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Interfacial Charge Transfer Events of BODIPY Molecules: Single Molecule Spectroelectrochemistry and Substrate Effects

Jia Liu[a], Caleb M. Hill[a], Shanlin Pan[a*] and Haiying Liu[b]

Corresponding Author: span1@bama.ua.edu

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Abstract

We present single molecule fluorescence and spectroelectrochemistry characteristics of 4, 4′-difluoro-4-bora-3a, 4a-diaza-s-indacene (BODIPY) dye bearing two carboxylic acid groups at its 2 and 6 positions. Our study shows a heterogeneous half redox potential distribution for the BODIPY molecules embedded in polystyrene film due to the heterogeneity in their charge transfer rates. Single molecules adsorbed onto a TiO_2 surface with ordered nanostructures show surprising fluorescence emission with the shortest ON duration time in comparison to bare glass and indium-tin oxide (ITO) surfaces. Single molecule stability tests show longer ON duration time and stable fluorescence feature when dispersed in polystyrene thin film than molecules exposed to air. Shorter ON times are observed for molecules coated onto ITO in comparison to glass substrate. Such decrease in their fluorescence stability or intensity is explained by charge transfer activities from the dye molecules to metal oxide surface. Electron transfer and back transfer rates are calculated to illustrate the substrate effects by using a well-established model.

1. Introduction

Precise and accurate determination of interfacial charge transfer events with ultrasensitive methods with high spectral and spatial resolution are highly desirable for providing insight into designing improved optoelectronic devices (e.g., light-emitting diode, fuel cell, solar cell, and batteries). It is unpractical to use traditional electrochemical methods to achieve such high accurate and precise electrochemical measurement. Signal amplification methods (e.g., catalytic redox reaction[1] and electroluminescence[2]) are usually applied to improving detection sensitivity in electrochemical measurements. Single molecule electrochemistry has been demonstrated by trapping the redox molecules in a small environment to increase the turnover rate at a nanoelectrode in a confined geometry for appreciable Faradaic current.[3, 4] This signal amplification method is often with poor temporal and spatial resolutions and also limited by the reproducibility of the nanoelectrode fabrication; no spectroscopic information of the redox species can be obtained to fully address the structure-function relationship at the nanoelectrode in an electrochemical environment.

Progresses made in resolving single molecules and single nanoparticles events using optical methods hold the promise of resolving photophysical and redox processes at the nanometer scale.[5] For example, single-molecule spectroelectrochemistry (SMS-EC) has been developed by Barbara and co-workers[6-8] for studying redox events of single molecules of intrinsically fluorescent organic polymer poly (9, 9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly [2-methoxy-5-(2-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV). This technology is based on single molecule fluorescence imaging technique with fluorescence characteristics modulated by charge transfer events for studying single molecule electrochemistry indirectly. SMS-EC has the capability of measuring redox properties of single molecules based on their fluorescence quenching without being obscured by non-specific redox reactions and double-layer charging effect. Interfacial charge transfer and catalytic activities of individual nanoparticles can also be studied using SMS-EC. For example, Chen and co-workers demonstrated the heterogeneous reaction pathways and catalytic dynamics of single catalytic nanoparticles using this combined electrochemical and optical spectroscopic methods.[9, 10] Singlet oxygen radical generation at photocatalyst surface such as TiO_2[11] and interfacial charge transfer dynamics of a porphyrin complex of zinc[12] have been recently studied with this technique.

BODIPY dyes are of great interests for dye sensitized solar cells (DSSCs) and can be used as molecule probe for sensing molecule recognition events because of their high extinction coefficients (> 80,000 $cm^{-1}M^{-1}$) and resistance to photobleaching.[13-16] Recently, we studied the photoelectrochemical characteristics and interfacial charge transfer dynamics of two (4, 4′-difluoro-4-bora-3a, 4a-diaza-s-indacene) BODIPY dyes attached to nanostructured TiO_2 electrodes.[17] The performance of DSSC was found to be dependent on the link molecules and hole-transport redox mediators. Transient absorption spectroscopy results suggests that interfacial charge transfer dynamics of the DSSC are highly dependent on how the BODIPY dyes are linked onto TiO_2 surface. Such charge transfer processes are yet to be studied at single molecule level to uncover the charge transfer mechanism at the nanometer scale.

