Solvent Effect on the Efficiency of Triphenylamine-Based Dye-Sensitized Solar Cells, Molecular Approach

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Research Article

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Solvent effect on the efficiency of triphenylamine-based dye-sensitized solar cells, molecular approach

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Abstract

In this research, dynamics, and kinetics of some metal-free organic dyes based on triphenylamine having a D- π -A type structure were investigated in the gas phase and solvent (ethanol, dichloromethane, toluene, tetrahydrofuran, chloroform, and dimethylformamide) using the quantum chemistry calculations. These structures consist of triphenylamine as the donor linked to the acceptor units of cyanoacrylic acid and benzoic acid via different π -conjugated systems. The obtained results show that TC601 dye having the ethynyl anthracene phenyl π -conjugated system has the preferred charge/hole transfer properties ($\Delta G_{inj}/\Delta G_{reg}$), which in ethanol as the solvent, the lowest values of ΔG_{inj} and ΔG_{reg} were evaluated. Molecular spectroscopic properties of the studied dyes reveal that H-P and F-P dyes have favorable molar absorption coefficients in all media. Also, the behaviors of the light-harvesting efficiency (LHE) and incident photon to current efficiency (IPCE) as the

functions of the wavelength were analyzed, which show that the presence of solvent increases the values of IPCE and LHE for most studied dyes in comparison with the gas phase. Finally, based on different analyses, TC601 as the dye and ethanol as the solvent are proposed as the preferred candidates to be applied in the DSSCs.

Keywords DSSCs; Sensitizer; Molecular design; Solvent effect; Kinetic processes; Intramolecular charge transfer

1 Introduction

The expansion of renewable energy sources is necessary due to the limited fossil fuels, the problems caused by greenhouse gas emissions, and irreparable damage to the environment [1, 2]. One of the largest sources of renewable energy is solar energy, which due to features such as huge reserves, abundant energy sources, and non-polluting has attracted a lot of attention [3, 4]. One of the safest and efficient devices for using solar energy is the solar cell, which can convert solar light into electricity based on the photovoltaic effect [5, 6]. Dye-sensitized solar cells (DSSCs) were developed by Grätzel and O'Regan in 1991 [7] which is a promising alternative to other solar cells due to its unique characteristics such as low cost in fabrication, environmentally friendly, high efficiency, flexibility, and non-toxicity [8-10]. The DSSCs device is composed of nanocrystalline semiconductors (TiO_2), fluorine-doped tin oxide (FTO), redox mediators (I^-/I_3^-), dye-based sensitizers anchored on the TiO_2 surface, and counter electrode (Pt) [11, 12]. In general, the main processes

related to DSSC including photon absorption by sensitizer, the formation of an exciton (e-h pair), and transferred to the conduction band (CB) of TiO₂. Then, injected electron to the counter electrode through the external circuit and finally reduces the electrolyte and regenerates the dye molecule [13, 14].

The sensitizer is an essential component that plays a primary role in the sunlight absorption and production of the electric charges and effects on the performance of the DSSC [15, 16]. Metal-free organic photosensitizers, which usually have a donor- π spacer-acceptor (D- π -A) architecture, show good performance in DSSC [17]. As an example of these dyes, triphenylamine-based dyes is used as an electron donor in organic structures, due to strong electron-donating nature [18]. In this compound, steric hindrance, and non-planar structure prevent undesirable aggregation of dye on the semiconductor surface. Moreover, the presence of π conjugated linkers, the ability of light-harvesting, and the low cost of triphenylamine-based dyes have made to be used in DSSC extensively [19, 20].

In addition to selecting proper and efficient dye, the use of appropriate solvents in the efficiency of solar cells is very important. According to the reports, the interaction of solvent with sensitizer affects the electronic properties, absorption spectrum, and photovoltaic processes of the solar cell and can improve the final efficiency of the cell [21, 22].

Metal-free organic dyes (L156 and L224) containing triphenylamine as the electron donor, 4-(benzo[c] [1,2,5]thiadiazol-4-yl)benzoic acid as electron acceptor and thiophene and 4,8-bis(4-hexylphenyl)benzo[1,2-b:4,5-b']dithiophene as π bridges are applied in DSSCs as photosensitizers [23]. The absorption spectra of the dyes in dichloromethane exhibited two different absorption peaks. The shorter peaks region (325–343 nm) can be assigned to the π - π^* transitions and longer peaks region (487–491 nm) according to the intramolecular charge-transfer (ICT) transitions between triphenylamine donor and the acceptor segment.

In 2021, Arslan and co-workers reported photovoltaic properties of three organic dyes having diphenylamine as electron-rich, benzene, benzothiadiazole, and N-ethylhexylbenzotriazole as auxiliary electron-withdrawing groups, quinoline as π -bridge, and cyanoacrylic acid as anchoring group [24]. Theoretical studies on these dyes show that BIM2 dye having benzothiadiazole electron acceptor represents a red shift compared to other dyes (BIM1 and BIM3) due to advanced electron acceptor group ability. Moreover, the photovoltaic properties of these compounds were evaluated in the gas phase and DMSO. According to the results, all three dyes have superior open-circuit voltage, short circuit current density, and higher efficiency in the presence of DMSO solvent in comparison with gas, which can be attributed to the interactions of the solvent-sensitizer.

