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A new class of triphenylamine based novel sensitizers for DSSC: A comparative study of three different anchoring groups

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In this paper, we report a new class of triphenylamine based sensitizer with different anchoring groups to rationalize the effect of anchoring group on power conversion efficiency (PCE) in dye sensitized solar cells (DSSCs). The Photophysical properties of the TPACA, TPARN and TPASA sensitizers were recorded in acetonitrile solvent. DSSCs based on TiO2 photoanodes were fabricated using these dyes. Chromophore TPACA, based DSSC, containing triphenylamine as a donor group and cyanoacetic acid as an anchoring group connected by π linkage produces a maximum power conversion efficiency of 5.8%, short circuit current J_{sc} =11.92 mA cm⁻², open circuit voltage V_{oc} =0.702 V and a fill factor ff= 0.716. This enhanced efficiency of the chromophore TPACA, based DSSC, is attributed to the presence of a strong electron withdrawing cyanoacetic acid anchoring group. The electron transfer kinetics was investigated by transient absorption spectroscopy (TAS). All the three chromophores TPACA, TPARN, and TPASA were extensively studied using density functional theory (DFT) and time dependent density functional theory (TD-DFT) to correlate the effect of anchoring modification on absorption and photo conversion efficiency.

Introduction

In the past two and half decades, attention is paid towards clean renewable energy sources to overcome the scarcity of energy consumption and environmental pollution ¹. In 1991 Grätzel and O'Regan reported first ruthenium based dyesensitized solar cells (DSSCs) with power conversion efficiency (PCE) of 7.9%² and gained momentum in solar cell research² ⁶. Researchers have synthesized ruthenium based sensitizers with remarkable PCEs 7-10 but dyes incorporated in DSSCs are still strapped by various issues, such as- heavy metal toxicity ¹¹, environmental impact ¹², high cost ¹³, low molar extinction coefficients ¹³ and hectic purification process ¹⁴.

To overcome the limitations of ruthenium based sensitizers metal free organic sensitizers have been developed in recent times ¹⁵⁻¹⁸. They have the benefit of being low cost ¹⁹, ecofriendly ²⁰, with a high molar absorption coefficient ^{21,22}, tuneable spectral electrochemical properties ²³ and involve easy synthetic approach ²⁴. Generally, DSSCs are constructed with a photoanode, dye as the light absorber, and a counter electrode. The dyes constructed via sensitizers play a crucial role in obtaining PCE²⁵. An ideal sensitizer should contain a typical donor- π -acceptor chromophore with anchoring group having lowest unoccupied molecular orbital (LUMO) energy level above the conduction band of TiO₂ with efficient electron injection and highest occupied molecular orbital (HOMO) energy level below the redox potential of the electrolyte with effective dye regeneration ²⁶⁻²⁸. Some of the efficient donor moieties in DSSCs are constructed with coumarins 29,30 merocyanines 31,32 , cyanines 33 , indoles 23,34 , triphenylamines $^{12,35-38}$, triarylamine 39 , thiophenes 40 , carbazoles 41,42 , phenothiazines ^{43,44}, julolidine ⁴⁵ and phenoxazines ⁴⁶. Among these donors, triphenylamine (TPA) is extensively used in DSSCs due to their favourable electronic structures and exceptional light capturing capability ^{47,48}. TPA attached to cyanoacetic acid to form TPA-1 shows 3.3% efficiency which is lower than TPACA and TPARN^{47,48}. Zeng W et al have reported TPA based best sensitizer with an efficiency of 8.9% ⁴⁹.

Along with the electron donor moiety, the anchoring group also plays a significant role in DSSC performance $^{50-53}$. The sensitizer covalently bonded on TiO₂ surface with the help of anchoring groups shows strong coupling and good stability of device ^{54,55}. Usually, the functionalized carboxylic acid with electron withdrawing group in conjugation is used as standard accepting group 56-60. Cyanoacetic acid is usually most preferred acceptor which is being used in many sensitizers ^{40,61,62}. The other successful reported anchoring groups are rhodanine-3-acetic acid, sulfonic acid, 4-aminobenzoic acid, phosphoric acid, acid chloride, ester, and salicylic acid ^{63,64}. The

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anchoring group rhodanine-3-acetic acid has an extension of the π -conjugation, and hence it shows red shift but cyanoacetic acid favours better properties in DSSC because of its co-planarity with respect to spacer unit and good electron combination with TiO₂⁶⁵. In 2015, Adhikari et al. have demonstrated Schiff's base as superior anchoring group over cyanoacetic acid and rodhanine-3-acetic acid ³⁴. The importance of hydroxy group as a lateral anchoring group along with carboxylic group is demonstrated by Faliang Gou et al ⁶⁶. This lateral anchoring group enhances the adsorption of dye on TiO₂ which results in better charge transfer rate ⁶⁷.

