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Computational Studies of Suitability of Triarylmethane-Coumarinsas Sensitizer for Dye Sensitized Solar Cells

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Abstract:
Triarylmethanes are low cost synthetic dyes with intense absorption in the visible spectrum. This makes it attractive to explore their suitability as sensitizer for dye sensitized solar cell. Using malachite green as a lead dye, we made intuitive structural modifications: incorporation of coumarin-3-carboxylic acid as acceptor/anchor, and substituting one or the two N, N-diethylaniline donors with N-propyl-1,6dimethyllutidine(s). The three resulting triarylmethane-coumarin structures were subjected to DFT calculations to investigate their suitability as sensitizers for DSSC applications. The calculation results showed that triarylmethane-coumarins with cationic type chromophores are unsuitable as DSSC sensitizer. The acceptor/anchor, coumarin-3-carboxylic acid, is basically excluded in the intramolecular charge transfer processes of the cationic dyes. Also, the LUMO levels of the cationic dyes are below the conduction band of TiO2, which is energetically uphill to electron injection into TiO2. Ultimately, the cationic triarylmethane-coumarin derivatives are unsuitable as sensitizer for DSSC. However, a charge-free triarylmethane-coumarin derivative shows promise as a sensitizer candidate for DSSC application.

Keywords: Triarylmethane, Coumarin-3-carboxylic acid, Sensitizer, DFT, DSSC

1. Introduction

Global energy demand is growing due to increase in population and improve standard of living. The bulk of the energy demand is currently being met by fossil fuels[1]. However, green house of carbon dioxide release from fossil fuel combustion is linked to global warming and climate change [2]. Hence there are quests to increase the proportion carbon-free energy in the global energy mix. A lot of attention is solar energy as a vast energy carbon-free resources that can be exploited to meet the growing energy demand [3,4]. Although silicon-based photovoltaic is at the market leader among technologies for harnessing solar electricity, its energy payback time is long and disadvantage. Dye sensitized solar cell (DSSC) is one of emerging photovoltaic technologies with very short energy payback time [5].

DSSC is a molecular photovoltaic (PV) system. It mimics nature's photosynthesis principle by using a dye molecule to absorb radiant energy to generate charge carriers which are then separated, transported and collected as harnessed solar electricity [6]. Since the seminal report by O'Regan and Grätzelin1991 [7], DSSC continued to attract research and commercial interests as low-cost photovoltaic technology. Atypical DSSC device is composed of dye, TiO_2, redox mediator and counter electrode, and advances in DSSC has focussed on the dye and the redox mediator [8]. In line with the low-cost tag, the quest for high efficiency and low-cost dyes is a recurring theme in DSSC research, resulting in evolution of high efficiency DSSC dyes

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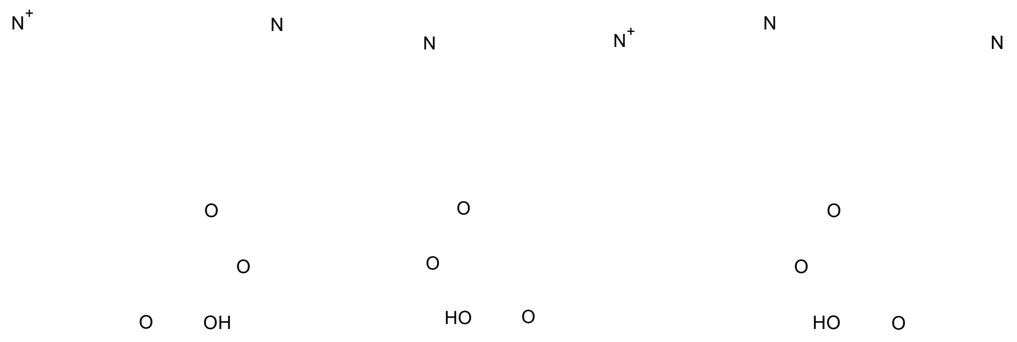
has evolved from Ru-based to Zn-porphyrin and metal-free dyes [9], yet the quest continues.

