

Donor-enhanced bridge effect on the electronic properties of triphenylamine based dyes: density functional theory investigations

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Abstract The geometries have been optimized by using density functional theory. The highest occupied molecular orbitals are delocalized on triphenylamine moiety while lowest unoccupied molecular orbital are localized on anchoring group. Intramolecular charge transfer has been observed from highest occupied molecular orbitals to lowest unoccupied molecular orbital. By replacing the vinyl hydrogens with methoxy as well as one benzene ring as bridge leads to a raised energy gap while extending the bridge decreases the energy gap compared to parent molecule. The HOMO energies bump up by extending the bridge. The LUMO energies of all the investigated dyes are above the conduction band of TiO₂ and HOMOs are below the redox couple except 3c. The distortion between anchoring group and triphenylamine can hamper the recombination reaction.

Keywords Density functional theory · Dye sensitized solar cell · HOMO · LUMO

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Introduction

The search for substitutes of fossil-energy sources and the growing environmental awareness worldwide have strengthened interest in photovoltaics as long-term available, cheap, environmental-friendly and reliable energy technology. Titanium dioxide (TiO₂) based dye-sensitized solar cells (DSCs) developed in the 1990s have attracted attention [1–6]. The DSCs constructed using dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have attractive features of high energy conversion efficiency [1]. During recent years, however, increasing interest has been shown in the application of organic materials in various solar cells, due primarily to easy processability [7–9].

The DSCs based on wide band gap nanoporous oxide semiconductors are of great interest as some of them have shown efficiencies comparable to their silicon counterpart. However, these devices generally consist of expensive sensitizers such as ruthenium(II) polypyridyl complexes and electrolytes with volatile solvents [1, 5]. These factors, especially the fact that the liquid electrolyte causes significant technological problems associated with device sealing and stability, affect the commercial application of DSCs. Therefore, there is considerable interest in both the development of a solid-state electrolyte for these devices and replacement of expensive dyes with inexpensive and readily available materials [10, 11].

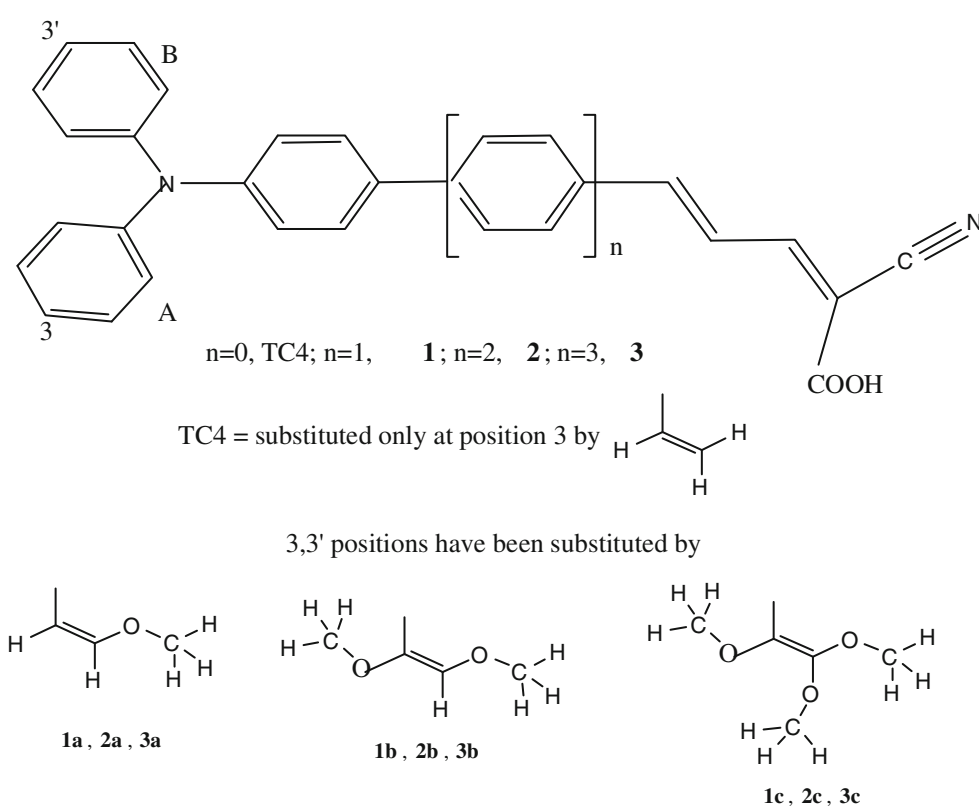
To improve the efficiency of the UV/vis photoinduced intramolecular charge transfer most of the organic sensitizers are made of a donor, a bridge and acceptor (DBA) moieties. The good conjugation across the donor and anchoring group determines the large charge transfer character of the electronic transition. The dye aggregation and charge recombination can lead to the lower efficiency in organic

