Supporting Information

Single-Molecule Interfacial Electron Transfer Dynamics of Porphyrin on TiO₂ Nanoparticles: Dissecting Interfacial Electric Field and Electron Accepting State Density Dependent Dynamics

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Experimental Section

Materials and Sample preparation

Zn(II)-5,10,15,20-tetra (3-carboxyphenyl) porphyrin, *m*-ZnTCPP and dichloromethane were purchased from Frontier Scientific (research and development purpose only) and EMD chemicals (HPLC grade), respectively. Isopropyl alcohol (ACS reagent, \geq 99.5%), ethanol (200 proof; anhydrous, \geq 99.5%), acetone (CHROMASOLV Plus, for HPLC; \geq 99.5%), and NaCl (BioXtra, \geq 99.5%) were purchased from Sigma Aldrich. All the reagents were used without further purification. Indium tin oxide (ITO)-coated transparent coverslips (SPI[®] Supplies; 18 mm × 18 mm; 8-12 ohms; thickness ~ 170 μ m) were thoroughly cleaned by sonication in deionized water, acetone, isopropyl alcohol and deionized water, each for 15 minutes, and dried in a jet of nitrogen gas before their use. Silver wire (0.25 mm diameter) and platinum wire (0.30 mm diameter) were purchased from Alfa Aesar[®]. Nanometer-size TiO₂ particles were prepared by the hydrolysis of titanium isopropoxide (Aldrich, 99.999%) as precursor according to a literature protocol.¹ The size range (diameter) of the TiO₂ nanoparticles was found to be 4–12 nm (Figure S1), as determined by atomic force microscopy (AFM).



Figure S1: AFM images of 0.62 μ M colloidal TiO₂ nanoparticles solution spin-coated on ITO-coated coverslip: (a) before washing with water and (b) after washing with water, showing no morphological change of the sample surface after washing with water. (c) and (d) are topographic profiles along the line indicated in (a) and (b). (e) and (f) are 3D view of images (a) and (b), respectively. All the images are obtained by tapping mode in air.

For the single-molecule experiments, we prepared the sample following our earlier reported procedures.^{2,3} Briefly, the transparent ITO-coated coverslip was first spin-coated with TiO₂ NP solution (25 μ L, 0.62 μ M) at 3000 rpm followed by overlaying 25 μ L of 0.1 nM *m*-ZnTCPP in ethanol.

Single-molecule Fluorescence Spectroscopy and Imaging

Single-molecule fluorescence spectroscopy and imaging were recorded by an Axiovert 135 inverted scanning confocal microscope equipped with a 100 \times 1.3 NA oil immersion objective (Zeiss FLUAR) and a close-loop nanoscale-precision piezoelectric scanning stage (PI (Physik Instrumente) L.P.) to control the position of a sample. A picosecond pulsed laser (532 nm, Coherent Antares, YAG) was used to excite the sample with a repetition frequency of 76 MHz (excitation power at the sample was kept between 400 to 1200 nW). A beam splitter Z532rdc (Chroma) was used to reflect the excitation light into the objective (excitation spot size \sim 300 nm). The emission light passed through the emission filter HQ545lp (Chroma, for *m*-ZnTCPP, the emission wavelength typically ranges from 570 to 750 nm, Figure S2⁴) and collected by a single-photon counting avalanche photodiode (APD) detector (Perkin-Elmer SPCMAQR-14, pinhole size of APD is 170 µm). Photon-stamping data was recorded by a time-correlated single-photon counting (TCSPC) system (SPC-830, Becker & Hickl GmbH) in a FIFO (first-in first-out) mode.



Figure S2: UV-vis absorption and fluorescence emission spectra of *m*-ZnTCPP and *m*-ZnTCPP bound to TiO_2 in ethanol (Adapted with permission from ref. 4. Copyright 2014 American Chemical Society).

