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Can elongation of the π-system in triarylamine derived sensitizers with either benzothiadiazole and / or *ortho*-fluorophenyl moieties enrich their light harvesting efficiency? – A Theoretical Study

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Abstract

The structural and electronic properties of five known triarylamine derived sensitizers (**A1, A1-F, C218, D2** and **Y123**) and their associated hypothetical dyes (**C218-F, D2-F, Y123-F, Y1234** and **Y1234-F**) have been studied using density functional theory and time-dependent density functional theory. The sensitizers primarily comprise of a triphenylamine, a 4,4′-dihexylcyclopenta[2,1-*b*:3,4-*b*]dithiophene and a cyanoacrylic acid as the electron donating, π-spacer and accepting units, respectively. The π-system is extended by incorporation of either a benzo[*c*][1,2,5]thiadiazol-4,7-diyl unit or an *ortho*-fluorophenyl unit or both. To gain insight into the effect of elongation of the π-system on the electronic properties of dye sensitized TiO_2 interfaces, first-principles calculations have been carried out on sensitizer molecules co-adsorbed on the (101) surface of the anatase TiO_2. The theoretical results revealed that elongating the π-system of the sensitizers with both the benzothiadiazole and *ortho*-fluorophenyl units increases the molecular extinction coefficient, the excited state lifetime and the light harvesting efficiency but decreases the band gap and the reorganization energy relative to the structurally comparable reference dye **Y123**. The calculated short circuit current density and level alignment quality showed that the π-system in the triarylamine sensitizers elongated with both benzothiadiazole and *ortho*-fluorophenyl units broadens their potential use in DSSCs due to the enhanced values as compared to the reference dye. The results obtained in this study will provide a valuable reference for the strategy of inserting various π-spacers in triarylamine sensitizers for dye sensitized solar cell applications.

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1. Introduction

In the past decade, organic dyes have fascinated many researchers due to a wide variety of high-tech applications, such as light-emitting diodes,[1] field effect transistors[2-3], and dye sensitized solar cells (DSSCs).[4-6] Especially, over the last few years a number of researchers have paid increasing attention towards experimental and theoretical investigations of metal free organic dyes (MFOD) due to their possible benefits, such as relatively low cost, general ease of preparation and routinely higher molar extinction coefficients, relative to metallo-organic dyes (MOD). It is perceived that, in DSSCs the efficiency of MFOD falls beneath the MOD. For example, DSSCs based on either ruthenium[7] or zinc porphyrin[8] sensitizers have demonstrated overall conversion efficiencies reaching 13 % under standard air mass (AM) 1.5 G sunlight. On the other hand, MFODs based on coumarin[9-11], merocyanine[12,13], cyanine[14,15], indoline[16,17], hemicyanine[18-20], triarylamine[21-30], dialkylaniline[25,31,32], [bis(dimethyfluorenyl)amino]phenyl[33-36], phenothiazine[37], tetrahydroquinoline[38,39] and carbazole[40,41], offer efficiencies between 4 and 10 %. Among all the MFODs, the triarylamine based sensitizer (**Y123**) achieved respectable conversion efficiencies up to 10% with the $[Co_{II}(bpy)_3](B(CN)_4)_2/[Co_{III}-(bpy)_3](B(CN)_4)_3$ redox system, owing to the promising electron-donating and steric properties of the donor group.

In DSSCs, the sunlight-to-electricity conversion efficiency (η) of solar cell devices is determined by the open-circuit photovoltage (V_{OC}), short-circuit current density (J_{SC}), and the fill factor (FF), as related to incident solar power (P_{inc})

$$\eta = \frac{(V_{OC})\ (J_{SC})\ (FF)}{P_{inc}} \qquad (1)$$

According to Equation (1), the product of V_{OC} and J_{SC} must be augmented to improve the efficiency of η. However, the quantity J_{SC} directly depends on the dye properties, such as, the dye light-harvesting, kinetics of the electron injection, dye regeneration and charge transport within the cell.

A key factor that has a significant impact on the power conversion efficiency of DSSCs is the energy gap (E_g) of the sensitizer, since the rate of charge transfer (CT) is directed by the free energy of the transition that is correlated to the energy gap between the electronic potential energy levels [highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs)] of both the donors and the acceptors[42]. In order to attain superior performance of DSSCs the sensitizer must have good conjugation throughout the molecule and a low energy gap between the HOMO (E_H) and the LUMO (E_L) to stimulate the intramolecular charge transfer and a strong absorption band in the visible and near-infrared region to maximize the light-harvesting efficiency[21,43]. Briefly, for the sake of an efficient electron injection from the dye excited state onto the semiconductor surface, there must be a strong electronic coupling between the LUMO of the dye and the semiconductor conduction band (CB). The LUMOs of the triarylamine dyes are generally too low to provide perfect electron injection, and must be further improved by the optimizations. The characteristic electronic absorption spectrum of triarylamine dyes[21] involves a strong transition to the first excited state ($S_0 \rightarrow S_1$) at about 400 – 600 nm and a weak transition to the second excited state (S0 → S2) at about 300 nm. The first transition belongs to the ICT character, whereas second transition is assigned to $\pi \rightarrow \pi^*$ transition. Although notable

progress has been made with triarylamine dyes, the major problem is that they show very low molar extinction coefficients in the region of 500−600 nm as well as in the longer wavelength region, which greatly decreases the light harvesting abilities. Thus, the J_{SC} of the cell decreases. In order to overcome this problem, it is essential to tune the electronic and optical properties of the sensitizers by modifying their chemical structures. As a result, the electron transfer process[21] of the DSSCs will be enhanced.

Figure 1

A survey of the literature indicated that the photo-conversion efficiencies of DSSCs fabricated with triarylamine derived dyes was critically dependent upon the molecular structure (i.e., donor (D) and acceptor (A) groups) of the dyes and also on the amount of dye adsorbed on the TiO_2 surface[21]. Triphenylamine (**TPA**) is commonly employed as the electron donor[23] and acid groups, such as cyanoacrylic acid, carboxylic acid, phosphonic acid and sulfonic acid, function as electron acceptors, which form the vital link between the dye molecules and the semiconductor surface. On the other hand, the conjugated π-system plays a vital role in the charge transfer process between the donor and the acceptor, in enhancing light harvesting, and in the suppression of the dark current. Tian *et al.*[23] in their review article demonstrated that D-π-A structure can facilitate the electron injection due to the directional electron transfer from the donor site to the acceptor site along the D-π-A system, and the elongation of the π conjugation and loss of symmetry could also cause broadening and a red shift of the absorption bands in triphenylamine dyes. For instance, in 2010, Chen et *al.*[44] verified that elongation of π-conjugation with the highly electronegative fluorine substituted phenyl group in dye **A1**, leading to dye **A1-F**, caused broadening and a red shift of the absorption bands and subsequently decreased the band gap and improved the photo-current response. As a consequence of the fluorinated dyes exhibiting higher hydrophobicity and offering large shielding, they moderate the direct interaction between the electrolyte and anode. Thus, water-induced desorption of the dye from the TiO_2 surface is significantly reduced. Improved results were achieved with the 1,4-phenylene group with a fluorine substituent at C-3 i.e., *ortho*-fluorophenyl group (**O-FP**). On the other hand, the steric repulsion between the *ortho*-substituted fluorine atom and the carboxylic acid group not only influenced the D–A strength, but also increased the electronic coupling with nanostructured TiO_2 electrode[21]. In 2013, Gabrielsson et *al.*[45] confirmed that higher photocurrents and solar energy conversion efficiencies can be achieved by encompassing the linker fragment, 4*H*-cyclopenta[2,1-*b*:3,4-*b′*]dithiophene (CPDT), in dye **D35**. Similarly, Zhang et *al.*[43] showed that the chromophoric core comprising of CPDT and benzo[*c*][1,2,5]thiadiazol-4,7-diyl (**BT**) in conjunction with a **TPA** unit and a benzoic acid (**BA**) anchor leads to power efficiencies of over 11%. Wang et *al.*[46] revealed that extending the **CPDT** π-bridge in C218 dye[47] with a strong electron-withdrawing **BT** unit, leads to dye **D2**, which exhibited enhanced absorption in the long wavelength region with efficiency greater than 9%. Recently, Yella et *al.*[48] demonstrated that the efficiency and short circuit current density of **C218** and **Y123**[49] dyes can be further enriched by tuning their donor fragments with a fluorine moiety. The foregoing discussion indicates that further enhancement of power conversion efficiency of DSSCs can be achieved by the rational molecular design of new triphenylamine dyes with good light

harvesting ability, and also informs us that the electron-withdrawing units (O-FP and BT) increase the co-planarity of a bridged π-system without inducing intermolecular aggregation and consequently enhance the red shifted absorption spectra of triphenylamine dyes. Contrary to the report by Wang *et al.*[46] in which improved DSSC performance was noted for incorporation of a benzothiadiazole spacer between the triphenylamine donor group and the π-system of the sensitizer, Bauerle *et al.*[50] have explored the incorporation of a benzothiadiazole unit placed adjacent to the cyanoacrylic acid anchoring group. In the latter study, low efficiency of the derived DSSC was noted as a consequence of enhanced back electron transfer and an increased recombination rate. The structure of our hypothetical dyes were guided by these reports and thus we have discounted hypothetical structures which incorporate the benzothiadiazole and cyanoacrylic acid grouping adjacent to one another. Therefore, for a full understanding of the dye solar cell performance and the roles of donor and π-spacer groups, the structural and electronic properties of the dyes is of crucial importance. In this concern, quantum mechanical calculations centered on DFT and TDDFT are believed to be most promising way ahead. Such state-of-the-art theoretical calculations have been successfully employed to select triarylamine derived sensitizers[51-55].

