Tuning the HOMO Energy of the Triarylamine Molecules with Orthogonal HOMO and LUMO Using Functional Groups

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Abstract

Tuning the HOMO and LUMO energy strategically of triphenylamine derivatives plays an important role towards understanding and design of high performance organic photovoltaics. To improve on the charge separation and electron transfer properties, twenty one D-π-A organic dyes with nitrostyryl triphenylamine-based structures (NTPAs) were designed and computationally studied, in which triphenylamine, carbazole, or indoline structures were used as donor and NO₂ group as acceptor. The LUMOs of these dyes are more localized at the nitrostyryl moiety with almost the same energy and the HOMOs, which are orthogonal to the LUMOs, can be conveniently tuned by changing the donor structure and using different functional groups substituted on the donor. Compared with triphenylamine molecules, carbazole molecules decrease the HOMO energy of NTPA, whereas cis N-phenylindoline structure increase the HOMO energy. In addition, the exciton sizes generated by these dyes are also tuned in a range of 7.0~12.7 Å. These results show that introduction of dimethylamino group on the triphenylamine moiety greatly increases the HOMO energy and prolongs the maximum absorption wavelength as well as increases the exciton size, indicating that NTPA dyes containing strong electron donating dimethylamino group on the donor part are promising candidates as sensitizers in the dye-sensitized solar cell applications. The results of the structural and spectral properties show good correlation with the experimental results, which confirms that the DFT method employed in this work is an effective way to design organic small molecule based sensitizers.

Keywords: Styryl triphenylamine, Donor-acceptor molecules, HOMO, Exciton, UV-Vis spectrum, Density functional theory
1. Introduction

Dye-sensitized solar cells (DSSCs) using organometallic or organic dyes have attracted sustained interest in recent years for their potential application in the next generation solar cells compared with the silicon-based inorganic photovoltaic devices.\(^1\)\(^-\)\(^{21}\) The energy conversion efficiency using ruthenium-based organometallic and metal-free organic dye sensitizers under AM 1.5 irradiation can routinely achieve 11% and 9%, respectively. Though the Ru(II) complexes, such as N3 and N719 sensitizers, exhibit higher conversion efficiency than metal-free organic dyes, the higher cost and purification difficulties prevent the large-scale application of these dyes. Consequently, the metal-free organic dyes with low-cost and environmentally benign, as well as high molar extinction coefficient and high conversion efficiency have been developed as alternatives.

Triphenylamine and its analogous such as carbazole and indoline have been extensively studied as metal-free sensitizers for their excellent hole mobility, isotropic charge transport and other interesting properties.\(^2\)\(^,\)\(^{16,22-31}\) Moreover, these functional structures show excellent electron-donating ability and have been widely used as donors in the design and synthesis of various D-π-A type dyes.\(^32\)\(^-\)\(^{40}\) Compared with organometallic dyes, the internal charge transfer in triphenylamine-based dye lead to a broaden UV-vis absorption spectrum, a lower HOMO energy level and a smaller HOMO-LUMO energy gap, which make these sensitizers more efficient in the application in DSSCs. Among these triphenylamine-based dyes, the styryl triphenylamines are the simple structures not only easily accessible but also efficient.\(^41\)\(^-\)\(^{49}\)

Recently we have reported a series synthetic and theoretical studies based on the triphenylamine structure (TPA).\(^50\)\(^-\)\(^{62}\) Five styryl triphenylamines or indoline derivatives have been synthesized, and the UV-vis spectrum of the styryl indoline derivative showed obvious red
shift of 20 nm than the styryl triphenylamine, indicating a better electron-donating ability of the indoline ring.\textsuperscript{63} In addition, a new type of DSSC dye with a donor-acceptor1-acceptor2 architecture using a styryl triphenylamine moiety as the donor and a triazine and an anthraquinone molecules as serial acceptors was designed and synthesized by our group, and a sequential electron transfers together with effective hole transfer and a charge separated state with lifetime of 650 ns in this D-A\textsubscript{1}-A\textsubscript{2} dye were observed.\textsuperscript{64} Recently, Akhtaruzzaman reported the novel donor-\pi-spacer-acceptor type organic dye incorporated with indoline donor was synthesized for dye-sensitized solar cells with high efficiency, and the conversion efficiency was 6.2\% under AM 1.5 illumination.\textsuperscript{65} We also reported the synthesis and photochemical properties of seven styryl triphenylamine molecules with different functional groups on the styryl end, and the electron-hole distance of the excitons generated by these dyes can be tuned in the range of 2.0-8.6 Å. Among these functional groups, NO\textsubscript{2} showed strongest electron withdrawing capability and generated the exciton with a larger electron-hole distance of 8.6 Å.\textsuperscript{66}