Han and co-workers examined the application of different solvents such as N, N-dimethylformamide (DMF), methanol (MeOH), and tetrahydrofuran (THF) on the performance of phenothiazine-based metal-free organic dye (WY5) [25]. The results of the calculations reveal that WY5 dye has a longer lifetime, higher open-circuit voltage, short circuit current density, and molar absorption coefficient in methanol in comparison with other solvents and improves the performance of the corresponding DSSCs.

Therefore, based on the above-mentioned reports and achieving better results, the study of solvent effects on the performance of solar cells has been attracting widespread attention in recent years.

In this research, molecular engineering and the study of optoelectronic properties of metal-free organic dyes based on triphenylamine including TC201 ((E)-2-cyano-3-(4-(10-(4-(diphenylamino)phenyl)anthracene-9-yl)phenyl)acrylic acid (C₄₂H₂₈N₂O₂)), TC202 ((E)-2-cyano-3-(4-((E)-2-(10-(4-diphenylamino)phenyl)anthracene-9-yl)vinyl)phenyl)yl)vinyl)phenyl)acrylic acid) (C₄₄H₃₀N₂O₂)), TC203 ((E)-2-cyano-3-(4-((10-(4-(diphenylamino)phenyl)anthracene-9-yl)ethynyl)phenyl)acrylic acid (C₄₄H₂₈N₂O₂)), TC601 ((E)-2-cyano-3-(4-(10-((4-diphenylamino)phenyl)ethynyl)anthracene-9-yl)phenyl)acrylic acid) (C₄₄H₂₈N₂O₂)), H-P ((E)-3-(4-((E)-3-(4-((E)-4-diphenylaminostyryl)phenyl)-2-cyanoacrylic acid) (C₃₀H₂₂N₂O₂)), F-P ((E)-3-(4-((E)-4-diphenylaminostyryl)-2-fluorophenyl)-2-cyanoac

rylic acid) (C₃₀H₂₁N₂O₂F)), FF-P ((E)-3-(4-((E)-4-diphenylaminostyryl)-2,6-difluorophenyl)-2-cyanoacrylic acid) (C₃₀H₂₀N₂O₂F₂)), T-F ((E)-2-cyano-3-(5-(E-4-(diphenylamino)styryl)furan-2-yl)acrylic acid) (C₂₈H₂₀N₂O₃)) and P1B ((E)-p-(p'-(diphenylamino)styryl)benzoic acid) (C₂₇H₂₁NO₂)) were performed in different media [26-29]. The structures of the dyes contain triphenylamine as an electron-rich, cyanoacrylic acid and benzoic acid as the electron-withdrawing groups and different π -conjugated system such as anthracene phenyl, anthracene vinyl phenyl, anthracene ethynyl phenyl, ethynyl anthracene phenyl, styryl phenyl, styryl-2-fluorophenyl, styryl-2,6-difluorophenyl, styryl furan, and styryl. In addition to analysis of the electronic structure of dye in the ground state, the investigation of excited state properties of dyes, intramolecular charge transfer interactions, dynamic/kinetic of charge transfer, physical chemistry/spectroscopy properties and the efficiencies of the photosensitizers in the presence of different solvents (ethanol, dichloromethane (DCM), toluene, tetrahydrofuran (THF), chloroform and dimethylformamide (DMF)) were analyzed to provide better understanding of the function of these cells and the selection of proposed dyes as efficient sensitizers in the solar cells.

2 Theory and computational details

Density functional theory (DFT) [30] and time-dependent density functional theory (TD-DFT) [31] were applied to optimize geometries and obtain the excited

state properties of the dyes at the M06-2X/6-311++G(2d,2p) level of theory, respectively. Quantum chemistry descriptors such as the electronic chemical hardness (η_e), electronic chemical potential (μ), electrophilicity (ω), and work function (WF) were calculated through the natural bond orbitals (NBO) analysis [32]. To evaluate the effects of solvents, a conductor-like polarizable continuum (CPCM) model was applied [33, 34]. In this study, all computational works were performed by using the Gaussian 09 package [35].

One of the important parameters for describing the performance of DSSC is incident photon to current efficiency (IPCE), which is theoretically calculated by Eq. 1 [36].

$$\text{IPCE} = \text{LHE}(\lambda) \cdot \Phi_{\text{inj}} \cdot \eta_{\text{coll}} \quad (1)$$

where Φ_{inj} and η_{coll} are the net electron injection efficiency and electron collection efficiency, respectively. LHE is the light-harvesting efficiency that can be obtained from Eq. 2 [37].

$$\text{LHE} = 1 - 10^{-f} \quad (2)$$

where f is the oscillator strength that indicates the probability of electron transfer between the molecular levels. Gibbs energies of electron/hole injection ($\Delta G_{\text{inj}}/\Delta G_{\text{reg}}$) are determined from Eqs. 3 and 4, respectively [38, 39].

$$\Delta G_{\text{inj}} = E_{\text{OX(dye)}^*} - E_{\text{CB}} \quad (3)$$

$$\Delta G_{\text{reg}} = E_{\text{OX(dye)}} - E_{\text{redox(electrolyte)}} \quad (4)$$

where $E_{\text{OX(dye)}}$, $E_{\text{OX(dye)*}}$, E_{CB} , and E_{redox} are the oxidation potential of the dye in the ground state, oxidation potential of the dye in the excited state, the energy of the semiconductor conduction band (TiO_2), and redox potential of the electrolyte, respectively.