We studied the interfacial ET dynamics of individual *m*-ZnTCPP molecule anchored to TiO_2 NP surface using single-molecule photon-stamping spectroscopic approach. This approach is capable of recording each detected photon with its chronic arrival time (absolute arrival time or real time) and the time delay between the photoexcitation and emission of the specific exited state of the individual molecule (Figure S3).^{2,3,5}



Figure S3: (A), (C) represent typical experimental photon-stamping trajectories for high emission intensity state (in red) and low emission intensity state (in blue) of single-molecule fluorescence trajectory shown in (B). For each detected photon (each data point in A and C represents a detected photon) two parameters were recorded: chronic arrival time or real time (x-axis of A and C) and delay time between the laser pulse excitation and the photon emission from the excited state (y-axis of A and C). The distribution of the delay times gives a typical single-molecule fluorescence decay curve, and the histogram of chronic arrival times yields fluorescence intensity trajectories with a given time bin resolution.

Electrochemical Cell Configuration and Spectroelectrochemistry

We used a home-built electrochemical cell with three-electrode configuration (working electrode: spin-coated TiO₂/ITO-coated coverslip; counter electrode: platinum wire; quasi-reference electrode: silver wire) for all the electrochemical measurements. The electrode calibration was reported using the Ru^{3+/2+} redox-couple of [Ru(bpy)₃] (PF₆) and it was found that the quasi-reference electrode is offset from the normal hydrogen electrode by 0.31 ± 0.01 V.⁶ It is also important to note that the specific applied potential does not always guarantee the same potential sensed by all single molecules owing to the inhomogeneous potential distributions in the semiconductor and at the semiconductor-electrolyte interfaces. This inhomogeneous surface electric work functions.⁷ Electrochemical experiments were performed by a CHI 600C electrochemical workstation (CH Instruments, Inc.), equipped with a three-electrode system connected to the home-built cell. For correlated electrochemical measurement with photon-stamping measurements the home-built cell was incorporated in the sample stage of same optical setup described above (Figure S4).



Figure S4. Schematic representation of experimental setup for single-molecule fluorescence imaging correlated with photon-stamping spectroscopy and electrochemistry. APD, avalanche photodiode; ITO, indium tin oxide; SPC, single photon counting. For electrochemical measurement we used a home-built electrochemical cell with three-electrode configuration, working electrode (W): spin-coated TiO₂/ITO-coated coverslip; counter electrode (C): platinum wire; quasi-reference electrode (R): silver wire.

The electrochemical experiments were performed using an aqueous solution of 0.1 M NaCl as supporting electrolyte. All potentials reported in this work are referenced to a silver wire quasi-reference.

The Selection of *m*-ZnTCPP Molecule and Aqueous Solution with a Particular Range of Applied Potential

The choice of four carboxylic acid group containing *m*-ZnTCPP as a sensitizer emerges from the fact that the four anchoring groups (-COOH group) in the *meta*-position of *meso*-phenyl rings of the porphyrin macrocycle provides a planar binding geometry as well as strong bonding of *m*-ZnTCPP with TiO₂ NPs.^{4,8,9} Porphyrin dyes and its various derivatives are also widely used as sensitizer in dye sensitized NP systems.⁸⁻¹² Recently, using different derivatives of Zn-porphyrin as a sensitizer, an efficiency as high as 13% was reported.¹⁰ These studies demonstrated the Zn-Porphyrin–TiO₂ system as an efficient photosensitization solar energy conversion system.⁸⁻¹²

The surface stabilization of dye molecules, catalysts, and dye-catalyst assemblies attached to metal oxide surfaces plays important role in dye sensitized solar cells, electrocatalysis, and photoelectrocatalysis. So replacing expensive solvents with water requires extensive research on long term stability of dye-catalyst assemblies in water.^{13,14} Considering the electrochemical window of water¹⁵ as well as the reported redox behavior of Zn-Porphyrin systems⁹ (due to insolubility of *m*-ZnTCPP in water we are not able to do electrochemical measurements) we have chosen -0.6 to +0.6 V potential range. In this potential range the *m*-ZnTCPP molecule remains stable towards any reduction or oxidation due to applied potential.

