Electronic Effects on a D- π -A Organic Sensitizer Upon Heteroatom Substitutions in the π -Bridge

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Abstract: Organic donor- π -acceptor sensitizers are a promising path to achieving cheaper and more efficient dye sensitized solar cells. The π -bridge plays an important part in the photovoltaic properties of the dye, and sulfur systems, like thiophene, have been favorites for this role. We aim to investigate the change in photovoltaic properties for systems that utilize heteroatoms besides sulfur. Using density functional theory, we have investigated the spectroscopic and electronic properties of the D5 organic dye upon heteroatom substitution for sulfur in the π -bridge. We substituted for sulfur with pnictogens, chalcogens, and various other elements in the second row of the periodic table. We find the larger elements reduce the HOMO-LUMO gap, red shift the absorption spectrum, increase the dipole moment and are energetically favorable for electron injection. In particular, π -bridge systems utilizing selenium or phosphorus, instead of the more prevalent sulfur, could prove to be more efficient based on our analysis of photovoltaic properties.

Keywords: Dye-sensitized solar cell, organic, π -bridge, D5

1. Introduction

With growing energy demand, the need for sources other than fossil fuels has been brought into focus. In particular, the conversion of solar energy has gained momentum as a technology that could meet this increase in demand [2, 3]. Dye-sensitized solar cells (DSSCs), introduced by O'Regan and Gratzel in 1991 [4], have shown great promise as next-generation photovoltaics. Ru(II)-based dyes have a power conversion efficiency of approximately 11% [5]. However, ruthenium is a rare metal, so widespread application will prove difficult. Alternatively, organic sensitizers possess a number of attractive attributes, most notably cost and availability of raw materials [6]. The leading organic sensitizers utilize the donor- π -acceptor (D- π -A) framework [7-9]. In this structure, electron donor and acceptor groups are connected by a π -conjugated bridge. The acceptor is linked to the semiconductor surface, typically TiO₂, by a carboxylic acid.

When examining a potential sensitizer, multiple factors must be considered. The lowest unoccupied molecular orbital (LUMO) must lie above the semiconductor conduction band (CB) so it is energetically favorable for the excited electrons to inject into the surface [10]. The highest occupied molecular orbital (HOMO) energy level must lie below the electrolyte redox potential, allowing the dye to gain back the lost electron [4]. Other factors include the presence of an anchor group to bond with the semiconductor [11, 12], directed charge transfer from the sensitizer to the semiconductor, and having a high molar extinction coefficient [13]. The latter implies less of the compound is needed in the cell to obtain the same power input, which could lead to thinner and more efficient cells [14]. More fully utilizing the entire solar spectrum is also highly desirable. Most sensitizers absorb in the ultraviolet or the shorter wavelengths of

the visible light range. Therefore, concurrently accessing longer wavelengths may lead to significant improvements in efficiency.

One D- π -A framework utilizes a triphenylamine donor group, a thiophene π -bridge, and a cyanoacrylic acid acceptor, with excitation involving a charge transfer

Figure 1: Chemical structure of D5 solar dye.

from the donor to acceptor group (SI

Figure 1). The chemical structure of

the dye is shown in Figure 1. This dye,

known as D5, was synthesized in 2006

[1] and showed promise as an organic

sensitizer [15]. Since then, many studies on D- π -A dyes have focused on optimization of the donor and acceptor groups [16, 17], while the π -bridge portion has received less attention. The π -bridge is very influential to the dynamics of electron transfer within the sensitizer and, if optimized, could increase the efficiency of intramolecular electron transfer.

This study utilizes a theoretical approach to examine potential π -bridge systems, ultimately aimed at improving the properties of D- π -A sensitizers for photovoltaic applications. Using elements from the second row of the periodic table, along with pnictogens and chalcogens up to the fourth row, we have investigated how changing the heteroatom of the π -bridge ring affects the spectroscopic and photovoltaic properties of the dye. D5 was chosen for this study because it is a relatively simple dye with only a single heteroatom in the π -bridge, so the effects of elemental substitution can be analyzed in a straightforward manner. We find these simple atomic substitutions can have

interesting effects on the electronics of the D- π -A dye, which may prove beneficial toward development of new molecules for DSSCs.

