# Supporting Information: BODIPY Chemisorbed on SnO<sub>2</sub> and TiO<sub>2</sub> Surfaces for Photoelectrochemical Applications

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# 1. Photophysical and Electrochemical Properties



**Figure S1.** a) UV-vis of **2** after 20 h sensitization (purple) compared to 1 h sensitization (blue). The 20 h sensitization has been repeated three times. The spectrum is the average of the different repetitions and the error bar on  $\lambda_{max}$  indicates the variability found. b) Stability of **2**/TiO<sub>2</sub> in pH 2 and pH 7 aqueous solutions, comparing the stability of the films sensitized for 1 h with the ones sensitized for 20 h. No differences in the behavior have been observed with increasing the sensitization time.

#### Spectroelectrochemistry

Spectroelectrochemistry experiments were performed using a CH Instruments CHI1200B potentiostat with a honeycomb cell (Pine Instruments) with Pt working and counter electrodes and a silver wire as the pseudoreference electrode. A 0.2 mM solution of the compound in acetonitrile with 0.1 M TBAPF<sub>6</sub> was placed in a cuvette (2 mm path length). For oxidation, a fixed potential was applied, and visible spectra were recorded at regular intervals using a Shimadzu UV-2600 UV-visible spectrophotometer. The applied voltage was consistent with the onset of the oxidation peak as seen by CV. The oxidized spectra of the 1 and 2 were obtained by applying a constant potential of 0.6 V vs Ag/AgCl in MeCN, the onset of the oxidation feature, using a quartz cuvette which was designed to fit a platinum working electrode with holes for the light to pass through. The counter electrode was a platinum electrode, and the reference electrode was Ag/AgCl. UV-visible spectral traces were taken every 3 seconds until they converged on the spectrum of the oxidized species (Figure S2).



**Figure S2.** Spectroelectrochemistry of **1** (left) and **2** (right) in 0.1 M TBAPF<sub>6</sub> in MeCN. Spectra were taken every 3 seconds after application of a constant potential of 0.6 V vs Ag/AgCl and converged on the spectrum of the oxidized species.



Figure S3. Absorption and emission spectra of 1 and 2 in MeCN solution.



Figure S4. Cyclic voltammetry of 1 and 2 in 0.1 M TBAPF<sub>6</sub> MeCN.



Figure S5. Differential pulse voltammetry of 1 and 2 in 0.1 M TBAPF<sub>6</sub> MeCN.



Figure S6. UV-vis of 1 and 2 on SnO<sub>2</sub> normalized to the extinction coefficients of the dyes.





**Figure S7.** OPTP data of sample a of 1/SnO<sub>2</sub> photoexcited with a 100 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.



**Figure S8.** OPTP data of sample b of 1/SnO<sub>2</sub> photoexcited with a 100 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.



Figure S9. OPTP data of sample a of  $2/\text{SnO}_2$  photoexcited with a 100 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.



**Figure S10.** OPTP data of sample b of  $2/SnO_2$  photoexcited with a 100 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.

	$a_i$	$a_r$	FWHM	$\mathcal{Y}0$	
	(%ATHz)	(%∆THz)	(fs)	(%∆THz)	
1/5=0	-0.1266	-0.2306	400	-0.1067	
$1/ShO_2$	(-0.1859, -0.0673)	(-0.2312, -0.2299)	400	(-0.1803, -0.0330)	
2/SnO <sub>2</sub>	-0.4180	-0.2890	400	-0.04109	
	(-0.4928, -0.3432)	(-0.3089, -0.2083)	400	(0, -0.08217)	
<sup>a</sup> The average values are reported and the fit values of the individual traces are in parentheses.					
<sup>b</sup> The FWHM was fixed at 400 fs due to the pulse width of the excitation beam.					

**Table S1.** Fit parameters for OPTP traces measured with a 100 mW excitation pulse using Equation 1 (see Experimental Methods).<sup>a</sup>



**Figure S11.** OPTP data of sample c of 1/SnO<sub>2</sub> photoexcited with a 40 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.



**Figure S12.** OPTP data of sample d of 1/SnO<sub>2</sub> photoexcited with a 40 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.



**Figure S13.** OPTP data of sample c of 2/SnO<sub>2</sub> photoexcited with a 40 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.



**Figure S14.** OPTP data of sample d of **2**/SnO<sub>2</sub> photoexcited with a 40 mW 400 nm excitation pulse. Terahertz data are plotted as square markers, whereas fitted models are plotted as solid lines.