In this paper, we utilized Schiff's base of 4-aminosalicylic acid for the first time as an anchoring group to explore superiority of Schiff's base over conventional anchoring groups along with utilization of hydroxy group as a lateral anchoring group. To understand the structural correlations and photovoltaic performance of different anchoring groups, we have synthesized three novel sensitizers containing triphenylamine based modified donor with chloro group suitably placed on π linker and cyanoacetic acid, rhodanine-3-acetic acid or 4amino salicylic acid as acceptor as shown in scheme-1 (SI). These moieties show better photovoltaic performance compared to the reported TPAC1 containing triphenyl amine donor group and cyanoacetic acid as anchoring group ⁶⁸. The newly synthesized molecules have been characterized by ¹H NMR, ¹³C NMR, and elemental analyses. The electronic and photo physical properties of these novel sensitizers have been studied. The HOMO and LUMO energy levels diagram have been obtained by theoretical calculation. These TPACA, TPARN, and TPASA dyes have been used for DSSC fabrication and their photovoltaic performances were investigated. TPACA (5.8%) and TPARN (5.8%) were compared with their reported analogue 2a (without Cl group on π -bridge) to establish the impact of π -linker modification on photophysical and photovoltaic properties ⁶⁹. It is important thing say in our study that the more complex conjugated structure is not essential for higher PCE, and TPACA, as well as TPARN, are perfect examples. Additional, the strategy of insertion of Cl group on π -bridge is quite successful for development of high efficient D- π -A organic TPA based sensitizers for improving J_{sc} , V_{oc} and n.

Results and discussion

Design and Synthesis of sensitizers

Scheme S1 shows our synthetic work starting from commercially available triphenylamine and the synthetic approach for the three sensitizers: **TPACA**, **TPARN**, and **TPASA**. Compound 2 was synthesized by Friedel craft acylation of triphenylamine, followed by Vilsmeier–Haack formylation. Knoevenagel condensation with cyanoacetic acid and rhodanine 3-acetic acid in the presence of piperidine or ammonium acetate resulted in the sensitizer **TPACA** (71% yield) and **TPARN** (79% yield) as products. The sensitizer **TPASA** with 65% yield (after silica gel column chromatography) was obtained after condensation with 4-aminosalicylic acid in ethanol. The detailed experimental procedure is given in experimental section.

Photophysical properties





Figure 1 a) UV Visible spectra of TPACA, TPARN and TPASA recorded in Acetonitrile (10-6M). and b) Emission spectra of TPACA, TPARN, and TPASA recorded in Acetonitrile (10-6M).

In Figure 1 the absorption and emission spectra of **TPACA**, **TPARN**, and **TPASA** in acetonitrile (2×10⁻⁶ M) is shown. **TPACA** and **TPARN** show a broad absorption peak in the range of 451-500 nm and **TPASA** shows a weak blue shifted peak in the region of 350-400nm. The bathochromic shift was observed from **TPASA**, **TPACA** and **TPARN** with a λ_{max} value of 369 nm, λ 462 nm, and 488 nm respectively. The absorption spectra of **TPARN** shows bathochromic shift which is due to the extension of the π -conjugated system and rhodanine-3-acetic acid. The sensitizer with a high molar extinction coefficient usually shows good light harvesting capability. The values of molar extinction coefficients for **TPACA**, **TPARN** and **TPASA** are 23.5x10⁴ M⁻¹ cm⁻¹, 11.8x10⁴ M⁻¹ cm⁻¹ and 7.03x10⁴ M⁻¹ cm⁻¹, respectively. The high value of molar extinction coefficient of Published on 28 May 2018. Downloaded by University of California - Santa Barbara on 28/05/2018 08:42:03

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TPACA is due to the presence of cyanoacrylic unit in the sensitizer. The emission spectra of the





sensitizer was recorded by using their λ_{max} wavelength as excitation wavelength.

In Table 1 the absorption and emission data are shown. The results clearly indicate that the sensitizers exhibit strong fluorescence maxima in the region of 484-637 nm. The sensitizer **TPACA** shows fluorescence λ_{max} value at 621 nm which is less than the **TPARN** with fluorescence λ_{max} value of 637 nm. The lowest fluorescence λ_{max} value at 484 nm is shown by **TPASA** dye. The sensitizer **TPACA** shows highest Stokes shift value at 159 nm whereas **TPASA** has the lowest Stokes shift value of 115 nm (Table S1). **TPACA** show higher value of absorption maxima (462 nm) as compared with the reported analogue (without chloro on π -bridge)⁶⁹. It has been noted that among the studied three sensitizers, **TPACA** showed the highest value of Stokes shift (Table S1).