The foregoing discussion clearly indicates that influence of the o-fluorphenyl unit and the thiadiazole unit have been examined independently in triarylamine derived dyes, but the examination of (i) their combined effect in triarylamine derived dyes and (ii) their combined effect in substituted triarylamine derived dyes has thus far been overlooked. Our present work redresses this oversight and aims to assess the combined effect of these individually beneficial groups. Several unique combinations of such desirable structural units are presented in the work for the first time. In order to achieve an advanced understanding of the physical properties of DSSCs, theoretical investigations of the ground and excited-state properties of five known reference dyes **A1**, **A1-F**, **C218**, **D2** and **Y123** and five hypothetical dyes **C218-F**, **D2-F**, **Y123-F**, **Y1234** and **Y1234-F** are presented (see Fig. 1 for structures and their interrelationships). **A1** dye contains a **TPA** and **CPDT** units with a cyanoacrylic acid acceptor unit. The substitution of either alkoxy or benzene-2,4-bis(hexyloxy) at the *para*-position of the phenyl rings of the **TPA** unit in **A1** leads to **C218** and **Y123** dyes, respectively. The long chain alkoxy substituents on the triphenylamine unit delay contact between the donor moiety and the TiO$_2$ surface and suppress the charge recombination to achieve high fill factor values. Such an alkoxy moiety also protects the TiO$_2$ surface, preventing access of the electrolytes to the interface and retarding the back electron transfer. However, using cyanoacrylic acid as a terminal anchoring group increases the electron affinity (**EA**) in regions close to the TiO$_2$ surface and forms a molecular dipole that is orientated away from the TiO$_2$ surface, enabling both open-circuit voltage (V$_{OC}$) and short-circuit current density to be increased simultaneously. The absorption spectra of **C218** and **Y123** covers only the short wavelength region of visible light. So it is possible to enhance the absorption of **C218** and **Y123** dyes in the long wavelength region by inserting a conjugated group **BT** between donor and spacer groups, forming dyes **D2** and **Y1234**. An additional fluorine substituted phenyl group incorporated between **CPDT** and the cyanoacrylic acid acceptor in the series of dyes **A1**, **C218**, **D2**, **Y123** and **Y1234** leads to structures **A1-F**, **C218-F**, **D2-F**, **Y123-F** and **Y1234-F**, respectively, with the aim of further elongating the π-conjugation. A special emphasis is placed on the use of standard computational strategies for

the study of the absorbance, the injection and recombination lifetimes at the dye/TiO$_2$ interface. This study is organized to provide the information concerning the methodology and full computational details (Section 2), followed by the theoretical results and discussion (Section 3) and finally the conclusions.

2. Theory and computational details

In DSSCs, incident photon to charge carrier Efficiency (IPCE) is represented as a function of wavelength. IPCE is obtained by the following equation[24]:

$$\eta_{IPCE}[\%] = \frac{1240[eV] \times J_{SC}[mAcm^{-2}]}{\lambda[nm] \times \phi_{ph}^{source}[mWcm^{-2}]} \times 100 \qquad (2)$$

where J$_{SC}$ is the short-circuit photocurrent density for monochromatic irradiation, λ is the wavelength, and $\phi_{ph}^{source}(\lambda) = 100 \text{ mW}/\text{cm}^2$. Here, J$_{SC}$ can be expressed as[56]

$$J_{SC}(\lambda) = q \int \eta_{IPCE} \phi_{ph}^{source}(\lambda) d\lambda \qquad (3)$$

IPCE is also given by the following equation:

$$\eta_{IPCE} = LHE \ \phi_{inject} \ \eta_{collect}$$

Therefore

$$J_{SC}(\lambda) \approx q \int \frac{LHE(\lambda) \times \phi_{inject} \times \eta_{collect} \times \lambda \times \phi_{ph}^{source}(\lambda)}{1240} d\lambda \qquad (4)$$

where LHE is the light-harvesting efficiency, ϕ_{inject} is the quantum yield of electron injection, and $\eta_{collect}$ is the efficiency of collecting the injected electrons at the back contact and q is charge of electron. According to equation, if ϕ_{inject} and $\eta_{collect}$ are almost equal to unity, IPCE is determined by the LHE of the dye adsorbed on the film. Here, LHE is expressed as[56]

$$LHE = 1 - 10^{-A} = 1 - 10^{-f} \qquad (5)$$

where A and f are the absorbance and oscillator strength of the dye associated to the λ_{max}^{ICT}. The oscillator strength is directly derived from the TDDFT calculations and writes[56]

$$f = \frac{2}{3} \lambda_{max}^{ICT} |\vec{\mu}_0 - ICT|^2 \qquad (6)$$

where $\vec{\mu}_0 - ICT$ is the dipolar transition moment associated to the electronic excitation. In order to maximize f, both λ_{max}^{ICT} and $\vec{\mu}_0 - ICT$ must be large. The amount of adsorbed dye on the surface Γ (in mol cm^{-2}) can be calculated from the absorbance A = 1000·ε·Γ, where ε is the molar extinction coefficient (units M^{-1} cm^{-1}). The Langmuir adsorption isotherm can be written as $\Gamma = \Gamma_{max}$ KC/(1+KC), with K the binding constant for adsorption, Γ_{max} the maximum load on TiO$_2$, and C is the dye concentration in the dye bath.[57]

The molecular structure and electronic properties of a series of hypothetical triarylamine dyes and associated reference dyes were investigated using quantum chemical program Gaussian 03[58] and GAMESS US[59] in this paper. The equilibrium geometry of the molecules in neutral, cationic and anionic states were determined in the gas phase using the B3LYP/cc-PVDZ approach. Vibrational frequencies were calculated to confirm that the geometries correspond to minima on the potential energy surface. In order to reduce the

computational cost, the hexyl groups have been replaced with methyl groups in each of the investigated dyes. The excited state properties have been examined using the CAM-B3LYP functional. Solvation effects, assuming acetonitrile solvent, were examined using an integral equation formalism variant Polarizable Continuum Model (IEFPCM) within the self-consistent reaction field (SCRF) theory[60,61]. In order to calculate the excited state life time, firstly we optimized the excited states of dyes using the TD-B3LYP/cc-PVDZ method, then we used the excited geometries to calculate the dye relaxation in acetonitrile solvent with TD-CAM-B3LYP/DGDZVP method. To understand the nature of electronic excitations, the excited states were analysed by constructing the frontier molecular orbitals (FMOs) within the Avogadro program[62]. The lambda diagnostic parameter concerning to charge transfer characteristic was calculated using GAMESS program. The reorganization energy of investigated dyes were calculated at the B3LYP/cc-PVDZ level in gas phase.

To gain insight into the electronic injection capability of dyes, the adsorption of dyes on the $(TiO_2)_{28}$ cluster was investigated with DFT calculations using DMol^3 program [63]. The $(TiO_2)_{28}$ configuration was fully optimised using the generalized gradient-corrected approximation (GGA) method. The Perdew-Burke-Ernzerhof (PBE) functional was used to take into account of the exchange-correlation effects with the double numerical polarization (DNP) basis set. The core electron was treated with all electrons. After optimization, the adsorption energies (E_{ads}) of dyes on the $(TiO_2)_{28}$ cluster were obtained using the equation:

$$E_{ads} = E_{dye+TiO_2} - E_{dye} - E_{TiO_2} \qquad (7)$$

where E_{dye} was the total energy of isolated dye, E_{TiO_2} was total energy of $(TiO_2)_{28}$ cluster, and $E_{dye+TiO_2}$ was the total energy of dye/$(TiO_2)_{28}$ complex. Following the above expression, a negative E_{ads} indicates that the molecule adsorption is exothermic and thus the adsorption system is energetically stable. It is believed that the numerical basic sets implemented in DMol^3 could minimize BSSE compared with the Gaussian basis sets.[64] Since DMol^3 uses the exact DFT spherical atomic orbitals, the molecules can be dissociated exactly to its constituent atoms. The binding energies still contain some small BSSE errors, but in the present study we have not consider the corrections.

Finally, making use of optimized geometries of Dmol^3, we have calculated the excited state properties of the dye/TiO$_2$ complexes at the CAM-B3LYP/3-21G(d) level using the Gaussian 03 program.

Table 1
Figure 2

3. Results and discussion
3.1. Structural and electronic properties of the isolated molecules
3.1.1. Molecular geometry

The ground state optimized structural parameters of the ten triarylamine derived dyes (see Fig. 1) in neutral, cationic and anionic states computed at the B3LYP/ cc-PVDZ level are

presented in Table 1. The geometry optimization shows that the ten structures were non-planar. Mostly, the delocalization of the nitrogen lone pair into the phenyl rings is strongly influenced by the molecular conformation and electronic character of the three phenyl rings. Molecular structures of A1 and D2 together with some important structural parameters are presented in Fig. 2. The results showed that the structure of the central NCCC moiety in **A1** and **A1-F** dyes is almost planar (θ_{NCCC} = 179 - 180˚). From Table 1, we noticed that the introduction of substituents at the *para*-position of the phenyl rings hardly influence the nearly planar conformation of the central NCCC moiety, and the N–C bond length decreases from 1.410 Å to 1.403 Å as the electron donating strength of the donor group increases. In addition, the three phenyl rings in the propeller-shaped triphenylamine unit twist symmetrically from the central NCCC plane. Experimental results reported for the triphenylamine molecule showed a torsion angle θ_1 of 41 – 44 ˚ in the gaseous phase[65], whereas our calculations show that θ_1 is 44 - 45˚ for dyes **A1** and **A1-F**. However, the substitution of either alkoxy or bis(hexyloxy)benzene groups at the *para*-position of the phenyl rings leads to an increase in torsion angle θ_1 by approximately 1 – 6 ˚. This slight increase in the torsion angle does not significantly influence the conjugation between the π-electrons of the phenyl groups and the central lone pair of the nitrogen atom. The steric repulsion between the inter-ring hydrogen atoms would leads to minimum energy configuration. We have also measured dihedral angles θ_2 and θ_3 between the donor group and the π-conjugation system, and the results were presented in Table 1. The dihedral angle θ_2 is in the range ~ 20.5 to 24.5 ˚ for **A1**, **A1-F**, **C218** and **Y123** dyes, whereas for **D2**, **Y1234** and **Y1234-F** dyes, the insertion of **BT** between triphenylamine donor and **CPDT** leads to a decrease in torsion angle θ_2 by 20˚. This showed that the spacer and acceptor groups are almost co-planar with the central NCCC moiety. Therefore, the elongation of rigid, planar and bulky **CPDT** with **BT** and **O-FP** moieties, which serve as efficient linkers connect the donor and the acceptor moieties and reduce the recombination, resulted in the high V_{OC} values. The rigidity constrains side paths that quench the excited states and most likely increases the lifetime of the dyes as compared with the flexible and heteroatom-containing conventional linkers[21]. The calculated results clearly indicate that the dihedral angles are not only affected by the substituent (alkoxy or bis(hexyloxy)benzene) at the *para*-positions of the triphenylamine group, but also affected by the π-elongation of the spacer group. From Table 1, we can observe that in cationic and anionic states the C-N bond length of the investigated molecules decreases and increases, respectively, as compared with the neutral structures. However, the bond angle Φ (C1-N-C1´) of the dyes in different states increases in the order as anionic < neutral < cationic. It is worthy to mention that in the anionic and cationic states the π-conjugated spacer group in the investigated dyes is more planar with the central NCCC plane as compared with the netural structures.