To investigate the effect of frontier energy levels of dye molecules to the energy conversion efficiency, dyes with systematic changes of HOMO or LUMO energies are needed. Herein, 21 dyes sharing the same 4-nitrostyryl moiety were designed and studied using Density Functional Theory (DFT) calculations. Triphenyl amine, N-phenylcarbazole, and N-phenylindoline were chosen as the donor. As shown in Figure 1, these dyes are divided into three groups according the donor structures, that is, 1\textsubscript{a}-1\textsubscript{h} with a triphenylamine structure, 2\textsubscript{a}-3\textsubscript{f} with an N-phenylcarbazole structure, and 4\textsubscript{a}-5\textsubscript{c} with cis and trans N-phenylindoline structure.

The strategy in designing the donor structures is to use a C-C single bond to connect the adjacent phenyl rings in a three-dimensional propeller-like triphenylamine structure to form a coplanar carbazole structure and use a non-conjugated indoline structure instead of the
conjugated carbazole structure. Thus the generated dyes will allow us to systematically compare the influence of different donor structures and different functional groups substituted on the donors.

Scheme 1. Structures of nitrostyryl triphenylamine derivatives in three groups, 1a-1h with a triphenylamine structure, 2a-3f with a N-phenylcarbazole structure, and 4a-5c with cis and trans N-phenylindoline structure

2. Computational details

All the calculations were performed using Gaussian 09 program package\textsuperscript{67} and the molecular orbitals were visualized using Gaussview 5.0. All the ground state geometries and the electronic excitations of these dyes were calculated by density functional theory (DFT) at B3LYP/6-31+g(d,p) level and time-dependent DFT (TD-DFT) at CAM-B3LYP/6-31+g(d,p) level, respectively. During the geometry optimization, the convergence criteria for all self-consistent field, gradient, and energy were $10^{-8}$, $10^{-6}$, and $10^{-6}$ a.u., respectively. The optimized structures were confirmed by frequency analysis at the same theory level. Frequency
calculations were performed to ensure the structures are the minima. The TD-DFT calculations were based on the optimized ground state geometries. For all calculations, dichloromethane was used as solvent and treated using the polarized continuum model (PCM). The procedures and convergence criteria were used in the previous calculations.\textsuperscript{68-70}

The sizes of the excitons generated by these dyes are calculated by the distance between the electron in the lowest unoccupied molecular orbital (LUMO) and the hole located at the highest occupied molecular orbital (HOMO) during the excitation process from $S_0$ to $S_1$ according to the reported method.\textsuperscript{[66]}

3. Results and discussion

3.1 The optimized molecular structures

The optimized structures show that the styrylaryl moieties are planar, which indicate a strong conjugation across the donor-$\pi$-acceptor structures. According to the literatures, the synthesized indoline derivatives always have cis conformation, because the indoline was produced by the platinum-catalyzed hydrogenation of 1,2,3,4-tetrahydrocyclopent[b]indole.\textsuperscript{71,72} The reduction of C=C double bond on the platinum surface lead to the commercial available cis indoline (Scheme 2).

![Scheme 2](image)

Scheme 2. The synthesis of cis indoline structure

![Scheme 3](image)

Scheme 3. Styryl indoline derivatives containing cis and trans isomers

It is interesting that the energy difference between the cis isomer 4b and trans isomer 5b was 58.2 kJ·mol$^{-1}$, indicating the cis isomer was more stable than the trans isomer (Scheme 3). These
two isomers show different properties.