Herein, we present single molecule fluorescence and spectroelectrochemistry studies of one of the BODIPY dyes bearing two carboxylic acid groups at its 2 and 6 positions on various substrates, including a TiO_2 nanostructured surface onto which this dye can covalently bond. Their blinking dynamics on various surfaces in air and coated with polystyrene are studied. Spectroelectrochemistry of single molecules in a real electrochemical cell suggests heterogeneous redox reaction characteristics of BODIPY dye at the nanometer scale.

2. Experimental

2.1 Materials

KOH, hydrochloric acid, ethanol, dimethylformamide (DMF) and acetonitrile were purchased from Fisher Scientific Corporation. Acetone was purchased from EMD Chemicals. Chloroform, titanium tetraisopropoxide and $LiCl_4$ were purchased from Sigma-Aldrich Corporation. P123 surfactant was purchased from BASF SE.

2.2 SMS-EC

Single molecule fluorescence was collected using a 100× oil-immersion objective (NA = 1.3) of an inverted optical microscope (Olympus IX-71) coupled with an electron-multiplying charge-coupled device (EM-CCD) camera (Andor, 512 x 512, 16 um, BV, 10MHz, 100C EX, South Windsor, CT). A 488 nm self-contained Argon-ion Laser (Edmund Optics Inc., Barrington, NJ) was used to excited the molecules and their emitted fluorescence was collected with the same objective and passed through a 500 nm long pass filter (Z488LP, Chroma Technology, Brattleboro, VT) and a 488 nm notch filter (Edmund Optics Inc., Barrington, NJ). Laser intensity used was 238.96W/cm^2. Same laser was used in single molecule fluorescence of BODIPY on different substrates. For spectroelectrochemistry study of single molecule BODIPY, we used a 0.15 mm thick ITO glass slide (Rs=50 Ω/□, SPI suppliers) as working electrode attached to the bottom of a Teflon cell. A bipotentiostat (CHI 760) was used for controlling the potential of the ITO substrate. The electrolyte used in the electrochemical cell was 0.1M $LiClO_4$ in MeCN. ITO glass was the working electrode. Pt wire was used as the counter electrode and Ag wire as the quasi-reference electrode (QRE). We calibrated the QRE with a standard calomel electrode (SCE) electrode in the same electrolyte solution and then converted all potentials to be versus a normal hydrogen electrode (NHE).

2.3 Preparation of Single BODIPY Molecule on ITO Glass

ITO glass was sequentially sonicated in 25.0 g/L acetone solution of KOH, DI water, acetone and DI water. ITO glass was then treated with UV-O_3 (UV/Ozone procleaner, Bioforce nanosciences) after drying with nitrogen stream. 1.0 nM chloroform solution of BODIPY-1 with or without 0.01% polystyrene was spin-casted on cleaned glass or ITO glass.

2.4 Preparation of Single Molecule BODIPY-1 on Ordered TiO_2 Substrates

Ordered TiO_2 substrates are synthesized using a previously reported method.[18] The preparation of spin-cast solution was done in the glove box, namely oxygen-free environment. Concentrated hydrochloric acid (35.5 wt%, 0.74g) was added into titanium tetraisopropoxide (1.05g) under vigorous stirring. After 10 min, this hydrolyzed solution was slowly added into an ethanol solution (3g) of P123 (0.2 g) and the mixture was stirred for another 15 min. The precursor solution was then spin-casted on cleaned glass slides. These spin-casted glass slides were then aged at -20 °C for at least 12 hours (overnight). After aging, the glass slides were heated at a ramp rate of 1 °C/min to 400 °C and kept at this temperature for 4 hours to generate ordered TiO_2 substrates on them. Before using, those TiO_2 substrates were put under UV-O_3 for 20 min. 1nM chloroform solution of BODIPY-1 with or without 0.01% w/w polystyrene were spin-casted on precursor ordered TiO_2 substrates.

2.5 Preparation of Self-assembled BODIPY-1 on Ordered TiO_2 Substrates

Precursor ordered TiO_2 substrates on glass slides were dipped in DMF containing 1.0 nM BODIPY dye for 2.5 hours, and then rinsed with DMF to remove excess BODIPY molecules that were not chemically bonded on TiO_2. Some of those TiO_2 substrates after self-assembling were spin-casted with 0.5% w/w chloroform of polystyrene to ensure that single molecules are embedded in the polystyrene.

2.6 Fluorescence lifetime measurements

The fluorescence lifetime experiment set-up has been described in a previous paper[19]. We used spin-casted samples with high concentration solution (1 mM $CHCl_3$ solution of BODIPY) on various substrates and self-assemble samples on TiO_2 with high concentration solution (1mM DMF solution of BODIPY) for the fluorescence lifetime measurements. 450 nm pulse laser was used as an excitation source.