Table 2

3.1.2. Electronic properties

As a general rule, a red shift in the absorption spectrum is needed to decreases the energy gap between the HOMO and the LUMO of the dye. Therefore we have calculated the potential levels of the sensitizers investigated in this work using B3LYP/ cc-PVDZ level. The

calculated energy levels of E_H, E_L and energy gap (E_g) were listed in Table 2. Results showed that the energy level obtained from the B3LYP method is close to the experimental values.

In order to design efficient triarylamine-dye sensitizers, the potential levels of the HOMO and LUMO must match to the conduction band level of the semiconductor electrode and to the I^-/I_3 - redox potential[21]. To accept electrons, i.e., for the dye regeneration process, the HOMO level must be lower than the iodine redox potential, and to inject electrons, the LUMO level must be higher than the conduction band level of the semiconductor[21]. However, in dye sensitizers the low LUMO level matches with the conduction band of TiO_2, which limits the further improvement of the energy conversion efficiency of DSSCs. Thus, it is very important to screen novel sensitizer candidates with a higher LUMO level. From Table 2, it can also be noted that the calculated LUMO of the dyes lies above the conduction band of the TiO_2, which ensures fast and efficient electron transfer from the excited dye to the TiO_2 conduction band, indicating that there will be a sufficient thermodynamic driving force for charge injection from the excited sensitizer molecule to the TiO_2 conduction band. Furthermore, the calculated HOMO level of dyes lies in the gap between the conduction band and valence band, more negative than the iodide/tri-iodide redox potential (I^-/I_3: -4.8 eV), indicating energetically favorable ground-state dye regeneration. Although we have compared the E_H value with the experimental oxidation potential, the theoretical redox potential of the electrolyte is difficult to obtain accurately, so another reference compound was used as a benchmark in assessing the sensitizer candidates. The previously reported dye **Y123**, (see Fig. 1) the most effective dye from the triarylamine sensitizer family, is a good choice as the reference.[49] It is predicted that sensitizer candidates with a HOMO level close to that of **Y123** would be promising for dye regeneration, as **Y123** can be regenerated efficiently. The calculated results in Table 2 showed that the HOMO level of hypothetical dyes are close to that of **Y123**, indicating that hypothetical dyes will have sufficient driving force for dye regeneration.

3.1.3. Dipole moment and Polarizability

A high molecular polarizability is a prerequisite for a dye to be employed in an efficient organic solar cell[66]. Such dyes with high polarizabilities exhibit strong interactions with surrounding species and induce an increase in the local concentrations of acceptor species.[67] Similarly, dyes with higher dipole moment can enhance the effective charge separation between donor and acceptor units and consequently increase the open circuit voltage V_{OC}.[68] Our calculations concerning dipole moment and polarizability (see Table 2) showed that **Y123-F**, **D2-F**, **Y1234** and **Y1234-F**, with elongated spacer groups, are highly polarized that would induce an increase in the local concentration of acceptor species at the TiO_2 surface. This enhanced concentration increases the possibility of acceptor species penetrating the adsorbed dye layer leading to electron recombination within a short electron lifetime.

Figure 3

3.1.4. Energy Gap

In DSSCs smaller energy gaps render the electrons more easily excited and thus beneficial for absorbing longer wavelength light. Hence, more photons can be absorbed at any given time,

which guarantees a higher short circuit current density J_{SC} and overall power conversion efficiency η[21]. The band gap (E_g), the energy gap between the filled valance band and unfilled conduction band, of the dye can be obtained by the difference between E_H and E_L. It is well-known that DFT calculations often lead to overestimate the band gaps. Even though it is obtained approximately, the band gap obtained by the B3LYP method is closely related to the actual band gap (see Table 2). In order to better understand how the HOMOs and LUMOs are influenced by the π-elongation of the spacer group and substituents (alkoxy or bis(hexyloxy)benzene) at the *para*-position of the phenyl ring of the triphenylamine group of structure **A1**. We have presented the molecular energy levels of the ten dyes in Fig. 3. We can observe that the energy gap of the molecules is decreasing in the order of **A1 > C218 > Y123 > A1-F> C218-F > Y123-F > D2 > D2-F > Y1234 > Y1234-F**.

In general, the substituent at the *para*-positions of each of the phenyl rings of the triphenylamine moiety makes an important contribution to the device efficiency. The energy gap of **C218** decreases by 7% when compared to **A1** due to the *para*-alkoxy substituents of the triphenylamine phenyl rings. As a result, the power conversion efficiency of **C218** increases to 8.6%. In **C281**, the energy levels are well separated from the HOMO and LUMO, but HOMO-4, HOMO-5; LUMO+4, LUMO+5 are energetically very close. Mostly these orbitals (HOMO-4, HOMO-5 and LUMO+4, LUMO+5) have contributions from carbon atoms of the triphenylamine group. From Fig. 3, it can also be seen that as the electron donating strength of the triphenylamine moiety increases, the energy difference between the HOMOs decreases. Similarly, introducing a bis(hexyloxy)benzene moiety at the *para*-position of the donor group in **A1** leads to the structure **Y123** in which the energy levels are well separated from each other and the HOMO – LUMO gap decreases by nearly 19 % when compared to **A1**.

Fluorine substitution provides a significant contribution for promoting the cell performance. Elongating the π-system of the dye molecule with the **O-FP** group lowers both the HOMO and LUMO levels, and enriches the spatial separation between electrons and holes and reduces the dark current. When the π-system in **A1** is elongated by the **O-FP**, structure **A1-F**, led to an upward shift of the HOMOs and downward shift of the LUMOs. As a result the energy gap of the molecule **A1-F** decreases by 8.6% compared to **A1**. Here HOMO-1 and LUMO+1 are energetically well separated from the HOMO and LUMO levels in all molecules. It is also interesting to note that HOMO-3 and HOMO-4 are energetically close and well separated from HOMO, HOMO+2 and HOMO+5 in **A1** and **A1-F**. This is due to the HOMOs of **A1** and **A1-F** having a significant contribution from the nitrogen in the triphenylamine group, whereas HOMO-3 and HOMO-4 have hardly any contribution from nitrogen. The energy gap in **C218** and **Y123** can be further decreased by up to 15% compared to **A1** by elongating the π-spacer with **O-FP**. From Fig. 3, it can be observed that in **C218-F**, the spacing between HOMOs is much less when compared to **A1** and **A1-F**. Whereas the gap between LUMO and LUMO+1 increases with the increasing electron donating strength of the triphenylamine moiety and decreases with the π-elongation of the spacer group.

Similarly, incorporation of the electron-deficient **BT** group between triphenylamine unit and **CPDT** in **C218**, leading to structure **D2**, lowers both the HOMO and LUMO energy levels, decreases the energy gap by 18% and enhances the spatial separation between electrons and holes. As a result, the efficiency of **D2** (η = 9.31 %) increases up to 7.62 %

when compared to **C218** (η = 8.6 %). The band gap of **D2** can be further decreased by elongating the π-system with **O-FP** unit. The elongation of the π-system in reference dye **Y123** and dye **Y123-F** with the **BT** (leads to hypothetical structures **Y1234** and **Y1234-F**) decreases the energy gap by 18 and 11%, respectively. Therefore the hypothetical sensitizers **C218-F**, **Y123-F**, **D2-F**, **Y1234** and **Y1234-F** have a smaller HOMO–LUMO gap than that of the more efficient dye **Y123**, showing potential for providing red-shifted electronic absorption spectra.

<center>

Figure 4
Table 3

</center>

3.1.5. Optical Properties

The absorption spectra of **A1**, **A1-F**, **C218**, **D2** and **Y123** dyes using three different LRC-DFT XC functionals (CAM-B3LYP, LC-ωPBE and ωB97XD) with DGDZVP basis set in acetonitrile solution with IEFPCM solvent model have been investigated firstly and compared with available experimental data. The calculated results were presented in Fig. 4. The results obtained with the CAM-B3LYP and ωB97XD functional are close to the experimental data (Fig. 4). Generally, the long-range corrected CAM-B3LYP offers the most stable and more rational descriptions on the relative intensities and energy spacing of energy bands, the discrepancy between the calculated and experimental excitation energies was found to be 0.2 – 0.3 eV. Secondly, we have adopted the CAM-B3LYP functional for calculating absorption spectra of the hypothetical dyes. The computed vertical excited singlet states, oscillator strengths of the ten dyes in acetonitrile solvent along with available experimental data were presented in the Supporting Information (Table S1†). The simulated absorption spectra of ten dyes (Fig. 5) exhibit maxima from the localized aromatic π→π* transitions in the range 250–390 nm, while those at 400 – 600 nm originates from the charge transfer π→π* transition. As expected, the electronic absorption bands of the triarylamine dyes are sensitive to substituents at the *para*-position of the phenyl rings of the triphenylamine unit and the elongation of the π-spacer.

<center>

Figure 5

</center>

The absorption spectra of **A1** in a 1: 1 solution of acetonitrile/*tert*-butyl alcohol exhibit an intense band at 477 nm. This band is attributed to the π→π* charge transfer transition (CT) originating from the **TPA** entity and part of **CPDT** to the electron accepting cyanoacrylic acid. Increasing the electron donating strength of the donor moiety in **A1** by inserting an alkoxy group at the *para*-position of the **TPA** group, forming **C218** dye, provides a ~ 72 nm red shift of the absorption maximum with a similar molecular extinction coefficient to that of **A1**. Whereas, the calculated results show that there is a ~10 nm red shift of the absorption spectra in acetonitrile solvent. Thus, the power conversion efficiency of **C218** (η = 8.6%) increases by 135% compared to **A1** (η = 3.62%). Replacement of the electron-donating alkoxy substituent at the *para*-position of the **TPA** rings in **C218** with a bis(hexyloxy)benzene unit (leading to **Y123**) causes slight changes in the absorption properties with the absorption maximum of **Y123** blue shifted by 6 nm. Generally, a dye with

<center>

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a low band gap can generate more electrons in the visible and near infrared regions and enhance the efficiency of DSSCs. But the probability of absorption by a molecule depends on the molecular extinction coefficient (ε). Larger values of ε indicate a high probability of absorption at a given wavelength leading to larger conversion efficiencies[69]. Even though absorption bands of **Y123** is blue shifted, its energy gap and molecular extinction coefficient are lower and higher than the dye **C218**, respectively. Therefore, the light harvesting efficiency of **Y123** dye is larger than **C218**.

