

# Ultrafast Charge Separation Dynamics of Twisted Intramolecular Charge Transfer State (TICT) in Coumarin Dye Sensitized TiO<sub>2</sub> Film: A New Route to Achieve Higher Efficient Dye-Sensitized Solar Cell

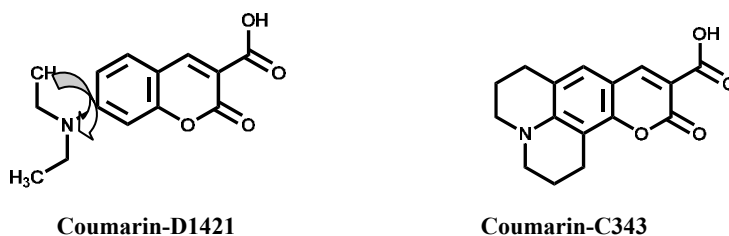
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**Abstract.** Ultrafast transient spectroscopy of 7-diethyl amino coumarin 3-carboxylic acid (D-1421) sensitized TiO<sub>2</sub> film reveals that TICT states facilitate higher charge separation and slow recombination and proved to be new route to design higher efficient solar cell.

## Introduction

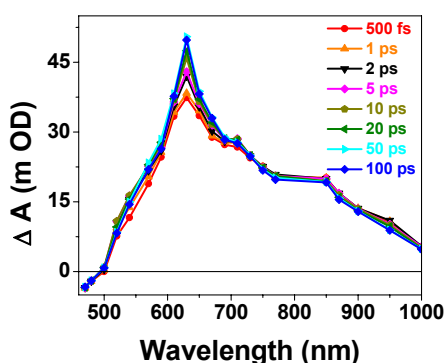
Interfacial electron transfer (ET) between molecular adsorbate and semiconductor nanoparticles is an intense area of current research work [1]. Investigations in this area are strongly motivated by both its fundamental importance and practical applications such as solar energy conversion [2]. Development of higher efficient dye-sensitized solar cell (DSSC) through designing proper sensitizing molecule is still a challenging task. It is strongly believed designing a proper sensitizer molecule can do the wonder. The photophysical properties of coumarin dyes are very sensitive towards rotational hindrance of 7-amino derivatives. The rotation of amine functionality results in excited state conformers viz. near planar and near perpendicular twisted conformers<sup>3</sup>. Photoexcitation to locally excited (LE) states leads to intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) states which depend upon rotating ability of 7-amino moiety in local environment [2]. D1421 and C343 dyes are known to form TICT and ICT excited states, respectively [3]. The rotating ability of -NEt<sub>2</sub> group stabilizes intramolecular charge separation of TICT state more than that of ICT state [4]. Thus, TICT states can be useful in achieving an efficient charge separation across dye/TiO<sub>2</sub> system. So, in order to explore the role of TICT and ICT excited state on interfacial charge separation (CS) in dye/TiO<sub>2</sub> system, femtosecond transient absorption studies has been carried out on TiO<sub>2</sub> film sensitized with D1421 and C343 dyes (Scheme 1) in acetonitrile (ACN) medium under neutral and acidic condition. The kinetic overdrive of electron injection with respect to LE→ICT/TICT internal conversion and then secondary electron donating effects of NEt<sub>2</sub> on back electron transfer (BET) reactions are addressed in present studies.



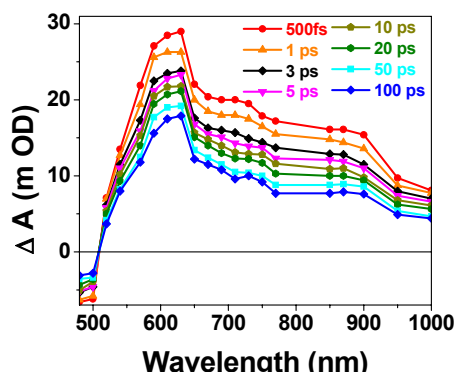
**Scheme 1:** Molecular structure of Coumarin D1421 and Coumarin 343