2.7 Data analysis programs

The data analysis software was developed in MATLAB. Typically, the data was input as Tagged-Image File Format (TIFF) image stack. Every frame of the image stack was first summed to create a "Raw" image. Gradient and Laplacian images were then computed from the Raw image. The Raw, Gradient, and Laplacian images were mixed to generate a composite image which best resolves individual molecules. Upon setting an appropriate threshold, the active pixels were grouped together into "spots", each representing a single molecule. Fluorescence trajectories for single molecules were then extracted by adding the intensities for each pixel in a given spot on a frame-by-frame basis. For each trajectory, blinking statistics were obtained by setting an intensity threshold and counting the time spent above and below for each "on"/"off" event. Thresholds were determined by the histogram of the measured intensity vs. occurrence graph as shown by Figure 4A.

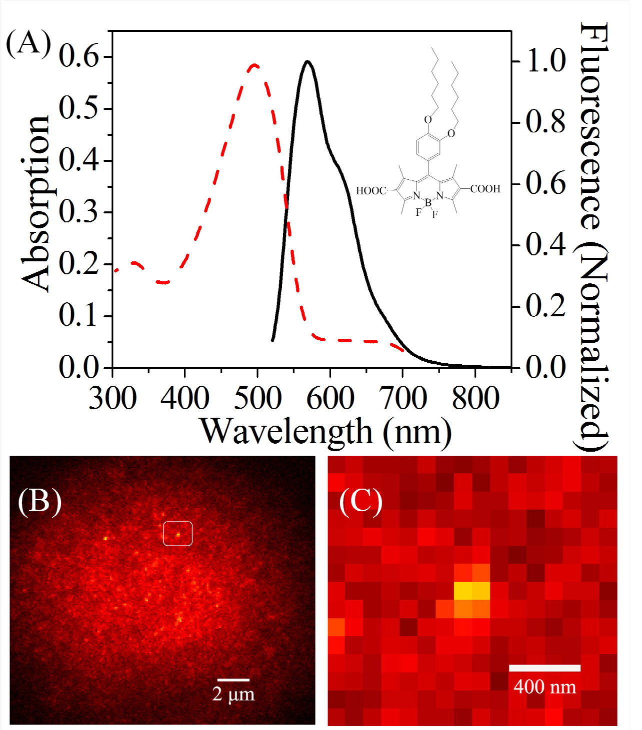

Fig. 1 (A) Absorption and fluorescence spectra of the BODIPY dye and its molecular structure; (B) a typical single molecule BODIPY fluorescence image obtained on glass substrate; and (C) a zoom-in image of (B).

3.Results and Discussion

3.1 Single molecule spectroelectrochemistry of BODIPY molecules

Figure 1A illustrates the absorption and fluorescence spectra of the BODIPY dye whose molecular structure is depicted as inset of the figure. This dye shows absorption maxima at 500 nm and fluorescence spectrum peaks at 580 nm. This typical BODIPY dye shows low fluorescence quantum yields of 28.1 % due to efficient photo-induced hole transfer from the excited BODIPY core to the electron-rich phenyl group at the meso position[17] (BODIPY dyes without the phenyl group usually give quantum yield greater than 50%[20]). The two carboxylic acid groups are designed for covalent attachment of the BODIPY onto a TiO_2 surfaces for characterizing the direct charge inject effect on single molecule blinking activities. Figure 1B shows a typical single molecule fluorescence image obtained for this BODIPY dye on glass substrate when 1 nM BODIPY molecule was spin-casted from chloroform solution containing 0.01% w/w polystyrene. Polystyrene is presumably to function as inert matrix to help maintain the stability of the single BODIPY molecules. Figure 1C shows a zoom-in image of one selected molecule from Figure 1B. It clearly shows good fluorescence contrast to the background signal. This high signal to noise contract would allow us to obtain the temporal response of single molecule with high accuracy. However, background subtraction was done using a custom MATLAB programs developed in our group[21] to obtain images of single molecules coated onto metal oxide surfaces, such as ITO and TiO_2 due to their intrinsic fluorescence from defect emission.[22]

