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SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF TRIPHENYLAMINE BASED SENSITIZERS AND ITS INTERACTION WITH TiO₂ NANOPARTICLES

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Abstract:

Two triphenylamine based Donor- π -Acceptor (D- π -A) organic dyes (TD1 and TD2) whose structures were slightly different from one to another were synthesized. Further, their photophysical and electrochemical properties were examined and their results were presented. TD1 are more suitable material as compared to TD2 for photovoltaics, because of the presence of additional donor on triphenylamine core in TD1. Hence, the present study will pave a way for further molecular design of highly efficient organic dyes for making photovoltaic devices, particularly; dye sensitized solar cells (DSC's) in future as environmental friendly energy sources.

Keywords: donor- π -acceptor organic dyes, additional donor and dye sensitized solar cells

Introduction

As petroleum and coal are depleted, renewable energy sources have attracted increasing attention, and solar energy is considered as a good alternate for fossil fuel energy because of their potential advantages of low cost and environmental friendly aspects. Metal free organic dyes have much stronger light -harvesting ability than metal complexes (e.g., ruthenium complexes) because of their high molar extinction coefficients, ecofriendly and easily accessible spectral response (M. Marszalek et al., 2012; G. Wu et al., 2014). Donor- π bridge -acceptor (D- π -A) dye design has been successfully used in various applications, such as organic light emitting diodes (S. Y. Chen et al., 2005; P. Kochapradist 2013), non-linear optics (K. R. Yoon et al., 2007), fluorescent sensors (Y-L. Tsai et al., 2007) and photovoltaic cells (S. Roquet et al., 2006). These kinds of dyes mainly used in dye sensitized solar cells (DSC's) because of the possibility of fine tuning their optical and electrochemical properties. Additionally, organic dyes having the D- π -A architecture are considered to be one of the promising types because of their low cost, easy purification environmental friendly and widespread molecular design (A. Mishra et al., 2009).

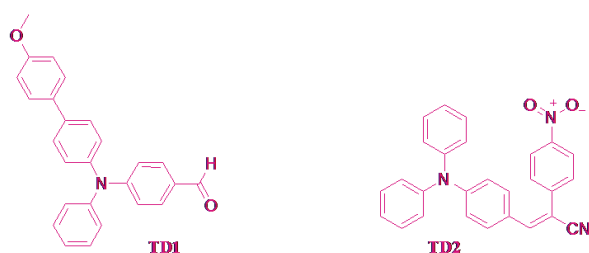
In DSC's device, light is absorbed by the dye anchored on the TiO₂ surface, and then electrons from the excited dye are injected in to the conduction band (CB) of the semiconducting TiO₂, generating an electric current. Meanwhile, the ground state of the dye is regenerated by the electrolyte to give efficient charge separation. Hence, the dye is essential in DSC's for efficient light harvesting and electron generation and transfer (Z. Ning et al., 2008). Besides, the performance of DSC's depends on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level of the relative sensitizers and the kinetics of electron transfer process (S. A. Haque et al., 2005). The HOMO of the organic dyes should be below the energy levels of the redox mediator (e.g., I⁻/I₃⁻) and the relative LUMO should be above the conduction band edge of the semiconductor (e.g., TiO₂) electrode. The electron distribution of HOMO should be mainly localized on the donor part, which further away from the semiconducting surface, and the electron distribution of the

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LUMO should be mainly localized near the anchoring group (C. Chen et al., 2012) Among donor groups, triphenylamine (TPA) derivatives have been used as sensitizers and displayed promising properties in the development of photovoltaics (N. Satoh et al., 2003 ; 2005), hence, the triphenylamine group has a tendency to reduce the aggregation on TiO₂ surface via., its non-planar structure (H. Zhang et al., 2013).