Triphenylmethanes are subclass of polymethines, specifically they are monomethine dyes with three terminal aryl systems. One or more of the aromatic rings usually have donor or acceptor groups at the para positions. These dyes are known for their brightness i.e high extinction coefficients, and are inexpensive to produce [10,11]. Malachite green is a member of these dyes. Two of its aromatic rings is substituted with dialkylamines and the third ring unsubstituted.With two dialkylamines as donor groups, introduction of an acceptor/anchor group on the third aryl ring should promote intramolecular charge transfer and electron injection into TiO_2 thereby transform malachite green into DSSC dye. Harlé et al., introduced carboxylic on the para position of unsubstituted aromatic ring of malachite green, but the resulting dyes displayed low DSSC performance [12]. Yet, probing further simple and easy molecular to malachite green remained a very attractive its prospect towards new low-cost high performance DSSC dyes.

The carboxylate group is a good anchor, but it a weaker acceptor compared to cyanoacetic acid, the ubiquitous acceptor group in DSSC dye design [13]. Moreover, 7-(Diethylamino)coumarin-3-carboxylic acid, is a popular laser having strong intramolecular charge transfer and coumarin-3-carboxylic changes acid is the acceptor fragment [14]. Hence, we opined that the low performance of the carboxylic acid malachite green derivative is due to weak acceptor strength of the carboxylate group. Therefore, employing coumarin-3-carboxylic acid, a stronger electron acceptor groups will lead to malachite green derivative that will display high DSSC performance. This hypothesis was explored using density function theory (DFT) computations.

2. Computational Method

Two dimensional (2D) structures of the studied triarylmethane-courmarin dyes are shown in Figure 1 [15]. Three dimensional (3D) of the dye were obtained using Avogadro. All computations were performed using the Orca 4.2.1 quantum chemistry package [16]. Orca is a versatile general purpose quantum chemistry package. It is useful for performing mainstream computational chemistry tasks including density functional methods. Geometry optimization of the structures of the dyes was carried out initially using BP86 functional and def2-SVP def2/J D3BJ basis set. In order to obtain a more accurate geometry a further geometry optimization was performed using PBEh-3c [17]. TD-DFT calculations were performed using B3LYP functional and def2-TZVP def2/J basis set with RIJCOSX approximation and TightSCF. The calculation outputs were visualised using Avogadro [18], and GaussSum[19] softwares.



A B C

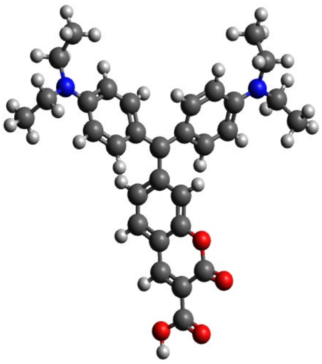
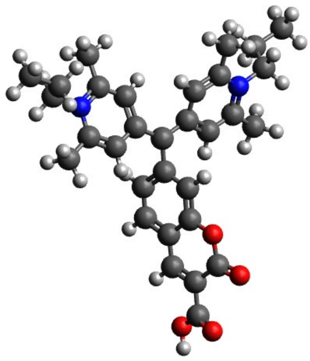
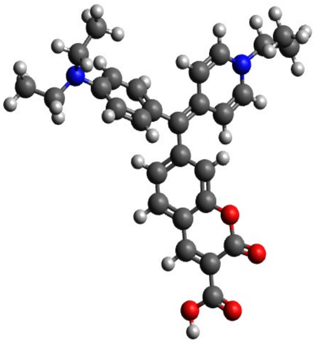
Figure 1. Triarylmethane-courmarin dyes

3. Results and discussion

Malachite green, the lead triarylmethane dye in this study is a monomethine, made up two N,N-dialkylanilineand a phenyl group, the three aryl groups bonded to a methine centre.One of the aniline groupshas to be in quinoid cation form and the structure of the malachite is a resonance hybrid of two canonical structures. With respect to the methine carbon, the N, N-dialkylanilinesare electron donors and transforming the unsubstituted phenyl group into coumarin-3-carboxylic acid, electron acceptor, the resulting dye A, is D-A dyad. Dye B is lutidine analogue of A, while C is hybrid of A and B. For DSSC application, photoinduced intramolecular charge transfer from the donor groups to the acceptor group is a requirement for dyads to qualify as candidates for DSSC application. In addition, the acceptor group should in close proximity to the anchor; in some instances, the acceptor doubles as the anchor. The anchor binds the dye to TiO_2 and thus serves a channel of electron injection into TiO_2.