The efficiency of the sunlight-to-electricity conversion in the solar cell (η_0) can be expressed by using the open-circuit voltage (V_{OC}), short circuit current density (J_{SC}), and fill factor (FF) Eq. 5 [40].

$$\eta_0 = \frac{J_{\text{SC}} \cdot V_{\text{OC}} \cdot \text{FF}}{P_{\text{in}}} \quad (5)$$

where P_{in} is the incident power of the solar cell, which is under the standard sunlight illumination (air mass 1.5 global). J_{SC} and V_{OC} parameters are theoretically determined by Eqs. 6 and 7 [41, 42].

$$J_{\text{SC}} = \frac{\text{IPCE} \cdot P_{\text{in}} \cdot \lambda}{1240} \quad (6)$$

$$V_{\text{OC}} = \frac{E_{\text{CB}}}{q} + \frac{K_B \cdot T}{q} \ln \left(\frac{n_c}{N_{\text{CB}}} \right) - \frac{E_{\text{redox}}}{q} \quad (7)$$

where q , K_B , T , n_c , and N_{CB} denote the unit charge, the Boltzmann constant, the temperature of the solar cell, the number of electrons in the conduction band, and the accessible density of conduction band (CB) states, respectively. Also, the total current density (J) is calculated from Eq. 8 [43].

$$J = J_{\text{SC}} - J_0 (e^{qV} / (K_B T_{\text{cell}}) - 1) \quad (8)$$

where J_0 is the saturation current density and estimated according to Eq. 9 [44].

$$J_0 = 2.95 \times 10^5 \exp \left(\frac{-E_g}{K_B T_{\text{cell}}} \right) \quad (9)$$

J_0 is extremely dependent on the bandgap energy of dye (E_g). *FF* Parameter is calculated according to Eq. 10 [43].

$$FF = \frac{g_{oc} - \ln(g_{oc} - 0.72)}{(g_{oc} + 1)} \quad (10)$$

where g_{oc} is the normalized V_{OC} that can be obtained by using Eq. 11 [43].

$$g_{oc} = \frac{q \cdot V_{oc}}{K_B \cdot T} \quad (11)$$

One of the quantum chemistry reactivity indices of the solar cell is work function (WF), which is estimated from NBO data Eq. 12 [45].

$$WF = \frac{(IE + EA)}{2} \quad (12)$$

where IE ($-E_{HOMO}$) and EA ($-E_{LUMO}$) are the ionization energy and electron affinity, respectively. E_{HOMO} is the energy of the highest occupied molecular orbital and E_{LUMO} is the energy of the lowest unoccupied molecular orbital.

The rate constant of the electron injection on the dye/ TiO_2 interface (k_{inj}) is one of the main kinetic parameters of the photovoltaic processes in DSSCs, which is evaluated by Eq. 13 [46].

$$k_{inj} = \frac{\pi^{0.5}}{\hbar (\lambda K_B T)^{0.5}} |V_{RP}|^2 \exp \left[\frac{-(\Delta G_{inj} + \lambda)^2}{4\lambda K_B T} \right] \quad (13)$$

where $\hbar$ is the reduced Planck constant ($\hbar/2\pi$), λ is the reorganization energy of the system and V_{RP} is the coupling constant between the photosensitizer and TiO_2

surface, which increases in $|V_{RP}|$ leads to enhance in rate constant and improve performance of DSSC. $|V_{RP}|$ can be calculated by Eq. 14 [47].

$$|V_{RP}| = \frac{E_{HOMO} - E_{CB, TiO_2}}{2} \quad (14)$$

The rate of photon absorption for a singlet excitation in the dye (R_a^s) is estimated by Eq. 15 [48].

$$R_a^s = \frac{4 k e^2 (E_{LUMO} - E_{HOMO})^3 a_x^2}{3 c^3 \epsilon^{1.5} \hbar^4} \quad (15)$$

where e is the electronic charge, $\hbar$ is the reduced Planck's constant, ϵ is the dielectric constant of the donor component, $k = (4\pi\epsilon_0)^{-1} = 9 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$, c is the speed of light and a_x is the radius of Bohr's exciton, which can be obtained by Eq. 16 [49].

$$a_x = \frac{\alpha^2 \mu \epsilon}{(\alpha - 1)^2 \mu_x} a_0 \quad (16)$$

where α is the material-dependent constant, which indicates the ratio of Coulomb and exchange interactions between the excited electron and hole, $a_0 = 5.29 \times 10^{-11} \text{ m}$ is Bohr radius, μ and μ_x are the reduced mass of the electron in the hydrogen atom and the reduced mass of the exciton, respectively.

The singlet exciton dissociation rate (R_d^s) can be evaluated through Eq. 17 [50].

$$R_d^s = \frac{8 \pi^2}{3 \hbar^3 \epsilon^2 E_B} [E_{LUMO}^D - E_{CB}^A - E_B]^2 (\hbar \omega_g) \mu_x a_x^2 \quad (17)$$

where E_B is the electron-hole binding energy and $\omega_g (c/\lambda_{\max.})$ is the frequency of the incident phonon to the dyes.

3 Results and discussion

3.1 Photovoltaic properties and electron injection processes

Figure 1 shows the optimized geometry of the studied photosensitizers within corresponding electronic energy in the gas phase, which is performed at the M06-2X/6-311++G(2d,2p) level of theory.

Fig. 1 Optimized structures of the studied dyes in the gas phase at the M06-2X/6-311++G(2d,2p) level.