To reduce synthetic hardness, it would be useful to develop a more efficient way for π -extension to tune the absorption range of the dyes. Although TPA seems promising for extending π - conjugation effectively, hence, we focused on triphenylamine derivatives as π - spacer materials. Many researchers have reported on D-D- π -A types of metal free organic dyes based on triphenylamine (Z. Ning et al., 2008), which shows more promising characteristics as compared with the D- π -A type. These studies have suggested that the HOMO and LUMO energy level tuning of organic dyes can be achieved by attracting additional donor moieties to increasing the hole transporting ability of dyes. Moreover, these donors avoid the charge recombination process of injected electrons with the electrolyte and the formation of aggregates between the neighbor dye molecules. Besides, methoxy phenyl groups could be used as additional donor in the organic dyes due to the following reasons, 1) it has the conjugation which is advantage to the charge transfer transition from the auxiliary donor to the first electron donor (X. Chen et al., 2014); 2) charge recombination after electron injection may be retarded, due to the decrease in positive charge density at the donor by the electronic delocalization.

Herein, special consideration was given to the design of molecular structure to determine its photophysical properties, two triphenylamine based organic dyes whose structure were slightly different from one to another were synthesized and characterized by NMR spectroscopy and structures displayed in Scheme 1.



Scheme 1. Structure of the Synthesized Compounds

Materials and methods

Reagents and Materials

All the chemicals were commercially available and they were used without further purification. Spectroscopic or HPLC grade solvents were used for all spectral measurements. All the experiments were performed with ambient temperature.

TiO₂ nanoparticles were prepared, based on the reported procedure (G. Paramaguru et al., 2011) as follows, Titanium (IV) 2-propoxide (15 μ l) in 2-propanol (150 μ l) was injected 50ml of doubly distilled water (prior to experiment, pH of water adjusted to 1.5 using 1 M HClO₄) with constant stirring under nitrogen atmosphere for 8hrs.

The resulting solution of titania has a concentration of 1mM which is stable for 5-7 days. The absorption of these nanoparticles in water is observed at 330nm, and the diameter of the particles determined from the relationship between band gap and radius of quantum size particles is about 4.1nm.

Synthesis

The compound TD1 and TD2 were synthesized and the synthetic pathways are shown in Scheme 2. And Scheme 3. and characterized by NMR spectroscopy (given as supporting information)

General procedure for the synthesis of 4-Diphenylamino benzaldehyde (TPA MA) via., Vilsmeier-Haack formylation

A mixture of DMF (2 mmol) and POCl₃ (1 mmol) in 2 ml of 1, 2-dichloroethane (DCE) were allowed to cool for 0 °C and stirred for 30 minutes. To this, Triphenylamine (1 mmol) in DCE (3 ml) was added and the mixture was stirred at 100 °C for 8 hours. The mixture was quenched with ice cooled water and filtered, washed with water, dried in vacuum and the compound was purified by column chromatography (silica gel 60-120 mesh, hexane/EtOAc) (5:1 v/v) as a eluent to afford the compound (TPA MA) as a pale yellow solid. Yield: 80%, ¹H NMR (400MHz, CDCl₃): δ _H 7.01 (d, 2H, 8.8 Hz), 7.16 (q, 5H, 5.6 Hz), 7.34 (q, 4H, 15.6 Hz), 7.67 (d, 2H, 8.8 Hz), 9.81 (s, 1H)

General procedure for the synthesis of 4-[(4-Bromo-phenyl)-phenyl-amino]-benzaldehyde (TPA MA Br) via., Bromination

A mixture of acetic acid (1 mmol) and TPA MA (1 mmol) with 0.1 ml of toluene were allowed to stirred at room temperature for 7 hours. The mixture was quenched with water and extracted with EtOAc and filtered, washed with water, dried in vacuum and the compound was purified by column chromatography (silica gel 60-120 mesh, hexane/EtOAc) (5:1 v/v) as a eluent to afford the title compound TPA MA Br as a orange semi solid. Yield: 96%, ¹H NMR (400MHz, CDCl₃): δ _H 7.02 (q, 4H, 7.2 Hz), 7.18 (m, 3H), 7.34 (t, 2H, 14.8 Hz), 7.43 (q, 2H, 3.2 Hz), 7.69 (q, 2H, 7.2 Hz), 9.82 (t, 1H, 14.4Hz)