sensitizers [12–14]. It has been found that triphenylamine (TPA) [15] derivatives as electron donor and the cyanoacetic acid moiety as electron acceptor are good choices to improve the efficiency [12, 16]. It is expected that TPA can incarcerate the cationic charge from the semiconductor surface therefore obstructing the recombination. TPA also features a steric hindrance that can prevent unfavorable dye aggregation at the semiconductor surface [16]. To model and design efficient metal-free sensitizers for DSCs, appropriate DBA systems are required whose properties can be tuned by applying the passable structural modifications. The DSC based on 2-cyano-5-(4-(phenyl(4-vinylphenyl)amino) phenyl) penta-2,4-dienoic acid (TC4) showed efficiency 4.82% [17]. Xu et al. attached vinyl unit at position 3 of A-ligand to enhance the electron-donor ability of TPA [17]. In the present study we designed DBA systems where TPA moiety as donor, cyanoacetic acid as acceptor and benzene rings (extended 1–3 in number) as bridge. In our previous study it was examined that positions 3 (A-ligand) and 3' (B-ligand) are favorable to design better sensitizer [18]. Thus in the present study we have modeled new systems by replacing the hydrogens of vinyl with OCH₃ at position 3 and 3' to boost up the donor ability of TPA moiety, see Fig. 1 (detail can be found in computational details). The quantum chemical calculations have been performed to gain insight into electronic properties of the new designed sensitizers.

Computational details

The ground state geometries have been computed using density functional theory (DFT) with Gaussian09 package [19]. The HF method is not adequate to describe virtual orbitals thus Politzer and Abu-Awwad [20, 21] proposed a reparametrization of the Becke-3 hybrid exchange-correlation functional that predicts orbital energies which are in good agreement with the experimental evidence. Preat et al. have explained the mechanism of electron injection in TPA sensitizers. They have optimized the ground state geometries of the TPA dyes at B3LYP/6-31G(d,p) level of theory. They concluded that this level of theory is adequate for TPA based sensitizers [22, 23]. Xu et al. optimized TC4 by means of the B3LYP/6-31G(d,p) level of theory. The geometrical and electronic properties of the TC4 were calculated at the B3LYP/6-31G(d,p) level [17]. Recently geometries of TPA based sensitizers have been optimized by using different Pople basis sets such as 6-31G(d,p), 6-31+G(d,p), 6-311G(d,p), 6-31G(2d,2p), 6-311G(2d,2p), and 6-311G(2df,2pd) [23]. They showed that the B3LYP bond lengths do not depend upon the basis set and are almost identical to the MP2/6-31G(d,p) values. They validated B3LYP for optimizing the geometry of TPA based sensitizers. Moreover, B3LYP/6-31G(d,p) level which is adequate for TPA based sensitizers has been applied to optimize the ground state geometries and shed light on the electronic properties

Fig. 1 The structures of **1a–3c** investigated in the present study



[17, 22–27]. Thus in the present study, ground state geometries have been computed by using the popular three parameter

B3LYP functional [24], in which the exchange is a combination of Hartree-Fock exchange, Slater functional, and Becke's

