Computational Study of the Influence of the π-bridge Conjugation Order of Quinodimethane-based Derivatives for Dye Sensitized Solar Cells (DSSCs) Using Density Functional Theory (DFT)

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Abstract. Several series of quinodimethane-based derivatives with different conjugated π-bridge groups (phenyl ring, thiophenyl ring and benzothiadiazoyl ring) were investigated by different conjugation orders using density functional theory (DFT) at B3LYP /6-31g(d) level. Computational results show that, all three π-bridge groups obviously improve the optoelectronic properties of dyes compared with the reference, with more suitable energy levels and wider absorption bands. For the series of dyes with different numbers (n) of phenyl rings, larger order of π-bridge conjugation leads to a larger band gap from 2.501 eV to 2.547 eV, while the other series with thiophenyl rings has a wider absorption band and a red shift of the first absorption peak from 522.86 nm (2.371 eV) to 565.25 nm (2.193 eV) when the conjugation order increases. Benzothiadiazoyl ring was also studied as a part of π-bridge conjugation. The structure of donor - phenyl - benzothiadiazoyl - thiophenyl - anchor shows the lowest LUMO level (-2.929 eV) and a relatively high HOMO level (-5.049) among all the derivatives, but with a wide absorption band since it has two strong absorption peaks (489.24 nm and 400.41 nm with strengths of 0.7883 and 0.6625 respectively). Generally, dyes with thiophenyl rings shows more suitable optoelectronic properties for being candidate sensitizers for dye sensitized solar cells, and a combination of different aromatic rings as π-bridges is also a valuable way for designing new dye molecules in the future’s work.

1. Introduction
Since 1991, O’Regan and Gratzel firstly reported a highly efficient dye sensitized solar cells (DSSCs) using nano-structured titanim oxide layers and ruthenium-based dyes [1]. DSSCs have become one of the most promising photovoltaic devices. According to NREL yearly report, the highest confirmed efficiency of DSSC devices has reached to 11.9% by Sharp [2] and one of the most efficient metal-free DSSC has reached an efficiency of 14.3% [2]. Organic sensitizers are regarded as the most potential materials due to its unlimited categories and could be easily combined with molecular engineering [3]. Quinodimethane-based dyes used in DSSCs was firstly proposed by Jacqueline Cole and her co-workers using a data-mining method, and a quinodimethane backbone was at the top of the most suitable candidate sensitizer list. [3] A further experimental and theoretical validation of these dyes used in DSSCs was reported later [4], showing the best one, with a single phenyl ring as its π-bridge,
reached an device efficiency of 1.41% without extra experimental optimization. This is not a satisfying result for devices but the basic structure shows a large potentiality since its donor group could be twisted under excited state and apparently this basis structure is not fully developed and optimized since only two simple anchor groups and donor groups were studied.

The Donor–π-bridge–Acceptor (D-π-A) is a typical structure of organic dyes used in DSSCs, and the π-bridge has a positive effect on optoelectronic properties of organic dyes [5]. Arakawa and Hara [6] developed several donor–π-bridge–acceptor (D-π-A) coumarin derivatives with an increased efficiency about 8%.

Therefore, in this study, to further improve quinodimethane-based dyes, phenyl ring, thiophenyl ring and benzothiadiazoyl ring were adopted to form different π-bridges for the quinodimethane backbone (dye 0, Figure 1(a)). Three series of dyes were designed and denoted as shown in Figure 1(b) and (c). Series A contains phenyl rings from one to four as their π-bridges, and series B contains thiophenyl rings with the same numbers. Dye C adopts a combination of thiophenyl ring, phenyl ring and benzothiadiazoyl ring as its conjugated π-bridge, which was reported in RK-1 dye, obtaining an efficiency of 10.19% in DSSC devices [7]. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were used to calculate optoelectronic properties of these dyes.

![Chemical structures of dye 0 (quinodimethane backbone) and three series of quinodimethane-based derivatives: dye A(n), dye B(n) and dye C with phenyl rings, thiophenyl rings and a combination of aromatic rings as their π-bridges respectively.](image)

**Figure 1.** Chemical structures of dye 0 (quinodimethane backbone) and three series of quinodimethane-based derivatives: dye A(n), dye B(n) and dye C with phenyl rings, thiophenyl rings and a combination of aromatic rings as their π-bridges respectively.

### 2. Computational details

All dyes were firstly optimized at the b3lyp [8]/3-21g [9] level of theory using NWChem 6.6 software package [10], and then a further geometry optimization with a higher level of theory, b3lyp [8]/6-31g(d) [9] were carried out to get preciser molecule structures. Theoretical first excited energies were calculated using TD-DFT with m062x [11]/6-31g(d) [9] basis set based on optimized structures. All models were calculated in vacuum. All optimized structures were checked with frequency calculation.

### 3. Results and discussion

#### 3.1. Frontier molecular orbitals

For series A (shown in Figure 2), quinodimethane backbone offers an overlap between the HOMOs and LUMOs since both of the two types of molecular orbitals are located on this moiety. Besides, for all the series A dyes, the HOMOs are also located on the -N(CH3)2 group, which is used as electron donor. The LUMOs are located mainly on the the first phenyl ring in the conjugated π-bridge, which means that the increased length of phenyl ring composed π-bridge fails to improve the charge transfer ability of these dyes. In addition, the values of HOMOs of series A dyes (-5.205 eV, -5.139 eV, -5.106 eV and -5.089 eV for n=1 to 4 respectively) become higher with the increase of the number of phenyl rings, and the values of LUMOs changes in a reversed trend (-2.448 eV, -2.363 eV, -2.310 eV for n=1 to 4 respectively).
and -2.282 eV). Taken the balance of frontier molecular orbitals distribution and their values, dye A (n=1) may be the most suitable candidate for utilization in DSSCs.

