Electronic Excitation and Injection of Ru-N3 Dye Anchored to TiO₂ Surface

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A step-by-step theoretical protocol based on the density functional theory (DFT) and time-dependent DFT (TD-DFT) has been performed to study a Ruthenium polypyridyl complex named cis-dithiocyanatobis-(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (N3) sensitized TiO₂ solar cell including dye excitations and electronic injection. Three binding structures of N3 anchored to a TiO₂ nanoparticle (TiO₂)₃₈ have been adopted. The electronic structures and optical properties of N3 dye in gas phase, in solutions (with the explicit and implicit solvent models), and interfaced with TiO₂ have been calculated. The hybrid DFT exchange-correlation (XC) functional B3LYP and PBE0, the newly-modified PBE0 functional PBE0-1/3, and the long-range corrected DFT (LRC-DFT) XC functional Cam-B3LYP have been applied. It is found that both the DFT XC functionals and molecular environments play a crucial role on molecular properties, which affect both the spectral lineshapes and peak positions. Coupled with PCM model, TD-PBE0-1/3 produces the best result compared with the experimental spectrum of N3 in CH₂Cl₂, TD-B3LYP slightly underestimates the excitation energies, and TD-Cam-B3LYP overestimates the excitation energies of 0.4 – 0.5 eV. As the solvent polarity increases, the electronic absorption spectra of N3 dye blue shift. The absorption manners of N3 anchored to (TiO₂)₃₈ affect the electronic excitations, leading to different electronic injection pathways. Two of three anchoring manners favor the interfacial electronic transfer. In the end, three possible electronic injection pathways from the different parts of the excited dye to TiO₂ nanoparticle have been suggested, indicating the different timescales of electron injections.

I. INTRODUCTION

To satisfy the currently increased global electricity needs, reduce air pollution and cut global warming emissions, it is urgent to develop the practical and affordable renewable energy sources. Silicon solar cells have been commonly used for converting solar radiation to electricity. However, the complex manufacturing processes and high production costs involved limit their commercial application. Dye-sensitized solar cells (DSSCs) or Grätzel cells are an efficient type of thin-film photovoltaic cell.¹ They promise viable solutions to future large-scale solar-energy conversion issues on the basis of high efficiency and low cost, and have thus attracted considerable research activities involved to design and optimize DSSCs. DSSC technology arises from the concept of "artificial photosynthesis". In DSSCs, chlorophyll is replaced by a light absorbing dye. We know that the main components of a DSSC is a wide band gap semiconductor that is able to accept

an electron injected into its conduction band from the excited photosensitizer. Since the semiconductor is transparent to the major part of the solar spectrum, a light absorbing dye is required to allow the absorption of light. A good photosensitizer not only should have broad and strong absorption bands but also should adsorb to the semiconducting antiparticles firmly and infuse electron from a high energy state generated by absorption of the light that can inject the photoexcited electron into the conduction band of semiconductors. Charge injection occurs very rapidly, often requiring less than 1 ps.

To enhance the performance of DSSCs, the improvement of semiconductor, redox mediator and dye-sensitizer has been the focus of previous publications. Among them, the development of more efficient dye-sensitizer is the key aspect for advancing these devices. A variety of dye sensitizers have thus been suggested, such as the metal-organic or fully organic dyes or porphyrin derivatives. Organic dye as an alternative to the dye-sensitizer generally possesses a common character of donor- π -bridge-acceptor (D- π -A) structure. When an organic sensitizer absorbs light, intramolecular charge transfer occurs from the subunit D to A through the bridge. To date, organic dyes exhibit high efficiencies in DSSCs. Porphyrin sensitizers were amongst the first examined natural types of dyes,^{2,3} and this day they continue to be one of the most frequently studied sensitizers.⁴⁻¹¹ Based on Zn-porphyrin dye and Cobalt(II/III)-based redox electrolyte, the power conversion efficiency of the best DSSC device has reached a record of 12.3%.¹² Among the organometallic complexes, Ruthenium polypyridyl complexes, such as N3 and N719 dyes, have shown the best photovoltaic properties due to their broad light absorption and relatively long excite-state lifetime.^{13,14} The best of Ru complex-based DSSCs has been reported to convert solar energy to electrical energy with an efficiency around 11%.¹⁵