To demonstrate redox characteristics of single BODIPY molecules and their difference from bulk counterparts, we used SMS-EC methods to study redox activity of single BODIPY molecules to compare with fluorescence stability at open circuit voltage (OCP). Figure 2A shows the schematic of single molecule spectroelectrochemistry. Florescence signals are collected using an EM-CCD camera, while a transparent electrode ITO is used as a working electrode along with a silver quasi-reference and Pt counter electrode arranged in a home-built electrochemical cell. Single molecules are spin-casted from polystyrene solution. The electrochemical cell contains acetonitrile and electrolytes to provide conductive media so that we can control and measure the redox reaction taking places at the working electrode using a potentiostat. Figure 2B shows the cyclic voltammogram (CV) of 1 nM BODIPY spin-casted along with polystyrene onto an ITO electrode in comparison to the CV of a dry-coated concentrated BODIPY sample. The bulk sample shows pronounced faradaic current due to the oxidation of this dye while the single molecule sample only shows double layer

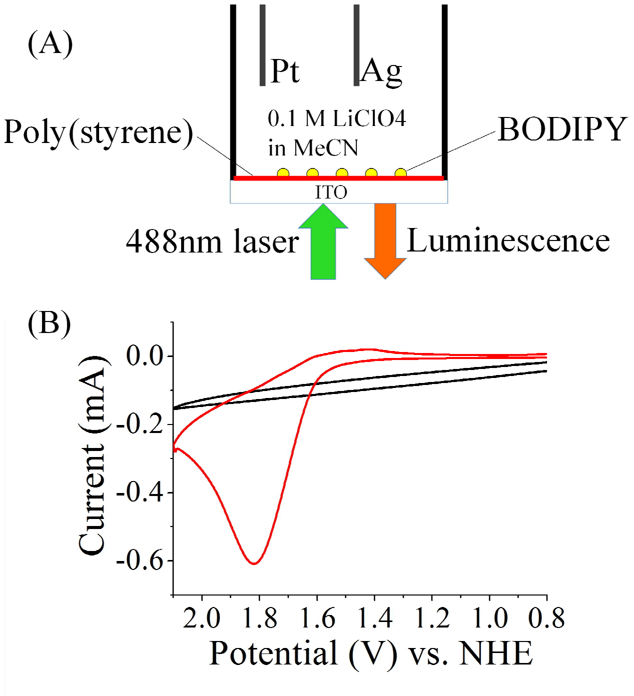

Fig. 2 (A) Schematic of SMS-EC setup; (B) cyclic voltammogram of 1 nM BODIPY casted along with polystyrene onto an ITO electrode (black curve) and a dry-coated concentrated BODIPY sample (red curve).

charging current. Spectoelectrochemistry result of the bulk sample with high concentration of dye (Figure 3A) shows that the PL of BODIPY dyes decreases with the oxidation of the molecules, and the total intensity decreases over several potential cycles because of the irreversible oxidation of BIDIPY molecules. Figure 3A illustrates the spectroelectorchemistry characteristics of a BODIPY sample. The fluorescence peaks near 1.1 V (vs. NHE) because BODIPY molecules are fully in reduced states and decrease in the fluorescence intensity above 1.1 V (vs. NHE) indicates the oxidation reaction takes places as the potential was scanned to 2.3 V (vs NHE). A fluorescence minimum peak near 1.9 V vs. NHE indicates all molecules are fully oxidized.

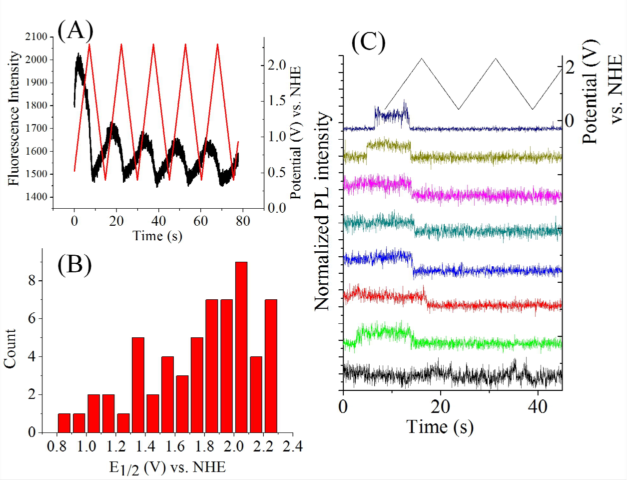

Fig. 3 Spectoelectrochemistry of the bulk sample of BODIPY dye (A), histogram of measured single molecule half potentials (B), and fluorescence responses of selected BODIPY molecules to substrate potential (C). The black curve at the bottom in C is a selected control BODIPY molecule fluorescence trace at an open circuit potential.

