Molecular Engineering of Quinodimethane-based Dyes with Different Anchor Groups for Dye Sensitized Solar Cells (DSSCs)

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Abstract. This paper mainly works on changing different anchoring groups of quinodimethane-based dyes, which represent a twisting phenyl ring during the excitation process, for dye-sensitized solar cells (DSSCs). Five different groups, (1) cyanoacrylic acid (-CHC(CN)COOH), (2) carboxylic acid (-COOH), (3) pyridine (-C5H5N), (4) sulfonic acid (-SO3H), (5) phosphoric acid (-PO3H2), were adopted as anchors on the quinodimethane moieties forming dyes 1-5, to further explore their effects on optoelectronic properties via molecular engineering methods. Density functional theory (DFT) and time-dependent DFT (TD-DFT) were used to calculate their electronic structures and electro-optical properties. Computational results show that all dyes show suitable molecular orbital energy levels between the conductive band of TiO2 and the potentials I-/I3- redox couple so that all of 1-5 can be potential candidates for DSSCs application. Also, TDDFT results exhibit that dye 1 has the widest absorption band in UV-visible region, with the first excitation energies of 2.782 eV, while other dyes show similar first excitation energies about 0.2 eV higher than that of dye 1. In particular, dye 3 with pyridine as anchor group shows a very excellent charge transfer properties from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO), with the highest HOMO level of -5.16 eV, which offers a strong driving force for dye regeneration, and a LUMO level of -2.36 eV, which enables excited electrons successfully to be injected in to titania film. Also, this pyridine anchor group offers a larger $\pi$ conjugation, which may improve the ability of electron injecting and further strengthen the photovoltaic performance in DSSCs.

1. Introduction

In 1991, Grätzel published a paper about dye sensitized nanocrystals solar cells on Nature, and the photoelectric conversion efficiency reached 7% with a low cost, and this work exploits a new age of the history of solar cells. Since then, people are working on improving the performances of DSSCs. So far, the most efficient metal-free DSSCs have reached power-conversion efficiency (PCE, $\eta$) values of up to 14.3%.

When exposed under illumination, dye molecules will be motivated from ground state to excited state. Meanwhile, electrons are excited from HOMO to LUMO, and then injected into...
semiconductor’s conductive band, transported to conductive substrate, and finally “flowed” into external circuit. On the other hand, the dyes at oxidation state are reduced by redox couples in electrolyte. The circulation is completed when the redox couples accept electrons at the interface of counter electrode from external circuit.

Dye molecules attach to metal oxide substrate’s surface through many ways, such as covalent attachment, electrostatic interaction, hydrogen bonding, hydrogen-phobic interaction, van der waals forces, and physical entrapment. In DSSCs, the most common way is the covalent bonding between the dyes and the TiO2 surface atoms in order to guarantee a strong coupling, a homogeneous dyes distribution, and device stability. While other kinds of interactions usually involve weaker bonds, leading to a quasi-reversible and unsteady adsorption.

Recently, a series of quinodimathane-based dyes were designed for DSSCs and investigated systematically, showing that the dyes with cyanoacrylic acid and carboxylic acid showing better performances compared to other dyes in this series, caused by a large twist of donor groups in its excited state which successfully blocked electron recombination. Thus, in this study, to further improve the properties of these dyes, the dimethylamino group was retained, as electrons donor, trying to maintain the property of the large ring twists in the donor group during ground-to-excited-state transition, and five anchoring groups: (1) cyanoacrylic acid (-CHC(CN)COOH), (2) carboxylic acid (-COOH), (3) pyridine (-C5H5N), (4) sulfonic acid (-SO3H), (5) phosphoric acid (-PO3H2) were investigated. Geometries at ground and excited states, frontier molecular orbitals and first excitation energies of dye 1-5 were calculated using DFT and TDDFT methods. Chemical structures of 1-5 are listed in figure 1.

![Chemical structures and systematic names of 1-5](image_url)

**Figure 1.** Chemical structures and systematic names of 1-5

### 2. Computational Methods
Gas-phase structures of 1–5 were firstly optimized at the B3LYP6/6-31g(d)7 level of theory using NWChem 6.6 software package. Single-point energy calculations were performed at the B3LYP/6-31g++(d,p) level of theory. Theoretical first excited energies were calculated using time-dependent density functional theory (TD-DFT) in combination with the M06-2X functional and the 6-31g (d) basis set, based on the optimized ground-state structures.

### 3. Results and Discussion

#### 3.1 Optimized ground state geometries in vacuo
All frontier molecular orbitals and ground-state (GS) geometries of 1-5 were
calculated and optimized as mentioned in computational methods. Selected structural parameters of the optimized structures are summarized in table 1.

