Theoretical Study of Effects of Anchoring Groups on Photovoltaic Properties of a Triarylamine-Based p-Type Sensitizer

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ABSTRACT: The effects of anchoring groups on triarylamine-based p-type dyes were studied by substituting the strong electron-withdrawing carboxyl group with the weak electron-withdrawing pyridyl and the electron-rich catechol groups. Judged by the index \( t \), the charge separation would be improved greatly when the carboxyl group of \( P_4 \) is replaced by the pyridyl or catechol groups. Although carboxyl as an anchoring group lowers the HOMO energy and facilitates the hole injection in comparison with pyridyl and catechol groups, the weak electron-withdrawing pyridyl and the electron-rich catechol groups facilitate the charge separation. \( E_g \) becomes narrow as the electron-withdrawing abilities of the anchoring groups decrease or as the conjugation extends. Both the extended \( \pi \)-spacers and the substitution of carboxyl with pyridyl and catechol groups promote the redshifts of adsorption wavelengths. The oscillator strengths for all dyes are over 2.00, indicating that all the dyes are able to harvest the sunlight strongly. The \( \Delta G_{\text{t}} \) values of \( P_4, \ DF_4, \) and \( DZ_4 \) are smaller than those of the other dyes. Also, these dyes have larger adsorption over infrared visible light, indicating that these dyes may be good candidates for p-type DSSCs.

1. INTRODUCTION

There is an increasing demand for renewable energy sources in recent decades. Solar energy has been paid great attention by many researchers because of its everlasting supply and nonpollution.\(^1\) An earlier n-type dye sensitized solar cell (DSSCs) developed by O’Regan and Grätzel achieved a power conversion efficiency (PCEs) of 7%.\(^2\) Recent n-type solar cells based on TiO\(_2\) are able to achieve exceeding 15%, which is much larger than the 2.5% PCEs of p-type DSSCs.\(^3\) In order to increase the PCEs of solar cells further, a tandem pn-type DSSC needs to be developed. Consequently, promoting the PCEs of p-type DSSCs is an essential and urgent task.\(^4\)

Organic sensitized dyes are the most key components in DSSCs, and play an important role in lots of aspects like hole or electron injection, charge redistribution, and photochemical reaction. Many optimal modifications have been performed to raise the PCEs of DSSCs. Earlier dyes basically consist of a central conjugated \( \pi \)-spacer that is flanked on opposite sides by an electron-rich donor and an electron-deficient acceptor (D–\( \pi \)–A), \( D \). Afterward, many improved structures such as D–D–\( \pi \)–A, D–A–\( \pi \)–A, and D–\( \pi \)–A–D etc., came into being.\(^7,8\)

When an additional donor group is inserted into the D–\( \pi \)–A, the electron pull–push effect is amplified because of an enhanced electron donation of the donors. This facilitates the charge transfer of the D–D–\( \pi \)–A dyes and a red shift in the absorption spectrum. In D–A–\( \pi \)–A, the inclusion of one more acceptor extends the conjugation by fusing A into \( \pi \)-spacers. This improves photon harvesting, lowers the bandgap, and enhances the open circuit voltage and short circuit current.

The attachment of another acceptor on the periphery of the acceptor increases the electron-pulling ability of D–\( \pi \)–A–A dyes. Furthermore, all dyes need to have acidic hydrophilic groups (anchoring group), like –COOH or –SO\(_2\)H, to combine them on the anode surface. For p-type sensitizers, the anchoring group is on the side of the donor group.