To calculate the energy levels of the frontier molecular orbitals (FMO) of the sensitizers, the NBO analysis was applied. As shown in Fig. 2, LUMO energy levels of all dyes are higher than of TiO₂ semiconductor conduction band edge, which demonstrates that the electron transfer from the dye excited state to the

semiconductor is efficient. Meanwhile, the HOMO levels of the photosensitizers are adjusted with the redox potential of iodide/triiodide electrolyte, which guarantees that the dye regeneration process is favorable and effective in all media. Therefore, the corresponding properties show that these dyes are suitable sensitizers to be applied in the DSSCs.

Fig. 2 HOMO-LUMO energy levels of the studied dyes in different phases.

To investigate the charge transfer processes in DSSCs, quantum chemistry reactivity descriptors such as the electronic chemical hardness (η_e), electronic chemical potential (μ), electrophilicity (ω), and work function (WF), Gibbs energy change of the electron injection at the dye/ TiO_2 interface (ΔG_{inj}), Gibbs energy

change of the hole injection ($\Delta G_{\text{reg.}}$), and the electron-driving force (eV_{OC}) in different media were calculated and represented in Table 1.

Table 1 Electronic chemical hardness (η_e), electronic chemical potential (μ), global electrophilicity (ω), work function (WF), Gibbs energy of the electron injection (ΔG_{inj}), Gibbs energy of the dye regeneration (ΔG_{reg}) and electron-driving force (eV_{OC}) in different media.

Dye	η_e (eV)	$-\mu$ (eV)	ω (eV)	WF (eV)	$-\Delta G_{\text{inj}}$ (eV)	$-\Delta G_{\text{reg}}$ (eV)	eV_{OC} (eV)
TC201; ethanol	4.50	4.30	2.05	4.30	0.65	1.71	1.95
TC202; ethanol	4.32	4.37	2.21	4.37	0.42	1.68	1.79
TC203; ethanol	4.19	4.47	2.38	4.47	0.25	1.72	1.62
TC601; ethanol	4.54	4.34	2.07	4.34	1.39	1.74	1.93
H-P; ethanol	4.28	4.33	2.19	4.33	0.47	1.63	1.81
F-P; ethanol	4.21	4.39	2.29	4.39	0.38	1.68	1.71
FF-P; ethanol	4.31	4.35	2.19	4.35	0.49	1.72	1.81
T-F; ethanol	4.26	4.30	2.17	4.30	0.30	1.53	1.82
P1B; ethanol	4.98	3.97	1.58	3.97	0.88	1.55	2.52
TC201; DCM	4.49	4.31	2.06	4.31	0.62	1.70	1.94
TC202; DCM	4.31	4.38	2.22	4.38	0.40	1.67	1.78
TC203; DCM	4.19	4.47	2.39	4.47	0.23	1.70	1.62
TC601; DCM	4.53	4.34	2.08	4.34	1.35	1.72	1.92
H-P; DCM	4.29	4.33	2.18	4.33	0.43	1.62	1.82
F-P; DCM	4.22	4.39	2.29	4.39	0.35	1.65	1.72
FF-P; DCM	4.33	4.35	2.19	4.35	0.46	1.66	1.81
T-F; DCM	4.26	4.30	2.17	4.30	0.26	1.52	1.83
P1B; DCM	4.99	3.96	1.57	3.96	0.85	1.53	2.53
TC201; toluene	4.46	4.33	2.10	4.33	0.63	1.69	1.90
TC202; toluene	4.28	4.39	2.26	4.39	0.41	1.66	1.74
TC203; toluene	4.17	4.49	2.41	4.49	0.21	1.70	1.60
TC601; toluene	4.48	4.36	2.11	4.36	1.36	1.72	1.88
H-P; toluene	4.32	4.32	2.16	4.32	0.43	1.62	1.84
F-P; toluene	4.27	4.40	2.26	4.40	0.35	1.67	1.74
FF-P; toluene	4.37	4.35	2.17	4.35	0.44	1.69	1.83
T-F; toluene	4.25	4.29	2.17	4.29	0.26	1.50	1.83
P1B; toluene	5.00	3.93	1.54	3.93	0.87	1.51	2.57
TC201; THF	4.49	4.31	2.07	4.31	0.62	1.70	1.94
TC202; THF	4.30	4.38	2.22	4.38	0.41	1.67	1.78
TC203; THF	4.18	4.47	2.39	4.47	0.24	1.71	1.62
TC601; THF	4.52	4.34	2.09	4.34	1.35	1.73	1.92

Table 1 (Continued)