2. Methods

A standard exchange-correlation functional used by density functional theory tends to underestimate the excitation energies for charge transfer of molecules, with the error increasing as the overlap between orbitals decreases. This poses a problem when investigating D- π -A dyes due to the donor and acceptor portions being separated spatially by the π -bridge, which leaves little overlap of the HOMO and LUMO orbitals. Using a hybrid functional reduces the error by including Hartree-Fock exchange, and when using a functional with long-range corrections, the errors are decreased even further [18]. We have examined several different functionals to determine which is most suitable to describe the excitations in the D5 dye variants being studied here. All ground state geometries were optimized by DFT using the B3LYP functional and the 6-31G(d) basis set. Diffuse functions were not added for they have negligible effects on the electron density in these molecules and are computationally more expensive [19]. Electronic absorption spectra and excitation energies were calculated using several DFT functionals including B3LYP, HSE06, PBE0, ω B97xD, CAM-B3LYP, and M06-HF. For calculations in solution, the SMD model was used, which has been shown to produce accurate results for organic dyes [20],[21]. All calculations were done using the Gaussian09 software package [22].

The total sunlight-to-electricity conversion efficiency (η) is an important parameter to evaluate the performance of a DSSC, and is related to the fill factor (FF), open-circuit voltage (V_{OC}), incident solar power (P_{inc}), and short-circuit density (J_{SC}) via:

$$\eta = FF \frac{V_{OC} J_{SC}}{P_{inc}} \quad (1)$$

By increasing the V_{OC} and J_{SC} , we can enhance the total conversion efficiency. A number of factors contribute to V_{OC} , such as the conduction band edge of the semiconductor, the reduction-oxidation potential of the electrolyte, and the density of accessible states in the conduction band; however, Ruhle *et al.* observed that V_{OC} was linearly dependent on the dipole moment of the dye in the ground state [23], which is what we will consider here. The J_{SC} value is associated with the light absorption capability and the electron injection efficiency from the dye to the semiconductor. For DSSCs, J_{SC} is determined by the equation [24]:

$$J_{SC} = \int LHE(\lambda) \Phi_{inject} \eta_{collect} d\lambda \quad (2)$$

where $LHE(\lambda)$ is the light harvesting efficiency, $\eta_{collect}$ is the charge collection efficiency, and Φ_{inject} is the electron injection efficiency. For calculations in which the dye is being changed only moderately, and not the surface the dye will be attached to, $\eta_{collect}$ can be presumed the same for each molecule. Based on Beer's law the LHE can be approximated with the following equation

$$LHE = 1 - 10^{-f} \quad (3)$$

where f is the oscillator strength. The Φ_{inject} value is related to the driving force (ΔG^{inject}) of injection from dye to the semiconductor. Electron injection occurs very rapidly in these systems, and there has been experimental evidence that the electron transfer event occurs much faster than the vibrational relaxation of the dye [25-27]. Therefore, the

charge transfer can be assumed to take place from an unrelaxed excited state, and ΔG^{inject} can be estimated by [28, 29]:

$$\Delta G^{\text{inject}} = E^{\text{dye}^*} - E_{\text{CB}} = E^{\text{dye}} - E_{\text{EX}} - E_{\text{CB}} \quad (4)$$

where E^{dye^*} is the oxidation potential of the dye in the excited state, E_{CB} is the reduction potential of the conduction band edge for the semiconductor, E^{dye} is the redox potential of the dye in the ground state ($-E_{\text{HOMO}} = E^{\text{dye}}$), and E_{EX} is the excitation energy for the transition associated with the intramolecular charge transfer. Obtaining a correct value of E_{CB} is difficult since it is sensitive to experimental conditions. For TiO_2 , E_{CB} has been shown to equal 4.00 eV [28, 30], which will be used for this study.