The high energy conversion efficiency of the widely used N3 sensitizer and other related Ru(II) polypyridyl complexes comes from the efficient exciton generation and exciton separation processes. Ru polypyridyl complexes are typical organometallic complexes and they adsorb to the semiconducting surface via polypyridyl ligands. When Ru polypyridyl complexes are excited, the photo-induced intramolecular electron transfer from Ru metal center to the ligands takes place. The small spatial separation between the dye's polypyridyl ligands and the semiconductors (such as TiO₂) surface facilitates the interfacial electron injection and inhibits the charge recombination. The injection time of the electron from excited dye to semiconductor is dominated by the alignment of the excited electron energy level of the dye and the conduction band minimum (CBM) of the semiconductor. Because this alignment is affected by the anchoring manner, the adsorption structure of the dye is still an essential property, especially for the initial electron injection to the semiconductor surface. Microscopic examinations of the adsorption manner in DSSC are therefore very important for a better understanding of the working principle of the solar cell, as well as for the design of new DSSC device with improved high performances. The improvement based on the atomistic understanding from both the time-resolved experiments and theory as well as modeling is crucial for further breakthroughs. In the recent years, many works have been devoted to atomistic simulation of DSSCs.¹⁶⁻³³

In this work, we focus on one representative prototype organic dye molecule N3. We use the density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches to investigate the effects of the solvent and the absorption manners of N3 anchored to TiO_2 surfaces on the molecular properties as well as the electronic injection pathways from excited dye to TiO_2 . Through the studies on the geometric and electronic structures of isolated dye and the dye- TiO_2 complexes, we give a deeper insight into the working principle of N3-sensitized DSSC device. In detail, we show the adsorption geometries of N3 anchored on $(\text{TiO}_2)_{38}$ nanoparticle, the UV-visible absorption spectroscopies of isolated dye and dye- TiO_2 complexes, and the energy alignment of molecular levels with respect to the substrate band edges. The interactions between the N3 dye and TiO_2 will be revealed. Especially, the mechanisms of interface electron separation of N3-sensitized TiO_2 system will be revealed. The overall picture extracted from these works indicates an important role of the dye adsorption energy and geometry on the electrochemical properties and the DSSCs efficiency.

The paper is organized as follow. Section II briefly introduces the theoretical methods and the computational details. Section III presents the calculated results and discussions. Finally, a summary is provided in section IV.

II. COMPUTATIONAL DETAILS

All the calculations were carried out within the Gaussian 09 program package.³⁴ The DFT and TD-DFT approaches with different DFT exchange-correlation (XC) functional have been applied. The 6-31G** basis set was used for all the atoms except Ru and Ti. For 3d transition metals Ti and 4d transition metal Ru, the effective core potential LANL2DZ³⁵ was adopted. Solvent effects were introduced by means of the explicit solvents or the implicit conductor-like polarizable continuum model (PCM).³⁶

TD-DFT has been confirmed to provide efficient description to the electronic excitation of organic dyes.^{37,38} However, TD-DFT with conventional DFT XC functional has been found to give a poor description on the delocalization excitation and long-range charge transfer excitation due to the nonlocality and incorrect asymptotic behavior of the XC potential. The long-range-corrected DFT (LRC-DFT) XC functionals (e.g. those in Refs. 39–42) have thus been constructed to overcome the drawback of the traditional XC functionals. In this work, we will check the effect of DFT XC functionals on the optical properties of Ru-N3 molecule and the dye- TiO_2 complexes. Four different DFT functionals including the widely-used hybrid functionals B3LYP⁴³ and PBE0⁴⁴, the LRC-DFT functional Cam-B3LYP⁴², and the newly-modified functional PBE0-1/3⁴⁵ will be adopted. PBE0-1/3 was constructed by combining the PBE generalized-gradient functional with a predefined amount of exact exchange of 1/3 and has been shown to have an increased performance of PBE0-1/3 with respect to the widely used PBE0.⁴⁶

To understand the nature of electronic excitations, we analysis the excited states by constructing the

Figure 1: The geometry of Ru-N3 Dye.

