Exploring the effect of mono- and di-fluorinated triphentylamine-based molecules as electron

donors for dye-sensitized solar cell

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Scheme SD 1: Synthestic route of T2FC and T3FC from [1], and the accordingly proposed synthetic route for the designed dyes T26FC and T35FC.

2. COMPUTATIONAL DETAILS

2.1 Isolated dyes

The excited state lifetimes have been computed using the Einstein transition probabilities [2]:

$$\tau = \frac{c^3}{2(E_{flu})^2 f} \tag{1}$$

Where *c* is the speed of light (in a.u. c = 137.036), E_{filu} is the fluorescent energy and *f* is the oscillator strength (in a.u. unit). Note that, 1 a.u. of time = 2.419×10^{-17} sec.

A series of organic solar cell devices employing 26 polymer donor moieties having a common acceptor and different HOMO levels have been investigated [3]. Based on [3], An empirical equation to obtain the theoretical value of open-circuit voltage (V_{oc}) has been proposed. It is to be noted that the V_{oc} loss of 0.3 V indicated is empirical and the actual loss could be greater or smaller than 0.3 V. In this study, the 0.3 V is chosen to predict the trend in the V_{oc} variation among the four dyes studied and the emphasis is not on finding the exact V_{oc} values:

$$V_{oc} = \left| E_{HOMO}^{Donor(Dye)} - E_{LUMO}^{acceptor(TiO_2)} \right| - 0.3$$
⁽²⁾

 $E_{LUMO}^{acceptor(TiO_2)}$ is energy condition band -4.0 eV. To quantify the light harvesting efficiency (*LHE*), Lambert–Beer's law is used [4]:

$$LHE = 1 - 10^{-f_{max}^{abs}} \tag{3}$$

Where f_{max}^{abs} is the oscillator strength of the maximum absorption band. The driving force ΔG_{inj} of electrons injected was calculated according to the following equation [5]:

$$\Delta G_{inj} = E^{D^*} - E_{CB} \tag{4}$$

Where E^{D^*} is the oxidation potential energy of the compound in the excited state and E_{CB} is the reduction potential of the conduction band of the semiconductor surface. The oxidation potential energy is given by:

$$E^{D^*} = E^D - E \tag{5}$$

Where E^D is the oxidation potential energy of the dye in the ground state (*i.e.* $-E^D_{HOMO}$) and *E* is electronic vertical transition energy. Also, using the oxidation potential energy the driving force for dye regeneration ΔG_{reg} can be calculated as:

$$\Delta G_{reg} = E_{I_3^-/I^-} - E^D \tag{6}$$

Where $E_{I_3^-/I^-}$ is redox potential energy of I_3^-/I^- redox electrolyte (-4.8 eV) [6]. The driving force (*DF*) is calculated using the following equation [7]:

$$DF = |E^0 - \Delta E - E_{CB}| \tag{7}$$

Where ΔE is the vertical excitation energy and E^0 is the redox potential of the ground state. The redox potential is determined by the following equation:

$$E^{0} = \frac{\Delta G_{sol} - \Delta G_{NHE}}{nF} \tag{8}$$

Where *F* denotes the Faraday constant (23.06 kcal mol⁻¹ V⁻¹), *n* is the number of electrons involved in redox couple (here, n = 1), ΔG_{NHE} is Gibbs free energy change of normal hydrogen electrode,

(-4.43 eV) [8], and ΔG_{sol} is Gibbs free energy change due to the oxidation of dye in solvent (here it is DMF). It can be calculated according to the Born–Haber cycle (as shown in Scheme SD 2: Born–Haber

cycle that used to computed redox potential E^0 , reproduced from [9].