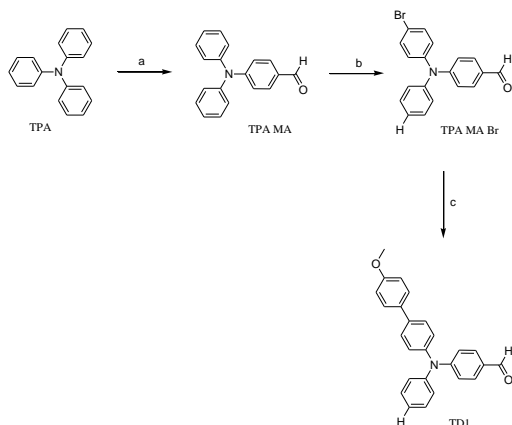
Procedure for the synthesis of 4-[(4'-Methoxy-biphenyl-4-yl)-phenyl-amino]-benzaldehyde (TD1) via., Suzuki coupling

A mixture of THF: H₂O (5:1) and TPA MA Br (1 mmol) and 4-Methoxyphenyl boronic acid (3 mmol) with Pd(PPh₃)₄ as catalyst (0.1 mmol), were allowed to stirred under nitrogen atmosphere for 2 hours. Then allowed to reflux at 90°C for 26 hours. The mixture was quenched with water and extracted with EtOAc and filtered, washed with water, dried in vacuum and the compound was purified by column chromatography (silica gel 60-120 mesh, hexane/EtOAc) (5:1 v/v) as a eluent to afford the title compound TD1 as yellow solid. Yield: 52%, mp: 210-212° C, ¹H NMR (400MHz, CDCl₃): δ _H 3.84 (d, 3H, 4.8 Hz), 6.96 (t, 2H, 17.2 Hz), 7.06 (d, 2H, 8.4 Hz), 7.19 (q, 5H, 6.8 Hz), 7.34 (q, 2H, 7.2 Hz), 7.49 (q, 4H, 4.6Hz), 7.69 (d, 2H, 8.0 Hz), 9.81 (s, 1H)

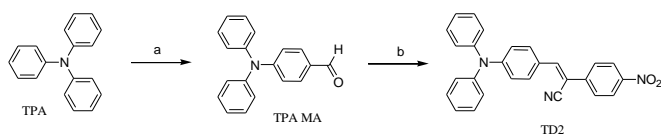
Procedure for the synthesis of 3-(4-Diphenylamino-phenyl)-2-(4-nitro-phenyl)-acrylonitrile (TD2) via., Knoevenagel condensation

A mixture of TPA MA (1 mmol) and 4-Nitrophenylacetonitrile (2 mmol) with 0.1 ml of piperidine were allowed to reflux at 90°C for 7 hours. The mixture was quenched with water and extracted with

EtOAc and filtered, washed with water, dried in vacuum and the compound was purified by column chromatography (silica gel 60-120 mesh, hexane/EtOAc) (5:1 v/v) as a eluent to afford the title compound TD2 as bright red solid. Yield: 82%, mp:184-186 ° C, $^1\text{H NMR}$ (400MHz, CDCl_3): δ_{H} 7.03 (d, 2H, 8.8 Hz), 7.16 (t, 6H, 17.2 Hz), 7.34 (t, 4H, 15.6 Hz), 7.54 (s, 1H), 7.66-7.83 (m, 4H), 8.27 (d, 2H, 8.8Hz)



Scheme 2. Synthesis of TD1 ; Regents : a) POCl_3 , DMF, DCE, 95°C, 7h, b) NBS, Acetic acid, Toluene, RT, 4h, c) 4- Methoxyphenylboronic acid, $\text{THF}:\text{H}_2\text{O}$, K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, 90°C



Scheme 3 Synthesis of TD2; Regents: a) POCl_3 , DMF, DCE, 95°C, 7h, b) 4- Nitrophenylacetonitrile, Piperidine, 110°C, 3h, CHCl_3