In comparison to bulk sample, single molecule PL signals only show dramatic decrease with a broad half potential $E_{1/2}$ distribution as shown in Figure 3B. $E_{1/2}$ is the half potential where PL of a single molecule decreases to the half of its initial intensity as shown by the selected PL traces in Figure 3C. There is around 50% of PL curves show instant decrease when applied with high potential, indicating the electron transfer to single BODIPY molecule (Figure 3C). Several selected fluorescence trajectories only show slow decrease upon applied electrode potential because of the presence of agglomerated BODIPY molecules in the polymer matrix. Negative potential scan does not reverse the PL intensity because of the irreversible electrochemical reaction as clearly shown in the CV in Figure 2B. We then analysed the PL responses of around a hundred single molecules and the measured average $E_{1/2}$ is 1.78 (+/-0.19) V vs. NHE. The heterogeneity in their half oxidation potential has to do with the heterogeneity in their charge transfer rates yielded by the difference of their spatial distribution inside the polymer layer. Measured redox potential of BODIPY dye in acetonitrile solution of 0.1 M $TBAPF_6$[17] is around 0.9 V, which is much less than above single molecule redox potential. This is because that polymer matrix can also increase the redox over potential due to their poor conductivity.

3.2 Single molecule fluorescence characteristics of BODIPY molecules and substrate effects

In order to understand redox activities and their stability of BODIPY molecules without using polymer matrix and electrolyte, single molecule fluorescence of BODIPY on different substrates (glass, ITO glass and ordered TiO_2) in air or nitrogen were studied at OCP and compared with molecules embedded in polystyrene. We also investigated whether molecules chemically bonded to TiO_2 would cause difference in their blinking dynamics in order to reveal the mechanism of charge transfer between substrates and BODIPY single molecules. The obtained fluorescence image of BODIPY molecules on a TiO_2 surface seems unusual as they are expected to be fully quenched in the presence of an electron accepting material such as TiO_2. As shown in Figure 4A and B, a typical single molecule on glass substrate shows ON and OFF fluorescence blinking behaviour. To ensure that only single molecule fluorescence signals to be collected, BODIPY dye solution with concentration as low as 1.0 nM was used to for coating all substrates. In addition, only single molecules with blinking dynamics were extracted using our Matlab program for further analysis. The duration of OFF states ranges from a few milliseconds to seconds, while the ON states are shorter than 50 milliseconds. The duration distributions of both ON and OFF states show non-Poisson behaviours because they exhibit second-order exponential decay processes as shown in Figure 4C. All parameters obtained by second-order exponential data fitting are listed in Table 1. This phenomenon is similar to dynamic disorder fluctuation behaviour of single molecule interfacial charge transfer activities reported previously in literature [23, 24].

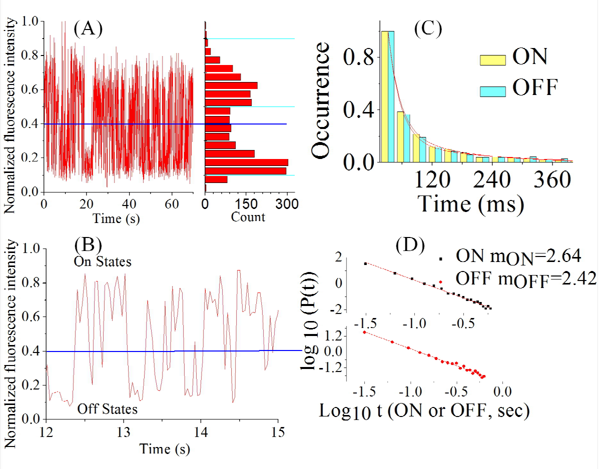

Fig. 4 (A) Photoluminescence intensity curve vs. time showing the blinking behaviour; blue curve is the threshold determined by histogram of the measured intensity vs. occurrence; (B) a zoom-in of (A); (C) the statistical distribution of occurrence of blinking and its corresponding time duration and fitting curves (red curves); and (D) log-log plot of P(t) and t-m and fitting curves (red curves) for BODIPY spin-casted on glass.

To analyse such dynamic disordered blinking behaviour, we constructed probability density distribution, P(t)=Occurrence(t)/Δt, for both ON and OFF states as shown in

Table 1. Single molecule blinking dynamics and statistical analysis for BODIPY molecules on various substrates.