![Figure 1. The optimized structures of 1a, 1g, 1h, 2a, 3a, 4a, 4h and 5a with the dihedral angles between the N-phenyl ring and the diarylethene plane (for 3a, the dihedral angle is between the carbazole plane and the diarylethene plane).](image)

The optimized structures of 1a, 1g, 1h, 2a, 3a, 4a, 4h and 5a as well as the dihedral angles between the N-phenyl ring and diarylethene are shown in Fig. 1 to exemplify the typical conformations of NTPA dyes. Triphenylamine derivatives are well-known electron donating compounds with three dimensional propeller-like structures that prevent the aggregation in solid state and exhibit excellent solubility. The dihedral angles in 1a and 1h are 68.1° and 67.4°, respectively, whereas a relatively larger dihedral angle of 75.4° in 1g may be explained that the steric hindrance between the two 1-naphthyl groups is higher than that in 1a and 1h. 2a and 3a with carbazole moieties show similar dihedral angles between carbazole and phenyl rings of 64.0° and 60.0°, respectively. Compared with 1a, both 4a and 4h containing the cis indoline structures have a smaller dihedral angle of 40.7°, which indicates that the conjugation in 4a and 4h are better than that in 1a. However, the dihedral angle in 5c containing trans indoline structure is 56.6° which is larger than that in 4a containing cis indoline due to the congested steric effects between phenyls and the cyclopenta ring in trans indoline.

We note that synthesis of these compounds will be interesting to explore using various
methods with investigation of catalysis. Finally, we mention that the structures are sensitive to the environments, such as presence of other ligands, and aggregation. The suitability of these molecules in the application of solar cells and compatibility with the acceptors for electron transport will need detailed electronic properties, which are discussed below.

3.2 The UV-Vis absorption spectra

The calculated UV-vis absorption spectra of 1a~1h, 2a~3f, and 4a~5c are shown in Fig. 2, and the calculated and experimental UV-vis spectra data are listed in Table 1.

![Image](https://via.placeholder.com/150)

Figure 2. Calculated UV-vis absorption spectra of 1a~5c in three groups. (A) the spectra of 1a~1h with triphenylamine structure; (B) the spectra of 2a~3f with N-phenylcarbazole structure; (C) the spectra of 4a~5c with cis and trans N-phenylnindoline structure.
Table 1. The calculated and experimental absorption maximums of 1a–5c

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Calculated λ&lt;sub&gt;max&lt;/sub&gt;/nm (Exp.)</th>
<th>Dyes</th>
<th>Calculated λ&lt;sub&gt;max&lt;/sub&gt;/nm (Exp.)</th>
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<tr>
<td>1a</td>
<td>429(436)</td>
<td>3e</td>
<td>434</td>
</tr>
<tr>
<td>1b</td>
<td>438(449)</td>
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<td>386</td>
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<tr>
<td>1c</td>
<td>444(455)</td>
<td>4a</td>
<td>451</td>
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<tr>
<td>1d</td>
<td>394</td>
<td>4b</td>
<td>456(470)</td>
</tr>
<tr>
<td>1e</td>
<td>470</td>
<td>4c</td>
<td>461</td>
</tr>
<tr>
<td>1f</td>
<td>425</td>
<td>4e</td>
<td>476</td>
</tr>
<tr>
<td>1g</td>
<td>425</td>
<td>4h</td>
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<td>1h</td>
<td>431</td>
<td>5a</td>
<td>426</td>
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<tr>
<td>2a</td>
<td>406(410)</td>
<td>5b</td>
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<tr>
<td>3a</td>
<td>379</td>
<td>5c</td>
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</tr>
<tr>
<td>3d</td>
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Different methods such as ZINDO/1-CI and TD B3LYP/6-31G(d,p)/B3LYP/6-31G(d,p)<sup>107</sup> for the UV-vis spectra prediction of TPA derivatives have been reported, and the average errors were 0.63 eV and 0.64 eV from the experimental data, respectively. Preat reported the comparison of six functionals for the UV/vis spectra calculation and found that BHandH with average errors of 18 nm/0.11 eV was the best choice.<sup>37</sup> Moreover, literature reported that the TD CAM-B3LYP can be successfully applied to the conjugated charge transfer systems with better results than the other functionals.<sup>108-111</sup> Therefore, the TDDFT calculations of the NTPAs 1a–5c in this paper were carried out at the CAM-B3LYP/6-31+g(d,p) level. As shown in Table 1, the theoretical results of 1a, 1b, 1c, 2a and 4b are well consistent with the experimental maximum absorption peaks with the largest deviation of only 14 nm, which shows that TD-DFT calculation at CAM-B3LYP/6-31+g(d,p) level based on the optimized structure at B3LYP/6-31+g(d,p) level is a suitable method to predict the UV-vis absorption spectra of such solar cell dyes with high accuracy.