When the p-type dyes are excited by photons, the electron leaps from the donor that is close to the anode to the acceptor that is far away from the anode. Carboxyl as an anchoring group is able to adsorb on the semiconductors firmly. However, its electron-withdrawing ability hinders the hole injection from the dye into the anode because carboxyl refrains the electron transition from the donor to acceptor. To overcome this issue and improve the charge separation, the rational design of anchoring groups is needed. An optimal anchoring group for the p-type dye should have weak electron-withdrawing or electron-donating abilities, under the premise of strong adsorption on the semiconductor, which will enhance the charge separation and consequently the power conversion efficiencies.
It was found that the N atom in porphyrin dyes shares an electron pair and forms a co-ordinated bond with TiO₂ when the pyridine unit acts as the anchoring group, thus the electron injection efficiency in n-DSSCs is improved. Research on p-DSSCs showed that the weak electron-withdrawing ability of the pyridine unit, when being used as the anchoring group, can efficiently overcome the issue raised by strong electron pulling of carboxyl. As a result, the charge recombination rate was delayed, and open circuit voltage was improved. Inspired by the success of an alternative anchoring group and in the pursuit of higher PCEs, the effects of different anchoring groups on p-DSSCs were investigated in this article. Three anchoring groups of carboxyl, pyridyl, and catechol groups, with electron-withdrawing, weak withdrawing, and donating ability, respectively, were selected. Based on the prototype P₁ (triphenylamine flanked on either side by π-spacers and electron-deficient acceptor units, and carboxyl as the anchoring group), DZ and DF series of dyes were constructed by altering the anchoring groups with pyridyl and catechol groups, respectively (Figure 1). Influences of the anchor groups on the electronic structures, optoelectronic properties, hole injections, dye regenerations, and charge redistributions were probed. Two types of π-spacers, thiophene and benzothiadiazole, were included in the dyes.

2. RESULTS AND DISCUSSION

2.1. Energy and Bandgap of Frontier Molecular Orbitals. The energies of the HOMO and LUMO for an ideal p-type dye should match well with the valence band of a semiconductor and the redox potential of the redox mediator. The energy of the dye’s HOMO should be well below the valence band of semiconductor NiO (EᵥB = −4.98 eV) to guarantee enough driving force for hole injection. In the meantime, the energy of the LUMO should be well above the redox potential of the mediator [E(1+)/1−) = −4.80 eV]. The energies of the frontier orbitals are displayed in Figure 2. The energies of the HOMO and LUMO for the dyes basically meet the requirements for an ideal dye with the exception of DF₃ and DF₄. When the π-spacer is the same, the HOMO energies increase in the order of P series < DZ series < DF series, indicating that the carboxyl as an anchoring group lowers the HOMO energy and facilitates the hole injection in comparison with pyridyl and catechol groups. To compensate the raising of the HOMO caused by the replacement of carboxyl with pyridyl and catechol groups, an electron-withdrawing group is suggested to attach to the acceptor moiety. In contrast, the influence of the anchoring group on the LUMO energy is very small.

A low bandgap of the dye in DSSCs makes an easier electron excitation and large light adsorption. This guarantees a large short circuit current and PCEs. The bandgap is usually expressed as the energy difference between the HOMO and the LUMO. As can be seen in Figure 2, the Eᵥ values increase in the order of DF series < DZ series < P series. When the π-spacer is different, the Eᵥ values for DF series increase in the order of DF₄ < DF₃ < DF₂ < DF₁. The same order is applicable to the other two series. Eᵥ becomes narrow as the electron-withdrawing abilities of the anchoring groups decrease or as the conjugation extends. Therefore, either the reduced electron-withdrawing or electron-donating groups or the extended π-spacer facilitate PCEs.

2.2. Constituents of Frontier Molecular Orbitals. Figure 3 shows the spatial distributions of the HOMO and LUMO, by which the electron excitation and electron leap can be comprehended. The HOMO of the dyes is mostly located on the electron-donating triphenylamine unit and the conjugated π-spacer. The LUMO is mostly located on the electron acceptor unit and the π-spacer. However, the anchoring groups influence the contours of the HOMO more than those of the LUMO. Among dyes P₁, DF₁, and DZ₁, the HOMO of DF₁ extends more to the anchoring group, which is beneficial to hole injection from the dye to semiconductor NiO. When the π-spacer is a thiophene unit, the HOMO is located on the whole electron-donating groups, with the LUMO being located on the π-spacer and the electron-withdrawing group and being extended partially to the central triphenylamine unit. This large overlap of the HOMO and LUMO spatial distribution improves the oscillator strength of the acceptor. However, it also causes the charge recombination of the dye and holes. As the conjugated area of the π-spacer increases, the HOMO gradually shrinks to the electron-rich group, while the LUMO is away from the anchoring group, which lowers the charge recombination.