Upon inserting the **O-FP** group into **A1**, forming **A1-F**, the power conversion efficiency (η) increases from 3.62 % to 4.86 %. Due to the lack of planarity between **CPDT** and the **O-FP** in **A2-F**, the absorption maximum blue shifts by ~ 20 nm with a slightly larger ε ~ 53740 ± 130 M^{-1} cm^{-1} than that of **A1**. From Table 3, the calculated maximum absorption peak of dye **A1-F** in acetonitrile solvent is red shifted by ~11 nm compared to **A1**. The π-conjugation in dyes **C218** and **Y123** is extended by inserting an **O-FP** group; forming hypothetical dyes **C218-F** and **Y123-F**. The maximum absorption band red shifts and the molecular extinction coefficient increases. As a result, the photocurrent response for these dyes is predicted to be higher than that of the **C218** and **Y213**. Similarly, extending π-system by inserting **BT** group in **C218**, **C218-F**, **Y123** and **Y123-F**, forming **D2**, **D2-F**, **Y1234** and **Y1234-F** dyes, enhances the absorption in the long wavelength regions. The experimental results showed that the absorption maximum of **D2** is red-shifted by 44 nm as compared to **C218**, due to better delocalization of electrons over the entire molecule. Whereas, the calculated results showed that the absorption maxima of hypothetical dyes **D2-F**, **Y1234** and **Y1234-F** red shift by 110, 106 and 108 nm, respectively, with enhanced molecular extinction coefficients, as compared to the reference dye **Y123**.

The calculated results showed that the first absorption maxima of the ten dyes are derived from the HOMO → LUMO electronic transition. The HOMOs of all dyes are fairly delocalized over the **TPA**-donor and spacer moieties, and the LUMOs are extended over the cyanoacrylic acid unit and part of the spacer. Such a spatially well-separated orbital distribution is highly desirable for efficient intramolecular charge separation upon photoexcitation. In order to understand the charge transfer character, Tozer et al.[70] introduced a spatial overlap, Λ, a quantity which measures the spatial overlap for each excitation using the formula

$$\Lambda = \frac{\sum\limits_{i,a} \kappa_{ia}^{2} O_{ia}}{\sum\limits_{i,a} \kappa_{ia}^{2}} \qquad (7)$$

where $O_{ia} = \langle |\varphi_i| \, || \, |\varphi_i| \rangle = \int |\varphi_i(r)| \, |\varphi_i(r)| \, dr$ is the inner product of the moduli of the two orbitals, φ_i and φ_a, involved in the excitation, and $\kappa_{ia} = X_{ia} + Y_{ia}$ is a measure of the contribution of the i-a orbital transition to the excitation. Because the maximum absorption of all our analogues corresponds to the HOMO→LUMO transition, the degree of CT can be approximated by simplifying equation 7. This is done by calculating the product of the absolute value of the molecular orbital coefficients of the HOMO and LUMO as given in equation 8.

$$\Lambda_{HL} = \sum_{i=j=1}^{N} |c_{iH}||c_{jL}| \qquad (8)$$

The spatial overlap takes the value $0 \leq \Lambda_{HL} \leq 1; 0 \leftarrow \Lambda_{HL}$ and indicates long-range excitation, and $1 \leftarrow \Lambda_{HL}$ signifies short range excitation. Recently, Peach *et al.*[71] suggested that Λ values > 0.4 have the greatest reliability for charge-transfer states. If Λ values < 0.4, there is little overlap and significant long-range charge transfer character. Therefore, we have calculated the Λ diagnostic values for the excitation of each ground state structures using TD–CAM-B3LYP/ 6-31G(d) level of theory. The results were reported in Table 3 for all the dyes in the gas phase. Note that smaller values of Λ (i.e. a smaller overlap between the HOMO and LUMO orbitals) indicate a greater charge-transfer character (when $\Lambda = 0$, an electron is completely transferred).[72]

Figure 6
Table 4

Fig. 6 (bottom) showed the charge density difference between the excited and ground states of ten dyes with green regions representing a depletion of density and red regions an accumulation of density upon excitation. As depicted in Fig. 6 (bottom), the density depletion zones (green) are mostly located on the conjugation spacer segments, while the regions of density enhancement (red) are mainly localized on the acceptor moiety, indicating an intra-molecular charge transfer when the transition occurs. Molecular orbital compositions of the HOMO and LUMO energy levels of the ten dyes were listed in Table 4. For a greater understanding of the molecular orbital contribution to the energy levels, the partial density of states (PDOS) of the ten molecules were presented in the Supporting Information (Figure S1†). The results showed that the substituent at the *para*-position of the phenyl rings of the triphenylamine group does not affect the contribution of the anchoring group to the LUMO of **C218** and **Y123** when compared to **A1**. Whereas, upon the insertion of the **O-FP** group in **A1**, **C218** and **Y123**, leading to dyes **A1-F**, **C218-F** and **Y123-F** respectively, a 5% increase contribution of the anchoring group to LUMO was noted. The contribution of the anchoring group of our hypothetical dyes **C218-F** and **Y123-F** to LUMO is 45%, whereas the so far known best dyes **C218** and **Y123** contribute 40%. However the insertion of a **BT** group in **C218,** affording **D2,** reduces the contribution of the anchoring group LUMO to 16%, but the contribution increases up to 18% by elongating the π-system with an **O-FP** moiety (forming **D2-F**). By elongating the π-system, the contribution from the donor part in the HOMO decreases and the contribution from **CPDT** moiety increases. Therefore, we may anticipate that elongating the spacer group would certainly increase the electron coupling with the TiO$_2$ surface and would be more favourable for electron injection into the TiO$_2$ surface.

3.1.6. Reorganization energy

In non-adiabatic Marcus electron transfer theory[73] the charge transfer (Γ) between a weekly coupled electron donor and electron acceptor was defined as a function the electronic coupling, (J), the reorganization energy, (λ_{reog}), and the difference in free energy between the equilibrium states of products and reactants, $\Delta G^0 = G_{products} - G_{reactants}$, which is written as

$$\Gamma = \frac{2\pi}{\hbar} \frac{|J|^2}{\sqrt{4\pi\lambda k_B T}} \, e^{-[(\Delta G^0 + \lambda_{reog})^2 / 4\lambda k_B T]} \qquad (9)$$

where k_B is the Boltzmann constant and T is the temperature. Therefore, in order to enhance the J_{SC} one should focus on improving the LHE and ϕ_{inject} as well as decreasing the reorganization energy. Reorganization energy is the energy requisite for structural changes associated with the charge transfer of the molecules of interest (internal, inner-sphere, vibrational, or structural reorganization) and nearby molecules (external or outer-sphere reorganization). In the solid state, the external reorganization energy can be passed over because the surroundings are rigid, and the internal reorganization energy of isolated molecules can be used as an upper boundary for the charge transport energetics. Internal reorganization energy has been shown to decrease as the size of the conjugated portion of the molecule increases. So we computed the internal reorganization energy λ_{int} according to the following formula[74]

$$\lambda_{int} = \lambda^+ + \lambda^-$$
$$= E_0(Q_+) - E_0(Q_0) + E_+(Q_0) - E_+(Q_+)$$
$$+ E_0(Q_-) - E_0(Q_0) + E_-(Q_0) - E_-(Q_-) \qquad (10)$$

where E is energy, Q is geometry, and the subscripts 0, +, and − denote neutral, cationic, and anionic states, respectively. Table 2 reported the computed internal reorganization energies, the ionization potential (IP), and the electron affinity (EA). IP and EA were calculated as $E_0(Q_0) - E_+(Q_+)$ and $E_0(Q_0) - E_-(Q_-)$, respectively.

Figure 7

From the Table 2, we can observe that the total reorganization energy decreases with increasing strength of the donor moiety and elongation of the π-spacer and thus making the molecules more rigid and planar. As a result, the charge injection rate from the dye excited state to TiO$_2$ conduction band will increase, which is a prerequisite for enhancing the short-circuit current density. When the spacer group is elongated with the **O-FP,** λ^+ is increasing but λ^- is decreasing. But when the **BT** group is inserted as a spacer group, both the λ^+ and λ^- decrease. The reorganization energy also depends on the molecular energy levels, because the LUMO energy levels generally decrease with increasing EA, HOMO energy levels decrease with increasing IP. The calculated results show that as the HOMO level increased, the hole reorganization energy is decreases. Whereas, the LUMO level decreases, the electron reorganization energy decreases (see Fig. 7). The total reorganization energy λ_{int} for the hypothetical dyes **C218-F**, **D2-F**, **Y123-F**, **Y1234** and **Y1234-F** are smaller than the reference dye **Y123**. Therefore we can expect to obtain high electron injection rate from the excited states to the TiO$_2$ conduction band for the hypothetical dyes due to their low reorganization energy. As a result, the J_{SC} for these dyes is predicted to be larger than that of the reference dye **Y123**.

3.1.7. Charge injection (ΔG^0_{inj}) and dye regeneration (ΔG^0_{reg})

The equation (3) and (9) clearly indicates that the ϕ_{inject} and rate of charge transfer are related to the free energy ΔG^0 of electrons injecting from the excited state of dye molecule to the TiO$_2$ substrate. Therefore, the change in electron injection ΔG^0_{inj} affects both the electron injection rate and short circuit current density. The yield of charge collection and dye regeneration can be determined by the driving force, which is defined as the potential difference between the oxidized dyes and the electrolyte. For a fast and an efficient regeneration of the dye cation radical, the oxidation potential of the dyes must be more positive than that of electrolyte and avoiding the geminate charge recombination between oxidized dye sensitizers and the nanocrystalline TiO$_2$ film where the photo-excited electrons are injected. According to Preat's method[54], assuming the electron injection occurs from the unrelaxed excited state of the dye, the ΔG^0_{inj} can be calculated by the following Equation

$$\Delta G^0_{inj} = E^{Dye^*}_{OX} - E^{TiO_2}_{CB} \qquad (11)$$

where $E^{dye^*}_{OX}$ is the oxidation potential of the dye in the excited state, and $E^{TiO_2}_{CB}$ is the reduction potential of the semiconductor conduction band. Though it is often difficult to accurately determine $E^{TiO_2}_{CB}$, a highly sensitive datum to the conditions like the pH of the solution, thus we used the experimental value $E^{TiO_2}_{CB} = -4.0$ eV [75] which corresponds to conditions where the semiconductor is in contact with the aqueous redox electrolytes of fixed pH 7.0[76,77]. The excited state oxidation potential ($E^{dye^*}_{OX}$) can be approximated from the redox potential of the ground state (E^{dye}_{OX}),[54]

$$E^{dye^*}_{OX} = E^{dye}_{OX} - \lambda^{ICT}_{max} \qquad (12)$$

where λ^{ICT}_{max} is the energy of the ICT. Note that this relation is only valid if the entropy change during the light absorption process can be neglected. Compared with dye Y123, the other dyes containing either benzothiadiazole and/or ortho-fluorophenyl moieties in the π-conjugated bridge have the slightly lower $-\Delta G^0_{inj}$ values. The calculated results indicated that the $-\Delta G^0_{inj}$ values of all the dyes are greater than 1 eV. As a result, an efficient electron injection takes place from the sensitizers into the TiO$_2$.