) as follows:

$$\Delta G_{sol} = \Delta G_{gas} + \Delta G_2 - \Delta G_1$$

$$\begin{bmatrix} Dye]_{gas} & \Delta G_{gas} & [Dye]^+_{gas} & + e \\ & & & & \\ & & & \\ & & & & \\ &$$

Scheme SD 2: Born–Haber cycle that used to computed redox potential E^0 , reproduced from [9]. The total electronic energies of neutral, cationic, and anionic forms of these compounds were used to compute the reorganization energy ($\lambda_{\text{hole/electon}}$), according to the following equations: [10, 11] $\lambda_{\text{hole/electon}} = \lambda^{\pm} + \lambda^o = [E^{\pm}(M) - E^{\pm}(M^{\pm})] + [E(M^{\pm}) - E(M)]$ (9)

Where, $E^{\pm}(M)$ is the energy of cation/anion with neutral structure, $E^{\pm}(M^{\pm})$ is the energy of cation/anion with cationic/anionic structure, $E(M^{\pm})$ is the energy of neutral structure at cationic/anionic state, E(M) is the energy of neutral structure.

Table SD 1: Selected optimized parameters of the ground state (S_0) in its nuetral, cationic and anionic forms (regular font) and first excited state (S_1) (bold font) in DMF solvent of the four invistigated dyes as calculated at the PCM/CAM-B3LYP/6-31G+(d) level of theory. Note: bond lengths r1, r2, and r3 are in angstrom (Å) units, bond angle θ , and dihedral angles $\varphi 1$, $\varphi 2$, and $\varphi 3$ are in degrees (°) units.

		Bond length		Bond angle	Dihedral angle		ngle	
Dye	Form	r1	r2	r3	θ	<i>φ</i> 1	φ2	φ3
T2FC	NT 1	1.465	1.454	1.442	120.34	25.94	4.38	0.35
	Neutral	1.413	1.406	1.404	121.28	3.17	1.14	0.10
	^a Δ	0.052	0.048	0.038	-0.94	22.77	3.24	0.25
	Cation	1.425	1.457	1.448	121.49	4.82	11.02	0.31
	bΔ	0.040	-0.003	0.006	-1.15	21.12	-6.64	0.04
	Anion	1.464	1.453	1.409	120.06	22.96	7.64	0.15
	bΔ	0.00	0.001	0.033	0.028	2.98	-3.26	0.20
T26FC	Novtrol	1.465	1.454	1.448	120.33	25.63	5.07	28.79
	Neutral	1.411	1.406	1.404	121.30	2.71	1.74	10.35
	aΔ	0.054	0.048	0.044	-0.97	22.92	3.33	18.44
	Cation	1.427	1.459	1.454	121.44	4.21	15.44	32.53
	bΔ	0.038	-0.005	0.006	-1.11	21.42	-10.37	-3.74
	Anion	1.464	1.452	1.411	120.09	23.24	9.85	13.60
	bΔ	0.001	0.002	0.037	0.24	2.39	-4.78	15.19
T3FC	Neutral	1.466	1.462	1.453	120.22	26.38	46.24	1.04
		1.405	1.411	1.406	121.31	7.12	27.36	1.07
	aΔ	0.061	0.051	0.047	-1.09	19.26	18.88	-0.03
	Cation	1.426	1.463	1.457	121.56	7.81	47.79	1.68
	^b Δ	0.040	-0.001	-0.004	-1.34	18.57	-1.55	-0.64
	Anion	1.466	1.462	1.416	120.00	24.62	48.37	0.26
	^b Δ	0.000	0.000	0.037	0.22	1.76	-2.13	0.78
T35FC	Neutral	1.467	1.462	1.455	120.28	26.67	49.34	0.40
	Incuttat	1.415	1.412	1.405	121.38	1.41	29.87	0.27
	aΔ	0.052	0.050	0.050	-1.10	25.26	19.47	0.13
	Cation	1.429	1.463	1.458	121.44	4.56	50.23	0.33
	^b Δ	0.038	-0.001	-0.003	-1.16	22.11	-0.89	0.07
	Anion	1.467	1.462	1.415	120.12	24.42	53.22	0.24
	bΔ	0.000	0.000	0.040	0.16	2.25	-3.88	0.16