## Results and Discussion

Ultrafast transient absorption studies have been carried out in D-1421 and C-343 sensitized  $\text{TiO}_2$  film in acetonitrile solvent environment exciting the samples at 400 nm laser pulse and shown in Figure 1 and Figure 2 respectively. Transient spectra clearly shown absorption band at 550 nm to 700 nm regions which can be attributed to cation radical of coumarin dyes and broad absorption band at 700 nm to 1000 nm attributed to injected electron in  $\text{TiO}_2$ . The strong electronic coupling due to  $\beta$ -keto carboxylate binding of coumarin dyes on  $\text{TiO}_2$  NPs surface also known for its adiabatic electron injection process. Transient absorption studies clearly confirmed pulse width limited ( $<100\text{fs}$ ) electron injection kinetics in both C343/ $\text{TiO}_2$  and D1421/ $\text{TiO}_2$  systems. Separate ultrafast transient absorption studies [5] have been carried out for free C-343 and D-1421 system in both low polar (methyl cyclohexane) and high polar (acetonitrile) solvent, which revealed that the formation of TICT states takes place only in the excited state of D-1421. However ultrafast electron injection kinetics for both the systems establishes that the strong electronic interaction facilitates electron injection from LE states prior to  $\text{LE} \rightarrow \text{TICT}$  internal conversion. The coumarin $^{*+}$  cation of D1421 dye is then stabilized in TICT state (Scheme 2) which is evidenced by growth of 630nm TA signal in D1421/ $\text{TiO}_2$  system as compared to C343/ $\text{TiO}_2$  system (Figure 3A). Back electron transfer (BET) kinetics has been monitored by following the kinetics at both 640 nm (cation radical of coumarin) and at 1000 nm (injected electron in  $\text{TiO}_2$ ). Interestingly it has been observed much slower BET kinetics in D1421/ $\text{TiO}_2$  film (CS is 65% after 1ns) as compared to C343/ $\text{TiO}_2$  system



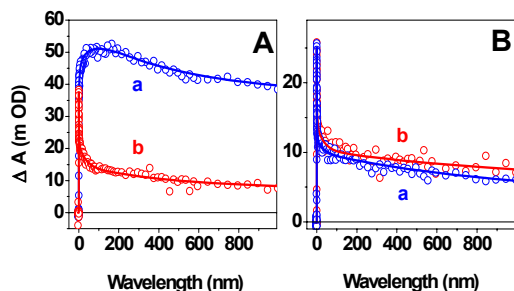
**Fig. 1.** Transient absorption spectra of D 1421 sensitized  $\text{TiO}_2$  film at different time delay after excitation at 400 nm laser light.



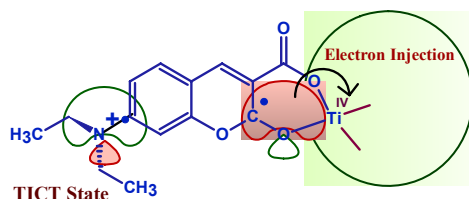
**Fig 2.** Transient absorption spectra of C-343 sensitized  $\text{TiO}_2$  film at different time delay after excitation at 400 nm laser light.

(CS is 18% after 1ns) (Figure 3A). To confirm the effect of TICT state in D-1421/ $\text{TiO}_2$  system, transient studies have been carried out in acidic condition in both the systems (Figure 3B).

Interestingly exactly similar transient kinetics has been observed in both the systems in acidic condition. In acidic condition, the protonation of  $\text{NEt}_2$  group of D1421 dye suppress the TICT state formation and both the dye comprises intrinsic ICT states only. As a result no difference in kinetics has been observed. The remarkable improvisation of BET process in D1421/ $\text{TiO}_2$  film as compared to C343/ $\text{TiO}_2$  film in ACN solvent is solely attributed to TICT behaviour of D1421 dye. Comparison of IPCE and IV characteristics of D1421/ $\text{TiO}_2$  and C343/ $\text{TiO}_2$  system clearly demonstrated that D1421 is better sensitizer for higher photocurrent and photo-voltage as compared to C-343 [5].



**Fig. 3.** Electron injection and BET kinetics monitored by coumarin $\bullet^+$  cation at 630nm in (a) D1421/ $\text{TiO}_2$  and (b) C343/ $\text{TiO}_2$  film; (A) Left Panel: ACN solvent; (B) Right Panel: ACN- $\text{HNO}_3$  solvent.



**Scheme 2:** Schematic diagram of IET process in D1421/ $\text{TiO}_2$  system.

## Conclusions

Ultrafast transient absorption spectroscopy has been carried out to study the effect of molecular structure in photoinduced electron-transfer dynamics in coumarin (D-1421 and C-343) dye-sensitized  $\text{TiO}_2$  film, where photoexcited D-1421 molecule exhibits TICT state. Electron injection dynamics found to pulse-width limited in both cases however back ET reaction found to be much slower in D-1421/ $\text{TiO}_2$  system as compared to that in D-1421/ $\text{TiO}_2$  system. On protonation both the systems show exactly same BET dynamics which clearly suggest that TICT state of D-1421 is responsible for higher electron injection yield and slower back ET reaction. This observation is also reflected in IPCE and IV characteristics of the above systems.

## References

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