The absorption spectra of the dyes **TPACA**, **TPARN**, and **TPASA** on TiO₂ electrode are shown in Figure 2. All sensitizers show broad absorption in 300–650 nm regions in the visible spectrum (Fig. 2). All the three sensitizers show red shifted absorption on TiO₂ films in comparison to results obtained from the acetonitrile solution, which is due to the interaction of anchoring group on the surface of titanium ion. Upon anchoring onto the TiO₂ surface, **TPACA**, **TPARN**, and **TPASA** energy absorption onset are red shifted by 48 nm, 62 nm, 42 nm, respectively, allowing the possibility to harvest light in the extended region. Band gap of TPACA, TPARN and TPASA dyes was calculated from absorption spectra and it is 2.29, 2.14 and 2.99 respectively. These spectral results motivated us to reveal the electrochemical and Spectro- electrochemical properties of **TPACA**, **TPARN** and **TPASA** sensitizers.

Electrochemical properties

We have measured the feasibility of thermodynamically allowed electron transfer from excited state dye to the conduction band of TiO_2 by photoemission yield spectrometer

(Riken Keiki, AC-3E). The measured ground state and excited state oxidation potential of the sensitizers **TPACA**, **TPARN** and **TPASA** are summarized in Table 1 and their pictorial representation about their energy diagram based on the absorption, electrochemical data are shown in Figure 3. Ground-state oxidation potential, $S^{+/0}$, values for **TPACA**, **TPARN**



Figure 3. A schematic representation of the ground and excited states oxidation potentials of TPACA, TPARN, and TPASA relative to TiO2 and triiodide.

Table 1 Photophysical and electrochemical properties of **TPACA**, **TAPRN** and **TPASA** sensitizing dyes

Dye	λ _{max} (nm) ^a	€(M ⁻ ¹ cm ⁻¹) x10 ⁴	λ _{emi} (nm) ^b	Λ _{onset} /nm ^c on TiO₂ film	(IP) ^d (eV)	<i>Е</i> ₀₋₀ (eV) ^е	S ^{+/*} (eV)
TPACA	462	23.5	621	642	-	1.99	-
TPARN	188	11.8	637	640	-	1.91	-
II ANN	-100	11.0	0.57	629	6.10	2.25	4.19
TPASA	369	7.03	484	030	- 6.18	2.25	- 3.93

^a Absorption maxima measured in acetonitrile at room temperature, ^b Emission maxima measured in acetonitrile at room temperature, ^c Absorption measured in a transparent TiO₂ film, ^d Ionization potential (IP) of absorbed dyes on the TiO₂ was determined by using the photoemission yield spectrometer, ^e $E_{a,o}$ was estimated from the absorption onset of dye loaded onto TiO₂ film.

and **TPASA** were observed at -5.78eV, -6.10eV, and -6.18eV respectively (Fig. S2-S4). These lonization potentials are sufficiently lower than the I_3/I^{-} a couple, indicating the thermodynamic electron accepting capability of the oxidized dyes from I⁻ ions in the electrolyte. The band gap energies $E_{0.0}$ of the three sensitizers are 1.99 eV (**TPACA**), 1.91 eV (**TPARN**) and 2.25eV (**TPASA**). The excited state oxidation potential, S^{+/*} levels were calculated from the expression of S^{+/*}=IP- $E_{0.0}$. The S^{+/*} of **TPACA**, **TPARN** and **TPASA** were calculated at -3.79 eV, -4.19 eV and -3.93 eV respectively. The S^{+/*} values for all three dyes are sufficiently above the conduction band edge of the TiO₂ film which indicates that excited states of these dyes are thermodynamically driven for electron injection into the conduction band edge of TiO₂.

Computational study

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The optimization of the three TPA based sensitizers in the acetonitrile solvent was carried out with the help of density functional theory, using the well-known B3LYP method ⁷⁰ with basis set 6-31G(d). B3LYP is a combination of Becke's three parameter exchange functionals (B3) ⁷¹ with the nonlocal correlation functional by Lee, Yang, and Parr (LYP) ⁷². The vibration frequency of each compound in all the solvents is computed using TD-DFT calculation at 6-31G (d) basis set was used for the



Figure 4 The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of all the three sensitizers. They were obtained at the B3LYP/6-31G(d) level in a vacuum. The corresponding HOMO-LUMO energy gap given in red.

optimization of the structure at first singlet excited state (S_1) of each sensitizer with its minimum energy geometry. Frequency computations were also carried out on the optimized geometry of the low-lying vibronically relaxed first excited state of molecules. The polarizable continuum model (PCM)^{73,74} was used for computations optimization in a solvent. The Gaussian 09⁷⁵ program was used for DFT computations.