The calculated structures and molecular electrostatic potential of the dyes are shown in Figure 2. The calculated structure indicated that in dye A, the N, N-dialkylanilines donor groups are in the benzenoid form, and the positive charge is on the methine carbon. In dye B, the input structure consists pyridinic cation and 4-methylidene-1,4-dihydropyridine as donor groups. But in the calculated structure the donor groups are in the pyridinic form, consequently the positive charge is resonating between the two pyridinic groups. This is consistent with the widely accepted structure of symmetrical cationic triarylmethanes that the positive resides on the central methine carbon [20]. For dye C, the input N, N-dialkylaniline and 4-methylidene-1,4-dihydropyridineremained unchanged as the donor groups in the calculated structure. Calculated surface molecular electrostatic potential (MEP) of the dyes indicated the methine carbons in dye A and B are electron rich. The amino nitrogens in dye A bears a net negative charge, but the adjacent aromatic carbons bears net positive charge. In dye B, the pyridinic nitrogens and the adjoining two ortho carbon atoms bear positive charge. High electron densities are delocalised over the methine carbons in dye A and B. The electron density on methane carbon of dye A and B may be attributed to the strong mesomeric pull on the lone pairs of electrons of the dialkylamino and pyridinic nitrogens respectively. However, electron density pyridinic nitrogens are lower than that of dialkyl amino nitrogens. On the contrary the methine carbon in dye C is charge neutral and its surface charge distribution is in line with relative electronegativity of the atoms of the dye molecule.

Dyes A and B are conjugated ionic type chromophores with odd (7) and even (6) π-bond system respectively. The positive charge centres in the dyes are electron traps. In fact, they are stronger electron accepting centres than coumarin-3-carboxylic acid fragment that is designated for this purpose in the dye design. Thus, dyes A and B are effectively A-D-A triads, in which the acceptors fragment, coumarin-3-carboxylic acid is competing with the delocalised positively charged on the donor fragments for electron distribution on the dye molecules. In dye A, the HOMO orbital is being localised on N, N-dialkylanilines but its LUMO is delocalised over the whole dye molecules. In dye B, the HOMO is localised on the methylene carbon and its LUMO localised on the pyridinic groups. As shown in Figure 3, the positive charge centre has an overriding influence on the chromophore properties of the two cationic dye A and B. Similar Overarching influence of positive charge centres on chromophore properties of triarylmethane species had been reported by Monezi et al. [21].

Dye	A	B	C
Optimized structure			

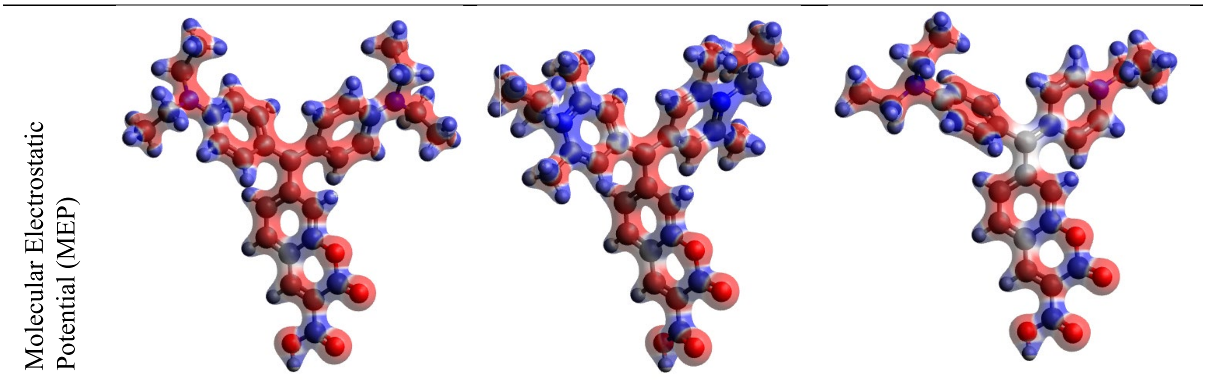


Figure 2. Calculated structures and molecular electrostatic potentials of the triarylmethane-coumarin dyes