Instrumental techniques

$^1\text{H NMR}$ was recorded on a Bruker Avance (400 MHz) NMR spectrometer. Chloroform (CDCl_3 -d) was used as solvent and tetramethylsilane (TMS) as internal standard. Absorption spectra of the compounds were obtained using JASCO V-630 Spectrophotometer. Photoluminescence spectra were recorded using JASCO FP-6500 spectrofluorimeter. The samples were carefully degassed with pure nitrogen gas for 15 min. Quartz cells (4 X 1 X 1) with high vacuum stopcocks were used for degassing. The electrochemical properties were investigated by cyclic voltammetry (CV) by using 0.1M tetrabutylammoniumhexafluorophosphate ($n\text{-TBAPF}_6$) as supporting electrolyte in Biologic SP-50 potentiostat. The experiments were performed in CH_3CN at room temperature (1 mM concentration of the sample in which nitrogen gas was purged for 5 min.) with a three-electrode cell consisting of a platinum wire as an auxiliary electrode, a saturated Ag/AgCl reference electrode and a platinum working electrode.

Fluorescence lifetime measurements were carried out with a nanosecond time correlated single photon counting (TCSPC) spectrometer Horiba Fluorocube-01-NL lifetime system with Nano LED (pulsed diode excitation source) as the excitation source and

TBX-PS as detector. The slit width was 8 nm. The time correlated single photon counting results fit to biexponential decay, DAS6 software was used for the fit and the χ^2 values are less than 1.2 and not less than 1.

Results and discussion

Ground state interactions

The maximum absorption wavelength (λ_{abs}) of TD1 and TD2 appears at 363nm and 366nm in CHCl_3 solution respectively. There is no significant change in absorption maximum of both compounds which is due to the presence of same number of aromatic rings in the sensitizers. The observed absorption is due to the presence of localized aromatic $\pi\text{-}\pi^*$ transition (X. Chen et al., 2014). Absorption measurements were performed with TiO_2 to analyze the ground state interactions of these sensitizers. Binding between these sensitizers and TiO_2 is one of the parameter to improve DSC's efficiency. The absorption of the compounds was increased by TiO_2 at different concentrations (shown in Figure 1.).

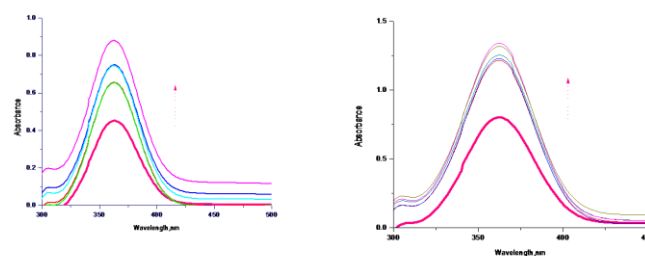


Figure 1. Absorbance spectra of TD1 and TD2 in CHCl_3 ($1 \times 10^{-6}\text{M}$) with various concentrations ($0\text{-}5 \times 10^{-5}\text{M}$) of TiO_2

Any change in the absorption spectrum reveals the ground state complex formation which facilitates static mode of quenching (C. Manivannan et al., 2013). Hence, we observed the increase in absorbance of the TD1 and TD2 during the addition of TiO_2 , which indicates the ground state complex formation between the sensitizers and TiO_2 .

Photoluminescence measurements

The emission maximum of TD1 and TD2 appears at 502nm and 515nm respectively. Interestingly, photoluminescence spectra of TD1 shows primarily one peak at 438nm and at 502nm attributed to the intramolecular charge transfer (ICT) based on auxiliary donor (methoxyphenyl group), which favor the electron injection. Moreover, the emission maximum of the TD2 was found to 515nm, which may be due to the presence of electron withdrawing $-\text{NO}_2$ group as auxochrome.

Figure 2 shows the photoluminescence spectra of the triphenylamine derivatives in CHCl_3 solution with different concentrations of TiO_2 . The fluorescence intensity of the triphenylamine derivatives was quenched by TiO_2 .