**Table S2.** Fit parameters for OPTP traces measured with a 40 mW excitation pulse using Equation 1 (see Experimental Methods).<sup>a</sup>

	$t_i$ (ps)	β	$<_{t_i}>^{\mathrm{b}}$ (ps)	$t_r$ (ps)	
$1/SnO_{2}$	6.91	0.6637	4.30	484.7	
1/51102	(1.69, 12.12)	(0.5341, 0.7932)	(1.93, 21.61)	(238.6, 730.7)	
	9.94	0.6818	14.06	621.6	
2/SIIO <sub>2</sub>	(7.20, 12.67)	(0.5828, 0.7809)	(8.31, 19.82)	(243.2, 1000.0)	
<sup>a</sup> The average values are reported and the fit values of the individual traces are in parentheses.					
<sup>b</sup> The average injection lifetimes were obtained using Equation 2 (see Experimental					
Methods).					

**Table S2 continued.** Fit parameters for OPTP traces measured with a 40 mW excitation pulse using Equation 1 (see Experimental Methods).<sup>a</sup>

	$a_i$	$a_r$	FWHM	$\mathcal{Y}0$		
	(%∆THz)	(%∆THz)	(fs) <sup>b</sup>	(%ATHz)		
1/SnO	-0.01415	-0.02882	400	-0.01407		
$1/5nO_2$	(-0.01736, -0.01095)	(-0.03351, -0.02413)	400	(-0.00700, -0.02113)		
2/SnO <sub>2</sub>	-0.09198	-0.04485	400	-0.03007		
	(-0.10200, -0.08195)	(-0.06087, -0.02882)	400	(-0.02984, -0.03029)		
<sup>a</sup> The average values are reported and the fit values of the individual traces are in parentheses. <sup>b</sup> The						
FWHM was fixed at 400 fs due to the pulse width of the excitation beam.						



Figure S15. OPTP data of SnO<sub>2</sub> photoexcited with a 100 mW 400 nm excitation pulse.



**Figure S16.** Transient absorption data for  $1/\text{SnO}_2$ , left, and  $2/\text{SnO}_2$ , right. The top spectra show changes in optical density plotted as a function of wavelength for various times; characteristic features at 514 nm for  $1/\text{SnO}_2$ , and 548 nm for  $2/\text{SnO}_2$ , are plotted below. The data indicate ultrafast oxidation of the dyes followed by reduction of the oxidized species over 1-5 ns.



Figure S17. a) Electron population on 1 over time for all ten trajectories. b) Mean electron population over time on 1 (red) and  $TiO_2$  (black) obtained by averaging over all ten trajectories. The standard deviation is represented by the shaded area.



Figure S18. a) Electron population on 2 over time for all ten trajectories. b) Mean electron population over time on 2 (blue) and TiO<sub>2</sub> (black) obtained by averaging over all ten trajectories. The standard deviation is represented by the shaded area.

**Table S3.** Slope and  $R^2$  for the linear fits on the electron injection traces for compounds 1 and 2, allowing for an estimate of the electron injection rate.

Molecule	Slope (fs <sup>-1</sup> )	$R^2$	Injection rate $(s^{-1})$
1	-0.00656	0.952	6.6×10 <sup>12</sup>
2	-0.00391	0.974	3.9×10 <sup>12</sup>

4. Stability in Acidic and Basic Environments



Figure S19. Absorption decay at  $\lambda_{max}$  of two different loaded 1/TiO<sub>2</sub> slides after 1 h at pH 2.

5. Photoelectrochemistry



Figure S20. Linear sweep voltammetry under chopped illumination of  $1/\text{TiO}_2$  and  $2/\text{TiO}_2$  in 0.075 M phosphate buffer solution and 0.025 M Na<sub>2</sub>SO<sub>3</sub> at pH 7.



**Figure S21.** Chronoamperometry of the  $1/\text{TiO}_2$  films in 0.075 M phosphate buffer solution and 0.025 M Na<sub>2</sub>SO<sub>3</sub> and  $1/\text{TiO}_2$  films in 0.1 M phosphate buffer solution at pH 7 under 5-min chopped irradiation (100 mW cm<sup>-2</sup> filtered with  $\lambda > 420$  nm) with an external bias of 0 V vs Ag/AgCl (KCl sat.).



Figure S22. UV/visible spectra of 1/TiO<sub>2</sub> and 2/TiO<sub>2</sub>.