Surface Stability of *m*-ZnTCPP Surface-Bound to TiO₂

The surface stabilization of dye molecules, catalysts, and dye-catalyst assemblies attached to metal oxide surfaces plays important role in dye sensitized solar cells, electrocatalysis, and photoelectrocatalysis.¹⁶⁻¹⁹ Different strategies evolved over the time for the surface stabilization of dye/catalyst molecule on metal oxide surfaces.¹⁶⁻¹⁹ Cooperative binding of dye molecule to metal oxide surfaces through anchoring groups is one of the strategies.¹⁷ Here, we have used four carboxylic acid anchoring group containing *m*-ZnTCPP as a sensitizer. To demonstrate the surface stabilization of *m*-ZnTCPP surface-bound to TiO₂ we have used single-molecule confocal fluorescence imaging. Figures S5A1 and S5A2 show the single-molecule confocal fluorescence images of *m*-ZnTCPP on TiO₂ NPs-coated ITO surface and

TiO₂ NPs-coated ITO surface after 30 minutes in presence of 0.1 M NaCl aqueous electrolyte, respectively. Figures S5B1 and S5B2 show the single-molecule confocal fluorescence images of *m*-ZnTCPP on TiO₂ NPs-coated ITO surface and TiO₂ NPs-coated ITO surface after 30 minutes with -0.60 V applied potential in presence of 0.1 M NaCl aqueous electrolyte, respectively. Each bright spot is attributed to a molecular fluorescence image of a single *m*-ZnTCPP molecule. A close look at the images indicates same position of the observed *m*-ZnTCPP molecule, clearly demonstrating the surface stabilization of *m*-ZnTCPP surface-bound to TiO₂ NPs even in presence of aqueous electrolyte and applied bias.



Figure S5. Single-molecule confocal fluorescence images of *m*-ZnTCPP on (A1) and (A2) TiO_2 NPs-coated ITO surface and TiO_2 NPs-coated ITO surface after 30 minutes (scan area is same for A1 and A2); (B1) and (B2) TiO_2 NPs-coated ITO surface and TiO_2 NPs-coated ITO surface after 30 minutes with -0.60 V applied potential (scan area is same for B1 and B2). All the images were taken in presence of 0.1 M NaCl aqueous electrolyte. Image sizes are 10 μ m x 10 μ m.

This observation can be accounted for by the fact that the four covalent anchor points^{8,9} of m-ZnTCPP lead to its strong bonding with TiO₂ NPs, which in turn provides resistance to the desorption. The surface stabilization of m-ZnTCPP surface-bound to TiO₂ NPs further indicates that the cooperative action of the four anchoring groups has a positive effect in stabilizing the dye on the TiO₂ NPs surface in aqueous electrolyte solution.²⁰





Figure S6: Single-molecule fluorescence intensity trajectories of *m*-ZnTCPP on TiO_2 NPscoated ITO surface in presence of 0.1 M NaCl aqueous electrolyte with (A), (B) 0.00 V, (C), (D) +0.60 V, and (E), (F) -0.60 V applied potential.

Here, we have shown six single molecule fluorescence intensity trajectories in addition to the three single molecule fluorescence intensity trajectories of main manuscript (Figure 2). Overall, the number of molecules studied in our system is more than 100 molecules (104 molecules are listed in Figure S7). To ensure that the observed dye molecules are representative of the ensembles, we compared our observed results with the literature reports on ensemble level measurement. The fluorescence lifetime of ZnTCPP in water was found to

be in the range of 1.9 ns to 3.0 ns.²¹⁻²³ So, we can expect the lifetime of *m*-ZnTCPP on TiO₂ NPs, in presence of water, will be less than 1.9 ns due to interfacial electron transfer from excited state of *m*-ZnTCPP to TiO₂. The lifetime distribution observed for *m*-ZnTCPP on TiO₂ NPs in absence of applied bias is in the range of 0.7 ns to 1.4 ns (Figure S7), which suggest that the observed single dye molecules are representative of the ensembles.