Substrate	ON					OFF					Lifetime
	m_{on}	A_1	t_1	A_2	t_2	m_{off}	A_1	t_1	A_2	t_2	(ns)
A	2.64±0.12	4.17	18.00	0.35	119.20	2.42±0.12	2.78	27.21	0.14	260.42	*2.07*
B	2.26±0.25	3.79	20.85	0.18	231.78	2.52±0.37	4.33	18.85	0.21	185.79	-
C	2.47±0.19	3.45	20.06	0.30	141.40	2.62±0.16	3.34	21.88	0.21	136.83	1.60
D	2.84±0.14	4.01	16.23	0.56	80.20	2.87±0.18	2.65	26.65	0.19	137.62	1.44
E	2.74±0.29	2.35	29.76	0.20	169.28	2.44±0.27	1.91	36.54	0.20	131.10	-
F	2.78±0.11	2.58	24.40	0.34	104.69	3.00±0.07	5.37	13.41	0.68	69.05	1.44
G	2.75±0.17	4.78	15.88	0.41	91.36	2.73±0.15	1.98	38.16	0.12	230.88	2.21
H	2.85±0.24	4.75	17.68	0.20	97.11	2.22±0.35	12.84	10.05	0.47	127.93	-
I	1.80±0.14	2.70	25.96	0.20	140.17	2.42±0.20	3.32	20.30	0.32	134.63	1.58
J	3.11±0.18	4.95	9.94	0.64	38.42	2.67±0.22	2.21	17.66	0.40	82.75	1.89
K	2.68±0.27	4.49	18.71	0.14	122.21	2.78±0.19	10.65	9.54	0.54	115.98	-
L	2.65±0.21	2.74	25.85	0.22	151.40	2.96±0.14	3.62	22.09	0.15	130.39	1.5834

** Data fitting was done using a formula with 2nd order exponential decays:* $A_1exp(-t/t_1) + A_2exp(-t/t_2)$.

*** 95% confidence intervals of m values are shown.*

A) glass in air; B) glass in N_2*; C) glass, coated with polystyrene; D) ITO in air; E) ITO in* N_2*; F) ITO, coated with polystyrene; G)* TiO_2 *spin-casted BODIPY, in air; H)* TiO_2 *spin-casted BODIPY, in* N_2*; I)* TiO_2 *spin-casted BODIPY, coated with polystyrene; J)* TiO_2*, self-assembled BODIPY, in air; K)* TiO_2*, self-assembled BODIPY, in* N_2*; L)* TiO_2*, self-assembled BODIPY, coated with thick polystyrene.*

Figure 4D. The calculated probability density distributions P(t) show typical power-law behaviour,[12, 25] which can be described by a linear function of t^{-m}, where m is a constant. We calculated the value of m by constructing a liner fitting of the log-log plot of P(t) and t^{-m} for both On and OFF states, and listed m values in Table 1. The On and OFF states distributions (Figure 4C) and the log-log plot of probability density (Figure 4D) were obtained from the aggregated data of at least 80 single molecules for each sample, and the same process was applied to all following data analysis. The power exponent m for BODIPY spin-casted on glass is found to be 2.64 ± 0.12 for ON states, and 2.42 ± 0.12 for the OFF state. According to the diffusion controlled model[12, 26] the m_{on} value represents the probability of the ON state time span: a larger m_{on} indicates higher probability of a shorter ON time span, thus suggesting a relatively poor fluorescence stability due to fast charge transfer between molecules and the substrate.

Direct charge transfer from photoexcited dye molecules to TiO_2 is of great interests to alternative energy conversion systems such as DSSCs. To study single BODIPY molecules blinking dynamics and statistical analysis on their ON and OFF states on electron accepting semiconductor material TiO_2, ordered nanostructure (Figure 5A) was prepared with the procedure in literature. [18] The TiO_2 substrate contains ordered nanopores with diameter of 10 nm that would presumably support high surface area for light absorption, efficient exciton diffusion and interfacial charge transfer for dye sensitized energy conversion system. High optical transparency of a TiO_2 substrate also enables single molecule fluorescence imaging in an inverted configuration. The duration distributions of both ON and OFF states for self-assembled BODIPY molecules exhibit 2nd order exponential decay processes as shown in Figure 5B with shorter average ON duration time in comparison to bare glass substrate. Probability density distribution analysis shows m value is 3.11 for ON state, and 2.67 for OFF state, indicating faster blinking activity on TiO_2 than on glass. We attribute this enhanced blinking behaviour to photo-induced charge transfer and back transfer in the presence of TiO_2 surface.

Blinking dynamics and occurrence population for ON and OFF states from several other control experiment results are further analysed to show the stability and charge transfer dynamics of the BODIPY molecules. These control experiments include single BODIPY molecules casted along with polystyrene

Table 2. Fluorescence kinetic parameters of BODIPY molecules on various substrates.