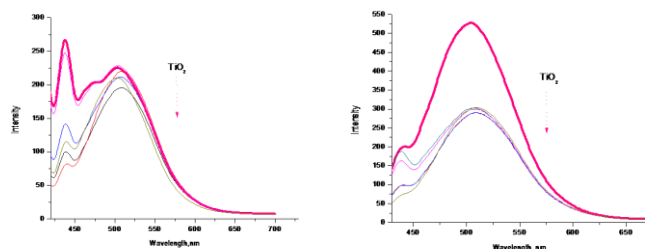


Figure 2. Photoluminescence spectra of TD1 and TD2 in CHCl_3 ($1 \times 10^{-6} \text{M}$) with various concentrations ($0-5 \times 10^{-5} \text{M}$) of TiO_2

It is interesting to discuss the mode of quenching mechanism resulting from the interaction of sensitizers with TiO_2 and the Stern–Volmer rate constant (K_{sv}) was determined using the Stern–Volmer Equation as written below,

$$I_0/I = 1 + K_{sv} [Q] = 1 + k_q \tau_0 \longrightarrow \text{(a)}$$

where I_0 is the fluorescence intensity of the fluorophore in the absence of TiO_2 , I is the fluorescence intensity in the presence of TiO_2 .

K_{sv} is the Stern –Volmer constant (Y. Zhang et al., 2009), $[Q]$ is the concentrations of TiO_2 . k_q is the bimolecular quenching rate constant, τ_0 is the lifetime of the fluorophore in the absence of quencher. The Stern –Volmer constant (K_{sv}) and bimolecular quenching rate constant (k_q) are summarized in Table 1. TD1 has high K_{sv} and k_q values as compared to that of TD2 which means, the binding interaction of TD1 is more as compared to TD2. Even though, TD2 has electron withdrawing anchoring group, it has a less tendency to bind on TiO_2 surface. This is mainly attributed to the presence of methoxyphenyl group as an auxiliary donor in TD1.

Evaluation of binding parameters

For static quenching, we can deduce the binding constants (K) because static quenching arises from the formation of ground complex between sensitizers (TD1 and TD2) and TiO_2 . Hence the binding constant deduced (H. R. Park et al., 2006) as follows, Since, the obtained bimolecular quenching rate constant (k_q) values found to be larger than the diffusion control limit; it indicates the existence of binding interaction between the sensitizers and TiO_2 nanoparticles. For static quenching, the relationship between the intensity and quencher can be described by binding constant formula, The relationship between the fluorescence intensity and the quencher concentration can be deduced from the following equation,

$$\log [(F_0-F)/F] = \log K + n \log [Q] \longrightarrow \text{(b)}$$

where, K is the binding constant of sensitizers with TiO_2 , n is the number of binding sites. The value of K was determined from the intercept of $\log [(F_0-F)/F]$ vs $\log [Q]$. The values are summarized in Table 1.

Sensitizer	$K_{sv} (\times 10^3 \text{M}^{-1})$	$k_q (\times 10^{12} \text{M}^{-1} \text{s}^{-1})$	K	n
TD1	2.747	1.301	5.674	1.5
TD2	2.155	0.471	2.204	0.51

Table 1. Stern -Volmer constant (K_{sv}), quenching rate constant (k_q) and binding constant (K)

This is because of the following considerations, 1) TD2 has no –COOH group in its anchoring part 2) the presence of –OCH₃ group on TD1 has binding capability with TiO_2 surface and also it extent the electron donating ability to the electron withdrawing aldehyde group (*via.*, triphenylamine) which has a binding ability on TiO_2 . Moreover, the correlation coefficients for both compounds were larger than 0.960, indicating that the interaction between sensitizers with TiO_2 , agrees well with the binding site model based on the binding equation mentioned above.

Fluorescence lifetime measurements

The presence of interaction between the sensitizers and TiO_2 were further characterized by time resolved fluorescence measurements (C.V. Lundgren et al., 2006). Fluorescence quenching can be due to collisional encounters between sensitizer and TiO_2 in excited state or static resulting from the formation of ground state complex between sensitizer and quencher (J.R. Lakowicz, 1983). The lifetime of TD1 and TD2 in the presence and in the absence of TiO_2 were recorded. The fluorescence lifetime of TD1 and TD2 is 2.11ns and 4.57ns respectively. The decay fitted based on bi-exponentially. The decay profile of the TD1 with TiO_2 is shown in Figure 2a.