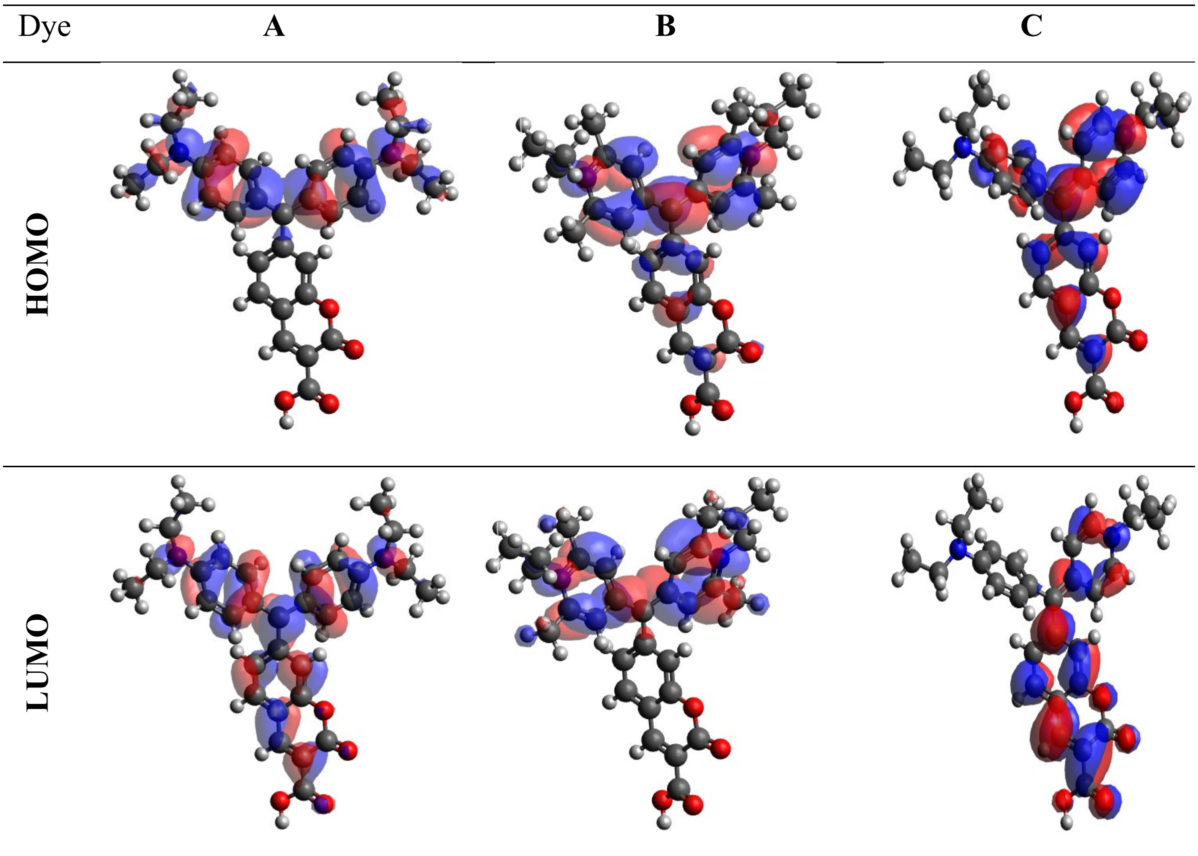
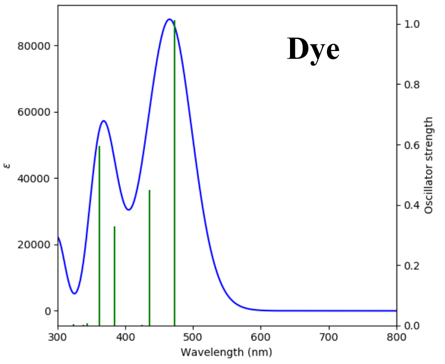