We note that the percentage of molecules that exhibited continual emission with applied potential varies from sample to sample but it is certainly higher than 25%. The lower percentage arises because the specific applied potential does not always guarantee the same potential sensed by each single molecule owing to the inhomogeneous potential distributions in the semiconductor and at the semiconductor-electrolyte interfaces. This inhomogeneity in potential distributions arises due to the inherent roughness of the TiO_2 NP surface, nanoscale gradient of dielectric constants and electric conductivity, and inhomogeneous surface electric work functions. Additionally, the quick photobleaching for some molecules is also responsible for lower percentage of molecules that exhibited continual emission with applied potential.

We also note that the intersystem crossing to the triplet state of *m*-ZnTCPP molecules is not likely to be the cause of fluorescence intensity fluctuation or blinking,⁴ because the triplet-state lifetime of ZnTCPP dye lies close to 1 ms or less.¹¹ The long dark time (from sub seconds to seconds) for *m*-ZnTCPP on TiO₂ shows that the fluctuation of fluorescence is not likely due to the triplet state. In our control experiment we have observed much less or no blinking for *m*-ZnTCPP on cover glass comparing to that in the *m*-ZnTCPP on TiO₂ systems, which rule out a significant contribution from the dark triplet state to the blinking.⁴ Had the triplet state of *m*-ZnTCPP molecules been responsible for the blinking, we should have observed similar blinking for *m*-ZnTCPP on glass.

Fluorescence lifetime distributions of *m*-ZnTCPP on TiO₂ NPs-coated ITO surface



Figure S7: Fluorescence lifetime distributions of m-ZnTCPP on TiO₂ NPs-coated ITO surface in presence of 0.1 M NaCl aqueous electrolyte with different applied potentials.

The single molecule fluorescence decays were fitted by biexponential function derived by deconvolution of instrument response function (IRF). The lifetime distribution from 0.7 ns to 1.4 ns with 0.00 V applied potential clearly demonstrates the individuality of each molecule in a specific environment, which cannot be observed by ensemble average measurements. This static disorder of the single-molecule interfacial ET process is closely associated with the inhomogeneous surface state distribution of *m*-ZnTCPP molecules on rough TiO₂ NP surface. The static disorder also leads to difference in lifetime as well as blinking pattern as we had discussed in our previous publications on the intermittent single-molecule interfacial ET dynamics.^{2,4,7}

We also considered the observed insensitivity of positive applied potential on blinking pattern as well as excited state lifetime of *m*-ZnTCPP molecule anchored to TiO_2 NP surface (Figure S7). Following earlier report ²⁴ we can attribute the bias independence at positive applied potentials to the fact that the electron occupancy induced by the applied positive potential reduced to less than one per nanoparticle. Under such low electron occupancy conditions, the effect of applied bias becomes less prominent than that induced by the laser excitation (approximately one photoinjected electron per nanoparticle). The charge recombination will therefore be dominated by electrons injected by the laser excitation only. The laser power in our experiment is so low that we can consider only one injected electron per nanoparticle, which in turn results in power independent recombination kinetics.

The charge screening effect and Stark effect reported by Meyer et al. $^{25-27}$ also suggest that the increased electron density into TiO₂ generate significant electric field across the interface, which in turn influence ET efficiency of the surface anchored molecules. The broader distribution of lifetime in case of -0.60 V applied potential can be accounted for by the inhomogeneous potential distributions in the semiconductor and at the semiconductor-electrolyte interfaces. This inhomogeneity in potential distributions arises due to the inherent roughness of the TiO₂ NP surface, nanoscale gradient of dielectric constants and electric conductivity, and inhomogeneous surface electric work functions. Furthermore, based on our intermittent single-molecule interfacial ET dynamics observations, we note that this electron density dependent inhomogeneity is likely to be dynamic rather than static due to the excess electron diffusion in the conduction band of TiO₂.²⁸

The change in electrostatic charge environment of the interface due to injected electrons into TiO_2 has influence on the surface anchored molecules. But, the effect of electric field on the absorption of dye molecules from the TiO_2 is thought to be diminished by the large dielectric constant of TiO_2 , $\varepsilon_r = 7-50$; high permittivity of water, $\varepsilon_r = 80.1$.²⁹ Extensive analysis of double layer effect and impact of different electrolyte composition and concentration at single-molecule level requires further investigation and is beyond the scope of this manuscript.