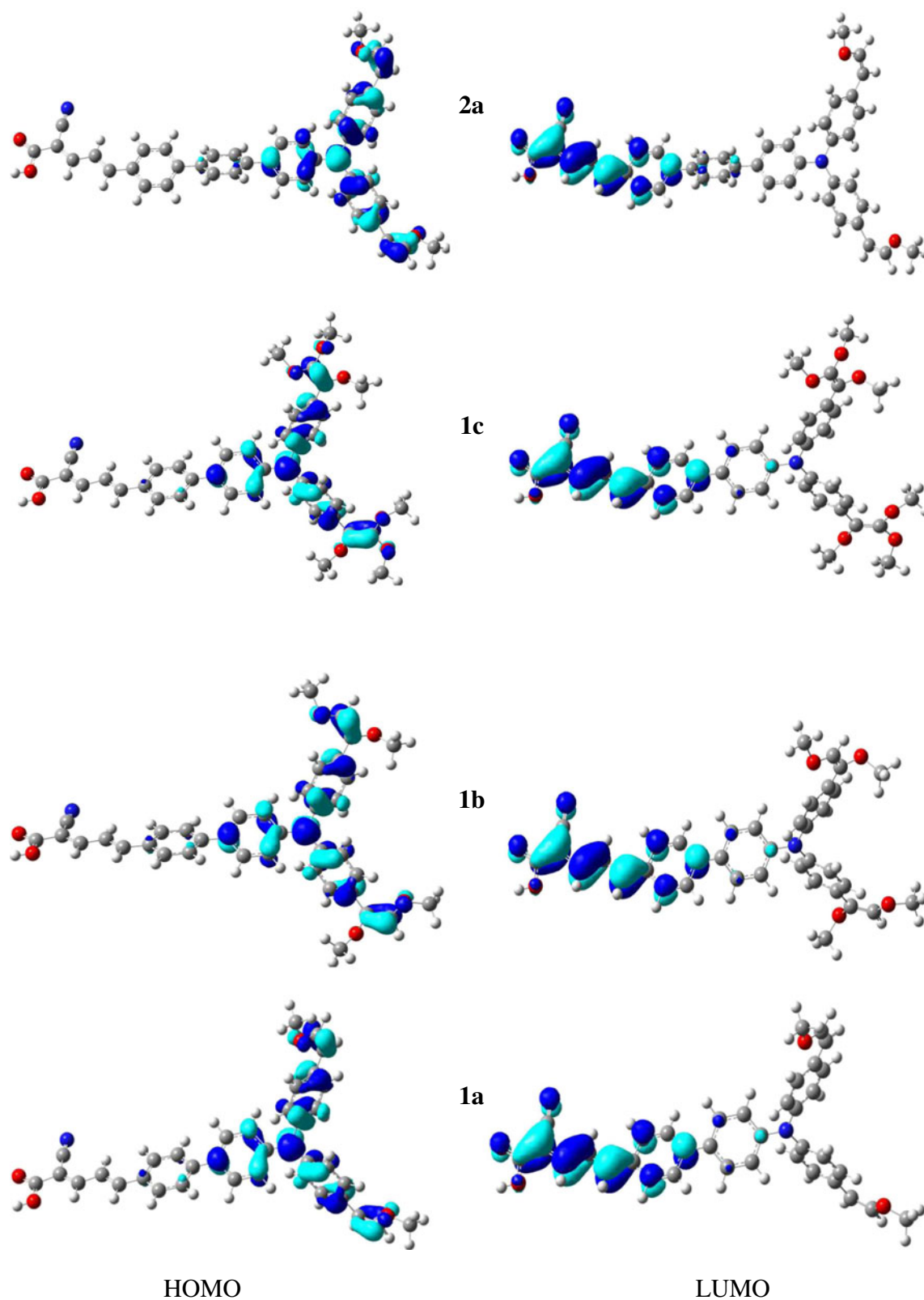


Fig. 2 The HOMOs and LUMOs distribution pattern