Table I: Calculated bond lengths (in Å) and bond angles (in degree) of N3. The experimental data are taken from the X-ray experiment.⁴⁸

Parameter	Expt.	N3	N3 (in water)
$R_{Ru-N1(N2)}$	2.048(12)-2.046(16)	2.057-2.057	2.080-2.080
$R_{Ru-N3(N6)}$	2.030(13)-2.013(14)	2.082-2.082	2.087-2.088
$R_{Ru-N4(N5)}$	2.036(15)-2.058(12)	2.085-2.085	2.076-2.076
$R_{N1(N2)-C1(C2)}$	1.162(21)-1.103(27)	1.185-1.185	1.181-1.181
$R_{C1(C2)-S1(S2)}$	1.615(18)-1.685(22)	1.628-1.628	1.646-1.647
$\angle N1RuN2$	88.7(5)	92.726	91.000
$\angle N3(N5)RuN4(N6)$	79.1(5)-79.8(5)	78.450-78.451	78.885-78.906
$\angle N4(N5)RuN3(N6)$	95.9(5)-97.8(5)	99.896-99.900	98.181-98.255
$\angle N3RuN6$	174.5(5)	177.624	175.903
$\angle N4RuN5$	90.6(5)	93.848	91.997

natural transition orbitals (NTOs). The NTOs are defined by transformations U and V obtained by singular value decomposition (SVD) of the transition density matrix T , i.e., $UTV^\dagger = \lambda$. The matrices U and V are unitary and λ is diagonal.

To have a clearer picture on the mechanism of interfacial photo-induced electron injection, we perform a calculation on the density of states (DOS) of the coupled N3-TiO₂ complexes along with their projection onto the dye. DOS and projected DOS (PDOS) are defined as⁴⁷ $DOS(E) = \sum_i \delta(E - \epsilon_i)$ and $PDOS(Subsys)(E) = \sum_{\mu \in Subsys} \sum_{\nu} \sum_i C_{\mu i} S_{\mu\nu} C_{\nu i} \delta(E - \epsilon_i)$, respectively. Here ϵ_i denotes the i -th MO energy, C and S denote the MO coefficient and the overlap matrices, respectively. The index $\mu(\nu)$ denotes the indices of atomic orbitals.

Figure 2: The calculated absorption spectra of the isolated N3 dye with different DFT XC functionals. TDDFT coupled with PCM is used to take account of the solvent effect. For the comparison, the experimental spectrum in CH_2Cl_2 ⁴⁹ is shown.

III. RESULTS AND DISCUSSIONS

A. Ru-N3 dye

The Ru-complex with a cis arrangement of the thiocyanate ligands as shown in Figure 1 is employed. The geometry was optimized both in vacuo and water solution without any constraint. Table I shows the calculated and experimental-measured⁴⁸ main geometric parameters of N3. The computed results agree well with the experimental measurement and the geometry of Ru-N3 dye is slightly affected by the solvent effect.

The computed absorption spectra of N3 molecule in gas phase and solutions are shown in Figures 2-3. TD-DFT coupled with the different solvent models have been employed. It is observed that both the DFT functional and solvent effects are significant. Several features of these spectra are noteworthy and are summarized in the follow.

(1) The absorption spectra in gas phase differ significantly with those in the solutions. In gas phase, the traditional DFT XC functionals, B3LYP and PBE0, predict an observable light absorption in the long wavelength range of 600 – 1100 nm, which may partially result from the underestimation of electronic excitation energies by B3LYP and PBE0 since those low-energy excited states possesses an explicit intramolecular charge transition character. TD-Cam-B3LYP and solvent effects push those low-energy states to high energy range. It is that the lower energy bands show appreciable solution- and XC functional-dependent characters.

(2) The experimental electronic absorption spectra of N3 dye have been measured in dichloromethane and

Figure 3: The calculated absorption spectra of isolated N3 in water solution. The explicit and implicit solvent models are adopted here.

methanol. In CH_2Cl_2 , the experiment⁴⁹ showed two absorption maxima with nearly same intensity centered around 420 and 560 nm, and a broad shoulder peak around 650 – 700 nm, while in methanol solution, two high-energy absorption peaks blue-shift 30 nm. Coupled with the PCM model, TD-B3LYP, TD-PBE0 and PBE0-1/3 predict a more consistent spectral lineshape with the experimental measurement in CH_2Cl_2 than TD-Cam-B3LYP. However, it is observed that B3LYP slightly underestimates the excitation energies, in contrast, Cam-B3LYP significantly overestimates the excitation energies of about 0.4 – 0.5 eV. PBE0-1/3 produces best result compared with the experimental spectrum of N3 in CH_2Cl_2 due to the larger percentage of HF exchange in this functional than in PBE0.