Figure 3: HOMO and LUMO orbitals of the triarylmethane-coumarin dyes



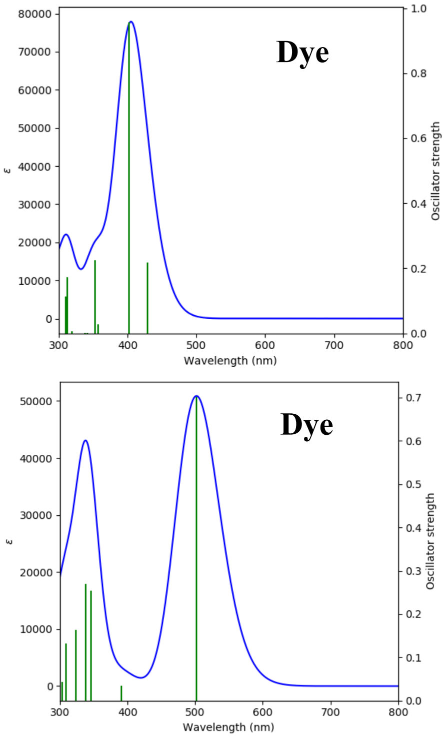


Figure 4: Calculated absorption spectra of the triarylmethane-coumarin dyes

Conversely, in dye C dyad, comprising the donor groups that is essentially an even (6) π-bonds polyene system and 3-cormarincarboxylic acid, as the acceptor group, the HOMO in dye C is delocalised over the on the six π-bonds polyene system and the LUMO delocalised over the coumarin-3-carboxylic acid group. Thus, charge-free dye C, possess intrinsic ability to exhibit vertical charge transfer from its donor to its acceptor/anchor fragments. This photoinduced vertical intramolecular charge transfer from the donor groups to the acceptor group is an important requirement for a dyad to qualify as candidates for DSSC application.

TDDFT calculation result provides further information photovoltaic properties of the studied dyes. Computed absorption spectra of the dyes are presented in Figure 3. The spectra indicate that the dyes have high extinction coefficient of absorption in the visible region. Light-harvesting efficiency (LHE) at the absorption peak wavelengths is given by equation 1:

$$LHE(\lambda_{max}) = 1 - 10^{-f} \qquad (1)$$

where *f* is the oscillator strength at the adsorption peak wavelength λ_{max} of the dye molecules [22]. Maximum obtainable open circuit voltage V_{OC} of a DSSC is determined by the difference between the energy levels of TiO_2 conduction band and redox potential of the mediator (I^-/I_3^-).

$$V_{oc} = E_{CB}^{TiO_2} - \mathrm{E}_{\text{redox mediator}}^{\text{redox pot}} \qquad (2)$$

The driving force of electrons injecting into TiO_2 ΔG_{inject} is the difference between the conduction band of TiO_2 and the LUMO level of a dye.

$$\Delta G_{inject} = -4.00 - \mathrm{E}_{\text{dye}}^{\text{LUMO}} \qquad (3)$$

While driving force of dye regeneration, ΔG_{reg}, is the difference between the HOMO level of the dye and the redox potential of the I^-/I_3^- redox mediator (-4.85).

$$\Delta G_{inject} = E_{dye}^{HOMO} - (-4.85) \qquad (4)$$

The values of the photovoltaic parameters listed above for the triarylmethane-courmarin dyes are presented in Table 1. Although reported voltammetric studies had shown that malachite green derivatives undergoes reversible one electron redox reactions in acetonitrile [23], this suggests that malachite green derivatives and by extension the triarylmethane-coumarin dyes in this study has potential for the photoelectrochemical cycles involved in DSSC. However, the data in Table 1 ruled out dye A and B as potential sensitizer candidates for DSSC device because their ΔG_{inject} is positive. Electron injection into TiO_2 from the LUMO level of the dyes is non-spontaneous. This is in addition to the competing lateral against vertical charge transfer charge transition in the dyes. In the lateral charge transfer the excited electron is far from the anchor group through which it can be ready injected into TiO_2. Thus, dye A and B are not good candidates for DSSC application.