Dye	η_e (eV)	$-\mu$ (eV)	ω (eV)	WF (eV)	$-\Delta G_{inj}$ (eV)	$-\Delta G_{reg}$ (eV)	eV_{OC} (eV)
H-P; THF	4.30	4.32	2.18	4.32	0.44	1.63	1.82
F-P; THF	4.22	4.39	2.28	4.39	0.36	1.66	1.72
FF-P; THF	4.33	4.35	2.18	4.35	0.46	1.66	1.81
T-F; THF	4.26	4.30	2.17	4.30	0.27	1.52	1.83
P1B; THF	4.99	3.96	1.57	3.96	0.86	1.53	2.54
TC201; chloroform	4.49	4.31	2.08	4.31	0.62	1.69	1.93
TC202; chloroform	4.30	4.38	2.23	4.38	0.41	1.67	1.77
TC203; chloroform	4.18	4.48	2.40	4.48	0.23	1.71	1.61
TC601; chloroform	4.51	4.35	2.10	4.35	1.35	1.73	1.91
H-P; chloroform	4.30	4.32	2.17	4.32	0.43	1.62	1.83
F-P; chloroform	4.24	4.40	2.28	4.40	0.35	1.66	1.72
FF-P; chloroform	4.34	4.35	2.18	4.35	0.45	1.67	1.82
T-F; chloroform	4.25	4.30	2.17	4.30	0.26	1.50	1.83
P1B; chloroform	4.99	3.95	1.56	3.95	0.86	1.53	2.55
TC201; DMF	4.51	4.30	2.05	4.30	0.60	1.70	1.95
TC202; DMF	4.32	4.37	2.21	4.37	0.40	1.65	1.79
TC203; DMF	4.19	4.47	2.38	4.47	0.24	1.70	1.63
TC601; DMF	4.54	4.34	2.07	4.34	1.34	1.71	1.93
H-P; DMF	4.28	4.33	2.19	4.33	0.43	1.61	1.81
F-P; DMF	4.21	4.39	2.29	4.39	0.35	1.65	1.71
FF-P; DMF	4.31	4.35	2.19	4.35	0.46	1.65	1.81
T-F; DMF	4.26	4.30	2.17	4.30	0.25	1.52	1.82
P1B; DMF	4.98	3.97	1.58	3.97	0.84	1.54	2.52
TC201; gas	4.43	4.35	2.14	4.35	0.67	1.72	1.86
TC202; gas	4.24	4.42	2.30	4.42	0.44	1.69	1.70
TC203; gas	4.16	4.51	2.44	4.51	0.27	1.74	1.57
TC601; gas	4.44	4.38	2.16	4.38	1.43	1.75	1.84
H-P; gas	4.38	4.31	2.12	4.31	0.55	1.65	1.88
F-P; gas	4.34	4.40	2.23	4.40	0.45	1.72	1.77
FF-P; gas	4.45	4.36	2.14	4.36	0.52	1.74	1.86
T-F; gas	4.25	4.28	2.16	4.28	0.39	1.56	1.84
P1B; gas	5.04	3.89	1.50	3.89	1.01	1.56	2.63

According to this Table, the values of ΔG_{inj} and ΔG_{reg} have a negative character in all studied dyes and media, which can confirm the favorable electron

transfer and dye regeneration, respectively. Among these compounds, TC601 dye has greater electron transfer from the dye to semiconductor and hole injection to the electrolyte in all media. According to the results, the theoretical trend of the $|\Delta G_{inj}|$ of the dyes in the solvents is as follows:

$$\text{TC203} < \text{T-F} < \text{F-P} < \text{TC202} < \text{H-P} < \text{FF-P} < \text{TC201} < \text{P1B} < \text{TC601}$$

Also, based on the data in Table 1, a decrement in the dye electrophilicity and less ability to electron acceptance is in agreement with increment in eV_{OC} parameter. The solvent improves the eV_{OC} character in TC201, TC202, TC203, and TC601 dyes, which can be due to the proper interaction of the dye and solvent.

Linear correlations between the global electrophilicity index, the electronic chemical potential, and work function with eV_{OC} in different media are illustrated in Fig. 3. A decrease in the absolute values of electronic chemical potential and work function reduces the system resistance to electron escaping and facilitates the electron transfer toward semiconductors. Also, the dyes having the lower electrophilicity show less tendency of electron capture, which improves electron injection and electron-driving force.

Fig. 3 Linear correlations of eV_{OC} against ω and μ .

Frontier molecular orbitals distribution of the studied dyes in different media are depicted in Fig. 4. According to this figure, the electron density distribution of the FMO of each dye is the same in different media, and the presence of various solvents does not affect this property in comparison with the gas phase. The electron density of HOMO is mainly localized on the electron donor moieties, while LUMO is delocalized over the electron acceptor parts, which facilitates charge transfer toward the anchoring groups.

Fig. 4 Distribution of the molecular orbitals of the dyes in different phases.

3.2 Kinetics of photovoltaic processes

Theoretical values of the exciton radius (a_x), electron-hole binding energy (E_B), the coupling constant of photosensitizers/ TiO_2 , (V_{RP}), charge transfer rate constant between the dye and TiO_2 surface, (k_{inj}), and the rate of the exciton formation/dissociation (R_d/R_d) in different media were calculated and represented in Table 2. Also, their possible correlation was analyzed.

According to the obtained data, TC601 dye is the preferred photosensitizer from the kinetic viewpoint in all media, due to the faster exciton formation/dissociation rate in comparison with other dyes, which may be related to

the grater electron injection rate constant, and more prominent coupling constant between the dye and TiO₂ surface. Also, all studied dyes have better kinetic properties in the gas phase in comparison with other solvents. Ethanol is the preferred solvent from these points of view. The obtained theoretical R_a/R_d trend of the photosensitizers in all media are respectively according to:

$$\text{T-F} < \text{TC203} < \text{F-P} \cong \text{H-P} \cong \text{TC202} < \text{FF-P} \cong \text{P1B} < \text{TC201} < \text{TC601}$$

and

$$\text{T-F} < \text{P1B} < \text{TC203} < \text{H-P} \cong \text{F-P} < \text{FF-P} < \text{TC202} < \text{TC201} < \text{TC601}$$

Table 2 Exciton radius (a_x), exciton binding energy (E_B), the coupling constant of photosensitizers/TiO₂, (V_{RP}), rate constant of the electron transfer at the dye/TiO₂ interface (k_{inj}) and the exciton formation/dissociation rate (R_a/R_d) in different media.