of new designed sensitizers

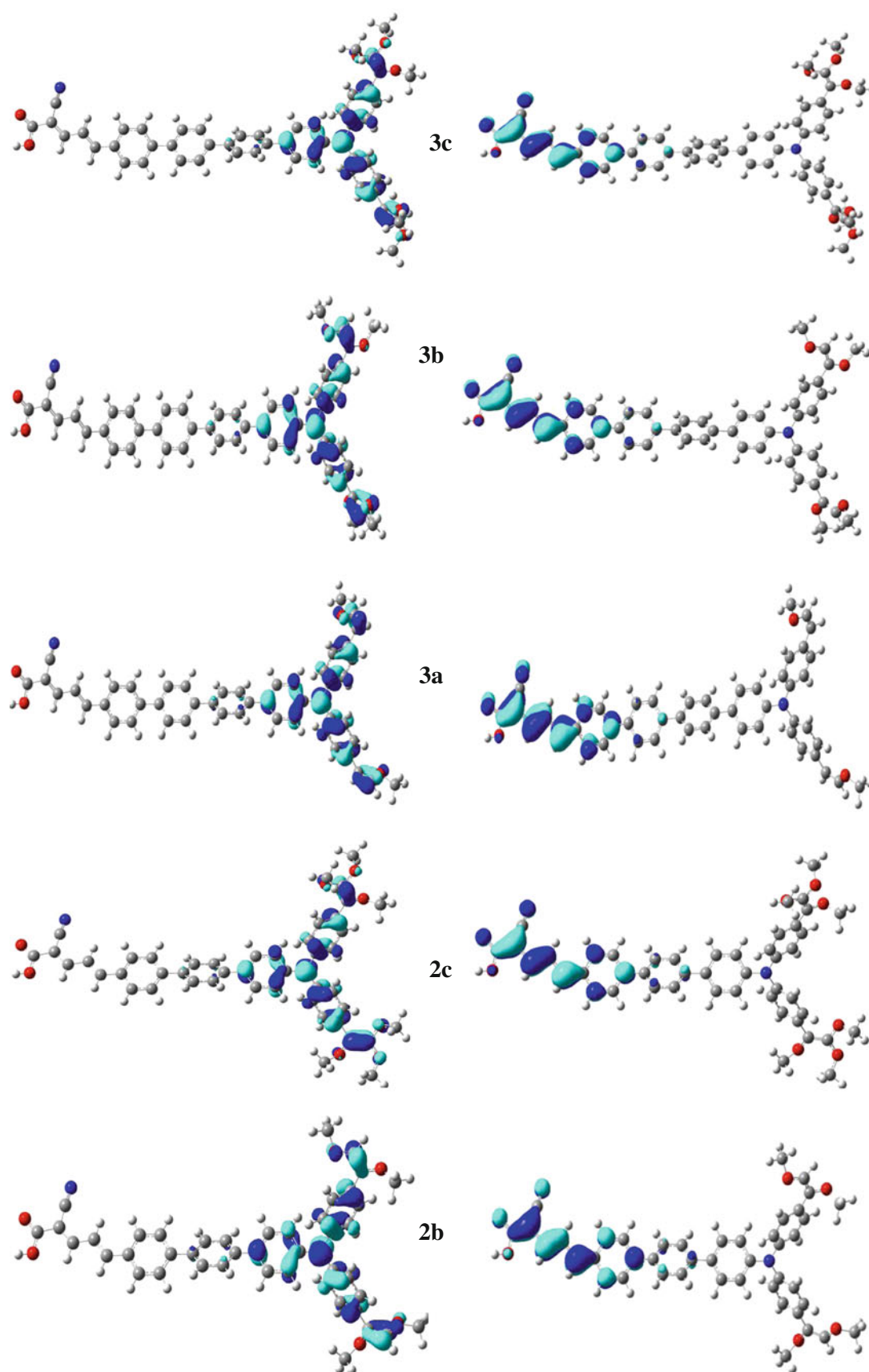


Fig. 2 (continued)