^a $\Delta = r/\theta/\varphi$ (S₀) $- r/\theta/\varphi$ (S₁)

^b $\Delta = r/\theta/\varphi$ (neutral) – $r/\theta/\varphi$ (cationic/anionic)

Table SD 2: Maximum absorption/emission wavelengths $\lambda_{max}^{abs}/\lambda_{max}^{em}$ (nm/eV), absorption/emission oscillator
strengths (f_{abs}/f_{em}) , the Stokes shift λ_{ss} (/nm) and excited state lifetimes τ (/ns) of the four invistigated
dves as calculated at the TDCAM-B3LYP/6-31G+(d) in the gas phase.

				()	0 1				
Due	_		Absorption			2			
Dye	λ_{\max}^{abs}	f_{abs}	Assign	LHE	λ_{max}^{em}	f_{em}	Assign	Λ_{SS}	l
T2FC	411 /3.02	1.503	$H-1 \rightarrow L (31\%);$ $H \rightarrow L (57\%);$ $H \rightarrow L+1 (21\%)$	0.969	485 /2.55	1.696	H−1←L (19%); H←L (64%); H←L+1 (17%)	75	2.05
T26FC	396 /3.13	1.420	H−1→L (30%); H→L (56%); H→L+1 (25%)	0.933	482 /2.57	1.448	H−1←L (21%); H←L (63%); H←L+1 (18%)	84	2.03
T3FC	398 /3.12	1.177	H−1→L (32%); H→L (56%);	0.962	480 /2.58	1.671	H−1←L (18%); H←L (64%);	84	2.37

Table SD 3 :Photovoltaic properties and ground state oxidation potential E_{ox} , E_{ox}^* (/eV) in DMF as computed at the PCM/CAM-B3LYP/6-31G+(d) level of theory.

L			v		
Dye	V _{oc}	E_{ox}	E_{ox}^*	ΔG_{inj}	ΔG_{reg}
T2FC	2.146	6.446	3.616	-0.384	1.646
T26FC	2.160	6.460	3.540	-0.459	1.660
T3FC	2.149	6.448	3.401	-0.598	1.649
T35FC	2.173	6.473	3.402	-0.598	1.673

Table SD 4: Gibb's free energy values (/a.u.), the redox potential of the ground state E^0 , and driving force *DF* (/V) of the invistigated dyes in DMF as computed at the CAM-B3LYP/6-31G+(d) level of theory.

	<u> </u>					v
Dye	ΔG_1	ΔG_2	ΔG_{gas}	ΔG_{sol}	E^{0}	DF
T2FC	0.0232	0.068	0.236	0.281	3.240	5.499
T26FC	0.0243	0.070	0.238	0.285	3.331	4.206
T3FC	0.0240	0.068	0.235	0.278	3.132	4.016
T35FC	0.0245	0.068	0.235	0.279	3.166	4.101

Table SD 5: Reorganization energies, adiabatic and vertical ionization potentials and electron affinities, hole and electron extraction potentials, and absolute hardness (/eV) of the four investigated dyes in DMF as calculated at the PCM/CAM-B3LYP/ 6-31+G(d) level of theory.

Due		Hole tr	ansfer		· · ·	Electron	transfer	anı	ba	h	
Dye	λ_{hole}	AIP	VIP	HEP	λ_{elec}	AEA	VEA	EEP	Δλ	λ _{int}	п
T2FC	0.332	5.176	5.321	0.183	0.428	3.402	3.184	0.133	0.096	0.760	0.887
T26FC	0.322	5.186	5.326	0.184	0.560	3.422	3.131	0.136	0.238	0.882	0.882
T3FC	0.350	5.157	5.306	0.182	0.488	3.416	3.171	0.134	0.138	0.838	0.871
T35FC	0.325	5.172	5.315	0.183	0.514	3.528	3.273	0.139	0.189	0.840	0.822

 ${}^{a}\Delta\lambda = |\lambda_{hole} - \lambda_{elec}|; {}^{b}\lambda_{int} = \lambda_{hole} + \lambda_{elec}$

Table SD 6: The Fermi energies, gab energies E_g , energy condition band E_{cb} , and E_{CB} shift compared to bare (TiO2)₂₄ cluster ΔE_{CB} (in eV), and adsorption energies E_{ads} (in kcal/mol) for the adsorption systems.