The electronic distribution in the HOMO and LUMO levels of the all sensitizers at B3LYP/6-31G (d) level and their corresponding energy gaps are shown in Figure 4. The electron density is uniformly distributed on TPA donor group and π bridge in HOMO upon excitation in LUMO level electron cloud which shifts towards the anchoring groups resulting in an effective intra-molecular charge separation in TPACA and TPASA as compared with the TPARN (Fig. 4). The variation in the band gap of the electrochemical data and DFT calculations were due to the energy values which were calculated by employing the B3LYP/6-31G(d) level of theory. These states encompass a complex orbital contribution, beyond that of the crude HOMO-LUMO, so considering these two frontier orbitals will not provide an accurate energy gap^{76,77}. The delocalization of electron density from the HOMO to LUMO levels favours the effective injection of electrons into the conduction band of TiO₂ through the carboxyl anchoring group. The optimized geometries of all sensitizers with selected bond length and bond angles at B3LYP/6-31G (d) level are shown in Figure S1. The bond angle between the nitrogen and three phenyl rings in all molecules are near about 120°. The bond lengths between the carbon atom and chlorine atom in all sensitizers

are about 1.7 Å and the bond lengths between the spacer carbon atom and acceptor group carbon atom are about 1.3 Å and its shown in Figure S1.

The DFT calculated electronic vertical transition energy, oscillator strengths (f), maximum absorption wavelength (λ_{max}) and nature of the transitions are collected in Table S2. From Table S2, the strongest absorption peaks for all sensitizers are mainly related to the transition from the HOMO to the LUMO. Moreover, the maximum absorption wavelength of **TPARN** was remarkably red-shifted as compared to the other TPA sensitizers and the increasing order of λ_{max} is **TPASA** < **TPACA** < **TPARN**. Computationally **TPARN** shows higher absorption value than the other TPA sensitizers. Such red shift in the absorption spectra of the sensitizers is desirable for harvesting the solar spectrum.

Photovoltaic performance



Figure 5 a) J-V curves of the DSSCs sensitized with TPACA, TPARN, and TPASA, b) % IPCE spectra of the DSSCs sensitized with TPACA, TPARN, and TPASA.

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Table 2 Photovoltaic performances of TPA based sensitizers in DSSCs

Dye	TBP %	Jsc[mA]	Voc[V]	F.F.	Eff [%]	
TPACA	TBP	11.62	0.70	0.72	5.84	
	0	11.02		0.72		
TPACA	TBP	8 07	0.73	0.72	4.65	
	0.5	0.92				
TPARN	твр	12 24	0.69	0.72	5 86	
	0	12.24	0.05	0.72	5.50	
TPARN	TBP	9 11	0.69	0.72	4 57	
	0.5	5.11			4.57	
τραςα	TBP	5 19	0.62	0.73	2.34	
II ASA	0	5.15				
τραςα	TBP	4 77	0.63	0.74	2.20	
	0.5	4.77				

The *J-V* characteristics of the three sensitizers based DSSCs are displayed in Table 2 and the corresponding *J-V* curves are depicted in Figure 5a and Figure 5b.

As summarized in Table 2, a moderate short-circuit current (Jsc) of **TPACA** based DSSC was recorded with 8.92 mA cm⁻² in presence of TBP but in absence of TBP the Jsc increased up to 11.62 mA cm⁻². The V_{oc} for the **TPACA** based DSSCs declined from 0.70 V to 0.73 V with TBP addition. A similar trend in the Jsc value was observed for the DSSCs fabricated with TPARN dye. Without the addition of TBP, 12.24 mA cm⁻² of Jsc has been observed, whereas a reduced Jsc of 9.11 mA cm⁻² was observed for the TPARN with the addition of 0.5% TBP. In comparison to TPACA, the open-circuit voltage (Voc) of the TPARN showed the lowest value, with and without TBP. Addition of 0.5mM TBP enhanced Voc for all the dyes. All dyes show high fill factors (FF) between 71% and 73.5%. TPASA based DSSCs showed lowest photovoltaic performance regardless of TBP addition. The TPASA based DSSC showed Jsc of 5.19 mAcm⁻², V_{oc} of 0.62V with a fill factor of 72%. Addition of TBP reduced the Jsc to 4.77 mAcm⁻² but increased the V_{oc} from 0.62 to 0.63V. TPACA based DSSCs showed highest power conversion efficiency of 5.84%, TPARN based DSSCs showed highest PCE of 5.86% and TPASA based DSSCs showed highest PCE of 2.34% without the addition of TBP. With the addition of 0.5 mM TBP TPACA, TPARN and TPASA based DSSCs showed reduced PCE of 4.65%, 4.57%, and 2.20%, respectively. TPACA and TPARN showed better efficiency than the reported analogue (5.30%) 69.