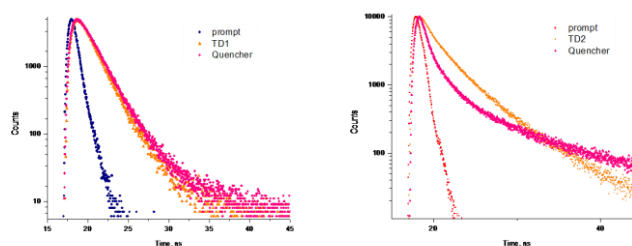


Figure 2a. Fluorescence lifetime decay profile of TD1 and TD2 ($1 \times 10^{-6} \text{M}$) with TiO_2 ($0-5 \times 10^{-5} \text{M}$)

Though the decay traces were actually plotted, however the life time remains same in both conditions (the presence and absence of TiO_2). Hence the plots looks like a single decay curve. This confirms the fluorescence quenching is static in nature (G. Paramaguru et al., 2010), which is primarily observed in UV/Visible spectral measurements.

While TD2, there is a change in lifetime decay curve, which implies dynamic in nature, but in UV/Visible studies, we observed ground state complex formation and also the quenching rate constant (k_q) was found to be beyond the collisional controlled limit. Hence, we conclude that the mode of quenching is based on static in nature.

Electrochemical properties

In order to study the possibilities of electron injection from the excited state of the sensitizers to conduction band of semiconductor and their regeneration (J. Shi et al., 2013), the oxidation potentials of the sensitizers were determined from cyclic Voltograms (in gms)

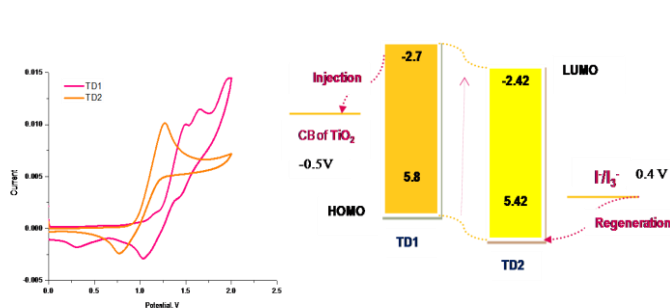


Figure 3. Cyclic voltammograms of TD1 and TD2 in CH₃CN (1X10⁻³M) and schematic energy levels of the sensitizers

The oxidation potential *vs* Ag/AgCl (E_{ox}) corresponded to the highest occupied molecular orbital (HOMO), while the reduction potential corresponded to the lowest unoccupied molecular orbital (LUMO), could be calculated from $E_{ox}-E_{0-0}$. The electrochemical properties of the sensitizers were summarized in Table 2. The quasi reversible oxidation wave was attributed to the oxidation of the triphenylamine group, and the oxidation potentials of the sensitizers TD1 and TD2 were 1.65V and 1.27V *vs* Ag/AgCl respectively. The reduction potentials (LUMO) of the two sensitizers were calculated to be -2.7V and -2.42V *vs* Ag/AgCl, which were more negative than the conduction band edge of the TiO₂ electrode (-0.5V *vs* NHE), ensuring favorable electron injection from the excited sensitizers to TiO₂. Sensitizer regeneration (X. Wang et al., 2013) was also ensured due to the more positive oxidation potentials (HOMO) of the sensitizers (5.8V and 5.42V *vs* Ag/AgCl) than that of I/I₃⁺ redox couple (~0.4V *vs* NHE).

Sensitizer	λ_{abs}^a (nm)	ϵ^a (M ⁻¹ cm ⁻¹)	λ_{em}^b (nm)	E_{ox}^c (V)	E_p^d (eV)	E_{HOMO}^e (eV)	E_{LUMO}^e (eV)
TD1	363	451700	502	1.65	3.1	5.80	-2.70
TD2	366	800000	515	1.27	3.0	5.42	-2.42

^aAbsorption spectra of the sensitizers measured in CHCl₃ and ϵ were calculated using $A=\epsilon cl$ (1X10⁻⁶M)

^bPhotoluminescence spectra of the sensitizers measured in CHCl₃ solution

^c E_{ox} were measured with 1mM solution of the sensitizer in CH₃CN with 0.1M *n*-TBAPF₆ as electrolyte (scanning rate, 50mV/s; working electrode and counter electrode, Pt electrode and Pt wire; reference electrode, Ag/AgCl) from cyclic voltametry

^dEstimated from the onset of absorption and emission spectra (1240/ λ_{onset})

^eThe HOMO and LUMO energies were determined by cyclic voltametrically *vs* Ag/AgCl with ferrocene as internal standard. $LUMO=E_{ox}-E_g$

Table 2. Optical and electrochemical properties of the sensitizers

According to the above results the two dyes are considered to have proper electronic energy levels (Figure 3.) as promising sensitizers in DSC's (J. He et al., 2014).