Substrate	τ_{on} (s)	τ_{off} (s)	PL lifetime (ns)	k_{fluor} (s^{-1})	k_{et} (s^{-1})	k_{bet} (s^{-1})	k_{et}/k_{bet}
A	18	27.21	2.07	4.83E+09	984.33	3.68E-02	2.68E+04
C	20.06	21.88	1.60	6.25E+09	1142.70	4.57E-02	2.50E+04
D	16.23	26.65	1.44	6.94E+09	1569.29	3.75E-02	4.18E+04
F	24.4	13.41	1.44	6.94E+09	1043.84	7.46E-02	1.40E+04
G	15.88	38.16	2.21	4.52E+09	1045.06	2.62E-02	3.99E+04
I	25.96	20.3	1.58	6.33E+09	894.18	4.93E-02	1.82E+04
J	9.94	17.66	1.89	5.29E+09	1952.25	5.66E-02	3.45E+04
L	25.85	22.09	1.58	6.32E+09	896.05	4.53E-02	1.98E+04

Substrate labels A-L represent the same substrates as the ones in Table 1.

onto glass, ITO and TiO_2 surface in comparison with the results obtained in the absence of polystyrene. All occurrence data is fitted using a 2nd order exponential function $A_1\exp(-t/t_1)+A_2\exp(-t/t_2)$ process and obtained amplitudes and time constants are compared in the Table 1. Our data clearly shows that all molecules casted from polystyrene show longer ON time constants (t_1 value) and smaller m values than the ones without polymer matrix. This has to do with the improved photostability enabled by polystyrene matrix preventing photo-oxidation of BODIPY molecules by eliminating oxygen. Relatively longer distance from BODIPY single molecule to substrate is also ensured in the presence of polystyrene, preventing interfacial charge transfer from single molecules to the substrate. We also preformed fluorescence measurement of single BODIPY molecule in N_2. As shown in Table 1, in N_2 atmosphere, samples all show longer ON time constant than that in air, indicating N_2 can improve the photostability of BODIPY spin-casted on substrate. Our data also shows that, for spin-casted BODIPY samples without polystyrene, the ON time constant of ordered TiO_2 surface (15.88) is the smallest followed by ITO and glass. This is because ordered TiO_2 and ITO both have intimate contact to BIDIPY molecules enabling improved charge transfer rate in contract to glass. The ON time constant at the ITO electrode is longer than bare glass in the presence of polystyrene. This is presumably due to the rough surface of our ITO electrode that would result in more polystyrene loading than bare glass substrate to improve molecule stability. The same reasoning can be used to explain the fact that ON time constant at the TiO_2 electrode with spin-casted BODIPY is also longer than glass in the presence of polystyrene. There is weak background fluorescence from defects of TiO_2.[19] Appropriate background subtraction is needed to extract useful information of single molecule on this substrate. We finally compare the occurrence dynamics for ON and OFF state of molecules spin-casted on TiO_2 surface with the ones self-assembled on TiO_2 via their carboxylic acid groups. The self-assembled molecules clearly show the lowest ON time constant (9.94) due to more efficient charge transfer rate when the molecules are bonded to the semiconductor surface. The calculated probability density distributions P(t) of all above substrates and sample preparation conditions show typical power-law behaviour that can be described as a linear function of t^{-m}, and m values for all samples are listed in Table 1 for both On and OFF states. It clearly shows that self-assembled BODIPY molecules on the ordered TiO_2 surface as the largest m followed by bare ITO and then glass in air.

3.3 BODIPY fluorescence lifetime and charge transfer kinetic parameters obtained from single molecule spectroscopy

To understand the dynamics of the unusual fluorescence from BODIPY molecules on TiO_2, we measured the fluorescence lifetime of BODIPY dye thin film sample at the various substrates, and the measured lifetime for each of the substrates are listed in Table 1. The average fluorescence lifetime of all cases is around 1.7 (+/- 0.3) ns and the ground state recovering rate of 8.3 (+/-0.8) ps was obtained by our previous transient absorption spectroscopy study of BODIPY film on TiO_2. With the fluorescence lifetime data, we can calculate the interfacial electron transfer rate (k_{et}) from BODIPY to substrates and the back electron transfer rate (k_{bet}) with a well-established model.[27] Following equations are used:

$$\frac{1}{\tau_{off}} = k_{bet} \quad (1)$$

$$\frac{1}{\tau_{on}} = k_{exc}\frac{k_{et}}{k_{et}+k_{fluor}+k_{isc}+k_{ic}} \quad (2)$$