generalized gradient approximation (GGA) correction [25], whereas the correlation part combines local and Lee-Yang-Parr (LYP) functionals [26]. We have used 6-31G(d,p) [27] basis set for the ground-state geometries. Molecular orbitals were visualized using Gaussview. To enhance the electron donor ability of TPA moiety Xu et al. synthesized the TC4 where vinyl unit has been substituted at position **3** [17]. Recently, we showed that substitution of vinyl at position **3** and **3'** are more favorable toward enhancing the electron injection and reducing the HOMO-LUMO energy gap [18, 28]. Energy gaps have been estimated for OCH₃ α,α' -substituted oligothiophenes [29], it is well known that OCH₃ enhance the electron donor ability. The sensitizers where charge transferred from donor to acceptor moiety are good toward high efficiency [23, 24]. Thus to augment the donor ability of TPA unit, we have replaced the hydrogens of vinyl by OCH₃. In the first step, we have replaced one hydrogen by OCH₃ (**1a**, **2a** and **3a**), second step we substituted two OCH₃ (**1b**, **2b** and **3b**) and finally three OCH₃ were substituted in place of three hydrogens (**1c**, **2c** and **3c**) of vinyl at positions **3** and **3'**. Moreover, to check the effect of bridge on the electronic properties we have extended the benzene rings; one benzene between TPA moiety and anchoring group (**1**), two benzenes (**2**) and three benzenes as bridge (**3**).

Results and discussion

Electronic structure

The distribution patterns of highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of studied systems in the S₀ states have been shown in Fig. 2. A reduced HOMO – LUMO gap can be used as an index of kinetic stability [30]. Kaur et al. provided the quantitative assessment of HOMO – LUMO gaps and photooxidative resistances [31]. Implications for predictions of HOMO – LUMO gaps of π -conjugated systems have been discussed and analyzed in terms of designing new materials with controlled properties by De Oliveira et al. [29]. The HOMO-LUMO gap refers to the potential energy difference between the HOMO and LUMO. Basically, it is the energy which has to feed into the molecule to kick it

from the ground state into an excited state. A large band gap means to use high-energy light, like UV wavelengths. A small band gap means not as much energy is needed to excite the molecule, like green or even red wavelengths [32]. On the basis of HOMO-LUMO energy gap liquid water electronic properties have been investigated as well [33]. It is esteemed that smaller energy gap leads toward red shift in the absorption spectra [34]. Generally, HOMOs are delocalized on TPA unit, oxygen of methoxy especially oxygen of mono- and di-methoxy take part in the formation of HOMO. The LUMOs are localized on anchoring group and the benzene ring near to the anchoring group in all the investigated sensitizers. This revealed that these materials would be excellent sensitizers as comprehensible charge transfer has been observed from donor to acceptor side thus electron injection from TPA moiety to TiO₂ conduction band would be favorable.

In Table 1, HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}) and HOMO-LUMO energy gap (E_{g}) has been tabulated. The TC4 has HOMO and LUMO energies -5.30 eV and -2.56 eV, respectively with energy gap 2.74 eV. By substituting the vinyl hydrogens with mono-, di-, and tri-methoxy as well as one benzene ring as bridge leads to lower the HOMO energies while raises the LUMO energies compared to TC4. Moreover these new designed systems have higher energy gap than the parent molecule, see Table 1 (**1a**, **1b** and **1c**). By extending the bridge (two or three benzene rings between TPA unit and anchoring group) with di- and tri-methoxy substituted sensitizers leads to increasing the HOMO and LUMO energies while decreasing the energy gap compared to TC4 (**2b**, **2c**, **3b**, and **3c**). However, in mono-substituted methoxy systems (**2a** and **3a**) extension of bridge have no effect on reducing the energy gap but raise the LUMO energy compared to TC4. By substituting the mono-, di- or tri-methoxy as well as extending the bridge change in the HOMO energies and LUMO energies has been observed compared to TC4. The HOMO energies augment by increasing the benzene rings as bridge. We have also observed that substitution of tri-methoxy (**1c** and **2c**) has no significant effect to elevating or lowering the HOMOs, LUMOs or energy gap. The HOMO energies of the systems containing one benzene ring as bridge have lowest HOMO energy while systems having three rings

Table 1 The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}) and HOMO-LUMO energy gap (E_{g}) of new designed derivatives in eV at B3LYP/6-31G(d,p) level of theory