![Chemical structure of dye 1-5](image)

### Table 1. Selected structural parameters for 1-5.

| Dye | α [°] | β [°] | C-anchor [Å] |
|-----|-------|-------|--------------|
| 1   | -46.36| -0.95 | 1.45         |
| 2   | -47.93| 0.34  | 1.49         |
| 3   | -47.20| -35.78| 1.48         |
| 4   | -48.72| -     | 1.79         |
| 5   | -48.27| -     | 1.80         |

For angle α, 1-5 show similar values to each other. 4 and 5 show relatively larger α in their structures, which might be caused by stronger electron-pulling abilities of SO3H and PO3H2. For β, anchors in 1 and 2 shows excellent planar structures, which guarantee a good electron injection from dye molecules to TiO2 layers. 3 shows a much larger twist since pyridine has a larger planar ring structure, which enlarged the π conjugation, may also promote the electron injection. The bond lengths of C-anchor show that !-3 have a typical C-C single bond, between their anchor and the adjacent benzene ring. While 4 and 5 have longer bond caused by S and P atoms which have larger electronic negativity. For structural parameters of other moities, such as the dihedral angles of the benzene rings connected to donor group and the quinodimethane rings, structural details are listed in the supporting information.

### 3.2 Frontier Molecular Orbitals (FMOs)

HOMO and LUMO levels are the most significant characters for dye molecules used in DSSCs. They directly exhibit the possibility of electron excitation and transportation in DSSCs. All the molecular
orbitals were calculated via DFT at the B3LYP/6-31g++(d,p) level of theory, listed in table 2 and figure 3. The HOMO energy levels of 1-5 are lower than the redox potential of the most commonly used DSSC electrolyte (I-/I3-), which renders the regeneration of the dye molecules possible. The LUMO energy levels are sufficiently high to provide the driving force for electron injection from the excited dye molecules into the TiO2 conduction band (CB).

Table 2. DFT- and TDDFT-derived HOMO and LUMO energy levels

| Dye | HOMO [eV] | LUMO [eV] | Energy gap* [eV] |
|-----|-----------|-----------|-----------------|
| 1   | -5.306    | -2.936    | 2.370           |
| 2   | -5.120    | -2.450    | 2.670           |
| 3   | -5.161    | -2.360    | 2.801           |
| 4   | -5.327    | -2.574    | 2.753           |
| 5   | -5.193    | -2.390    | 2.803           |

*: Energy gap = LUMO – HOMO

Figure 3. Calculated HOMO/LUMO energy levels of 1-5.
Figure 4. Calculated electron density distributions for the frontier molecular orbitals of 1-5 using DFT methods based on B3LYP/6-31++g (d,p), and shows the HOMO, LUMO, and HOMO-2 energy state.

As shown in figure 4, the HOMOs in the ground state is comparable for 1-5, and the electron density is located predominantly on the donor moiety and the quinodimethane backbone. The LUMOs are located mainly on the anchor groups and the quinodimethane backbone. In addition, small parts of the LUMO of 2-5 are situated on the phenyl ring that connects the quinodimethane moiety and the donor group. Generally, 1-5 exhibit very good HOMO-to-LUMO charge redistribution from the donor to the anchor moieties, which renders the injection of excited electrons into the CB of TiO2 possible. Distribution of 1-3 are much better than 4 and 5, and 4 is slightly better than 5, especially for 5, few LUMOs is located on P atom, which may lead to a worse performance than the other four dyes.

3.3 First excitation energies

The first excitation energies of 1-5 were studied by TDDFT calculations at the M062X/6-31g (d) level of theory. The results are listed in table 3.

The first excitation energies of 1-3 are smaller indicating wider absorption band compared to that of 4-5, which are much larger and lead to difficulties of absorbing longer wavelength light.

The compositions of the excitations in terms of molecular orbital transitions were also calculated (table 3), and the results show that for dye 1, the first excitation is mainly attributed to HOMO-LUMO transition (84.12%), which is obviously an intramolecular charge transfer (ICT) process. While for 2-5, the excitations were attributed mainly to the HOMO-2-LUMO and HOMO-LUMO transitions. So in order to discuss the excitation properties of 2-5, distributions of HOMO-2 were also shown in figure 4. The results show obvious charge redistribution from donor groups to anchor groups in the HOMO-2 -> LUMO transition, indicating that ICT occurs in such transition and also the first excitation.