We will be reporting λ_{max} , LHE, ΔG^{inject} , and μ of the dye after each π -bridge variation has been substituted. The sun's radiation output peaks at approximately 500 nm and is skewed toward longer wavelengths, so red-shifting the spectra is often beneficial for increasing the dye efficiency. In regards to J_{SC} , the goal is to increase the λ_{max} without sacrificing the LHE, and to maintain a favorable ΔG^{inject} . For the V_{OC} , we will be observing the change in the dipole moment after each substitution in hopes of enhancing V_{OC} alongside J_{SC} . We will use these values as an indicator to determine if a variation would increase or decrease the overall efficiency η .

3. Results and Discussion

3.1. Establishing benchmarks

For benchmarking purposes, six functionals have been tested, where we compared the calculated λ_{max} to experiment (Table 1). B3LYP, PBE0 and HSE06 are all hybrid functionals, while ω B97xD, CAM-B3LYP and M06-HF are long-range corrected DFT hybrids. The experimentally measured λ_{max} of the D5 dye in ethanol is 441 nm and the

experimental spectrum is shown in SI Figure 2 [15]. The hybrid functionals perform poorly in ethanol, being off from the experimental $\lambda_{\max}$ by over 120 nm when in solution (similar trends are present in gas phase; all peaks are red-shifted when accounting for solvation effects). The long-range corrected functionals

Table 1: TD-DFT functional test of D5 dye in gas phase and ethanol solution. The table shows the maximum absorption wavelength ($\lambda_{\max}$), oscillator strength (f), and the difference between the calculated and experimental $\lambda_{\max}$ ($\Delta\lambda$).

Functional	$\lambda_{\max}$ (nm)	f	$\Delta\lambda$ (nm)
Gas Phase			
B3LYP	534.5	1.11	-
HSE06	543.9	1.02	-
PBE0	510.2	1.24	-
ω B97xD	422.2	1.74	-
CAM-B3LYP	433.4	1.69	-
M06-HF	386.5	1.72	-
Ethanol			
Experiment	441.0[1]	-	-
B3LYP	594.0	1.25	153.0
HSE06	604.4	1.17	163.4
PBE0	562.1	1.37	121.1
ω B97xD	465.0	1.83	24.0
CAM-B3LYP	466.5	1.79	25.5
M06-HF	409.6	1.80	-31.4

predict $\lambda_{\max}$ to be much closer to experiment. M06-HF produces acceptable results when paired with a solvation model, only being off the experimental value by 31.4 nm. The best functional in ethanol using the SMD solvation model is ω B97xD, which predicts $\lambda_{\max}$ to be 24.0 nm from the experimental value. Based on these findings, the combination of ω B97xD and SMD will be used for further TD-DFT calculations. Additionally, this functional has been shown to produce accurate results for the spectroscopic properties of D- π -A dyes [21, 31].

3.2. Energy levels after substitution

Many studies have previously described the effects of altering the donor or acceptor portions of these sensitizers [5, 6, 16, 32]. However, the π -bridge also plays an

important role in the overall D- π -A system, and over the last few years, more papers have focused on modifying that region of the molecule [33-36]. These accounts have substituted various conjugated groups into the π -bridge but have not investigated the effect of heteroatom substitution. For the D5 dye, a thiophene group is used as the π linker between the triphenylamine donor group and the cyanoacrylic acid acceptor (Fig. 1). Instead of thiophene, here we substituted different heteroatoms for the sulfur. All heteroaromatic rings were kept as 5-membered to most closely mimic thiophene, and hydrogen was added to the heteroatom as necessary to fill the valence. This method maintains consistency in the length and rigidity between heterocycles; changes observed can be interpreted as effects of the heteroatom substitution primarily.