The maximum open circuit voltage (V$_{OC}$) of the DSSC is limited by the difference between the redox potential of the redox mediator and the quasi-Fermi level of electrons in the TiO$_2$ semiconductor. In principle, device efficiencies can be improved by choosing a redox couple with a potential closer to that of the dye, but sufficient driving force needs to be provided to ensure efficient dye regeneration by the redox mediator. Gratzel[78] reports that a minimum driving force of 0.2 – 0.3 eV is required due to the two-electron character of the iodide oxidation reaction, which passes through I$_2^-$ radicals as intermediates. Generally, at large thermodynamic driving forces for dye regeneration, energy dissipates as heat during the regeneration reaction and contributes to a major loss in energy efficiencies of DSSCs. In order to obtain the dye regeneration, we have calculated the driving force for oxidized dye regeneration as the difference between redox potential I$_3^-$/I$^-$ and redox potential of the dye ground state ($\Delta G_0^{reg} = E\left(I_3^-/I^-\right) - E^{dye}_{OX}$). The calculated results in Table 5 showed that the E^{dye}_{OX} values of the hypothetical dyes **C218-F**, **Y123-F**, **D2-F**, **Y1234** and **Y1234-F** match

well with the reference dye **Y123**. Whereas for dyes **A1**, **A1-F**, **C218** and **D2**, the E_{OX}^{dye} values are slightly lower than the reference dye Y123. Therefore the regeneration driving forces of the hypothetical dyes **C218-F**, **Y123-F**, **D2-F**, **Y1234** and **Y1234-F** are lower than the reference dye **Y123**. From Table 5, we can also note that the regeneration driving force of the dyes decreases as the electron donating strength of the donor group increases. This can be further decreased by π-elongation of the spacer group. Therefore, there exists a potential to obtain a higher voltage and higher power conversion efficiencies for hypothetical dyes **C218-F**, **Y123-F**, **D2-F**, **Y1234** and **Y1234-F** when compared to reference dye **Y123**.

<div align="center">

Figure 8
Table 5

</div>

3.2. Dye adsorption on $(TiO_2)_{28}$ substrate

The charge transfer kinetics depends largely on the configuration of the dye adsorbed on the semiconductor surface and the interface energy alignment. In order to understand the electron injection and charge recombination process, we have investigated the electronic and optical properties of the dye adsorbed on the $(TiO_2)_{28}$ substrate using the DFT method. Generally, the strength of the interaction between dye and the TiO_2 surface depends on the adsorption energy of the dye/TiO_2 system. In DSSCs, the electron-transfer rate (k_{ET}) also depends on the strength of the adsorption energy of the dye/TiO_2 system, i.e., the larger the adsorption energy, the stronger the electronic coupling strength between the anchoring group of the dye and the TiO_2 surface, and consequently the larger the k_{ET} value is. In order to calculate the adsorption energies, we first created the 84-atom titania nanoparticle $(TiO_2)_{28}$ by exposing the (101) surface of the anatase titania and then selected different initial adsorption configurations of the ten dyes onto the substrate and optimized each binding structure of them. The optimized structures of the lowest energy structures were presented in Fig. 8, in which the dyes bind onto the surface through their carboxyl group. In the initial configuration of the dye/$(TiO_2)_{28}$ system, the hydrogen of the –COOH anchoring group stays on the dye, but after optimization it was found to transfer to the substrate predominantly in a protonated state. As a result, the sensitizers bind almost perpendicular to the $(TiO_2)_{28}$ surface via bidentate bridging with the formation of two interface O-Ti bonds. Previous studies have shown that the dye links onto TiO_2 surface through a bridging bidentate coordination mode which is more stable and preferable[79,80] because the bidentate binding is shorter than the other binding modes and hence an increase in the rate of electron injection could be expected. The calculated bond distances between the Ti atom and the O atom of dyes are in the range 2.166 – 2.252 Å. The calculated adsorption energies of the most stable bidentate adsorption configurations were presented in Fig. 8. The results indicate that the adsorption energy of the known reference dyes increases with elongation of the π-system with **O-FP** and it decreases upon inserting the **BT** group between the **TPA** and **CPDT** moieties. Among all the investigated dyes, **Y123-F** has shown the largest adsorption energy, indicating a strong interaction between the dye and the TiO_2 surface. These results clearly indicated that the binding strength between the sensitizer and TiO_2 substrate can be improved by elongating the π-system with the **O-FP** group between the triphenylamine unit and the condensed thiophene system. As a result the

electron-transfer rate will increase significantly and lead to an enhanced photovoltaic performance.

Figure 9

3.2.1. Optical properties of the dyes adsorbed on the $(TiO_2)_{28}$ substrate

The electronic absorption spectra of the dyes on TiO_2 substrate were investigated using the CAM-B3LYP method with 3-21G* functional to determine the relationship between the solar energy conversion efficiency and spectroscopic properties. The HOMO and LUMO energy levels of the $(TiO_2)_{28}$ surface in acetonitrile were –8.24 and -2.87 eV, respectively, leading to a HOMO – LUMO band gap of 5.37 eV. Even though the calculated results overestimated the energy levels and band gap, the $S_0 \rightarrow S_1$ optical gap was calculated to be 3.33 eV, which is only slightly larger than the experimental band gap of ~3.20 eV for the nano-sized (15−20 nm) TiO_2[81], supporting the validity of the current theoretical approach based on the $(TiO2)_{28}$ cluster. The calculated results also showed that energy gap of the TiO_2 decreases upon dye adsorption. When the dye inserts the occupied orbitals within the HOMO – LUMO gap of the TiO_2 substrate, the energy gap of dye/TiO_2 complex decreases below the TiO_2 energy gap (5.37 eV). The energy level alignment of the dyes on the TiO_2 substrate was presented in Fig. 9. For dye/TiO_2 complexes, the orbitals near the HOMO and LUMO are free of the combining states and have no mixing MO character. The HOMO of the complexes nearly have the characteristics of dye molecules, while the LUMO of the complexes have the same characteristics as the TiO_2 substrate, which was manifested by the charge densities of the frontier MOs shown in Fig. 10.

Figure 10
Table 6

The absorption spectra of **A1** and **A1-F** on a mesoporous TiO_2 thin film show that there is a slight blue shift as well as a broadening of the absorption peak relative to the isolated dye. Fig. 11 showed the calculated absorption spectrum for the dye/TiO_2 complexes in acetonitrile solution. The electronic spectrum of the dye on the $(TiO_2)_{28}$ surface calculated with CAM-B3LYP/3-21G(d) is overestimated in comparision with the experimental results. For example, the calculated absorption spectrum of **A1-TiO_2** / **A1-F-TiO_2** complex has an absorption band extending from 400 – 1000 nm with the peak at 592 / 621 nm, whereas experimental band is at ~460 nm. The calculated band holds several excitations with the most significant transitions (highest oscillator strengths) being listed in Table 6. All of these transitions take place from the HOMO of the complex which is typically localized on the dye and keeps the HOMO character of the isolated dye (Fig.10). The unoccupied states involved in the transition from LUMO to LUMO + 12 in both **A1-TiO_2** and **A1-F-TiO_2**. In these excitations, LUMO + 12 in **A1-TiO_2** and LUMO + 6 in **A1-F-TiO_2** show significant involvement and have the major contribution to λ_{max}. Fig. 10 is an isosurface plot of LUMO + 12 / LUMO + 6 pertaining to **A1-TiO_2**/**A1-F-TiO_2**, showing contributions from both the dye and the titanium dioxide. All unoccupied orbitals below LUMO+11 in **A1-TiO_2** and LUMO + 6 in **A1-F-TiO_2** show contributions only from the surface without any dye character. On

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the other hand, the three highest occupied MOs (HOMO to HOMO-2) in both the complexes show localization only on the dye. This was confirmed by visualization of these MOs with Avogadro software.

An experimental study performed by Yella et al. [48] for **C218** and **Y123** on a TiO_2 film showed a blue shift as well as broadening of the absorption peak compared to the isolated dye. The calculated absorption spectra of **C218-TiO$_2$** and **Y123-TiO$_2$** have shown only a major excitation for λ_{max} at 608 and 615 nm, respectively. This excitation corresponds to the $S_0 \rightarrow S_1$ transition and shows the contribution from HOMO $\rightarrow$ LUMO + 18 and HOMO $\rightarrow$ LUMO + 19 for **C218-TiO$_2$** and HOMO $\rightarrow$ LUMO + 18 and HOMO $\rightarrow$ LUMO + 19 for **Y123-TiO$_2$** (Table 6). Among them, in **C218-TiO$_2$** (**Y123-TiO$_2$**), LUMO + 19 (LUMO + 20) shows largest contribution in the excitation and delocalizes over the linker and acceptor moieties of the dye as well as on the TiO_2 (Fig. 10). The unoccupied orbitals below LUMO + 18 (LUMO + 19) in **C218-TiO$_2$** (**Y123-TiO$_2$**) localize at the TiO_2 nanoparticle only. Similar to the **A1-TiO$_2$** complex, HOMO to HOMO-2 in both the complexes shows only dye character. This is also indicated in Fig. 10. In the case of **A1-TiO$_2$**, the optical gap (E_{opt}) between HOMO and LUMO+12 is 2.09 eV (Fig. 9). For **C218-TiO$_2$** and **Y123-TiO$_2$** complexes, the optical gap between the MOs involved in the highest intensity transition is 2.04 eV and 2.02 eV, respectively. On the other hand, the hypothetical **C218-F-TiO$_2$** and **Y123-F- TiO$_2$** complexes have shown maximum absorption at 631 and 635 nm, respectively. This excitation corresponds to $S_0 \rightarrow S_1$ and has a maximum contribution from HOMO$\rightarrow$LUMO+7 for each of the complexes. The MOs show that the HOMO exhibits the HOMO character of the dye and that LUMO+7 shows considerable involvement of both dye and TiO_2. The absorbance spectrum of **C218-TiO$_2$/Y123-TiO$_2$** shows a blue shift compared to **C218-F-TiO$_2$/Y123-F-TiO$_2$**.