(3) The solvent polarity is significant to the properties of N3 dye. Polar solvent water further blueshifts the spectra of N3 dye compared with that in dichloromethane as the Figure 2 shows. To check the effect of explicit hydrogen bonds formed between waters and N3 dye, here we put 4 – 6 explicit H_2O molecules around N3 and let H_2O hydrogen-bonded with N3 dye. Figure 3 shows that two additional H_2O molecules around the NCS ligands significantly blueshift the absorption band compared with that of $\text{N3}\cdot(\text{H}_2\text{O})_4$, which suggest that the solvent has different effect for the ligands of N3. The NCS ligands are more sensitive to the polar solvent than the other.

(4) The lower-energy absorption bands of $\text{N3}\cdot(\text{H}_2\text{O})_6$ in vacuo possess the intramolecular charge transfer features, which are evidenced by the charge distributions of “hole” and “particle” NTOs pairs with larger excitation amplitude values of λ as shown in Figure 4. In Figure 4, we visualize the charge distributions of

Figure 4: The electronic densities of “hole” and “particle” NTO pairs with largest values of λ for the low-lying dipole-allowed singlet excited states of $\text{N3} \cdot (\text{H}_2\text{O})_6$ calculated by TD-Cam-B3LYP.

three excited states of $\text{N3} \cdot (\text{H}_2\text{O})_6$, which correspond to the first, ninth and sixteenth dipole-allowed singlet excited states (simply noted as S_1 , S_9 , S_{16} in Table II). The results are produced by TD-Cam-B3LYP. These absorption bands come from the electronic excitations taken place between the ligands ($\pi \rightarrow \pi^*$) and metal-to-ligand CT (MLCT, $d \rightarrow \pi^*$) as Figure 4 shows. We observe that both the ligand-to-ligand charge transfers (LLCT) and MLCT transitions contribute to the lower energy bands. As Figure 4 shows, the densities on all “hole” NTOs, which are related to the initial states, are mostly centralized on Ru atom and two monodentate NCS ligands, while those in the “particle” NTOs, which are related to the final states, are

mainly delocalized on the two π -conjugated dcby ligands. It should be noted that there are some charges distributed on the Ru atoms in both “particle” and “hole” NTOs pairs, however, the charges in the “hole” NTOs of Ru atom are much larger than those in “particle” NTOs of Ru, which suggest that intramolecular MLCT occurs. There are significant LLCT occurred in these low-lying excited states.

Table II: The vertical excitation energies (in unit of eV) and oscillator strengths (in parentheses) of low-lying dipole-allowed singlet excited states of N3-(H₂O)₆ in vacuo and N3-(TiO₂)₃₈ in water solution.

	S1	S3	S4	S5	S7	S8	S9	S16
N3-(H ₂ O) ₆	2.05(0.043)						3.05(0.097)	3.39(0.109)
Type1	2.22(0.06)		2.63(0.23)		3.11(0.12)			
Type2	2.16(0.02)			2.56(0.10)		3.22(0.15)		
Type3	1.89(0.46)	2.33(0.13)			2.93(0.14)			

B. N3-TiO₂ complexes

1. Electronic Excitation of N3-TiO₂ complexes

Figure 5 shows the structures of N3-(TiO₂)₃₈ complexes with three different binding structures of the sensitizer anchored to TiO₂ nanoparticles. Here, the size of TiO₂ nanoparticle is as large as (TiO₂)₃₈, which was cut from anatase bulk structure and used by many other works.^{50–53} The plane (101) of TiO₂ is the most stable surface. Type1 adsorption manner is heteroleptic sensitizer, in which one of two bipyridine ligands has been bounded to nanocluster. Type2 adsorption manner has two equivalent ligands and the two carboxylate groups from the different ligands anchored to the surface of nanocluster. In the Type3 adsorption manner, the N3 dye is keen on adsorbing on the TiO₂ surface by a tridentate and bridging coordination mode which differs from the first two adsorption manners, and in this case there is a proton transfer from the dye to the surface of TiO₂. The structures of N3-(TiO₂)₃₈ are optimized in DMol3 program at the theoretical level of PBE/DNP. Theoretical calculations show that the anchoring mode of Type3 is most stable (setting its energy $E = 0.0$), and Type2 is the second ($E = 0.57$ eV) and Type1 is most unstable ($E = 0.92$ eV).