The IPCE spectra of the fabricated DSSCs with **TPACA**, **TPARN**, and **TPASA** are shown in Figure 5b. All the fabricated DSSCs showed IPCE > 60% in the 400-700nm region. The IPCE of the **TPACA** DSSCs peaks at 80% within the 400-800nm region. Further addition of 0.05mM TBP decreased the IPCE to 70% in the same region. **TPARN** based DSSCs showed 70% IPCE in the 450-700nm region. A high onset up to 760 nm is observed for the **TPARN** DSSCs. Further addition of 0.05mM TBP reduced the IPCE to 65% in the same region and reduced the onset wavelength to 680nm. Among the fabricated DSSCs, **TPASA** DSSCs showed lowest IPCE of 70% at a narrower range (400-580nm). The IPCE spectra of all the DSSCs based on **TPACA**, TPARN, and TPASA are in accord with the decreasing order of the photovoltaic performances. TBP (4-tert-butyl-pyridine) is well recognized for its influence on inhibiting the recombination of injected electrons with I^{3-} in the electrolyte. Due to the basicity of TBP, its addition causes a negative increase in the conduction band edge of TiO₂. The aim of using TBP is to cover the TiO₂ surface between dye molecules. Previously TBP has been used to improve the performance of solar cells based on ruthenium dyes ²⁷. According to these results, both the J_{oc} values and FFs were increased significantly on addition of TBP, while JSC was slightly decreased, so efficiency of TPACA-TO and TPARN-TO dyes were more than the TPACA-T0.5 and TPARN-T0.5 dyes. The IPCE spectra in Figure 5b show differences in IPCE between the three dyes which indicates that the photocurrent action spectrum for **TPACA** is higher than the other sensitizers.

CEM and IMVS characterization

In order to understand the differences between the V_{oc} observed for the DSSCs based on **TPACA**, **TPARN** and **TPASA**, the relative conduction band positions of TiO₂ were investigated by means of charge extraction method (CEM). As shown in Figure 6, The DSSCs sensitized with **TPACA**, **TPARN** and **TPASA** showed a similar linear increase in the electron density as a function of V_{OC}, which indicates that the respective cells, regardless of the different molecular dye structures have the same conduction band edge of TiO₂. The electron lifetime (τ) in DSSCs is an essential factor to determine the charge recombination rate of injected electrons in TiO₂ with I₃⁻ in the electrolyte which is ideally correlated with the open circuit voltage (V_{OC}) of the overall device. We have measured the electron lifetime by intensity-modulated photovoltage spectroscopy (IMVS). Figure 7 plots



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Figure 7 Electron lifetime (τ) as a function of VOC for DSSCs sensitized with TPACA, TPARN, and TPASA.

the electron lifetimes (τ) of the DSSCs as a function of V_{oc}. It is clear that at a fixed V_{oc} the lifetime increases as **TPASA** < **TPARN** < **TPACA**, which is in accord with the order of increasing V_{oc} observed in the fabricated DSSCs. The longer lifetime observed for **TPACA** based DSSC compared to the lifetimes observed for **TPARN** and **TPASA**, clearly reveals that **TPACA** sensitizer sufficiently surpassed the recombination of the electrons in the TiO₂ film with I₃⁻ in the electrolyte. In **TPACA** based DSSC, the sensitizer most likely arrayed regularly and formed blocking layers on the TiO₂ surface to suppress the electron recombination. The close packing of **TPACA** dye is in well accord by the broader absorbance on the TiO₂ film compared to **TPARN** and **TPASA** dyes (Fig. 2).

Transient Absorption Study

In order to obtain efficient charge injection from π^* -orbitals from the anchoring groups of **TPACA**, **TPARN** and **TPASA** dyes to the titanium 3d-orbitals, a good overlap of these orbitals is requested. This later has a great effect on DSSC charge transfer kinetics and impact on the electrical performance. Investigating these later kinetic will give an answer to the strength of the anchoring system. For this, we adopted nanosecond laser flash photolysis (Eidenburg LP920) to investigate and collaborate the transient kinetics of waste recombination routes and dye regeneration by electrolyte among the dyes with their respective DSSC performance parameters and electronic levels. Nanosecond laser flash photolysis has become an ideal tool for investigating DSSC interfacial kinetics and has been considered as one of the crucial steps for the DSSC performance ^{9,78–80}.