Feasibility of electron transfer

The fluorescence quenching of the sensitizers with TiO₂ semiconductor can be explained with the following pathways, such

as electron transfer, energy transfer, and proton transfer. Since, there is no overlap between the emission spectrum of sensitizer TD1 with absorption spectrum of TiO₂ (shown in Figure 4), which indicates the absence of energy transfer mechanism (C. Manivannan et al., 2010).TD2 shows similar behaviour

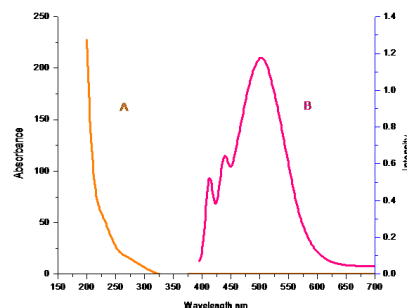


Figure 4. A) Absorbance spectra of TiO₂ and B) emission spectra of TD1 in CHCl₃ (1X10⁻⁶M)

In order to check the electron transfer mechanism, we employed the well known Rehm-Weller expression (D. Rehm et al., 1970) as follows,

$$\Delta G_{et} = E_{ox}(D) - E_{red}(A) - E^* + C \longrightarrow (c)$$

where, ΔG_{et} is the change in free energy, $E_{ox}(D)$ is the oxidation potential of the Sensitizer, $E_{red}(A)$ is the reduction potential of the quencher, E^* is the singlet excited energy of the sensitizer, C is the columbic term. We observed negative ΔG_{et} values (shown in Table 3) which indicate the thermodynamic feasibility of electron transfer (A. Kathiravan et al., 2008 ; S. Nad et al., 2006). Hence, the present study follows electron transfer mechanism.

The rate of electron transfer (k_{et}) was determined from the following equation based on the time resolved fluorescence measurements (J. He et al., 1998).

$$k_{et} = 1/\tau_{ads} - 1/\tau \longrightarrow (d)$$

Where, τ_{ads} is the lifetime of TiO₂ adsorbed fluorophore, τ is the lifetime of the sensitizer. The rate of electron transfer (k_{et}) was calculated and summarized in Table 3.

Sensitizer	$^a\Delta G_{et}$ (eV)	$^b k_{et}$ (X10 ⁸ s ⁻¹)
TD1	-1.35	1.552
TD2	-1.63	0.399

Table 3. Free energy change (ΔG_{et}) and rate of electron transfer (k_{et})

Higher value of k_{et} was observed for TD1 which implies the more electron transfer ability as compared to TD2 then, electron injection occur more feasibly to conduction band of TiO₂

Conclusions

In summary, triphenylamine based donor- π -acceptor frameworks (coded as TD1 and TD2) were synthesized and characterized by NMR spectroscopy. Synthesized compounds were studied with semiconductor TiO₂ nanoparticles and the Stern-Volmer constant (K_{sv}), bimolecular quenching rate constant (k_q) and binding constant (K) were evaluated. Feasibility of electron transfer