There are two peaks in the UV-vis spectrum of each compound. The weak absorption peak around 290 nm is assigned to the π–π* transition of the TPA, carbazole and indoline moieties.
connected with the styryl group.\textsuperscript{112-114} The main absorption from 350 nm to 550 nm in the UV-vis region are assigned to the intramolecular charge transfer (ICT) absorption.\textsuperscript{115-119} Since these compounds share the same 4-nitrostyryl moiety as the acceptor, their UV-vis spectra are dramatically influenced by the structures of the electron donors. We can tune the UV-vis spectra by changing the donor structure and changing the substituents on the donor.

As shown in Fig. 2 and Table 1, the maximum absorption of 3a, 2a, 5a, 1a and 4a are 379nm, 406nm, 426nm, 429nm and 451nm, respectively, which indicates that the N-carbazole group in 3a is the weakest electron donor and the cis-N-phenyl-indoline group in 4a is the strongest electron donor among these five NTPA dyes without substituents. Though 4a and 5a are cis and trans isomers, the cis indoline has stronger electron-donating ability than the trans indoline. This can be explained by the structures illustrated in Fig. 1. The dihedral angle between the N-phenyl and the cis indoline plane in 4a is 41.7° and that in 5a is 56.6°, which means there is a better conjugation of the N-phenyl ring with the cis indoline ring in 4a than that in 5a. In addition, the maximum absorptions of 4a, 4b and 4c increase gradually from 451nm to 461nm with stronger electron-donating groups from hydrogen, methyl to methoxy substituted on the N-phenyl ring, whereas the maximum absorptions of 5a, 5b and 5c are almost the same, which could be assigned to the poor conjugation between the N-phenyl ring and the trans indoline plane. Meanwhile, 2a and 3a are also isomers, the carbazole plane in 2a is conjugated with the 4-Nitro-stryl group, whereas the carbazole plane in 3a is separated from the diphenylethene plane, so the maximum absorption of 2a is red-shifted than that of 3a. For the 1a and 5a, they have very similar UV-vis spectrum, implying similar electron-donating ability of the 4-(diphenylamino)phenyl in 1a and the trans-N-phenylindoline groups in 5a.

Figure 2A shows the UV-vis spectra of the NTPAs containing TPA donor with different
substituents. The maximum absorptions of 1d, 1f, 1a, 1b, 1c and 1e increase gradually with the increasing electron-donating abilities of the substituents on the triphenylamine donor. 1d with two strong electron-withdrawing cyano groups shows shortest absorption of 394 nm, while 1e with two strong electron-donating dimethylamino groups show longest absorption of 470 nm. It is found that the maximum absorption of 1g and 1h containing two 1-naphthalenyls and 2-naphthalenyls are similar to that of 1a containing two phenyls, which discloses that changing the substituents on the TPA donor plays more important role in tuning the absorption properties of such solar cell dyes than changing the donor structure. The same trend of the influence of the substituents on the absorption properties of the other NTPAs can be found. Those dyes containing two dimethylamino groups on the donor part with longer UV-vis absorption can absorb the sunlight more efficiently and are more potential candidates in solar cell dyes.

3.3 The frontier molecular orbitals

The electron-density distribution of the highest occupied molecular orbit (HOMO), the lowest unoccupied molecular orbit (LUMO), and the calculated HOMO and LUMO energies of the optimized structures of NTPAs in ground state are illustrated in three groups in Figs. 3-5. These calculated HOMO and LUMO energies and energy gaps of 1a, 1b, 1c, 2a and 4b are in good agreement with the available experimental data. It is found that the LUMO energies and patterns of these NTPAs are almost the same and nearly all the electron density of the LUMO is delocalized on the nitrostyrylphenyl part. The calculated LUMO energy of 1d, 1f, 3d, and 3f containing cyano group are -3.19 eV, -3.13 eV, -3.23 eV, and -3.19 eV, respectively, which are lower by about 0.1~0.2 eV than that of the other analogues. These results show that the LUMO energies of the NTPAs are only slightly affected by the increase of the electron-withdrawing ability of the donor. On the other hand, the electron density of the HOMO is distributed on the
whole molecule especially focused on the donor, indicating that a charge transfer from the electron donor such as TPA group to the nitrostyryl acceptor will be generated during the excitation process. The HOMO energies of the NTPAs are greatly affected by the electronic properties of the donor and the substituents. The increase of the electron-donating ability of the donors and substituents will increase the HOMO energy. The HOMO energies of 1a, 3a and 4a containing 4-(diphenylanimo)phenyl, 4-(N-carbazolyl)phenyl, and N-phenyl indoline donor are -5.34 eV, -5.74 eV, and -5.64 eV. And that of 1a, 1b, 1c, 1d, and 1e containing the same TPA donors with different substituents are -5.34 eV, -5.24 eV, -5.16 eV, -5.79 eV and -4.82 eV, respectively. Based on these data, compared with the LUMO energies, the HOMOs of NTPAs are orthogonal orbitals, which the HOMO energies and HOMO-LUMO energy gaps can be effectively tuned by changing the donor structures and substituents to satisfy the requirement of new dyes for solar cell.