		<u> </u>			N N
Isolated/system	Fermi energy	E_{g}	E_{CB}	ΔE_{CB}	E_{ads}
Clean TiO ₂	-6.656	2.950	-5.164	_	_
T2FC@TiO ₂	-4.147	0.071	-4.135	1.029	-4.197
T26FC@TiO ₂	-4.156	0.074	-4.142	1.022	-4.289
T3FC@TiO ₂	-4.234	0.067	-4.224	0.940	-8.140
T35FC@TiO ₂	-4.294	0.067	-4.285	0.879	-5.673

Table SD 7: Ti–O bond distances (/Å) and dihedral angles (/°), and adsorption energies E_{ads} (in kcal/mol) for the adsorption systems.

System	(Ti-O)1	(Ti-O)2	${}^{a}\varphi 1$	$^{\mathrm{a}}\varphi 2$	^а <i>ф</i> З	${}^{\mathrm{b}}\varphi 4$	${}^{\mathrm{b}}\varphi 5$	E _{ads}
T2FC@TiO ₂	1.994	2.097	16.11	6.28	1.00	154.00	154.55	-4.197
T26FC@TiO ₂	2.040	2.011	15.92	2.51	24.27	116.21	153.64	-4.289
T3FC@TiO ₂	2.099	2.003	21.81	39.95	2.13	172.64	128.43	-8.140
T35FC@TiO ₂	2.028	2.065	24.00	41.58	3.73	164.21	99.54	-5.673

^a Refer to **Error! Reference source not found.** for the definition of dihedral angles $\varphi 1$, $\varphi 2$, and $\varphi 3$. ^b $\varphi 4$ (Ti-O -C-C)₁; $\varphi 5$ (Ti-O -C-C)₂.



Figure SD 1: The calculated maximum absorption wavelengths (λ_{max}^{cal}) for T2FC as a representive example using different TDDFT XC-functionals and different solvation models with 6-31G+(d) basis set in gas phase and DMF solvent. Note: numbers beside bars representing the %deviation $(=\frac{(\lambda_{max}^{cal}-\lambda_{max}^{exp})}{\lambda_{max}^{exp}})$ from the experimental value $(\lambda_{max}^{exp} = 420 \text{ nm from [1]}).$



Figure SD 2: % fragment contribution to the HOMO and LUMO orbitals of the four investigated dyes in DMF solvent as calculated at the PCM/CAM-B3LYP/6-31+G(d) level of theory. Note: TPA: triphenylamine, DHO: dihydrothieno-dioxine, FP: fluorophenylene, and CA: cyanoacrylic acid.



Figure SD 3: Simulated UV–Vis absorption and emmission (a) in the gas phase, (b) in DMF as copmuted at the TDCAM-B3LYP/6-31G+(d) and PCM/TDCAM-B3LYP/6-31G+(d) levels of theory, respectively.



Figure SD 4: 3D-visualization of electron density difference map (EDDM) upon the ground state to first excited state transition as calculated in the PCM/TDCAM-B3LYP/6-31+G(d) level of theory. Note: blue cloured region indicating electron density depletion region and cyan colored region indicating electron density gaining region.



Solid view Mish view Figure SD 5: Illustration of centroids of charge (C^+/C^-) , isoconour 0.004 a.u.) of T3FC dye as a representative example.



Figure SD 6: TDOS of T26FC@TiO₂ as a representative example as calculated by $Dmol^3$ using PBE functional with DNP basis set.

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