# Intermittent Single Molecule Electron Transfer Dynamics

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- **What is Single molecule spectroscopy (SMS)?**
  To detect one single molecule and record its spectroscopy
- **Why SMS?**
  SMS removes ensemble average :
  **(1)** allowing the exploration of hidden heterogeneity in complex condensed phases
  **(2)** direct observation of dynamical state changes
- **How SMS?**
  (1)Dilute sample (typically $10^{-9}$~$10^{-12}$ M)
  diffraction limit: Spot Size = 1.22 λ /N.A.
  (2)High spatial resolution (e.g. 1.2<NA, 40x<Magnification)
  (3)Sufficiently high SNR (by using filters with high OD)
  (4)Fine step stage and data processing

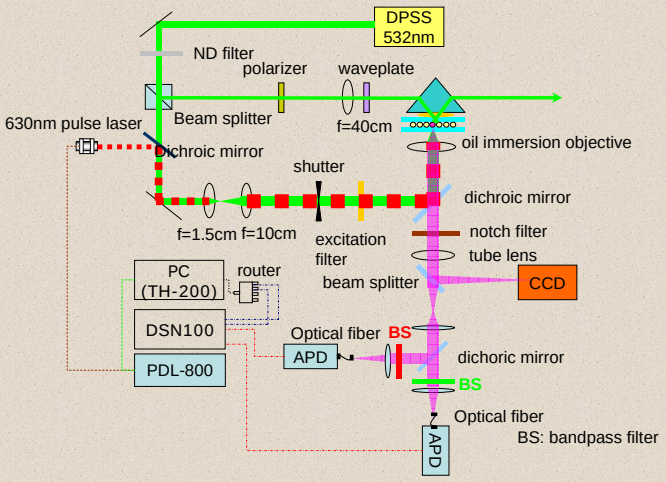


**Fig.1 System schematic diagram**

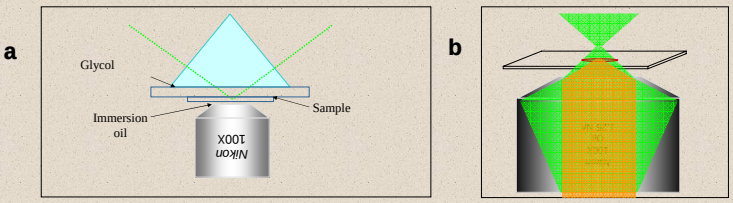


**Fig.2 (a) Prism type TIR and (b) Epi-fluorescence geometry**

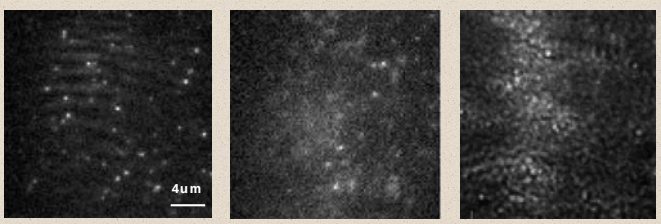


**Fig3. Image of (a)$10^{-10}$ M Cy5 single molecules on coverslip (b) 5x$10^{-11}$M Oxazine 1 on coverslip (c) 5x$10^{-11}$M Oxazine 1 on $TiO_2$ nanoparticle (NP) coated cover coverslip**

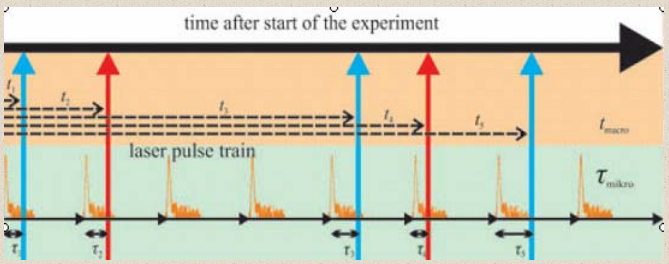


**Fig4. TTTR measurements differ from traditional TCSPC in that both the start-stop time (time between excitation pulse and single photon emission, $\tau_i$ ) and the absolute arrival time (time since the start of experiment, $t_i$ ) of each photon are measured.**