The transient absorption signals, ΔOD , in Figure 8, represent either the concentration of oxidized dye sensitizer (positive ΔOD) or the concentration of the bleached ground states of the dye sensitizer (negative $\triangle OD$), (both have same decay lifetime), following electron injection from the dye to the conduction band of TiO₂. As for the fitting of the transient decay graphs, a good approach has been adopted for a quantitative comparison of the data for the different dyes, with and without electrolytes ⁸¹. We used, instead, the weighted average of logarithmic lifetimes from a biexponential fit to the data

 $log < \tau > = \sum Ailog(\tau i)$

where A_i is the fractional amplitude for each component related to excited state relaxation, recombination or dye regeneration.

The absorption decays of the inert electrolyte (Fig. 8), in acetonitrile, show half-times ($\tau_{1/2}$) of 8.8, 13.6 and 39.7 µs, implying the waste recombination kinetics of the injected charges into TiO₂ conduction band with the oxidative dyes of **TPACA**, **TPARN**, and **TPASA**, respectively. After addition of redox electrolyte, the fitting of the decays clearly led to faster dye regeneration half-times ($\tau_{1/2}$) 2.3, 3.6 and 9.7 µs. This proves efficient dye regeneration by electrolyte redox system of the above organic dyes, respectively and, thus, a good prevention of electron recombination with oxidized dyes can be achieved, allowing, thus, a good collection of photoinjected electrons into the external circuit as shown in PV performance (Table 2).

In addition, Daeneke et al. ⁸² have established that Quantitative dye regeneration (theoretical regeneration yields 99.9%) can be achieved with a driving force of 20–25 kJ mol⁻¹ ($\Delta E \approx 0.20-0.25$ V). Based on highest occupied molecular orbitals (HOMO) from Figure 3, all respective dyes present driving forces higher than 0.25 V with respect to the redox potential of I-/I₃⁻ (around -5.20 V vs vacuum). Thus, much higher driving force (more than 0.25 V vs Vacuum), even for a lower performing DSSC as for **TPASA** dye, would not necessary make a difference since above 0.25 V the dye regeneration process is diffusion controlled ⁸². Thus, lower performance measured with **TPASA** dye compared to others, would not be originated from a lower anchoring of 4-amino salicylic acid with TiO₂ but from the lower absorbance



Figure 8 Transient absorbance decay profiles obtained upon nanosecond pulsed laser excitations (bandwidth 6 ns) on mesoporous TiO2 (7 μ m) films sensitized with TPACA, TPARN and TPASA dyes at a laser excitation of 470 nm and monitored at 550-680 nm, in the presence

overlap through the visible light spectrum. In light of this later, dye regeneration times recorded in presence of electrolyte do corroborate with the driving forces and with measured respective $J_{\rm sc}$.

Experimental

Materials and Methods

All the commercial reagents and the solvents were bought from S. D. Fine Chemicals Pvt Ltd. Mumbai and used without purification. The reaction was checked by TLC using 0.25 mm silica gel 60 F254 percolated plates, which were visualized with UV light. ¹H-NMR and ¹³C-NMR spectra were recorded on VARIAN 500-MHz instrument (USA using TMS as an internal standard). The UV visible absorption spectra of the compounds were recorded on a Perkins-Elmer Lambda 25 spectrometer and emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer. Transient absorption spectra were recorded using LP920 laser flash photolysis spectrometer (Edinburg) associated with a Continuum Nd: YAG laser (Surelite; 10 Hz repetition rate; fwhm 5 ns). The dye absorption amount on TiO₂ film of 15 µm thickness was estimated to be 1.04 X 10^{-7} , 1.03 X 10^{-7} and 1.02 X 10^{-7} mol cm⁻⁷ ² for the TPACA, TPARN, and TPASA, respectively, with the three values are almost equal.

Synthesis

2.2.1. 1-(4-(Diphenylamino) phenyl) ethan-1-one (1)

A solution of acetyl chloride (4.08 mmol) in a dichloromethane (100 ml) was added drop wise to a slurry of zinc chloride (4.48 mmol) suspended in a solution of triphenylamine (4.08 mmol). After the addition was completed, the mixture was heated under reflux for 24 h. The reaction was monitored using TLC (10% ethyl acetate in hexane). After completion of the reaction, the mass was poured on cold dilute hydrochloric acid. The organic layer was separated and

washed, several times with water until neutral pH, and then dried over anhydrous sodium sulphate. The dried organic layer was evaporated on a rotary evaporator. The resulting residue was purified by column chromatography using ethyl acetate/hexane (10:90), there by affording the desired product as a yellow solid (Yield: 79%)⁸³. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.81 – 7.78 (m, 2H), 7.31 (m, 4H), 7.18 – 7.10 (m, 6H), 7.01 – 6.97 (m, 2H), 2.52 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 196.46, 152.15, 146.48, 129.87, 129.78, 129.59, 125.94, 124.61, 119.66, and 26.22.