Dye	a_x (Å)	E_B (eV)	V_{RP} (eV)	k_{inj} (1/ns)	$10^{-8} R_a$ (s ⁻¹)	$10^{-49} R_d$ (s ⁻¹)
TC201; ethanol	1.91	1.25	1.28	0.05	0.16	0.79
TC202; ethanol	1.78	1.35	1.27	0.01	0.12	0.68
TC203; ethanol	1.73	1.38	1.28	0.00	0.11	0.63
TC601; ethanol	4.13	0.58	1.31	0.77	0.79	2.32
H-P; ethanol	1.74	1.37	1.23	0.02	0.12	0.64
F-P; ethanol	1.77	1.35	1.25	0.00	0.12	0.64
FF-P; ethanol	1.78	1.34	1.25	0.01	0.13	0.66
T-F; ethanol	1.53	1.56	1.22	0.00	0.09	0.51
P1B; ethanol	1.43	1.67	1.23	0.28	0.13	0.56
TC201; DCM	1.92	1.25	1.28	0.05	0.15	0.77
TC202; DCM	1.78	1.35	1.27	0.01	0.11	0.66
TC203; DCM	1.73	1.38	1.28	0.00	0.10	0.61
TC601; DCM	4.02	0.57	1.30	0.79	0.81	2.36
H-P; DCM	1.73	1.38	1.23	0.02	0.11	0.63
F-P; DCM	1.76	1.36	1.25	0.00	0.11	0.63
FF-P; DCM	1.76	1.36	1.26	0.02	0.12	0.65
T-F; DCM	1.53	1.57	1.22	0.00	0.08	0.50
P1B; DCM	1.42	1.68	1.23	0.29	0.12	0.55
TC201; toluene	1.94	1.23	1.28	0.04	0.15	0.78
TC202; toluene	1.79	1.33	1.27	0.01	0.11	0.66
TC203; toluene	1.73	1.39	1.29	0.00	0.10	0.60

Table 2 (Continued)

Dye	a_x (Å)	E_B (eV)	V_{RP} (eV)	k_{inj} (1/ns)	$10^{-8} R_a$ (s $^{-1}$)	$10^{-49} R_d$ (s $^{-1}$)
TC601; toluene	4.55	0.53	1.30	0.88	0.92	2.62
H-P; toluene	1.70	1.41	1.24	0.02	0.11	0.61
F-P; toluene	1.72	1.39	1.26	0.01	0.11	0.61
FF-P; toluene	1.72	1.39	1.27	0.01	0.12	0.63
T-F; toluene	1.53	1.57	1.21	0.01	0.08	0.50
P1B; toluene	1.40	1.70	1.22	0.35	0.12	0.55
TC201; THF	1.92	1.24	1.28	0.05	0.15	0.78
TC202; THF	1.78	1.34	1.27	0.01	0.11	0.66
TC203; THF	1.73	1.38	1.28	0.00	0.10	0.61
TC601; THF	4.25	0.56	1.30	0.81	0.82	2.40
H-P; THF	1.73	1.38	1.23	0.02	0.11	0.63
F-P; THF	1.76	1.36	1.25	0.01	0.11	0.63
FF-P; THF	1.76	1.36	1.26	0.02	0.12	0.65
T-F; THF	1.53	1.56	1.21	0.01	0.08	0.50
P1B; THF	1.42	1.68	1.23	0.29	0.12	0.55
TC201; chloroform	1.93	1.24	1.28	0.05	0.15	0.78
TC202; chloroform	1.78	1.34	1.27	0.01	0.11	0.66
TC203; chloroform	1.73	1.38	1.28	0.00	0.10	0.60
TC601; chloroform	4.33	0.55	1.30	0.83	0.85	2.46
H-P; chloroform	1.72	1.40	1.24	0.02	0.11	0.62
F-P; chloroform	1.74	1.37	1.26	0.01	0.11	0.62
FF-P; chloroform	1.75	1.37	1.26	0.01	0.12	0.64
T-F; chloroform	1.53	1.57	1.21	0.01	0.08	0.50
P1B; chloroform	1.42	1.69	1.22	0.31	0.12	0.55
TC201; DMF	1.90	1.26	1.28	0.05	0.15	0.77
TC202; DMF	1.77	1.35	1.27	0.01	0.11	0.66
TC203; DMF	1.72	1.39	1.28	0.00	0.10	0.60
TC601; DMF	4.06	0.59	1.31	0.74	0.76	2.26
H-P; DMF	1.73	1.38	1.23	0.02	0.11	0.63
F-P; DMF	1.76	1.36	1.25	0.01	0.11	0.63
FF-P; DMF	1.77	1.35	1.25	0.02	0.12	0.65
T-F; DMF	1.52	1.57	1.22	0.01	0.08	0.50
P1B; DMF	1.43	1.68	1.23	0.26	0.12	0.55
TC201; gas	2.00	1.19	1.28	0.04	0.17	0.81
TC202; gas	1.90	1.26	1.27	0.01	0.13	0.71
TC203; gas	1.83	1.30	1.29	0.00	0.12	0.66
TC601; gas	5.90	0.40	1.30	1.19	1.50	3.77
H-P; gas	1.80	1.33	1.25	0.03	0.13	0.68
F-P; gas	1.81	1.32	1.29	0.00	0.13	0.68
FF-P; gas	1.78	1.34	1.29	0.01	0.14	0.69

Table 2 (Continued)

Dye	a_x (Å)	E_B (eV)	V_{RP} (eV)	k_{inj} (1/ns)	$10^{-8} R_a$ (s ⁻¹)	$10^{-49} R_d$ (s ⁻¹)
T-F; gas	1.65	1.44	1.21	0.02	0.10	0.57
P1B; gas	1.47	1.62	1.21	0.84	0.14	0.59

Theoretical correlations of the rate of exciton formation and exciton binding energy, as well as the rate of the exciton dissociation with the exciton binding energy and exciton radius, are shown in Figs. 5a and 5b, respectively.