To show the variations in charge densities over the space, we used Multiwfn to draw the charge density difference maps (CDDM) between the excited and the ground states and to obtain some key parameters like hole and electron overlap degree index Sᵣ, the center of mass distance index Dₑᵥ, between the hole and the electron distributions, and hole and electron separation degree index t (Table 1). In the CDDM, green represents the increase of the electron density in the excited state relative to the ground state, and blue represents the relative decrease. The diagram indicates that the charge transfer is from the electron-donating group to the electron-withdrawing group via the π-spacers. Larger Sᵣ means more overlap of holes and electrons and a less degree of charge
separation. The charge separation efficiency of P4 is the least among all dyes. This is also shown in index t. The charge separation is inadequate when t < 0. For all the dye series, the charge separations are not perfect. When the carboxyl group of P4 is replaced by the pyridyl or catechol groups, judged by the index t, the charge separation would be improved greatly.

2.3. Adsorption Spectra. As mentioned above, the hybrid exchange–correlation functional CAM-B3LYP that combines the hybrid qualities of B3LYP and the long-range correction performs well for charge transfer excitations. As can be seen in Table 2, the wavelengths of maximum adsorption for the three series dyes increase in the order of P series < DZ series < DF series when the π-spacer is the same. If the π-spacer is a thiophene unit, the maximum adsorption wavelengths are 471 and 479 nm for anchoring groups being pyridyl and catechol groups, respectively. They are red shifted by 14 and 22 nm, respectively, in comparison with carboxyl as the anchoring group (λmax = 457 nm). There are also red shifts for the π-spacers other than the thiophene unit. The DF series are red shifted more than other series. The maximum adsorption wavelengths are in the order of DF1 (479 nm) < DF2 (508 nm) < DF3 (527 nm) < DF4 (584 nm). The red shift promoted by π-spacers is more than that by anchoring groups. DF4 has the most red shift because of its larger conjugation.

The oscillator strengths for all dyes are over 2.00. The corresponding light harvesting efficiencies (LHE) are over 0.99 according to the equation of LHE = 1 – 10−f, indicating that all the dyes are able to harvest the sunlight strongly. Furthermore, the main transitions are H → L and H → L + 1 for all dyes other than DF1 whose main transitions are H → L and H → L + 1.

As can be seen in Figure 4, the adsorptions are in the range of 200–900 nm, with two strong adsorption peaks at 300–350 and 400–600 nm. The adsorption variations with different π-spacers for the three series are similar. For example, the intensity in the absorption spectrum of DF3 is the most, while the red shift of DF4 is the most. The adsorption intensity could be promoted by more and more thiophene units, while benzoathiadiazole is more beneficial to red shift compared to other π-spacers. An extended coplanar conjugation enable the dyes to adsorb sun light more efficiently. It is worth noting that the dihedral angles of the DF and DZ series are much less than those of the P series, but the dihedral angles of DF1 to DF4 or DZ1 to DZ4 are similar (Table S1). This means that the coplanarity is improved by substituting the carboxyl group with pyridyl or catechol groups rather than by extended π-spacers. The π-spacers hardly enhance the coplanarity but increase the delocalization region of the conjugated π-electrons. It also needs to mention that when the dyes are anchored to the photoelectrode, their conjugated structures of the dyes are essentially similar to the isolated dyes because π-electrons do not take part in anchoring directly. Instead, the dyes are anchored to the electrode by donating their lone pair electrons of N or O atoms to the transition metal ion. However, the corresponding adsorptions over infrared visible light are somewhat red shifted because of the contributions of metallic orbitals to the LUMO. The energy of the LUMO is lowered and the HOMO–LUMO gap decreases.11

2.4. Performance of the Dye in DSSCs. Table 3 lists the predicted values of LHE, ΔGinj, ΔGreg and ΔGCR. The LHE values for all dyes are over 0.99, indicating high efficiencies for light harvesting. Both the ΔGinj and ΔGreg are negative, and more negative values are beneficial to the hole injection and dye regeneration. ΔGCR is positive, and a smaller value means less charge recombination losses. When the anchoring group of carboxyl is replaced by pyridyl and catechol groups, ΔGinj
Hole and Electron Separation Degree slightly or remains the same. As a whole, the replacement of blue colors indicate an increase and decrease of the electron density of increases, $\Delta a$ increases, $\Delta G_{inj}$ hardly changes, and $\Delta G_{CR}$ increases very slightly or remains the same. As a whole, the replacement of $\Delta a$ and $\Delta G_{CR}$ values essentially. As the conjugation of the $\pi$-spacer increases, the variations of $\Delta G_{inj}$, $\Delta G_{reg}$, and $\Delta G_{CR}$ become similar. The absolute values of $\Delta G_{inj}$ and $\Delta G_{reg}$ decrease, and those of $\Delta G_{CR}$ also decrease. Anyway, both values of $\Delta G_{inj}$ and $\Delta G_{reg}$ are less than $-0.2$ eV, which guarantees enough driving forces for hole injection and dye regeneration. Lower $\Delta G_{CR}$ leads to high PCEs. The $\Delta G_{CR}$ values of $P4$, $DF4$, and $DZ4$ are smaller than those of the other dyes, indicating that these dyes maybe have larger efficiencies of charge separations when used in the p-type DSSCs.