As shown in Table 2, upon heteroatom substitution the HOMO energy levels stay below the electrolyte reduction potential for I_3/I^- of -4.6 eV in vacuum [37] and -4.8 eV in ethanol [16], verifying the

dye can still regenerate the ground state and complete the circuit of the cell. The LUMO is most affected by the substitutions, due to the substitution occurring closer to the acceptor

Table 2: HOMO and LUMO energy levels of heteroatom substituted dyes with Δ_{H-L} denoting the energy gap between the HOMO and LUMO.

Dye	Gas			Ethanol		
	HOMO (eV)	LUMO (eV)	Δ_{H-L} (eV)	HOMO (eV)	LUMO (eV)	Δ_{H-L} (eV)
B	-5.07	-3.43	1.64	-4.92	-3.35	1.57
C	-5.02	-2.62	2.40	-4.86	-2.60	2.27
N	-5.00	-2.33	2.67	-4.87	-2.30	2.56
O	-5.06	-2.50	2.56	-4.93	-2.53	2.40
P	-5.09	-2.76	2.33	-4.92	-2.75	2.17
S	-5.11	-2.62	2.48	-4.94	-2.64	2.30
As	-5.09	-2.79	2.31	-4.90	-2.73	2.17
Se	-5.10	-2.65	2.45	-4.92	-2.63	2.29

region of the dye. It is important to note that all LUMO energy levels are above the TiO_2 conduction band of -4.00 eV [30]; therefore, electron injection into TiO_2 remains favorable throughout the substitutions.

Using the Pauling Electronegativity Scale [38, 39], a general trend is observed that as the electronegativity of the heteroatom increases, the energy gap also increases, as shown in Figure 2. (tabular data included in the supplementary information along with gas phase plots). In ethanol, the pnictogens follow this trend with nitrogen having the largest gap of 2.56 eV and arsenic with the smallest at 2.17 eV. The chalcogens follow this trend as well, with the energy gap being the

Figure 2: The HOMO/LUMO energy gap (A) and dipole moment (B) of each species plotted against the electronegativity of each substituted heteroatom in ethanol solution.

largest for oxygen at 2.40 eV and the smallest for selenium at 2.29 eV. However, when going along the second row of the periodic table nitrogen breaks the trend. Boron has the smallest of 1.57 eV and oxygen had a gap of 2.40 eV, but nitrogen is 0.16 eV higher than oxygen. This deviation is most likely caused by the strong polar interaction between hydrogen and nitrogen. Unlike with carbon, boron or phosphorus, when hydrogen is attached to nitrogen to fill the valence, the larger bond polarity contributes more to the charge on the heteroatom. This leads to a higher electron density around nitrogen than oxygen (SI Figure 4) and increases the energy gap of that dye.

3.3. Absorption spectra

Figure 3 displays the computed absorption spectra for all the D- π -A dyes in ethanol (gas phase data included in the SI). Our calculations show the same general appearance as the D5 experimental spectrum (SI Fig. 2) [15], including some weak excitations at less than ~ 350 nm and a large peak red-shifted from these features. The most intense peak in the spectra (430 - 520 nm) corresponds primarily to transitions from HOMO to LUMO (see SI Table 2). These excitations would be effective at moving electron density from donor to acceptor regions of the molecules. It can be noted that the third and fourth row elements exhibit wider, more red-shifted bands. The most unique spectrum is from the boron substitution, which has the smallest HOMO-LUMO gap. We see a broad peak at 942.5 nm, an intense peak at 446.0 nm, and another absorption at 337.4 nm. All other heteroaromatic substitutions did not have any peaks above ~ 520 nm, while the substitution of boron red-shifted the spectrum by a substantial amount. In this case, the broad feature at 942.5 nm is dominated by the HOMO to LUMO transition (See SI Table 2). This broad peak is attributed to a delocalized density near B in the LUMO, and a diffuse transition moment from HOMO to LUMO. The energy gap for the boron species is the smallest among the tested dyes by 0.70 eV.