Based on Fig. 5a, the lower required energy to separate the electron-hole leads to faster and more favorable exciton formation. Also, according to Fig. 5b, the dyes having less exciton binding energy and higher exciton radius show the efficient exciton dissociation that results in a greater ability of the electron transfer toward semiconductor.

Fig. 5 (a) The theoretical correlation of R_d/E_B and (b) R_d/E_B and R_d/a_x .

The theoretical trend of $IPCE$ and ΔG_{inj} in different solvents is depicted in Fig. 6. According to this figure, $IPCE$ is highly dependent on ΔG_{inj} changes and TC601 dye has a higher incident photon to current conversion efficiency and lower Gibbs energy of the electron injection in comparison with other dyes in all solvents, which is due to the presence of the extended π -conjugated system in this dye.

Fig. 6 The theoretical values of the $IPCE$ and ΔG_{inj} (a) in polar solvents, ethanol, THF, and DMF; (b) in nonpolar solvents, DCM, toluene, and chloroform.

Figure 7 shows differential plots of k_{inj}/V_{RP} in different environments. Based on this figure, it is concluded that an enhancement in V_{RP} enhances the rate constant of electron injection and facilitates the electron injection from the excited photosensitizer to the semiconductor.

Fig. 7 The possible correlation of differential behaviors of k_{inj} and V_{RP} in different media.

3.3 Absorption spectra and the efficiencies of the DSSCs

To evaluate the performance of the DSSCs, spectroscopic properties including the oscillator strengths (f), vertical excitation energy (E_{0-0}), maximum wavelength (λ_{max}), light-harvesting efficiency (LHE), incident photon to current conversion efficiency ($IPCE$), and major transition configurations of the excited dyes in different media were calculated using the TD-DFT method and listed in Table S1.

Fig. 8 The simulated absorption spectra of the dyes calculated at TD-DFT/M062X/6-311++G(2d,2p) level in different media.

Considering Table S1 and simulated absorption spectra in Fig. 8, it is indicated that H-P and F-P dyes have greater values of the molar absorption coefficient in all media. This may be originated from the higher oscillator strength and a greater probability of the electronic transitions between the frontier molecular orbitals in the excited states, which indicates that an increase in the oscillator strength is higher in the solvents than in the gas phase. Therefore, solvent improves the intensity of the

absorption wavelength of the dyes. Also, TC202, TC203, F-P, and T-F dyes show a red shift in the absorption spectra in the gas phase. In addition to the mentioned dyes, H-P and FF-P dyes show a red shift in the solvent, due to a lower HOMO-LUMO gap in comparison with other dyes.

To examine more accurately the efficiency of the solar cell, the predicted behaviors of the incident photon to current conversion efficiency (*IPCE*) and the light-harvesting efficiency (*LHE*) as the functions of absorption wavelengths were theoretically analyzed and shown in Figs. 9 and 10. According to these figures, *IPCE* behavior is different in comparison with the *LHE* pattern. This behavior shows that the photosensitizer ability for incident photon absorption is not according to the capability of light conversion into the current. Also, Figs. 9 and 10 show the interaction of dye and solvent represents the sensitizer light-harvesting efficiency in both UV and Visible regions, as well as enhances the incident photon to the current conversion efficiency of the dyes in the UV region, respectively. There is only one exception in the case of TC202, TC601, and P1B dyes, where the *IPCE* values of these dyes are higher in the gas phase than in the solvents.

Fig. 9 The predicted behavior of the light-harvesting efficiency (LHE) of the dyes as the functions of the maximum wavelength in different media.

Fig. 10 The behavior of the incident photon to current conversion efficiency (IPCE) of the dyes as the functions of the maximum wavelength in different media.

3.4 Photocurrent-voltage characteristics of the DSSCs

The DSSC performance parameters of dyes such as open-circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) and solar cell efficiency (η_0) in different media were calculated and represented in Table 3 and the corresponding current-voltage (J-V) curves are depicted in Fig. 11.

Table 3 Open-circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and solar cell efficiency (η_0) in different media.