Recently, Wang et al.[46] reported that the absorption peak for **D2** adsorbed onto 4.8 μm thick TiO_2 film is blue-shifted to 536 nm. In fact, **D2** had shown a hypsochromic shift by 20 nm in the absorption spectrum. The computed absorption band of the **D2-TiO$_2$** complex expands from ~400 to ~1200 nm with a maximum at 741 nm. This excitation corresponds to $S_0 \rightarrow S_2$ transition with high oscillator strength and shows a contribution from HOMO $\rightarrow$ LUMO+7. The LUMO + 7 is an admixture of π^* orbitals of the dye and the empty states derived mainly from d-orbitals of TiO_2. Here, LUMO + 7 is delocalized over the entire BT, CPDT, cyanoacrylic acid anchor and continues over to the TiO_2 substrate attached to the anchor. The delocalization of the LUMO demonstrates a strong coupling between the dye and the oxide surface. Fig. 9 showed that the optical gap between the HOMO and LUMO+7 is 1.66 eV. All unoccupied states below the LUMO + 7 are localized on the TiO_2 substrate. Whereas, hypothetical **D2-F-TiO$_2$** complex showed a maximum absorption band at 782 nm red-shifted by 20 nm as compared to that of the **D2-TiO$_2$** complex. In this case, the $S_0 \rightarrow S_2$ transition has the highest contribution from HOMO$\rightarrow$LUMO. The LUMO of the complex shows resemblance to the unoccupied orbital of the isolated dye with sufficient surface contribution from TiO_2 (Fig. 10). The top four occupied MOs in the **D2-F-TiO$_2$** complex are derived mostly from the dye. HOMO and LUMO are located at –5.95 eV and –3.01 eV respectively with E_g (E_{opt}) of 2.96 eV (1.59 eV). Fig. 11 shows another low intensity absorption peak at 565 nm for **D2-F-TiO$_2$**. This transition originates from the three highest occupied MOs (HOMO to HOMO-2). Several unoccupied MOs contribute significantly to

this transition. With the exception of the LUMO, the other unoccupied orbitals involved in the transition are localized on the TiO_2 substrate (Fig. 10).

Figure 11

The computed **Y1234-TiO$_2$** and **Y1234-F-TiO$_2$** complexes have shown maximum absorption around 744 and 748 nm, respectively. The main contribution to this excitation for **Y1234-TiO$_2$** (**Y1234-F-TiO$_2$**) is HOMO→LUMO+2 (HOMO→LUMO+3). The isosurface plot of LUMO+2 (LUMO+3) shows the contribution is from both the dye and the TiO_2. For the **Y1234-TiO$_2$** (**Y1234-F-TiO$_2$**) complex, the E_{opt} gap between the MOs involved in the highest intensity transition is 1.67 eV (1.66 eV). The excited state calculations for **Y1234-TiO$_2$** and **Y1234-F-TiO$_2$** show a red shift in the absorption spectrum as compared with the **Y123-TiO$_2$** complex.

In 2008, Jose *et al*. [82] indicated that the short circuit current density (J_{SC}) is directly related to the probability density at the anchor moiety. This observation was reinforced by Angelis *et al*.[83] who exposed an improved photocurrent with an increase in electron coupling between dye and the TiO_2 surface. Furthermore, the placement of the excited states in the conduction band of the complexes as well as their isosurface plots can throw light on the mechanism involved in the electron injection from excited dye to TiO_2. Therefore, in order to understand the charge transfer character of the complexes we have presented the electron density difference maps of the main excitation transition in Fig. 12. From Fig. 12, we can observe that upon insertion of the fluorophenylene and benzothiadazole groups in the triarylamine derivatives, the negative charge transfer from dye to TiO_2 substrate increases and consequently enhances the J_{SC}.

Figure 12

3.2.2. Factors influencing the photovoltaic performance

Equation 2 clearly indicates that η_{IPCE} is directly proportional to J_{SC}, so in order to enhance the J_{SC}, the LHE must be as large as possible. Therefore we calculated LHE of ten dye-titanium complexes at the CAM-B3LYP/3-21G(d) level of theory and the results were presented in Table 6. The results showed that the LHE of the dye is enhanced by increasing the strength of the donor moiety and elongating the conjugated system. The LHE of the hypothetical dyes are much better than **Y123-TiO$_2$**. As a result, the photocurrent response for the model dyes is predicted to be larger than that of the reference dye. In order to check this, we calculated the J_{sc} value using Equation 4 by considering approximate parameters $K \approx 10^4$ M^{-1}, $C \approx 10^{-6}$ M and $\Gamma_{max} \approx 5 \times 10^{-8}$ mol cm^{-2} for a 6 μm thick TiO_2 film.[56] The J_{SC} value obtained with DFT method are well comparable with the experimental results. From Table 6, we can observe that J_{SC} values for dyes **C218-TiO$_2$**, **D2-TiO$_2$** and **Y123-TiO$_2$** are larger than the complex **A1-TiO$_2$**, whereas for hypothetical systems **C218-F-TiO$_2$**, **D2-F-TiO$_2$**, **Y123-F-TiO$_2$**, **Y1234-TiO$_2$** and **Y1234-F-TiO$_2$**, J_{SC} values are larger than the reference dye **Y123**. As a result, the IPCE of the model dyes is greater than the reference system **Y123-TiO$_2$**.

In DSSCs, the V_{OC} is another important factor which effect the efficiency of the cell and is defined as the potential difference between the electrolyte redox potential and the

quasi-Fermi level of electrons in the semiconductor TiO$_2$; the V$_{OC}$ can be calculated with the empirical formula given below[84]

$$V_{OC} = \frac{E_C + \Delta CB}{q} + \frac{kT}{q} \ln\left(\frac{n_c}{N_{CB}}\right) - \frac{E_{redox}}{q} \qquad (13)$$

where N_{CB} is the density of accessible states in the conduction band; n_c is the number of injected electrons in TiO$_2$ due to dye adsorption; q is the charge of electron and ΔCB is the shift of E$_{CB}$ when dyes are adsorbed on TiO$_2$ and can be expressed as[84]

$$\Delta CB = -\frac{q\mu_{normal}\gamma}{\varepsilon\varepsilon_0} \qquad (14)$$

In this expression, μ$_{normal}$ denotes the dipole moment of individual dye molecules perpendicular to the surface of the TiO$_2$, q is the charge of electron and γ is the surface concentration of the dye. ε_0 and ε represent the vacuum permittivity and dielectric permittivity, respectively.

From the above equations it is clear that V$_{OC}$ is strongly influenced by the structural parameters of the dye. Because the dye adsorbed on the TiO$_2$ substrate induces the change in dipole moment and charge distribution, as a result, the conduction band edge of the TiO$_2$ substrate shifts upwards. Therefore we compared the important structural parameters of the dyes before and after the adsorption on the TiO$_2$ surface calculated at the same level of theory (GGA-PBE/DNP). The important structural parameters of the dyes were presented in the Supporting Information (Table S2†). From Table S2,† it can be observed that there are appreciable changes in the structural parameters of the dyes before and after adsorption on TiO$_2$ substrate, which leads to large changes in the electronic properties of dye-TiO$_2$ complexes. Normally, the dyes with a dipole pointing toward the TiO$_2$ surface plane cause a decrease of the V$_{OC}$, whereas the opposite is true for a dipole pointing away from the surface. In order to obtain higher V$_{OC}$, the dipole moment of the dye-TiO$_2$ complexes must be as large as possible and point away from the surface. The calculated results indicated that the dyes on the TiO$_2$ surface adsorb almost perpendicularly with their total dipole moments forming an angle of roughly 45º to the TiO$_2$ surface. The dipole moment of dye-TiO$_2$ complexes increases by up to 3 times (Table 6) when compared with an isolated dye, which is a prerequisite for enhancing charge separation between the dye and the TiO$_2$ substrate. The dipole moment of complexes **A1**, **A1-F**, **C218** and **D2** all fall beneath that of Y123, whereas for hypothetical complexes (**C218-F**, **D2-F**, **Y123-F**, **Y1234** and **Y1234-F**) the dipole moments are larger than the reference dye complex. This indicates that the CB shift of the hypothetical dye complexes will be larger than the **Y123** complex. However, from Fig. 9 we noticed that the CB shift of the hypothetical dye-complexes (except **C218-F**) is comparable to **Y123** complex, whereas, for **A1**, **A1-F**, **C218**, and **D2** the CB shifts are larger than **Y123**. Consequently, the V$_{OC}$ of **A1**, **A1-F**, **C218**, and **D2** complexes will be larger than **Y123**. But it is in contradiction with the experimentally observed V$_{OC}$[21]. Therefore, on the basis of dipole moment we predict that the V$_{OC}$ of **C218-F**, **D2-F**, **Y123-F**, **Y1234** and **Y1234-F** will be larger and **A1**, **A1-F**, **C218**, and **D2** complexes are lower than **Y123** complex. These results indicate that hypothetical dyes (**C218-F**, **D2-F**, **Y123-F**, **Y1234** and **Y1234-F**) offer potential for DSSCs applications.