Although the spectral intensities for the B substituted ring are generally not as strong as the other dyes, there are two transitions that bring electrons to the acceptor portion of the dye. However, the longer wavelength feature has a notably decreased LHE compared to other HOMO to LUMO transitions in the dyes (0.73 vs. ~ 0.98), and there is a dramatic dip in the AM1.5 solar spectral irradiance at ~ 950 nm. So while this spectral feature of the dye may ultimately be beneficial for harnessing NIR photons, we will concentrate on the global λ_{max} trends in the forthcoming analysis. This is reasonable because the boron peak at 446.0 nm gives a LHE of 0.935, which is comparable to the other substitutions and is only slightly blue-shifted from the original dye. Similarly, the transition at 446.0 nm puts electrons primarily in the LUMO and LUMO+1 like the others (SI Table 2), and these orbitals are

Figure 3: UV/Vis spectrum of the dye in ethanol upon heteroatom substitutions of elements from A) row 2 of the periodic table B) the pnictogens and C) the chalcogens.

also localized near the acceptor group of the dye (SI Figure 6). The HOMO for the boron species is more centralized in the pi-bridge than the donor portion of the dye, while the HOMO-1 has more density on the donor group phenyl rings. Compared to the transition at 942.5 nm, the band at 446.0 nm more closely represents the typical donor to acceptor intramolecular charge transfer as seen in the other dyes in this study. Therefore, photovoltaic data obtained from the transition at 446.0 nm for the B species will be used to compare with the other heteroatom substitutions. From this absorption data, we can now calculate other photovoltaic properties for each dye, based on the most intense spectral feature at ~500 nm.

3.4. Photovoltaic data

Our approach toward predicting the photovoltaic performance of these dye molecules is to maximize the conversion efficiency, η , via increases in V_{OC} and J_{SC} (Eq. 1). For this analysis, the dipole moment will be used to represent relative variations in V_{OC} , and the combination of large LHE and large free energy of injection represents enhancements in J_{SC} at a given wavelength. As shown in Table 3 (and Fig. 2B), we observe that as the electronegativity of the substituted heteroatom increases, the dipole moment decreases. Being in close proximity to the acceptor region, the character of the heteroatom can notably alter the charge distribution of the dye. As the atom becomes more electronegative, it will hedge electron density migrating to the carboxylic group in the acceptor region of the dye by localizing electrons around itself, and thus decrease the dipole moment. The least electronegative heteroatom, boron, provides the largest dipole moment for the dye. Other substitutions decrease the dipole moment of the dye in

accordance with atomic electronegativity trends (the O and N ordering is inverted as discussed above but they have comparable values). Therefore, a relative increase in V_{OC} is expected as the electronegativity of the heteroatom decreases.

Moving on to LHE and ΔG^{inject} , we observe more diffuse trends when going along the second row of the periodic table. The driving force generally increases from left to right, and λ_{max} fluctuates between 432 to 502 nm. LHE values are comparable for all except the B species (discussed previously). Table 3 shows clearer trends when moving

Table 3: Calculated properties of heteroatom substituted dyes in ethanol solution. The LHE is at the λ_{max} wavelength. E^{dye*} is the difference between E^{dye} and E_{EX} , while ΔG^{inject} is the difference between E^{dye*} and the accepted E_{CB} value of 4.00 eV.

Row 2								
Dye	E_{EX} (eV)	f	E^{dye} (eV)	E^{dye*} (eV)	ΔG^{inject} (eV)	LHE	λ_{DYE} (nm)	μ (D)
B	1.316	1.189	4.92	3.60	-0.40	0.935	446.0	22.83
C	2.468	1.676	4.86	2.40	-1.60	0.979	502.4	10.92
N	2.868	1.822	4.87	2.00	-2.00	0.985	432.3	7.98
O	2.724	1.669	4.93	2.21	-1.79	0.979	455.2	8.43
Chalcogen								
Dye	E_{EX} (eV)	f	E^{dye} (eV)	E^{dye*} (eV)	ΔG^{inject} (eV)	LHE	λ_{DYE} (nm)	μ (D)
O	2.724	1.669	4.93	2.21	-1.79	0.979	455.2	8.43
S	2.666	1.875	4.94	2.28	-1.72	0.987	465.0	10.58
Se	2.627	1.870	4.92	2.29	-1.71	0.987	472.1	10.79
Pnictogen								
Dye	E_{EX} (eV)	f	E^{dye} (eV)	E^{dye*} (eV)	ΔG^{inject} (eV)	LHE	λ_{DYE} (nm)	μ (D)
N	2.868	1.822	4.87	2.00	-2.00	0.985	432.3	7.98
P	2.420	1.707	4.92	2.50	-1.50	0.980	512.2	12.12
As	2.386	1.723	4.90	2.51	-1.49	0.981	519.6	12.87