Calculated orbital energy profiles of the dyes relative to that TiO_2 is presented Figure 4. As shown in the Figure 4, the LUMO, LUMO+1 and LUMO+2 orbitals of dye A; and the LUMO and LUMO+1 orbitals of dye B, are below the CB of TiO_2. Injection of excited electrons from these orbitals into TiO_2 is energetically uphill, thus precluding dye A and B as sensitizer candidate for DSSC applications. Dye C has LUMO energy level that is favourable for injection of excited electron into TiO_2, but its HOMO is about the same level as the CB of TiO_2. However, its HOMO-1 orbital is suitable positioned to receive electron from iodide/triiodide redox couple to regenerate oxidised dye C. While the absorption spectrum of Dye C will encompass HOMO → LUMO and HOMO-1 → LUMO transitions, only the later will contribute to obtainable cell voltage and cell performance. Further molecular engineering of dye C towards optimum positioning of its LUMO and HOMO with respect to CB of TiO_2 and standard potential of the iodide/triiodide redox couple (or other suitable redox mediator) respectively, will enhance its suitability for DSSC application.

Dyes	V_{OC} (eV)	LHE(λ_{max})	ΔG_{reg}(eV)	ΔG_{inject} (eV)
A	0.80	0.903	-3.437	1.853
B	0.80	0.889	-2.919	0.823
C	0.80	0.801	0.074	-1.784
			-1.116	

Table 1: Photovoltaic properties of the triarylmethane-coumarin dyes

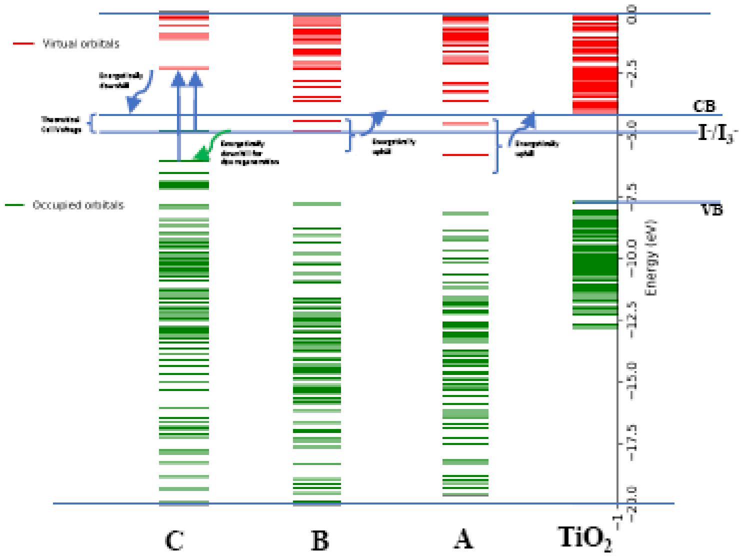


Figure 4: Orbitals energies profiles of the triarylmethane dyes and TiO_2

4. Conclusions

Triarylmethanes are low cost syntheticdyes with intense absorption in the visible spectrum. This makes it attractive to explore their suitability as sensitizer for dye sensitized solar cell. Using malachite green as a lead dye, we made intuitive structural modifications and carried out DFT calculations to investigate the TiO_2 sensitization suitability of three triarylmethane-coumarin derivatives. The DFT calculation results showed that triarylmethanes with cationic type chromophores are unsuitable as DSSC sensitizer.

Because the positive charge centre in such dyes constitute electron trap and controls the path of intramolecular charge transfer (ICT), dominantly resonating between the donor groups through the positive charge centre. Therefore, offering no path for ICT for electron injection into TiO_2. Moreover, the LUMO levels of the cationic type chromophores are below the CB of TiO_2 which energetically uphill to electron injection into TiO_2. Ultimately, the cationic triarylmethane-coumarin derivatives are unsuitable as sensitizer for DSSC. However, modifications leading to a charge-free triarylmethane-coumarin dye produce a promising sensitizer candidate for DSSC application.

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