Table 7

Another factor that influences the photovoltaic performance is the excited state lifetime of the dyes. The electron lifetime must be as large as possible,[85] i.e. to realize long-term stability, the dyes must remain stable in the cationic form for a long time. Jiang *et al.*[86] reported that the remarkable performance of the triarylamine dye **D35** is due to its stable excited state. In contrast, the longest electron lifetime with triarylamine dyes was ascribed to the blocking effect by steric hindrance of the nonplanar structure of the donor. Generally, in DSSCs, the excited state decay of the dye is dominated by the nonradiative process.[87] Therefore to calculate the nonradiative electron injection time (τ) between the sensitizer and the semiconductor surface, we employed the Newns−Anderson model[88,89] in the formulation used by Persson et al[90,91] The complete procedure for obtaining nonradiative electron lifetimes of the sensitizers were given in Supporting Information (ESI1[†]). The calculated results were presented in Table 6. The calculated results highlighted that the nonradiative electron life times of the **C218**, **D2** and **Y123** dyes will decrease and increase, respectively with the inclusion of **O-FP** and **BT** groups. The calculated results showed that the electron lifetime for hypothetical dyes containing both **BT** and **O-FP** moieties (**D2-F**, **Y1234**, and **Y1234-F)** is much larger than that of the reference dye **Y123**. As a result, the hypothetical dyes will retard the charge recombination process and enhance the efficiency of the DSSCs.

3.2.3. Level alignment quality (η)

A no-loss DSSC level alignment quality is another important factor which can be used to screen the organic sensitizers for DSSC applications. Recently, Ørnsø *et al.*[92] investigated the efficiency of a functionalized zinc porphyrin using level alignment quality. Level alignment quality is defined as

$$\eta = \frac{V_{OC} \int_{E_c - E_H}^{\infty} \Theta(E - E_1) . J_{SC}(E)\, dE}{\int_0^{\infty} E \bullet \phi_{ph}^{source} dE} \qquad (15)$$

where

$$\Theta(E - E_1) = \begin{cases} 1 \text{ for } E - E_1 \geq 0 \\ 0 \text{ for } E - E_1 < 0 \end{cases}$$

Here $E_c - E_H$ is the distance from the HOMO level to the conduction band, E_1 is the optical gap of the dye, $\Theta(E - E_1)$ is a step function representing the absorption of the dye molecules, $J_{SC}(E)$ is the short-circuit current density and $\int_0^{\infty} E \bullet \phi_{ph}^{source} dE = 100\ mW/cm^2$. In order to calculate the level alignment quality, we adopted two different models for open circuit voltage i.e., $V_{oc} = E_c - E_H$ and $V_{oc} = 1\ V$[92]. The calculated results presented in Table 7 showed that the η values of **A1** and **C218** dyes are lower than the reference dye **Y123**. This indicates that the η value can be improved with increasing the strength of the donor group. It is also interesting to observe that the level alignment quality of **A1** is enhanced by elongating the π-system with **O-FP**, leads to structure **A1-F**. However, when the spacer group in **C218** is elongated with the **BT** group, producing dye **D2,** the η value decreases. The calculated results

showed that η values for dyes elongated with **O-FP** (**C218-F, Y123-F**) or with both **O-FP** and **BT** (**Y1234-F**) are larger than the reference dye **Y123**. Whereas for the remaining dyes (**A1, A1-F, C218, D2 and D2-F**) the η values are smaller than the **Y123**. Based on the above results, we concluded that elongating the π-system in triarylamine dyes with both **O-FP** and **BT** offers more potential for DSSC applications.

4. Conclusions

        A first-principles study has been carried out to gain insight into the effect of π-elongation on the structural and electrical properties of ten triarylamine dye molecules adsorbed on the $(TiO2)_{28}$ anatase (101) surface. The geometry optimization of the isolated molecules in the gas phase showed that the central NCCC moiety is significantly influenced by the elongation of the π-system. As a result, the three phenyl rings of the triarylamine unit are twisted symmetrically from the central NCCC plane by 34 - 49°. The dihedral angles are affected not only by the π-elongation, but also by the substituent (alkoxy or bis(hexyloxy)benzene) at the *para*-position of the phenyl rings of the triphenylamine group. The energy gap between HOMO and LUMO energy levels decreases further by elongating the π-system with either **BT** or **O-FP** units or both. The absorption spectra of the isolated molecules containing either **BT** or **O-FP** units or both in the π-system show pronounced red shifts of the maximum absorption band with enhanced molecular extinction coefficient compared to reference dye **Y123**. The simulated absorption spectra of the ten dyes showed intense bands in the range 250 – 390 nm and 400 – 600 nm, which are ascribed to the localized aromatic π→π* transitions and the charge transfer π→π* transition, respectively. The calculated results also showed that the excited state life-times and reorganization energies of the investigated dyes are larger and lower, respectively, than the reference dye. The dye/TiO_2 results indicate that the adsorption energy of the hypothetical dyes increases with elongating the π-system with **O-FP** group but decreases with inserting **BT** group between **TPA** and **CPDT** moieties. However, the absorption spectra of dye/TiO_2 complexes show pronounced red shifts of the absorption maxima with large molecular extinction coefficients after the elongation of π-system. Due to elongation of the π-system, the optical gap and light harvesting efficiency of the dye/TiO2 complexes decreases and increases, respectively, as compared to reference **Y123**. The short circuit current density and level alignment quality factors of the hypothetical systems are larger than those of **Y123**. Finally, we concluded that elongating the π-conjugated spacer group in triarylamine dyes with **BT** and **O-FP** groups offers a potential approach for optimizing DSSC performance. The elongation of the π-system using carefully placed spacer groups guarantees the dyes with larger molecular excitation coefficient, electron lifetime, LHE, J_{SC}, level alignment quality and smaller electron reorganization energy and energy gap than the reference dye. Thus, to summarize, the elongation of the π-system in a series of hypothetical triphenylamine dyes by the judicious placement either a fluorophenyl or benzothiadiazole group, or a combination of both groups, results in an improved light harvesting efficiency in DSSC devices.

†**Electronic supplementary information (ESI) available:** Contains the computed vertical excited singlet states, oscillator strengths of ten dyes in acetonitrile solvent and PDOS of dyes calculated at the CAM-B3LYP/DGDZVP level of theory. The important structural

parameters of the dyes before and after the adsorption on TiO_2 surface calculated at the GGA/PBE/DNP level of theory using $Dmol^3$.

Acknowledgments

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Figure 1. Chemical structures of the triarylamine dyes investigated in the present study. Structures in black color are known (reference) dyes, whose experimental data are given below each structure and hypothetical structures are in blue color.

Figure 2. Molecular structure of (a) A1 and (b) D2 dyes. For C-N bond lengths, bond, and torsion angles, see Table 1.

Figure 3. Energy level diagram of isolated dye molecules calculated at the B3LYP/cc-PVDZ level.

Figure 4. Absorption maxima of the experimentally investigated dye molecules calculated in acetonitrile solution by TD-DFT coupled with IEFPCM.

Figure 5. Calculated absorption spectra of ten dyes in acetonitrile solution using TD-DFT-CAM-B3LYP method.

Figure 6. HOMO, LUMO, and electron density difference maps (EDDM) between the excited and ground states of ten dyes. The contour thresholds for molecular orbitals and density differences are 0.02 and 0.0002 a.u., respectively. The green and red colors indicate a decrease and increase of charge densities, respectively.

Figure 7. Comparison graphs between (a) HOMO vs IP and (b) LUMO vs EA of ten dyes. The colors map in the figure indicates the reorganization energy for the corresponding energy levels, IP and EA.

Figure 8. Optimized bidentate bridging mode of the ten triarylamine dyes on the $(TiO_2)_{28}$ cluster calculated by PBE/DNP on DMol^3 program.

Figure 9. Energy level alignment of isolated dyes and dye-TiO2 complexes calculated at the CAM-B3LYP/3-21G(d) level.

Figure 10. (a) HOMO (b) LUMO and (c) interacting orbital isosurfaces of ten triarylamine derivatives on $(TiO2)_{28}$ nanoparticle. The isovalue is 0.002 a.u.

Figure 11. Calculated absorption spectrum of investigated dyes on $(TiO2)_{28}$ nanoparticle.

Figure 12. Electron density difference maps of investigated dyes on $(TiO_2)_{28}$ nanoparticle. The contour threshold for isosurfaces is 0.0002 a.u. The green and red colors indicate a decrease and increase of charge density, respectively.

List of Tables

Table 1 Relevant bond lengths, angles, and dihedrals of triphenylamine derivatives at B3LYP/cc-PVDZ Level[a]

Compound	State*	Bond length (Å)	Bond Angle (°)	Torsion Angle (°)		
		N – C1	Φ (C1-N-C1´)	θ1 (C1-N-C1´-C2´)	θ2 (C-C-C-S) / (C-C-C-C)	θ3 (C-C-C-S)
A1	N	1.410	120.46	45.07	23.95	--
	C	1.378	121.29	23.55	2.25	--
	A	1.434	119.01	34.63	2.66	--
A1-F	N	1.412	120.25	44.73	24.35	--
	C	1.379	121.37	22.83	3.16	--
	A	1.431	119.17	36.48	7.42	--
C218	N	1.403	120.73	51.20	22.37	--
	C	1.389	120.89	29.29	4.64	--
	A	1.430	119.43	37.15	3.92	--
C218-F	N	1.405	120.81	28.76	23.29	--
	C	1.387	120.93	27.83	2.141	--
	A	1.426	119.77	39.09	8.44	--
D2	N	1.405	120.73	48.64	1.146	0.128
	C	1.388	120.85	28.80	0.466	0.044
	A	1.433	119.31	34.99	0.00	0.229
D2-F	N	1.402	120.84	27.81	0.281	0.678
	C	1.386	120.91	27.16	0.595	0.269
	A	1.426	119.85	40.20	0.454	0.021
Y123	N	1.403	120.50	46.60	20.54	--
	C	1.399	120.43	33.28	6.386	--
	A	1.433	119.05	34.03	0.379	--
Y123-F	N	1.410	120.40	46.00	20.98	--
	C	1.395	120.67	31.34	5.028	--
	A	1.431	119.22	35.15	0.942	--
Y1234	N	1.403	120.74	49.42	1.681	0.454
	C	1.398	120.47	33.00	0.012	0.591
	A	1.433	119.29	34.95	0.477	0.016
Y1234-F	N	1.404	120.67	49.07	1.926	0.666
	C	1.393	120.94	29.98	1.423	0.172
	A	1.430	119.41	36.67	0.036	0.148

[a] The bond lengths, bond angle and torsion angles are shown in figure 2.

Table 2 E_H (eV), E_L (eV) levels, E_g (eV), ionization potential (eV), electron affinity (eV), dipole moment ρ (Debye), polarizability α (a.u), reorganization energy λ (eV) of triphenylamine based sensitizers calculated at B3LYP/cc-PVDZ level.