Dye	V_{oc} (V)	J_{sc} (mA.cm ⁻²)	FF	η_0 (%)	Dye	V_{oc} (V)	J_{sc} (mA.cm ⁻²)	FF	η_0 (%)
TC201; ethanol	4.07	14.65	0.96	0.57	F-P; THF	3.79	12.20	0.96	0.44
TC202; ethanol	3.89	13.47	0.96	0.50	FF-P; THF	3.90	14.92	0.96	0.56
TC203; ethanol	3.74	8.29	0.96	0.30	T-F; THF	3.81	8.91	0.96	0.33
TC601; ethanol	4.13	28.88	0.96	1.15	P1B; THF	4.57	24.87	0.96	1.10
H-P; ethanol	3.85	14.82	0.96	0.55	TC201; chloroform	4.05	14.34	0.96	0.56
F-P; ethanol	3.77	12.41	0.96	0.45	TC202; chloroform	3.86	13.06	0.96	0.48
FF-P; ethanol	3.88	15.13	0.96	0.56	TC203; chloroform	3.73	7.75	0.96	0.28
T-F; ethanol	3.81	8.94	0.96	0.33	TC601; chloroform	4.10	29.05	0.96	1.14
P1B; ethanol	4.56	24.77	0.97	1.09	H-P; chloroform	3.87	14.57	0.96	0.54
TC201; DCM	4.06	14.56	0.96	0.57	F-P; chloroform	3.80	12.01	0.96	0.44
TC202; DCM	3.88	13.25	0.96	0.49	FF-P; chloroform	3.91	14.72	0.96	0.55
TC203; DCM	3.74	7.97	0.96	0.29	T-F; chloroform	3.81	8.87	0.96	0.32
TC601; DCM	4.11	28.95	0.96	1.15	P1B; chloroform	4.57	24.95	0.96	1.10
H-P; DCM	3.86	14.60	0.96	0.54	TC201; DMF	4.07	14.79	0.96	0.58
F-P; DCM	3.78	12.12	0.96	0.44	TC202; DMF	3.89	13.37	0.96	0.50
FF-P; DCM	3.89	14.87	0.96	0.56	TC203; DMF	3.75	8.07	0.96	0.29
T-F; DCM	3.81	8.79	0.96	0.32	TC601; DMF	4.13	28.84	0.96	1.15
P1B; DCM	4.57	24.77	0.97	1.09	H-P; DMF	3.85	14.52	0.97	0.54
TC201; toluene	4.03	13.89	0.96	0.54	F-P; DMF	3.77	12.11	0.96	0.44
TC202; toluene	3.84	12.65	0.96	0.47	FF-P; DMF	3.88	14.92	0.96	0.56
TC203; toluene	3.72	7.27	0.96	0.26	T-F; DMF	3.81	8.59	0.96	0.31
TC601; toluene	4.07	29.15	0.96	1.14	P1B; DMF	4.56	24.56	0.96	1.08
H-P; toluene	3.89	14.51	0.96	0.54	TC201; gas	3.99	10.78	0.96	0.41
F-P; toluene	3.83	11.78	0.96	0.43	TC202; gas	3.81	12.59	0.96	0.46
FF-P; toluene	3.94	14.40	0.96	0.55	TC203; gas	3.71	8.66	0.96	0.31
T-F; toluene	3.80	8.97	0.96	0.33	TC601; gas	4.02	29.31	0.96	1.13
P1B; toluene	4.59	25.26	0.97	1.12	H-P; gas	3.95	17.43	0.96	0.66
TC201; THF	4.06	14.48	0.96	0.56	F-P; gas	3.91	14.45	0.96	0.54
TC202; THF	3.87	13.25	0.96	0.49	FF-P; gas	4.02	16.1	0.96	0.62
TC203; THF	3.74	8.00	0.96	0.29	T-F; gas	3.82	12.39	0.96	0.45
TC601; THF	4.11	28.99	0.96	1.15	P1B; gas	4.63	27.72	0.97	1.24
H-P; THF	3.86	14.69	0.96	0.54

Fig. 11 The simulated diagram of the voltage-current studied dyes in different media.

Theoretical data in Table 3 and Figure 11 demonstrate that P1B and TC601 dyes have the highest open-circuit voltage and short circuit current density in all media, respectively. This behavior can be explained by the stronger ability of the electron-withdrawing of the benzoic acid in P1B dye and the presence of an extended π -conjugated system in TC601 dye. Moreover, the obtained theoretical data in Table 3 reveal that the solar cell based on P1B dye is superior in terms of the fill factor and solar cell efficiency in comparison with other dyes. Also, the obtained results show

that H-P, F-P, FF-P, T-F, and P1B dyes have the highest values of V_{OC} , J_{SC} , and η_0 in the gas phase in comparison with the solvents.

The possible correlation of the solar cell efficiency and short circuit current density with *IPCE* in Fig. 12 in various phases shows that the increase in conversion efficiency is according to the short circuit current density enhancement, which improves the final efficiency of the studied DSSCs.

Fig. 12 The theoretical correlation of the *IPCE* with (a) the final efficiency and (b) short-circuit current density.

4 Conclusion

In this work, photovoltaic, kinetics, and electrical features of some metal-free triphenylamine-based dyes, containing electron-rich triphenylamine, electron-deficit

cyanoacrylic acid, and benzoic acid, and disparate π -conjugated systems were analyzed in the gas and solvent media for highly efficient DSSCs by density functional theory (DFT) and time-dependent DFT (TD-DFT) approaches. The kinetic photovoltaic properties results indicate that TC601 dye has the highest values of photon absorption rate (R_a), exciton dissociation rate (R_d), and the lowest value of the exciton binding energy (E_B) in all media. Moreover, the obtained kinetic properties are more favorable in the gas phase in comparison with solvents and among the solvents, ethanol as the preferred solvent has the proper formation/dissociation of the exciton in most dyes. Also, on the basis of the voltage-current analysis, the highest values of the open-circuit voltage and short circuit current density belong to P1B and TC601 dyes in all media, respectively. Finally, ethanol as the solvent and TC601 as the sensitizer is introduced as the best candidates for application in the DSSCs.

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Conflicts of interest

There are no conflicts of interest to declare.

Appendix A. Supplementary data

Supplementary data to this article can be found online at...

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