Table 3. Energy (eV, nm) and oscillator strength values for 1-5, as well as sizable ($f > 0.1$) contributions of the molecular orbitals to the transitions

| Dye | 1st excitation energy | Oscillator strength (f) | Composition                  |
|-----|------------------------|-------------------------|------------------------------|
|     | [eV]                   | [nm]                    |                              |
| 1   | 2.782                  | 445.66                  | 0.5092 84.12% HOMO - LUMO    |
|   | 2.936 | 422.26 | 0.2663 | 38.26% | HOMO-2 - LUMO |
|---|--------|--------|--------|--------|---------------|
|   |        |        |        |        | 46.81% HOMO - LUMO |
| 3 | 2.959  | 419.02 | 0.2537 | 50.00% | HOMO-2 - LUMO |
|   |        |        |        |        | 34.65% HOMO - LUMO |
| 4 | 2.918  | 424.97 | 0.2373 | 49.91% | HOMO-2 - LUMO |
|   |        |        |        |        | 35.38% HOMO - LUMO |
| 5 | 2.946  | 420.85 | 0.2065 | 30.02% | HOMO - LUMO |
|   |        |        |        |        | 54.93% HOMO-2 - LUMO |

### 4. Acknowledge

For the first, I would like to express my gratitude to my teacher Dr. Yun Gong, who taught me the basic knowledge required in this project, and how to write an academic paper. And thanks to the organization Illume Research and my school Chongqing Foreign Language School, they provided the chance that I can be a part of the project; without them, I can never learn or reach about the correlation stuff.

### 5. Conclusion

This research investigated the effects of different anchors on quinodimethane dye molecules for dye-sensitized solar cells (DSSCs). Five anchors were selected in this research, (1) cyanoacrylic acid (\(-\text{CHC(CN)COOH}\)), (2) carboxylic acid (\(-\text{COOH}\)), (3) pyridine (\(-\text{C5H5N}\)), (4) sulfonic acid (\(-\text{SO3H}\)), (5) phosphoric acid (\(-\text{PO3H2}\)). Density functional theory (DFT) was used to calculate HOMO and LUMO levels, showing all the quinodimethane dyes are good candidates for DSSCs in terms of energy levels. The distributions of HOMOs and LUMOs show that dye 1-3 have better charge-transfer properties than 4 and 5. In TD-DFT study, the first excitation energies of 1-5 were calculated, and it is very clear that -\text{CHC(CN)COOH} is the best anchor in terms of the energy gap, since it requires the lowest first excitation energy (2.78 eV) for electrons to be excited, and also this excitation were mainly due to an intramolecular charge transfer process from HOMO to LUMO transition. Dye 3 with pyridine as its anchoring group is also an attractive one since it has a larger π conjugation, obvious intramolecular charge transfer from HOMO to LUMO transition and HOMO-2 to LUMO transition. Although the first excitation energy (2.959 eV) is slightly large, it may perform very well in shorter wavelength region and also in electron injection. And finally, as the results of 4 and 5, inorganic acid groups may not very suitable for these quinodimethane-based dyes due to their relatively worse charge transfer properties and large first excitation energies.

### 6. Reference

[1] O’Regan, B.; Graetzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO2 Films. Nature 1991, 353, 737–740.
[2] Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.-i.; Hanaya, M. Highly-Efficient Dye-Sensitized Solar Cells with Collaborative Sensitization by Silyl-Anchor and Carboxy-Anchor Dyes. Chem. Commun. 2015, 51, 15894–15897.
[3] Kalyanasundaram, K. Applications of Functionalized Transition Metal Complexes in Photonic and Optoelectronic Devices. Coord. Chem. Rev. 1998, 177, 347–414.
[4] Yun Gong, Jaqueline M. Cole, et al, Photoexcited Phenyl Ring Twisting in Quinodimethane Dyes Enhances Photovoltaic Performance in Dye-Sensitized Solar Cells, ACS Appl. Energy Mater. 1, 3, 1127-1139.
Lei Zhang, Jacqueline M. Cole, Anchoring Groups for Dye-Sensitized Solar Cells. ASC Appl. Mater. Interface 2015, 7, 3427-3455.

Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. The Journal of Chemical Physics 1993, 98 (7), 5648-5652; (b) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Physical Review B 1988, 37 (2), 785-789.

M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox., Gaussian, Inc., Wallingford CT 2016, Gaussian 09, Revision A.02.

Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; Van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; de Jong, W. A., NWChem: A comprehensive and scalable open-source solution for large scale molecular simulations. Computer Physics Communications 2010, 181 (9), 1477-1489.

Runge, E.; Gross, E. K. U., Density-Functional Theory for Time-Dependent Systems. Physical Review Letters 1984, 52 (12), 997-1000.

Zhao, Y.; Truhlar, D. G., Density Functionals with Broad Applicability in Chemistry. Accounts of Chemical Research 2008, 41 (2), 157-167.