$$k_{fluor} = \frac{1}{\tau_{fluor}} \quad (3)$$

$$\varphi_f = \frac{k_{fluor}}{k_{fluor}+k_{isc}+k_{ic}} \quad (4)$$

Where τ_{on} and τ_{off} are the time constants of ON and OFF distributions, respectively, obtained from Table 1. τ_{fluor} is the fluorescence lifetime. k_{isc} and k_{ic} are the rate constants of intersystem crossing to the triplet state and other nonradiative decay, respectively. The estimated photon absorption rate of single BODIPY molecules k_{exc} is 6.98×10^5 s^{-1} (calculated with the estimated light absorption cross section of 10^{-15} cm^2). We used fluorescence lifetime of ensemble samples to estimate other kinetics parameters in equation 1-4. This is because of the low fluorescence quantum yield of BODIPY, preventing us from measuring single molecule lifetime with our limited instrument capability. Calculated results of k_{et} and k_{bet} are collected in Table 2. The highest k_{et} value is observed for self-assembled BODIPY on TiO_2 without polystyrene (sample J), indicating very efficient charge transfer from BODIPY to TiO_2 because of their intimate contact with each other. For samples on ITO and TiO_2 coated with polystyrene, a smaller k_{et} than samples without polystyrene was obtained, indicating the impediment of polystyrene to the electron transfer from BODIPY to ITO or TiO_2. However, the same impediment is not observed for electron back transfer by analysing k_{bet} values. On the other hand, samples with polystyrene give smaller k_{et}/k_{bet} than samples coated with polystyrene; k_{et}/k_{bet} of glass substrate is smaller than ITO and TiO_2, which agrees with our previous conclusion that the enhanced blinking behaviour is due to photo-induced charge transfer and back transfer between BODIPY and substrate. Furthermore, according to the calculation, $k_{fluor} \gg k_{et}$, indicating that radiative decay is much faster than charge transfer, which is the reason why unusual fluorescence can be observed from BODIPY dyes on TiO_2 instead of being completely quenched by a charge transfer process. These parameters are only applied to those molecules whose fluorescence signals are detected by our EM-CCD when they are attached to TiO_2 surface. Our analysis cannot be applied to molecules completely quenched by a TiO_2 surface without charge back-transferring. Table 2 also shows that $k_{et} \gg k_{bet}$, indicating favorable electron transfer from BODIPY to substrate than back electron transfer process for blinking single moelcules.

4. Conclusions

BODIPY dye bearing two carboxylic acid groups at its 2 and 6 positions shows excellent single molecule PL stability in polymer matrix and allows us to study its spectroelectrochemistry at single molecules level in inert polymer matrix. Our study shows a heterogeneous half redox potential distribution of 1.78(+/-0.19) V vs. NHE for single molecules embedded in polystyrene film due to the heterogeneity in their charge transfer rates. Redox events and photostability of single BODIPY molecules are investigated at open circuit potential. Molecules self-assembled onto a TiO_2 surface exhibit surprising fluorescence emission with the shortest ON time duration constant and highest interfacial electron charge transfer rate. Polystyrene helps reserve the stability of the individual molecules. Single molecule fluorescence decreases in their stability and intensity upon charge transfer activity and/or exposure to air. Fluorescence lifetime of BODIPY is measured and electron transfer rates are calculated with a well-established model to understanding the unusual fluorescence from BODIPY molecules attached to TiO_2 surface.

5. ACKNOWLEDGMENTS

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Notes and references

[a] *Department of Chemistry, the University of Alabama, Tuscaloosa, AL, USA, 35487-0336; E-mail: span1@ua.edu*
[b] *Department of Chemistry, Michigan Technological University, Houghton, Michigan, USA, 49931;*

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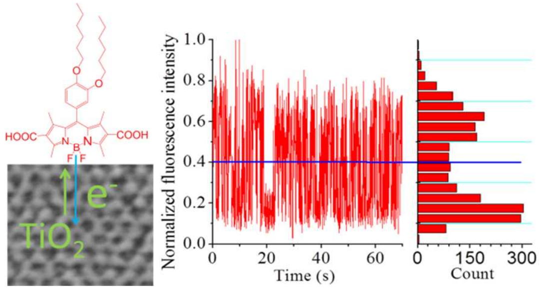

BODIPY dye single molecules on nanostructured substrates are studied with single molecule spectroelectrochemistry technique to reveal heterogeneous charge transfer mechanism.