2.2.2. (Z)-3-Chloro-3-(4-(diphenylamino) phenyl) acryl aldehyde (2)

DMF (2.11 g, 1.38 mmol) was added drop wise to (1.01 g, 1.38 mmol) POCl₃ at 0 ⁰C under nitrogen atmosphere. Compound 1 (4.0 g, 1.38 mmol) dissolved in DCM was added drop wise to POCl₃+DMF complex at room temperature. The reaction mixture was stirred at 42 ^oC for 2.0 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and poured into ice cold water. The crude product was extracted into ethyl acetate and the organic layer washed with water and dried over anhydrous sodium sulphate. After removing the solvent under reduced pressure, the residue was purified by column chromatography (eluent: toluene) to afford the yellow solid 2 (72% yield) ⁸⁴. ¹H NMR (500 MHz, CDCl₃) δ 10.20 (dd, J = 6.9, 0.5 Hz, 1H), 7.64 - 7.61 (m, 2H), 7.34 (dd, J = 8.4, 7.3 Hz, 4H), 7.17 (d, J = 8.5 Hz, 6H), 7.04 – 7.01 (m, 2H), 6.62 (d, J = 6.9 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 191.50, 152.07, 151.36, 146.33, 129.69, 128.44, 125.93, 124.81, 121.65, 120.14.

2.2.3. (2E,4Z)-5-Chloro-2-cyano-5-(4-(diphenylamino) phenyl) penta-2,4-dienoic acid (TPACA)

Two to three drops of piperidine were added to a solution of the compound 2 (0.35 g, 0.106 mmol) and cyanoacetic acid (0.089 g, 0.106 mmol) in acetonitrile (12 ml). The reaction mixture was refluxed for 9 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified bv column chromatography (dichloromethane/methanol, 95: 5) on silica gel to afford compound TPACA as a red solid (71% yield). ¹H NMR (500 MHz, DMSO) δ 13.91 (s, 1H), 8.18 (d, J = 11.6 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.39 (t, J = 7.6 Hz, 4H), 7.22 – 7.14 (m, 7H), 6.90 (d, J = 8.7 Hz, 2H). ¹³C NMR (125 MHz, DMSO) δ 163.55, 151.12, 148.75, 147.59, 146.10, 130.41, 129.91, 129.53, 129.34, 128.65, 126.83, 126.41, 125.62, 123.90, 123.11, 119.71, 117.40, 115.70, 106.67. CHN Analysis- Calculated: C, 71.91; H, 4.27; Cl, 8.84; N, 6.99; O, 7.98. Found: C, 71.94; H, 4.26; N, 6.98. MS Analysis: Calculated: 400.0979 and Found: 399.0977.

2.2.4. 2-((E)-5-((Z)-3-Chloro-3-(4-(diphenylamino) phenyl) allylidene)-4-oxo-2-thioxothiazolidin-3-yl) acetic acid (TPARN)

0.074 g (0.096 mmol) of ammonium acetate was added to a solution of compound 2 (0.32 g, 0.096 mmol) and Rhodanine-N-acetic acid (0.018 g, 0.096 mmol) in acetic acid (10 ml). The reaction mixture was refluxed for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and poured into ice water. The product filter was

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washed with water then the corresponding crude product was purified by column chromatography (dichloromethane/methanol, 95: 5) on silica gel to afford compound TPARN as a red solid (79 % yield). ¹H NMR (500 MHz, DMSO) δ 13.48 (s, 1H), 7.82 (d, J = 8.8 Hz, 2H), 7.67 (d, J = 12.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 4H), 7.20 - 7.16 (m, 3H), 7.13 (d, J = 8.4 Hz, 4H), 6.89 (d, J = 8.8 Hz, 2H), 4.68 (s, 2H). ¹³C NMR (125 MHz, DMSO) δ 192.97, 167.72, 166.29, 150.50, 146.30, 144.53, 137.55, 131.12, 130.36, 129.22, 128.77, 127.63, 126.14, 125.55, 125.36, 120.08, 118.27, 45.60. CHN Analysis- Calculated: C, 61.59; H, 3.78; Cl, 6.99; N, 5.53; O, 9.47; S, 12.65. Found: C, 61.61; H, 3.77; N, 5.54. MS Analysis: Calculated: 506.0526 and Found: 505.0527.