For dye C (shown in Figure 4), almost no LUMO remains on -N(CH$_3$)$_2$ group, and most LUMOs are re-distributed on thiophenyl and benzothiadiazolyl rings, and a small part of it is on the phenyl and carboxyl groups. Also, compared with series A and B, the LUMOs left on quinodimethane backbone are relatively fewer. Both points mentioned above imply that dye C has a stronger charge transfer ability due to the combination of thiophenyl and benzothiadiazolyl rings. In addition, dye C has the lowest LUMO level (-2.929 eV) and a relatively high HOMO level (-5.049) among all the dye molecules, implying the most suitable electronic properties for DSSCs.
3.2. Excited state

The first excitation energies of all dyes in vacuum were studied by TDDFT calculations at the M062X/6-31g (d) level of theory. For series A, with the increase of \(n\), the first excited energies grow up, which means a blue shift of absorption peak, and meanwhile the oscillator strengths become weaker. In addition, all the series A dyes’ first excited states are mainly contributed by the transition from HOMO-1 to LUMO. The above shows that longer chain of phenyl rings may not improve the charge transfer and absorption properties of quinodimethane-based dyes.

For series B, the first excited energy is obviously reduced by the increase of \(n\), from 2.3713 eV to 2.1934 eV, indicating that the absorption peak has a red shift (from 522.86 nm to 565.25 nm), which is an advantage of being sensitizers for DSSCs. When \(n > 1\), the major component transition contributed to the first excited state is HOMO to LUMO, which implies a typical charge transfer process occurs during the excitation.

For dye C, it has a relatively high first excitation energy which may not benefit for absorbing photon. However, it is found that there is a second absorption peak at 400.41 nm which has an oscillator strength of 0.6625, which offers dye C a much wider absorption band than the other studied dyes. Also, the major component of the first excitation state is the transition from HOMO to LUMO, implying an obvious charge transfer occurs. (see Table 1)

Table 1. First excited state energy (eV, nm) and oscillator strength values for all dyes, as well as the major contributions of the molecular orbitals to the transitions.

| Dyes   | 1st Excitation Energy | Oscillator Strength (f) | Major Component |
|--------|-----------------------|-------------------------|-----------------|
| dye A (n=1) | 2.5009 | 495.76 | 0.0749 | HOMO-1 \(\rightarrow\) LUMO | 75.63% |
| dye A (n=2) | 2.5300 | 489.28 | 0.0712 | HOMO-1 \(\rightarrow\) LUMO | 76.15% |
| dye A (n=3) | 2.5408 | 487.98 | 0.0696 | HOMO-1 \(\rightarrow\) LUMO | 76.58% |
| dye A (n=4) | 2.5473 | 486.72 | 0.0670 | HOMO-1 \(\rightarrow\) LUMO | 57.11% |
| dye B (n=1) | 2.3713 | 522.86 | 0.0927 | HOMO-1 \(\rightarrow\) LUMO | 66.24% |
| dye B (n=2) | 2.3097 | 536.80 | 0.2639 | HOMO \(\rightarrow\) LUMO | 68.23% |
| dye B (n=3) | 2.2528 | 550.35 | 0.5578 | HOMO \(\rightarrow\) LUMO | 88.50% |
| dye B (n=4) | 2.1934 | 565.25 | 1.0564 | HOMO \(\rightarrow\) LUMO | 94.62% |
| dye C | 2.535 | 489.24 | 0.7883 | HOMO \(\rightarrow\) LUMO | 84.66% |
4. Conclusion
In conclusion, three different types of conjugated π-bridges were investigated in this paper. Series A, of which π conjugation is offered by phenyl rings, shows a relatively weaker charge transfer ability and larger band gap with the increase of the rings’ number, and dye A (n=1) may be the best candidate in this series due to its relatively suitable HOMO and LUMO energy levels and band gap. Series B shows an obvious stronger charge transfer and separation ability in the frontier molecular orbital distribution. For dye B (n=4), even the furthest thiophenyl ring has enough LUMO distribution and extensively, all dyes of series B have absorption peaks more than 520 nm, which may be a strong feature for being a sensitizer in DSSC by using more lights in the long wavelength area. For dye C, two strong absorption peaks (489.24 nm and 400.41 nm) makes it a wider absorption band. Also, the distributions of HOMO and LUMO indicates that the exist of benzothiadiazoyl ring may effectively improved charge transfer ability of dye C since most LUMOs are located on the benzothiadiazoyl ring moiety, and less LUMOs remains on the quinodimethane backbone, which is not observed in neither series A nor series B. In summary, in terms of optoelectronic properties, the calculation of frontier molecular orbitals and first excitation energies, series B may be the best candidate for DSSCs as sensitizer compared with the others. However, all studied dyes, and the three aromatic rings used as a part of π-bridge, show their strength and weakness respectively, and a further molecular engineering work for designing better π-bridges by combining their advantages could be done in the future.

5. References
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