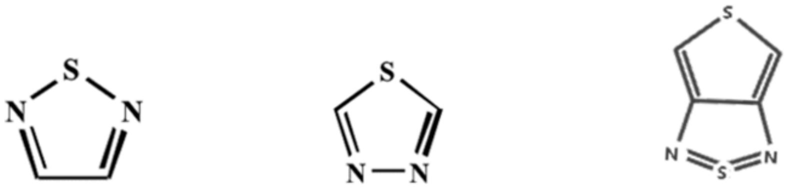
e6: 1.1 eV

Figure 5. Set e compounds and their HOMO-LUMO gap computed at B3LYP/6-311+G(d,p).



Compound #	LUMO (eV)	HOMO-LUMO Gap	Color on contour plot
b1	-3.2	2.1	🔴
b2	-3.7	2.2	🔵
c3	-3.2	1.7	🟡
e1	-3.2	2.3	🟢
e4	-3.7	1.4	🟠
e5	-3.7	1.4	🟣
e6	-3.9	1.1	🔵

Figure 6. Estimated power conversion efficiency of seven of the compounds designed. Adapted from Scharber and collaborators. [5]



1,2,5-thiadiazole 1,3,4-thiadiazole thieno[3,4-c] [1,2,5]thiadiazole

Figure 7. EWG's used.