### 3. CONCLUSIONS

Three series of p-type dyes were designed with different anchoring groups. Based on the optimized geometrical structures, TD-DFT calculations for the excited states were performed at the CAM-B3LYP/6-311+G(d,p) level with solvent effects being considered by the polarizable continuum model. The results showed that the HOMO and LUMO energies match with the valence band of NiO and the redox potential $E(1\text{}/1\text{)}$ of the mediator, respectively. When the anchoring group of carboxyl is replaced by pyridyl and catechol groups, the adsorption spectra are red shifted, indicating that the replacement is beneficial to the light harvesting. The red shifts are further enhanced by an increasing conjugation of $\pi$-spacers. Dyes $P4$, $DF4$, and $DZ4$ have the most red shifts among all the dyes, with all the values of LHE, $\Delta G_{inj}$ and $\Delta G_{reg}$ being less than $-0.2$ eV in addition to having the smallest $\Delta G_{CR}$. These features can improve their performances as p-type dyes. Although several factors influence the PCEs of DSSCs, the prerequisite is that the dyes must have larger adsorptions over infrared visible light. The important factor is that the least overlap possible achieved between the contours of the HOMO and the LUMO guarantees less charge recombination. An initial screening based on these factors is suggested prior to the dye synthesis.

### 4. METHODS

#### 4.1. Theoretical Background.

PCEs ($\eta$) are important parameters in evaluating the performance of solar cells. High PCE values need large short circuit current ($I_{sc}$), open circuit
The quantity of semiconductor. The quasi-Fermi potential of electrons ($E_{fi}$) and the driving forces for hole injection ($\Delta G_{inj}$), dye regeneration ($\Delta G_{reg}$), and charge recombination ($\Delta G_{CR}$) can be quantitatively expressed by their corresponding free energies:

$$\Delta G_{inj} = E_{VB} - (E_{00}(dye^*) + E_{red}(dye))$$

$$\Delta G_{reg} = E(I^-/I^+) - E_{red}(dye)$$

where $E_{VB}$ denotes the valence band potential energy of the semiconductor, $E_{00}$ (dye$^*$) the excited state energy of the sensitizing agent, $E_{red}$ (dye) the reduction potential energy of the sensitizing agent, and $E(I^-/I^+)$ the reduction potential energy of the electrolyte.

4.2. Computational Methods. The geometrical optimizations for the dyes were performed at the B3LYP/6-31G(d,p) level with consideration of solvent effects through the polarizable continuum model (PCM). Five functionals were used to calculate the properties of excited species on the basis of the optimized structures of ground states. The excitation energies for the prototype P1 are 2.71, 2.06, 2.20, 3.04, and 1.55 eV from the CAM-B3LYP, B3LYP, PBE0, LC-BLYP, and MPW1K methods, all with the basis set of 6-311+G(d,p), respectively. The values at the PBE0/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels are comparable to the experimental value of 2.25 eV (Table 4). The maximum adsorption wavelengths at these two computational levels, however, deviated from the experiment greatly. The larger error of excitation energy at the CAM-B3LYP/6-311+G(d,p) level is somewhat offset by its good result of the maximum adsorption wavelength that is more important in evaluating the performance of the dyes. Thereafter, the calculations of the excited states are carried out using the CAM-B3LYP/6-311+G(d,p)