The optical absorption of N3 also is affected by substrates (TiO₂ nanoparticle), resulting in the overall spectral lineshape of N3-(TiO₂)₃₈ complexes different with that of isolated N3. Furthermore, the different anchoring modes also lead the different spectral lineshapes as shown in Figure 5, implying that the electronic structures of N3 are effected by the anchoring modes. In Type1, two main high-energy absorption bands redshift about 30 nm and their relative oscillator strengths alter in comparison with these of free dye. The absorption in high-frequency range is reduced. Contrarily, the absorption in low-energy range is enhanced. The spectral lineshape of Type2 is more similar with that of free N3 except the overall spectra redshift about 45 nm, which mean that the electronic structures are weakly affected under Type2 anchoring mode. Quite

Figure 5: The optimized geometries of three anchoring modes of N3-(TiO₂)₃₈ and the calculated absorption spectra of N3-(TiO₂)₃₈ by TD-Cam-B3LYP. The spectrum of the isolated N3 is shown for the comparison.

differently, Type3 shows a overall different spectral lineshape with the first two anchoring modes and free N3. The lowest absorption band redshifts to around 660 nm and there is an additional absorption band in the range of 600 – 700 nm. However, the relative oscillator strengths in Type3 absorption are lower than those in the other anchoring modes.

To obtain a better clarification on electron transfer mechanisms from the photoexcited dye to the conduction band of the semiconductor, we conduct an additional analysis on the electronic excitations of the corresponding states. Figure 6 shows the pairs of “hole” and “particle” NTOs corresponding to the three low-lying bright excited states of each anchoring mode (see Table II). The “hole” NTOs of Type1 are analogous with that of S₁ of free N3. However, the “particle” NTOs are significantly different and localized on a π -conjugated dcby ligand, which has been bonded to the TiO₂ nanocluster, which is favorable toward electronic injection from the excited dye to the semiconductor. The two high-energy excited states of Type1 show that there are two “particle” NTOs localized on the different π -conjugated dcby ligands (namely up and down), which implies that the multiple time scales of the electron injections. From our intuition, the electron injection from the dcby ligand (down) should be faster due to the closer distance with the substrate. In

Figure 6: The electronic densities of “hole” and “particle” NTO pairs of the three anchoring modes with largest values of λ for the dipole-allowed singlet excited states of N3-(TiO₂)₃₈ complexes.

Type2, the two dcppy ligands of the N3 both anchor the surface of the TiO₂ and the “hole” NTOs are similar with those of Type1. As the energies of the singlet excited states increases, we find that the “particle” NTOs are delocalized from one of the dcppy ligand to both of the dcppy ligands, which suggests that the two dcppy ligands should have the same effect for the injection of the excited electron. Meanwhile, the “particle” NTOs of Type3 are similar with that of Type2. But, in the lower singlet states, the “particle” NTOs are more localized on the dcppy ligand which anchors the surface of the TiO₂ by a bidentate mode, which implies that the excited electrons seem to inject the surface by the bidentate ligand more effectively.

2. Electronic structures of N3-TiO₂ complexes

Figure 7 reported the total and projected density of states (DOS) of three adsorption structures of N3-TiO₂ complexes. The Fermi energy is defined as the middle point of HOMO and LUMO of N3-TiO₂ complex.

Figure 7: Total and projected DOS of N3-(TiO₂)₃₈ complexes.

The following features are observed. A significant feature is that total DOS curves show the intensities and shapes typical to the TiO₂ structure with distinctly different features of HOMO and LUMO, and a noticeable gap. For the N3-TiO₂ complexes, the molecular orbitals near the HOMO and LUMO are contributed by N3 and TiO₂ cluster, respectively. The (TiO₂)₃₈ nanocluster has a HOMO-LUMO gap of 6.5 eV, which is larger than the band gap of 3.2 eV in the bulk TiO₂ due to the overanimation of LRC-DFT functional and the small nanoparticle size. The N3 dye inserts states within the HOMO-LUMO gap of the TiO₂ cluster, which decreases the computed HOMO-LUMO gap from 6.7 eV for the free cluster to 4.0 eV for the N3-(TiO₂)₃₈ complexes. This type of DOS suggests a favored electron promotion from the HOMOs to the LUMOs, in line with the classical chemical understanding of dye-sensitized solar cells, in which optical excitation of the dye with visible light leads to excitation of the dye and injection of electrons into the conduction band of the semiconductor.