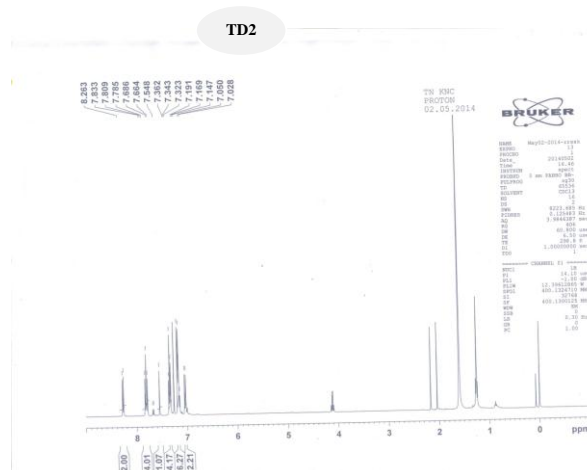
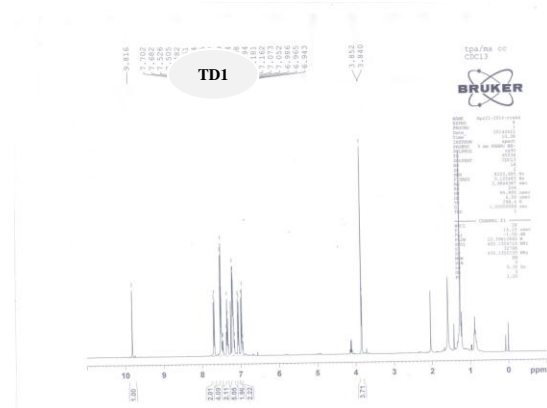
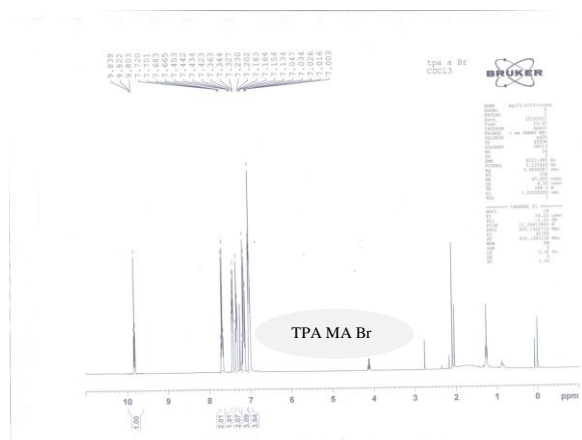
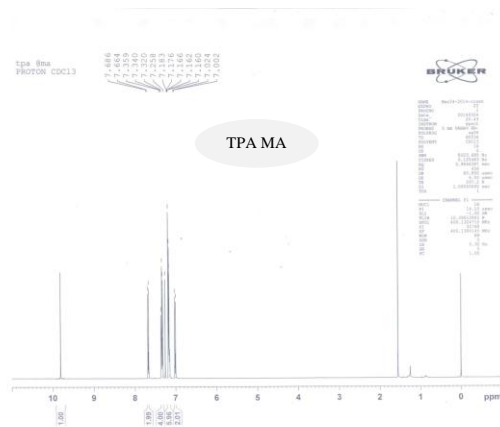
process was analyzed through Rehm-Weller expression and spectral overlap method. We obtained negative free energy change (ΔG_{et}), hence proving the electron transfer mechanism. Further the rate of electron transfer (k_{et}) was presented. The possibility of electron injection was studied *via.*, electrochemically using cyclic voltametric technique, in which we discussed the impact of electron injection and dye regeneration through the HOMO and LUMO energy levels. From the above results, TD1 has promising properties as compared with TD2, due to the additional donor presence in TD1. This contribution brings further credit to these molecular designs as efficient sensitizers for DSCs, *en route* for a cheap and less toxic substitute to ruthenium based sensitizers as potential eco-friendly energy candidates in future.

Acknowledgements

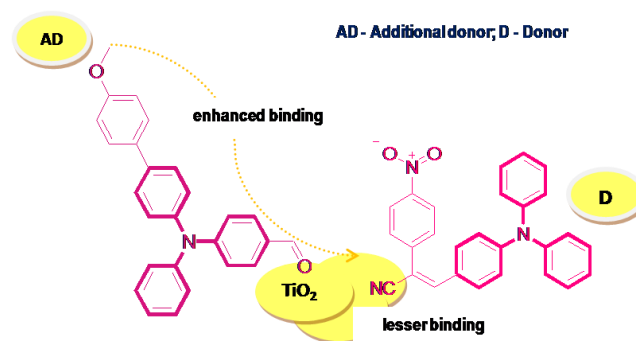
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Footnotes

^1H NMR spectra of the sensitizers and graphical abstract were included in supporting information as follows,



Graphical abstract



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