The photoreductant properties, weak photoreductant vs strong photoreductant can also affect (i) the interfacial ET dynamics and (ii) the extent of change in FET dynamics with applied bias. However, the consideration of photoreductant properties is advantageous if we compare two dye molecules having different photoreductant properties in similar environment at single molecule level.

Statistical Analysis on the Stochastic Durations of the Dark state

To quantify the emission intermittency recorded by the blinking single-molecule fluorescence trajectories it is always advantageous to performed statistical analysis on the stochastic durations of the dark state involving high ET reactivity compared to the bright state associated with low ET reactivity.⁴ In case of negative applied potential for most of the molecule we observed a quasi-continuous (intensity trajectory with no distinct bright and dark states) distribution of fluorescence intensities, so we cannot perform such statistical analysis. Nevertheless in our earlier manuscript⁴ we have performed detailed analysis on the stochastic durations of the dark state of *m*-ZnTCPP surface-bound to TiO₂ in absence of applied potential. We have shown non-Poisson behavior for *m*-ZnTCPP as indicated by the nonexponential distribution of dark times (Figure S8).⁴ Figure S8 also show probability density distribution of the dark states and histogram of power-law exponents (For detail discussion please see reference 4).

The theoretical model for our data analysis is clearly a simple two state model, and the focus is on the distinction of two states observed for all visible molecules: (i) the state in which the dye molecule interact strongly with TiO₂ surface leading to higher interfacial ET reactivity and dark state; and (ii) the state in which the dye molecule interact weakly with TiO₂ surface leading to lower interfacial ET reactivity and bright state. The main findings of this manuscript are (i) the blinking behavior of single-molecule anchored to TiO₂ NPs can be controlled with applied electric potential by effectively tuning electron density inside the TiO₂ NPs and (ii) systematic variation of parameters controlling blinking rate as well as blinking behavior at single-molecule level can yield mechanistic information about the complex FET and BET dynamics. However, there are a number of statistical analyses of the single-molecule data available other than thresholding method; for example, the change point detection analysis and code developed by Haw Yang.³⁰ Rigorous statistical treatment of the single-molecule data followed by comparison at different applied potential as well as comparison of different models to explain statistical results can be useful. However such detailed treatment is beyond the scope of this manuscript.



Figure S8: Distributions of dark-time durations of *m*-ZnTCPP on the TiO₂ NP surface for (A) 1 molecule and (B) 23 molecules. Probability densities of the dark-time durations of *m*-ZnTCPP on TiO₂ NP surface for (C) 1 molecule and (D) 23 molecules. In log–log scale plots (C, D) the solid lines are linear fits indicating power-law behavior. The power-law exponent, which is the slope of the linear fits, is also indicated in the panels. (E) Histogram of power-law exponents (m_{dark}), for 23 different molecules of *m*-ZnTCPP on the TiO₂ NP surface (Adapted with permission from ref. 4. Copyright 2014 American Chemical Society).

References:

- 1 D. Duonghong, E. Borgarello and M. Grätzel, J. Am. Chem. Soc., 1981, 103, 4685.
- 2 Y. Wang, X. Wang, S. K. Ghosh and H. P. Lu, J. Am. Chem. Soc., 2009, 131, 1479.
- 3 L. Guo, Y. Wang and H. P. Lu, J. Am. Chem. Soc., 2010, 132, 1999.
- 4 V. G. Rao, B. Dhital, Y. He and H. P. Lu, J. Phys. Chem. C, 2014, 118, 20209.
- 5 H. P. Lu, Chem. Soc. Rev., 2014, 43, 1118.
- 6 C. Galland, Y. Ghosh, A. Steinbrück, M. Sykora, J. A. Hollingsworth, V. I. Klimov and H. Htoon, *Nature*, 2011, **479**, 203.
- 7 V. Biju, M. Micic, D. Hu and H. P. Lu, J. Am. Chem. Soc., 2004, 126, 9374.
- 8 S. Rangan, S. Coh, R. A. Bartynski, K. P. Chitre, E. Galoppini, C. Jaye and D. Fischer, J. Phys. Chem. C, 2012, 116, 23921.
- 9 J. Rochford, D. Chu, A. Hagfeldt and E. Galoppini, J. Am. Chem. Soc., 2007, 129, 4655.
- S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nature Chem.*, 2014, 6, 242.
- 11 K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier and M. Grätzel, J. Phys. Chem., 1987, 91, 2342.
- 12 L.-L. Li and E. W.-G. Diau, Chem. Soc. Rev., 2013, 42, 291.
- 13 T. Daeneke, Y. Uemura, N. W. Duffy, A. J. Mozer, N. Koumura, U. Bach and L. Spiccia, *Adv. Mater.*, 2012, **24**, 1222.
- 14 C. Law, O. Moudam, S. Villarroya-Lidon and B. O'Regan, J. Mater. Chem., 2012, 22, 23387.
- 15 N. V. Plechkova and K. R. Seddon, Chem. Soc. Rev., 2008, 37, 123.
- 16 A. K. Vannucci, L. Alibabaei, M. D. Losego, J. J. Concepcion, B. Kalanyan, G. N. Parsons and T. J. Meyer, J. *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 20918.
- 17 D. G. Brown, P. A. Schauer, J. Borau-Garcia, B. R. Fancy and C. P. Berlinguette, J. Am. Chem. Soc., 2013, 135, 1692.
- 18 K. Hanson, M. K. Brennaman, H. Luo, C. R. K. Glasson, J. J. Concepcion, W. Song and T. J. Meyer, ACS Appl. Mater. Interfaces, 2012, 4, 1462.
- 19 K.-R. Wee, M. K. Brennaman, L. Alibabaei, B. H. Farnum, B. Sherman, A. M. Lapides and T. J. Meyer, *J. Am. Chem. Soc.*, 2014, **136**, 13514.
- 20 S. Cherian and C. C. Wamser, J. Phys. Chem. B, 2000, 104, 3624.

- 21 P. Liang, H. Y. Zhang, Z. L. Yu, and Y. Liu, J. Org. Chem. 2008, 73, 2163.
- Y. Kou, S. Nakatani, G. Sunagawa, Y. Tachikawa, D. Masui, T. Shimada, S. Takagi, D. A. Tryk, Y. Nabetani, H. Tachibana, and H. Inoue, *Journal of Catalysis* 2014, 310 57.
- 23 Y. Tachibana, S. A. Haque, I. P. Mercer, J. R. Durrant and D. R. Klug, *J. Phys. Chem. B*, 2000, **104**, 1198.
- 24 S. A. Haque, Y. Tachibana, R. L. Willis, J. E. Moser, M. Grätzel, D. R. Klug and J. R. Durrant, *J. Phys. Chem. B*, 2000, **104**, 538.
- 25 P. G. Johansson, A. Kopecky, E. Galoppini and G. J. Meyer, J. Am. Chem. Soc., 2013, 135, 8331.
- 26 S. Ardo, Y. Sun, A. Staniszewski, F. N. Castellano and G. J. Meyer, J. Am. Chem. Soc., 2010, 132, 6696.
- 27 R. N. Sampaio, R. M. O'Donnell, T. J. Barr and G. J. Meyer, J. Phys. Chem. Lett., 2014, 5, 3265.
- 28 G. M. Hasselmann and G. J. Meyer, J. Phys. Chem. B, 1999, 103, 7671.
- 29 R. M. O'Donnell, R. N. Sampaio, T. J. Barr and G. J. Meyer, J. Phys. Chem. C, 2014, 118, 16976.
- 30 L. P. Watkins and H. Yang, J. Phys. Chem. B 2005, 109, 617.