down the chalcogens that suggest the dye properties become more favorable for photovoltaic systems. λ_{max} red shifts and LHE as well as μ increase, while ΔG^{inject} decreases in magnitude slightly but still remains very favorable. The pnictogens follow a

similar trend as the chalcogens, except the LHE value generally decreases moving down the column from N. However there is a larger difference in the properties between the second and third row pnictogens when compared to the chalcogens, which can be attributed to the factors yielding the large band gap for the nitrogen species. Of all the elements being substituted that utilize additional hydrogens to fill valences, nitrogen forms the most polar bond with hydrogen, making it an electron density donor to nitrogen. The intramolecular effects of the polar bond in the π -bridge, coupled with enhanced solvent interactions, are likely the origin of the differences in the spectroscopic and photovoltaic properties of the nitrogen species. For the fourth row elements, Natural Bond Order (NBO) analysis revealed that the d_{xy} electrons of the fourth row heteroatom, the d-orbital in the plane of the molecule, delocalize throughout the π -bridge system, thus increasing the ease of electron transfer through the π -bridge.

This study has demonstrated that substituting other elements into the π -bridge of these D- π -A organic sensitizers can substantially change the photovoltaic properties. When comparing the effects from these substitutions, a number of factors should be considered in the overall assessment. For example, even though the boron species has the largest μ , it has the smallest ΔG^{inject} and LHE, which would lead to the smallest J_{SC} of the dyes tested. Most of the factors that affect V_{OC} are tied to the surface properties and the redox electrolyte, while J_{SC} is a better measure of dye contributions and is weighted more heavily here. Nitrogen has the most favorable ΔG^{inject} , but the smallest dipole moment and λ_{max} values. Selenium could be a potentially better suited heteroatom than sulfur due to it having a slightly more red-shifted λ_{max} and a larger dipole, without sacrificing its LHE or injection driving force. If looking for a more abundant heteroatom, Phosphorus is

attractive due to it being the most red-shifted having a large dipole moment, and the LHE is only slightly smaller compared to sulfur. Larger substituted heteroatoms had, on average, better photovoltaic properties and our results show introducing these heavier, less electronegative, heteroatoms into the π -bridge could improve photovoltaic efficiencies. Utilizing π -bridge systems with multiple heteroatoms could also yield interesting results.

4. Conclusion

Substituting different heteroatoms for the sulfur in the thiophene linker varied the properties of the sensitizer. In all cases the energy gap decreased, except for the substitution of oxygen or nitrogen, the two most electronegative atoms in our study. The substitution of boron provided the most dramatic results, by increasing the λ_{max} from less than 530 nm to 942.5 nm. This is attributed to a much smaller gap of the boron-substituted dye. The oscillator strengths are weaker, and the LUMO orbitals are not heavily localized on the acceptor portion of the dye, but the transition in the NIR could be further optimized to access the potential of that region of the solar spectrum. Even though the creation of dyes that use arsenic is not practical, this study has shown that large heteroatoms have a positive effect on the photovoltaic properties. Other third or fourth row elements may further improve the photovoltaic properties of these organic dyes. Future studies will examine dyes that utilize boron to enhance absorption in the NIR, potentially as a cosensitizer, and to further understand the chemical phenomena associated with its unique spectrum.

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