As shown in Fig. 4, it is worth noting that the electron density distribution of the HOMO and LUMO of 3a, 3e, and 3f are almost separated to each other. The HOMO of these three dyes focus on the N-carbazole donors and there is only tiny overlap of the HOMO and LUMO. In contrast, 3d containing two strong electron-withdrawing cyano shows contrary properties. The HOMO electron density of 3d delocalized over the whole molecular structure with very low energy of -6.26 eV and the energy gap of 3d is the highest one of 3.03 eV among these NTPA dyes. Tuning the polarizability of a molecule shown here is similar to creating intrinsic electric field in inorganic materials for better photocatalytic performances.
Figure 3. Calculated frontier orbital diagrams of 1a–5c

Figure 4. Calculated frontier orbital diagrams of 2a–3f
3.4 The exciton sizes

Intramolecular charge transfer (ICT) from the electron donor to the electron acceptor is one of the most important feature for the metal-free organic dye in the DSSC application.\textsuperscript{26,52,92} In order to investigate these photophysical properties of the NTPA dyes, the size of the excitons generated in the excitation process are theoretically studied by calculating the electron-hole distance of the exciton. Upon the light irradiation, an electron is excited from the HOMO to LUMO and leaves a hole in the HOMO. We can calculate the distance between the electron at the LUMO and the hole located at the HOMO, this distance is the size of excitons generated by the NTPAs. Our previous work also showed that the electron-hole distance of the excitons generated by MTPA derivatives were in the range of 2.0 ~ 8.6. Those MTPA derivatives have the same donor unit and use different substituents as the acceptors. The calculated results showed that the electron donating group decreased the size of the exciton, whereas the electron withdrawing group greatly increased the size of the exciton up to 8.61 Å.\textsuperscript{50,66}
Table 2. The exciton sizes generated in NTPAs

<table>
<thead>
<tr>
<th>Dyes</th>
<th>e⁻⁻h⁺ distance/Å</th>
<th>Dyes</th>
<th>e⁻⁻h⁺ distance/Å</th>
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<tr>
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<td>3e</td>
<td>12.18</td>
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<tr>
<td>1b</td>
<td>8.61</td>
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<td>12.73</td>
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<td>1c</td>
<td>8.81</td>
<td>4a</td>
<td>7.68</td>
</tr>
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4. Conclusions

In this work, we designed 21 dyes which share the same 4-nitro-styryl as the acceptor and contain triphenyl amine, carbazole or indoline moieties as donor. The optimized structures and HOMO and LUMO properties of these NTPAs were obtained from B3LYP/6-31+g(d,p) calculations, and the UV-Vis spectra were predicted at the TD-CAM-B3LYP/6-31+g(d,p) level. The DFT results are consistent with the available experimental data, which means the theoretical method used in this work is reliable for the prediction the photophysical properties of NTPA dyes with intramolecular charge transfer character. The most important property of these dyes is that the LUMO energies remain the same and the HOMOs are orthogonal to the LUMOs. The absorption, HOMO energies, and electron-hole distances can be easily tuned by changing the donor structure and substituents. The dimethylamino as strong electron donating group can be used not only increase the UV-vis absorption wavelength but also increase the electron-hole distance, which may greatly increase the performance in solar cells. It is interesting that the molecule contains one cyano and one dimethylamino has a bigger electron-hole distance, though the electron-hole distance of 3e is bigger than that of 1e, the maximum absorption of 3e is
blue-shifted than that of 1e. Considered the absorption and electron-hole distance, 1e is the best promising candidate for the application in DSSCs.

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Notes
The authors declare no competing financial interest.

References


(72) Scott, T. L.; Burke, N.; Carrero-Martínez, G.; Söderberg, B. C. G. Tetrahedron 2007, 63, 1183.