2.2.5. 4-(((1E,2Z)-3-Chloro-3-(4-(diphenylamino) phenyl) allylidene) amino)-2-hydroxybenzoic acid (TPASA):

The compound 2 (0.45 g, 0.135 mmol) and p-amino salicylic acid (0.208 g, 0.135 mmol) were added in ethanol (10 ml). The reaction mixture was refluxed for 6 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and poured into ice water. The product was filtered and washed with water then corresponding crude product was purified by column chromatography (ethyl acetate/hexane, 80:20) on silica gel to afford compound TPASA as a yellow solid (65% yield). ¹H NMR (500 MHz, DMSO) δ 10.10 (s, 1H), 8.21 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 7.8 Hz, 2H), 7.81 – 7.75 (m, 2H), 7.34 (t, J = 7.5 Hz, 4H), 7.24 (s, 1H), 7.12 – 7.07 (m, 7H), 7.05 (d, J = 7.8 Hz, 2H). ¹³C NMR (125 MHz, DMSO) δ 159.23, 156.05, 149.88, 148.89, 147.26, 136.96, 132.94, 130.12, 129.39, 128.68, 125.07, 124.11, 122.52, 121.49, 119.09, 115.64, 110.52. CHN Analysis- Calculated: C, 71.72; H, 4.51; Cl, 7.56; N, 5.97; O, 10.24. Found: C, 71.75; H, 4.50; N, 5.55. MS Analysis: Calculated: 468.1241 and Found: 467.1242.

Fabrication and measurement of DSSC

A double-layer TiO₂ based semiconductor photoelectrode with a thickness of 15 μ m and 0.25 cm² area was used for the preparation of the DSSCs. A 10 µm main transparent layer, a scattering layer of titania of 5 µm (particle size ~400 nm) was screen-printed on fluorine-doped tin oxide (FTO) conducting glass substrate. A Surfcom 1400A surface profiler from Tokyo Seimitsu Co. Ltd. has been used to determine the thickness of the TiO₂ film. These films were further sintered at 500°C for 1h and treated with 0.1M HCL solutions before usage. A dye solution in acetonitrile was used to coat the TiO₂ film with the respective dyes. A deoxycholic acid solution of 20mM concentration was added to the dye solution as a co-adsorbent which helped to reduce aggregation of the dye molecules on to the TiO₂ surface. The adsorption of dye was carried out by immersing the electrodes in the dye solutions for 15h at 25°C. Sandwich-type sealed cell configuration was prepared by using two electrodes for photovoltaic measurements. The TiO₂ electrode containing a monolayer of sensitizer adsorbed on the surface acts as a working electrode while platinum coated conductive glass was used as the counter electrode. A 40um thick Surlyn spacer was used for separation of the two electrodes and sealed by heating the polymer frame. The photovoltaic performances of TPACA, TPARN, and TPASA have been carried out by using the following electrolyte composition. The electrolyte 1 contained a mixture of 0.6 M dimethylpropyl-imidazolium iodide,

0.05 M I₂, 01 M Lil and 0.5 M tertbutyl pyridine in acetonitrile used for the fabrication. The current-voltage spectra have been measured under standard AM 1.5 sunlight (100 mW cm⁻², WXS-155S 10: Wacom Denso Co. Japan). The photovoltaic characteristics were measured by using the incident light of 1×10¹⁶ photons cm⁻² under 100 mW cm⁻² in direct current mode (CEP-2000BX, Bunko-Keiki).

Conclusions

Herein, we have employed novel metal-free organic sensitizers TPACA, TPARN and TPASA having TPA group as an electron donor unit and π -conjugation system but with different designed and synthesized electron anchoring groups namely: 2-cyanoacrylic acid, rhodanine-3-acetic acid, and 4-amino salicylic acid. Their electrochemical, optical properties and structural characterization were performed, and device fabrication studies were carried out. It is important to note that the absorption maximum red shifted in the order of **TPASA** < **TPACA** < **TPARN** is due to the longer π -conjugation in the TPARN due to rhodamine-3-acetic acid. The significant trend in molar extinction coefficient was observed in the order of TPASA < TPARN < TPACA, the sensitizer TPACA have a higher value of molar extinction coefficient than the other sensitizers. The photovoltaic characteristics showed that TPACA and TPARN exhibit the higher short circuit current density about 11.69 mA cm⁻² and 12.23 mA cm⁻², respectively, as compared with the TPASA. The higher power conversion efficiencies at 0% TBP of 5.84%, 5.86%, and 2.33% were obtained for TPACA, TPARN, and TPASA respectively. IMVS study shows that the electron lifetime increases as TPASA < TPARN < TPACA, which is in accord with the order of increasing V_{oc} observed in the fabricated DSSCs. The transient absorption study shows that the sensitizer regeneration times recorded in presence of electrolyte do corroborate well with the driving forces. These results show that the TPACA and TPARN are promising candidates in the development of DSSCs.

Conflicts of interest

There are no conflicts to declare.

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