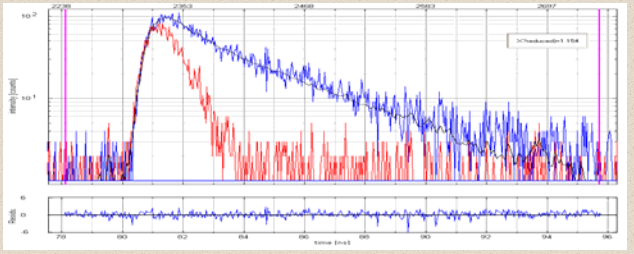

**Fig 5 Fluorescence decay of single Oxazine1 molecule dispersed on $TiO_2$ NP coated cover coverslip**

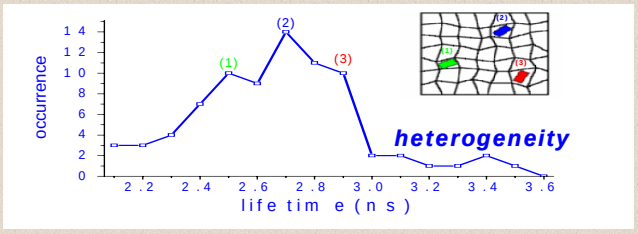


**Fig 6 Distribution of single molecule radiative lifetime for 80 different oxazine 1 molecules dispersed on TiO2 NP coated cover coverslip**

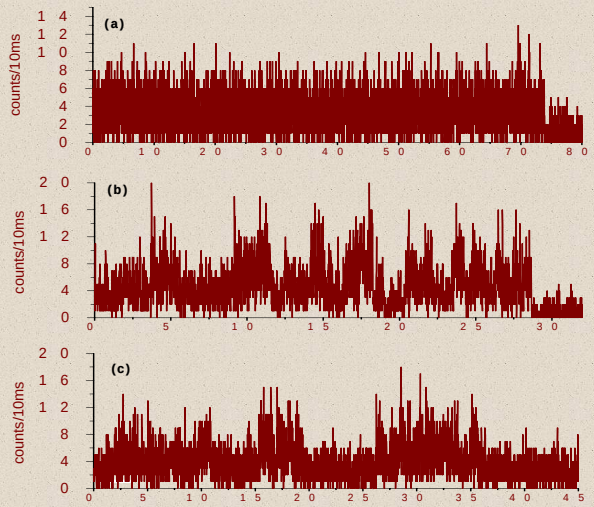


**Fig7. Fluorescence intensity trajectories of Oxazine 1 spin-coated dye solutions (0.1nM) on coverslips or on $TiO_2$ NP coated cover coverslips: (a) trajectory of Oxazine in the absence of $TiO_2$ NP; (b) and (c) trajectory of Oxazine in the presence of $TiO_2$ NP**

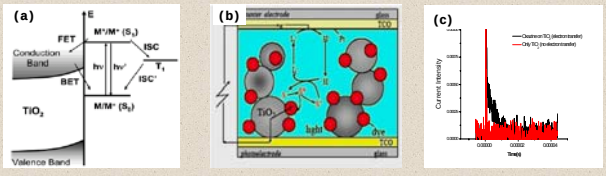


**Fig 8. (a) Schematic presentation of a model of photoinduced processes in a dye-sensitized $TiO_2$ system (b) principle of operation of dye-sensitized solar cell (c) current intensity trajectory of DSSC excited by 630nm pulse laser.**

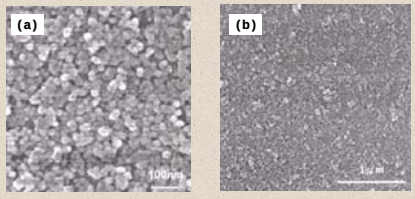


**Fig9. SEM images of $TiO_2$ NP with particle sizes ~20nm**

## Conclusions

**We report on single-molecule studies of photosensitized interfacial electron transfer (ET) processes in Oxazine1-TiO2 NP systems, using time-correlated single-photon counting coupled with confocal fluorescence microscopy. Fluorescence intensity trajectories of individual dye molecules adsorbed on $TiO_2$ NP surface showed fluorescence fluctuations and blinking, with time constants ranged from several milliseconds to seconds. Such fluctuations are attributed to discrete electron transfer events.**