Systems	E_{HOMO}	E_{LUMO}	E_{g}	Systems	E_{HOMO}	E_{LUMO}	E_{g}
1a	-5.41	-2.05	3.36	2c	-5.06	-2.48	2.58
1b	-5.45	-2.27	3.18	3a	-5.22	-2.44	2.78
1c	-5.36	-2.08	3.28	3b	-4.96	-2.46	2.50
2a	-5.32	-2.45	2.87	3c	-4.69	-2.44	2.25
2b	-5.04	-2.43	2.61	TC4	-5.30	-2.56	2.74

have the highest HOMO energy (3 rings > 2 rings > 1 ring) while for the LUMO energies the contrary effect has been observed as 3 rings < 2 rings < 1 ring. The HOMO-LUMO energy gap increases in the following order: 3 rings < 2 rings < 1 ring.

For good DSCs sensitizers following factors to be considered: a narrow band gap, with LUMO lying just above the conduction band of TiO₂ and HOMO below the redox couple. As a model for nanocrystallinity the HOMO and LUMO energies of bare cluster (TiO₂)₃₈ are -7.23 and -4.1 eV, respectively, resulting in a HOMO-LUMO gap of 3.13 eV [35]. Usually an energy gap more than 0.2 eV between the LUMO of the dye and the conduction band of the TiO₂ is necessary for effective electron injection [36]. The LUMO energies of all the investigated dyes are above the conduction band of TiO₂. The HOMO of the redox couple (I⁻/I₃⁻) is -4.8 eV [37]. It can be found that HOMOs of the dyes are below the redox couple except **3c** thus we discarded this system. The smaller HOMO-LUMO energy gaps of **2b**, **2c**, **3b** and **3c** revealed that these dyes would be efficient for DSCs. As designated by Fig. 2, the HOMO is delocalized over the pi-conjugated system with the highest electron density centered at the central TPA-nitrogen atom, and the LUMO is located in anchoring groups through the pi-bridge. We discern that the HOMO-LUMO excitation induced by light irradiation could move the electron distribution from the TPA-moiety to the cyanoacrylic acid moiety and the photo-induced electron transfer from the dye to the TiO₂ electrode can occur efficiently by the HOMO-LUMO transition.

Undeniably, the TPA moiety shows a sizable steric hindrance and is expected to greatly favor the detention of the cationic charge from the semiconductor surface and efficiently obstruct the recombination [16]. We have explained the recombination barricade on the basis of distortion and coplanarity. The coplanarity between the benzene near anchoring group having LUMO and the TPA unit is broken in new designed derivatives compared to TC4, i.e., 32–35° out-of-plane distortion, thus the positive charge may not be directly in drop line to the TiO₂ surface, consequently hampering the recombination reaction.

Conclusions

In the framework of our present quantum chemical investigation, we can draw the following conclusions:

1. The HOMO is delocalized over the pi-conjugated system and the LUMO is located in anchoring groups. Clear charge transfer has been observed in designed sensitizers.
2. By substituting the vinyl hydrogens with mono-, di-, and tri-methoxy as well as one benzene ring as bridge

leads to lower the HOMO energies while raise the LUMO energies.

3. Extending the bridge with di- and tri-methoxy substituted sensitizers leads to an increase in the HOMO and LUMO energies while decreases the energy gap.
4. In mono-substituted methoxy systems (**2a** and **3a**), extension of bridge has no effect to reduce the energy gap.
5. The LUMO energies of all the investigated dyes are above the conduction band of TiO₂. HOMOs of the dyes are below the redox couple except **3c**. The smaller HOMO-LUMO energy gaps of **2b**, **2c**, **3b**, and **3c** revealed that these dyes would be efficient for DSCs.
6. The coplanarity between the benzene near anchoring group having LUMO and the TPA unit is broken in new designed derivatives compared to TC4, i.e., 32–35° out-of-plane distortion, thus the positive charge may not be directly in drop line to the TiO₂ surface, consequently hampering the recombination reaction.

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