In the absorption structures of Type1, Type2 and Type3, we note that the occupied MOs are mainly localized on N3, in according with the similar shapes of the “hole” NTOs shown in three different absorption structures. However, there are some differences in the virtual MOs. It is found that Type3 shows smaller gap than those of Type1 and Typ2. Due to the proton transfer from the N3 dye to the substrate occurred in Type3, the lowest virtual MO is localized on the N3 which has lower energy level than the conduction band bottom (CBM) of TiO₂. It is interesting that the lowest virtual MOs of Type1 and Type2 have different gaps with the CBM of the TiO₂, which mean that the different energetic driving force for the interfacial charge transfer. In contrast, when the electron is excited to the lowest virtual MOs of Type3, the lower

Figure 8: The predictive pathways of the electron injection from N3 to TiO_2 nanoparticle

energy level of the excited state than the CBM would not lead the excited electrons to transfer to TiO_2 .

3. The predictive pathways of charge separation in $\text{N3-(TiO}_2\text{)}_{38}$ interface

Following the different types of electronic distributions in the initial and final states, we suggest that the possible injection mechanisms in N3-TiO_2 interface for the different anchoring modes (in Figure 8). With respect to our analysis above, we have known the excitations of the dye in the long wavelength are mostly contributed by the LLCT and MLCT. In Type1, the excited electrons of the lowest excited state is mainly localized on the dc bpy ligand (down) which is anchored on the surface of substrate, thus indicating a thermodynamically favorable injection of electron from the first excited state of the dye. For the higher excited states, the excited electron have some distribution on the dc bpy ligand (up), which has greater separation with TiO_2 surface and may not facilitate the electron injection. In Type2, the distances between two dc bpy ligands and the surface of TiO_2 are nearly same, and the electrons in "particle" NTOs are delocalized on two dc bpy ligands. The injection mechanism of Type2 is that the electron is excited to one of two dc bpy ligands, then injects into TiO_2 . For Type3, the lowest excited state could not provide sufficient driving force for the electron injection. Meanwhile, the distinct difference between the absorption spectra of theoretical calculations and the experimental measurement means that Type3 is not the major anchoring mode and the effect of Type3 anchoring mode in $\text{N3-sensitized DSSC}$ may be neglected.

The different pathways of electron injection in different anchoring modes indicates the different timescale,

which is in agreement with the experimental evidences that electron injection dynamics is multiexponential.^{56,57} It is worth mentioned that an injection from the thermalized triplet state exists in the experimental works, although in a longer timescale. By our calculations, the triplet state lie at lower energy than the excited singlet state, thus being energetically more stable than the first singlet excited state. So, the intersystem cross transit the electrons to lower-energy triplet state, then finish the injection.

IV. CONCLUDING REMARKS

We have presented a detail theoretical study on the electronic excitation and injection mechanism of Ru-N3 dye anchored to TiO₂ surface and provided a microscopic atomistic simulation of N3-sensitized solar cell system. Through the studies on the geometric and electronic structures of isolated dye and dye-TiO₂ complexes, we have given a deeper insight into the solvent effect on N3's properties and the working principle of N3-sensitized solar cell device. At first, we instigated the optical absorption spectra of N3 and the complexes of N3-TiO₂ by means of TD-DFT with different DFT XC functionals. Obvious CT characteristics has been visualized in low-lying dipole-allowed excited states of Ru-pyridine complex. By using TD-PBE0-1/3 functional, we have achieved a satisfied consistent with the experimentally-measured spectra and gotten insights into CT character of the lower-lying electronic transitions. It is noted that the LRC-DFT XC functional seems to overestimate the solvability for N3 molecule with PCM. Then, we have shown the adsorption geometries of N3 anchored on (TiO₂)₃₈ nanoparticle, the effects of absorption manners on UV-visible absorption spectroscopes, the energy alignment of molecular levels with respect to the substrate band edges, and the electronic injection pathways as well. Through the analysis of different anchoring modes, the electronic structures and excited states of dye-TiO₂ complexes, we suggested the possible pathways of electron injection for the different anchoring modes. The overall picture extracted from our work indicates an important role of the dye adsorption energy and geometry on the electrochemical properties and the DSSC efficiency. This calculation provides a detailed theoretical understanding of the interactions between the sensitizer and the substrate, and gets insight into the effect of the DFT XC functionals and solvent. It is an important step toward optimization of computational details in the later theoretical calculation.

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