Dye	E_H (eV)	E_L (eV)	E_g (eV)	ρ (D)	α (a.u)	Hole Transfer		Electron Transfer		λ_{int}
						IP	λ^+	EA	λ^-	
A1	-5.16	-2.69	2.47	10.21	596	6.05	0.25	1.71	0.42	0.67
A1-F	-5.08	-2.82	2.26	10.09	757	5.91	0.27	1.87	0.33	0.61
C218	-4.92	-2.61	2.31	10.95	661	5.81	0.20	1.63	0.41	0.61
	(- 4.99)[a]	(- 2.86)[a]	(2.13)[a]							
C218-F	-4.85	-2.74	2.11	13.53	825	5.69	0.21	1.78	0.33	0.54
D2	-4.99	-3.10	1.90	11.37	982	5.73	0.17	2.21	0.32	0.50
	(- 5.15)[b]	(- 3.20)[b]	(1.95)[b]							
D2-F	-4.86	-3.00	1.86	13.02	1174	5.63	0.18	2.24	0.28	0.46
Y123	-4.87	-2.59	2.27	12.38	885	5.66	0.18	1.64	0.41	0.60
	(- 5.08)[a]	(- 2.91)[a]	(2.17)[a]							
Y123-F	-4.81	-2.75	2.06	13.01	1054	5.57	0.19	1.80	0.33	0.52
Y1234	-4.88	-3.03	1.85	12.68	1225	5.62	0.16	2.23	0.36	0.52
Y1234-F	-4.83	-3.00	1.83	13.03	1420	5.53	0.16	2.26	0.30	0.46

[a] See ref 48
[b] See ref 46
* Values in parenthesis are calculated using experimental E_H and E_L Values.

Table 3   Absorption and emission properties of the ten dyes in acetonitrile solution calculated at the CAM-B3LYP/ DGDZVP level

Dye	Experimental			Theoretical									
	λ^{abs}_{max} (nm)	ε ($M^{-1}cm^{-1}$)	E_0^{exp*} (eV)	λ^{abs}_{max} (nm)	E_0^A (eV)	ε ($M^{-1}cm^{-1}$)	f	Λ	λ^{em}_{max} (nm)	ε ($M^{-1}cm^{-1}$)	f	E_0^{E*} (eV)	E_{00}^{Avg*}
A1	477[a]	51660[a]	2.59	484	2.56	50107	1.724	0.591	512	48676	1.676	2.42	2.49
A1-F	460[a]	53740[a]	2.69	494	2.51	62970	2.168	0.509	587	62746	2.155	2.11	2.31
C218	549[b]	46000[b]	2.25	498	2.49	51307	1.765	0.546	511	47990	1.627	2.42	2.46 (2.13)
C218-F	-	-	-	504	2.46	62112	2.131	0.467	521	61867	2.125	2.38	2.42
D2	556[c]	56000[c]	2.23	596	2.08	62062	2.168	0.630	633	50594	1.739	1.96	2.02 (1.95)
D2-F	-	-	-	603	2.05	71081	2.329	0.610	658	55983	1.929	1.88	1.97
Y123	542[b]	50500[b]	2.28	493	2.51	54040	1.857	0.496	510	50496	1.731	2.43	2.47 (2.17)
Y123-F	-	-	-	501	2.47	64799	2.219	0.419	516	62832	2.160	2.40	2.44
Y1234	-	-	-	599	2.06	64367	2.171	0.586	559	51225	1.633	2.21	2.14
Y1234-F	-	-	-	601	2.06	73550	2.424	0.568	647	58588	2.019	1.91	1.99

* Where average optical gap E_{00}^{Avg} is calculated using sum of the optical gap obtained from absorption and emission maximum i.e, $E_{00}^{Avg} = (E_o^A + E_o^E)/2$

[a] See ref 44

[b] See ref 48

[c] See ref 46

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Table 4   Percentage of donor, acceptor and spacer units contribution to HOMO and LUMO energy levels

Dye	Molecular Orbital Contribution (%)									
	HOMO					LUMO				
	D	CPDT	OFP	BT	A	D	CPDT	OFP	BT	A
A1	60	33	-	-	6	6	54	-	-	40
A1-F	48	45	5	-	2	2	21	32	-	45
C218	71	25	-	-	4	6	54	-	-	40
C218-F	60	35	4	-	1	2	21	32	-	46
D2	61	19	-	17	3	9	32	-	43	16
D2-F	50	28	3	18	1	7	23	16	36	18
Y123	73	23	-	-	4	6	54	-	-	40
Y123-F	61	34	4	-	4	2	21	32	-	45
Y1234	62	19	-	16	3	9	32	-	44	16
Y1234-F	50	29	3	17	1	7	23	15	37	18

Table 5 Ground and excited state redox potentials (E^{dye}_{ox} and E^{dye*}_{ox}); charge injection and dye regeneration driving forces (ΔG^0_{in} and ΔG^0_{reg}) of triphenylamine based sensitizers calculated at B3LYP/cc-PVDZ level.

Dye	E^{dye}_{ox} (eV)	E^{dye*}_{ox} (eV)	ΔG^0_{inj} (eV)	ΔG^0_{reg} (eV)
A1	-5.16	-2.60	-1.40	0.36
A1-F	-5.08	-2.57	1.43	0.28
C218	-4.92	-2.43	-1.57	0.12
	(- 4.99)[a]	(- 2.86)[a]	(-1.26)*	(0.19)*
C218-F	-4.85	-2.39	-1.61	0.05
D2	-4.99	-2.91	-1.09	0.19
	(- 5.15)[b]	(- 3.20)[b]	(-1.08)*	(0.35)*
D2-F	-4.86	-2.81	-1.19	0.06
Y123	-4.87	-2.36	-1.64	0.07
	(- 5.08)[a]	(- 2.91)[a]	(-1.20)*	(0.28)*
Y123-F	-4.81	-2.34	-1.66	0.01
Y1234	-4.88	-2.82	-1.18	0.08
Y1234-F	-4.83	-2.77	-1.23	0.03

Table 6 Calculated electronic properties of isolated dyes and dye-TiO_2 complexes at CAM-B3LYP/3-21G(d) level.

| Dye | Isolated Dye | | | | Dye on $(TiO_2)_{28}$ substrate | | | | | | | | | | | | | |
	E_H (eV)	E_L (eV)	E_g (eV)	ρ (D)	E_H (eV)	E_L (eV)	E_g (eV)	ρ (D)	λ^{abs}_{max} (nm)	E_o^A (eV)	ε ($M^{-1}cm^{-1}$)	f	LHE	t (μm)	J_{SC}^{exp} (mA cm^{-2})	J_{SC}^{cal} (mA cm^{-2})	$\Gamma\hbar$ ** (eV)	τ ** (fs)	Electronic Transition
A1	-6.43	-2.02	4.41	11.00	-6.28	-3.05	3.23	38.55	592	2.09	63399	2.13	0.992	1.6	6.37[a]	5.26	0.295	2.23	H→L+12 (18%), H→L+11(17%)
A1-F	-6.30	-2.07	4.23	13.94	-6.08	-2.98	3.10	38.37	621	2.00	79440	2.73	0.998	1.6	7.52[a]	6.82	0.305	2.15	H→L+6 (28%)
C218	-6.24	-2.02	4.23	13.96	-6.05	-2.96	3.09	39.29	608	2.04	65524	2.25	0.994	4.0	14.8[b]	12.77	0.306	2.15	H→>L+7 (20%), H→L+11 (17%)
C218-F	-6.15	-2.14	4.01	15.16	-5.88	-2.99	2.89	42.45	631	1.97	78567	2.70	0.998	4.0	-	15.45	0.310	2.12	H→L+7 (21%), H→L+9 (11%)
D2	-6.25	-2.48	3.77	13.64	-6.00	-2.99	3.01	39.90	747	1.66	65744	2.26	0.994	4.0	17.0[c]	15.74	0.300	2.19	H→L+2 (29%), H→L+3 (14%), H→L+4 (23%)
D2-F	-6.16	-2.38	3.77	15.01	-5.95	-3.01	2.94	48.89	782	1.59	89751	2.96	0.998	4.0	-	21.35	0.296	2.22	H→L (29%), H→L+1 (21%)
Y123	-6.23	-2.03	4.21	14.27	-6.04	-2.96	3.08	42.56	615	2.02	71001	2.43	0.996	4.0	14.1[b]	13.83	0.303	2.17	H→L+7 (16%), H→L+10 (11%)
Y123-F	-6.19	-2.15	4.04	15.34	-5.90	-3.00	2.90	48.98	625	1.98	79400	2.73	0.998	4.0	-	15.44	0.309	2.12	H→L+7 (22%), H→L+9 (10%)
Y1234	-6.28	-2.49	3.79	14.54	-6.02	-3.01	3.01	43.84	744	1.67	66042	2.27	0.994	4.0	-	15.73	0.303	2.17	H-1→L+2 (18%), H→>L+2 (60%)
Y1234-F	-6.19	-2.40	3.79	15.16	-5.92	-3.00	2.92	49.15	748	1.66	77931	2.68	0.997	4.0	-	18.19	0.289	2.27	H-1→L+3 (10%), H→L+2 (16%), H→>L+3 (37%)

[a] See ref 44
[b] See ref 48
[c] See ref 46
** These results are obtained for the dye – TiO_2 complexes with the B3LYP/3-21g(d) level.

Table 7   Calculated E_c -E_H, E_1 and η values for ten triarylamine dyes

Dye	$E_c - E_H$ (eV)	$E_1{}^a$ (eV)	$\eta^b{}_{con}$	$\eta^c{}_{dyn}$	η^{exp}
A1	4.00	2.09	0.11	0.21	0.036[d]
A1-F	3.57	2.00	0.14	0.24	0.048[d]
C218	3.65	2.04	0.26	0.47	0.086[e]
C218-F	3.45	1.97	0.30	0.53	--
D2	3.18	1.66	0.26	0.50	0.090[f]
D2-F	2.94	1.59	0.34	0.63	--
Y123	3.65	2.02	0.28	0.50	0.098[e]
Y123-F	3.45	1.98	0.31	0.53	--
Y1234	3.23	1.67	0.26	0.51	--
Y1234-F	3.20	1.66	0.30	0.58	--

[a] optical band gap calculate by E_1 = 1240 eV/ λ, where λ absorption maximum of dye-TiO_2 complex calculated at the CAM-B3LYP/3-21G(d) level.
[b]Voc = 1 V.
[c] Voc = E_c – E_H.
[d] See ref 44
[e] See ref 48
[f] See ref 46