Table 3. Calculated LHE, Redox Potential $E_{red}$ (dye), and Driving Forces for Hole Injection ($\Delta G_{inj}$), Dye Regeneration ($\Delta G_{reg}$), and Charge Recombination ($\Delta G_{CR}$) for the Dyes

| Dyes | LHE | $E_{red}$ (dye) | $\Delta G_{inj}$ | $\Delta G_{reg}$ | $\Delta G_{CR}$ |
|------|-----|----------------|-----------------|------------------|-----------------|
| P1   | 0.9938 | −2.98 | −0.71 | −1.82 | 2.00 |
| P2   | 0.9994 | −3.02 | −0.56 | −1.78 | 1.96 |
| P3   | 0.9997 | −3.04 | −0.46 | −1.76 | 1.94 |
| P4   | 0.9997 | −3.26 | −0.47 | −1.54 | 1.72 |
| DF1  | 0.9939 | −2.96 | −0.57 | −1.84 | 2.02 |
| DF2  | 0.9994 | −3.00 | −0.47 | −1.80 | 1.98 |
| DF3  | 0.9998 | −3.03 | −0.40 | −1.77 | 1.95 |
| DF4  | 0.9997 | −3.26 | −0.40 | −1.54 | 1.72 |
| DZ1  | 0.9939 | −2.97 | −0.62 | −1.83 | 2.01 |
| DZ2  | 0.9994 | −3.01 | −0.50 | −1.79 | 1.97 |
| DZ3  | 0.9998 | −3.03 | −0.42 | −1.77 | 1.95 |
| DZ4  | 0.9997 | −3.26 | −0.40 | −1.54 | 1.72 |

The units of $E_{red}$ and $\Delta G$ are eV.

The geometrical optimization for the dye with the best performance of DSSCs, and the FF is related to the output property of cells. $V_{OC}$ is dependent on the voltage difference between the electrolyte redox potential ($E_{red}/q$) and the quasi-Fermi potential of electrons ($E_{fi}/q$) in the semiconductor. The quantity of $J_{SC}$ depends on the dye light harvesting, the charge injection, dye regeneration, and charge recombination. For p-type dyes, high efficiency of hole injection and dye regeneration, and low efficiency of charge recombination are beneficial to $J_{SC}$. The efficiencies of these processes can be quantitatively expressed by their corresponding free energies:

$$\eta = \frac{J_{sc}V_{oc}}{I_{s}} \text{FF}$$

where $J_{SC}$ and $V_{OC}$ are so important that they are the basis for high performance of DSSCs, and the FF is related to the output property of cells. $V_{OC}$ is dependent on the voltage difference between the electrolyte redox potential ($E_{red}/q$) and the quasi-Fermi potential of electrons ($E_{fi}/q$) in the semiconductor. The quantity of $J_{SC}$ depends on the dye light harvesting, the charge injection, dye regeneration, and charge recombination. For p-type dyes, high efficiency of hole injection and dye regeneration, and low efficiency of charge recombination are beneficial to $J_{SC}$. The efficiencies of these processes can be quantitatively expressed by their corresponding free energies:

$$\Delta G_{hij} = E_{VB} - (E_{00}(dye^*) + E_{red}(dye))$$

$$\Delta G_{reg} = E(I^-/I^+) - E_{red}(dye)$$

Table 4. Adsorption Spectra of P1 From Different Functionals

| Functionals | $E$ (eV) | $\lambda_{max}$ (nm) | $\epsilon \times 10^{4}$ M$^{-1}$ cm$^{-1}$ | $f$ |
|-------------|---------|----------------------|----------------------------------------|-----|
| (expt.)     | 2.25    | 487                  | 5.7                                    |     |
| CAM-B3LYP   | 2.71    | 457                  | 11.0                                   | 2.21|
| B3LYP       | 2.06    | 601                  | 6.3                                    | 1.31|
| PBE0        | 2.20    | 563                  | 7.6                                    | 1.46|
| LC-BLYP     | 3.04    | 407                  | 12.0                                   | 2.41|
| MPW1K       | 1.55    | 801                  | 4.3                                    | 0.92|

where $E_{VB}$, $\lambda_{max}$, $\epsilon$, and f are excitation energy, maximum adsorption wavelength, absorption coefficient, and oscillator strength. The basis set of 6-311+G(d,p) was used.

Figure 4. UV–vis spectra of the dyes.
method. All calculations for the target dyes were performed with the Gaussian 09 package.\textsuperscript{15}

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03522.

Dihedral angles of the dyes; and full width and onset at half-maximum of the strongest absorption peak of the UV–vis absorption spectra (PDF)

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\section*{Notes}

The authors declare no competing financial interest.

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