**Figure S23.** Chronoamperometry of the dye-sensitized TiO<sub>2</sub> films in 0.075 M phosphate buffer solution and 0.025 M Na<sub>2</sub>SO<sub>3</sub> at pH 7 under 12-min irradiation (100 mW cm<sup>-2</sup> filtered with  $\lambda > 420$  nm) with an external bias of 0 V vs Ag/AgCl (KCl sat.). The inset shows a zoomed in view of the area where the current density of **2**/TiO<sub>2</sub> diminishes under **1**/TiO<sub>2</sub>.



**Figure S24.** Chronoamperometry of the dye-sensitized TiO<sub>2</sub> films in 0.075 M phosphate buffer solution and 0.025 M Na<sub>2</sub>SO<sub>3</sub> at pH 7 under 2-h irradiation (100 mW cm<sup>-2</sup> filtered with  $\lambda > 420$  nm) with an external bias of 0 V vs Ag/AgCl (KCl sat.).

# 6. Effects of Additives on BODIPY Loading



Figure S25. Effects of the presence of different additives in the loading solution on the absorbance at  $\lambda_{max}$  of the  $1/\text{TiO}_2$  films. Each acetonitrile sensitization solution is composed of 5 mM dye and 1 mM additive.



**Figure S26.** On the left, UV-visible spectra of  $1/\text{TiO}_2$  obtained from different sensitization solutions: 5 mM **1** in acetonitrile (red trace); 5 mM **1** in acetonitrile + 2% water (orange trace); 5 mM **1** in acetonitrile + 1 mM TBAF·3H<sub>2</sub>O (green trace); pre-sensitization of a TiO<sub>2</sub> film into a solution 1 M KF(aq) for 20 h, dried and then submerged into a solution of 5 mM **1** in acetonitrile (blue trace); pre-sensitization of a TiO<sub>2</sub> film into a solution of a TiO<sub>2</sub> film into a solution 1 M KF(aq) for 20 h, dried and then submerged into a solution of 5 mM **1** in acetonitrile (blue trace); pre-sensitization of a TiO<sub>2</sub> film into a solution 1 M TBAF·3H<sub>2</sub>O in acetonitrile for 20 h, dried and then submerged into a solution of 5 mM **1** in acetonitrile (blue trace); and bare TiO<sub>2</sub> control (black trace). On the right, UV-visible spectra of **2**/TiO<sub>2</sub> obtained from a sensitization solution of 5 mM **2** in acetonitrile (blue trace); from a sensitization solution also containing 1 mM TBAF·3H<sub>2</sub>O in acetonitrile (green trace) and bare TiO<sub>2</sub> control (black trace).

# 7. Computational Details

# Anatase surface

Structure optimizations were performed using the dftb+ program,<sup>1</sup> with GFN-xTB as electronic structure method.<sup>2</sup> A bulk optimization of anatase TiO<sub>2</sub> was performed, expanded and rotated so that the 101 plane was normal to the z direction. The box dimensions are 20.145 Å x 14.226 Å x 30.000 Å, with three layers and a total of 288 atoms. A mesh of  $1 \times 1 \times 1$  Kpoints was used. The lowest layer was kept frozen in bulk geometry, while the other two layers were allowed to relax to their preferred surface geometry. SCC convergence was set to 10-8. Geometries were treated as converged once the gradient was below  $10^{-4}$  Hartree/Bohr. The compounds **1** and **2** were then attached to the surface and reoptimized, as given in Figure S25.



**Figure S27.** Model systems for  $1/\text{TiO}_2$  (a) and  $2/\text{TiO}_2$  (b) as used in the present manuscript. Periodic boundary conditions are applied in x,y and z with a large vacuum layer preventing self-interaction along the z-direction.

# **Binding modes**

While 2 was attached via bidentate bonding of the carboxylate to two Ti atoms, with the proton adsorbing on a step oxygen, the adsorption of 1 is more involved. Initially, 1 was attached via its boron on a step oxygen, with one fluoride released and adsorbed onto a Ti site as given in Figure S26a. However, during the NVT nuclear dynamics, the step oxygen was plucked out of the surface, leaving an oxygen defect as shown in Figure S26b, and forming a bridge between the Ti surface site and the boron atom. We therefore reoptimized the system in this new binding mode, but also tested the thermodynamic requirements to refill this oxygen defect with a water molecule, releasing a proton and the adsorbed  $F^-$  on the surface, which was thermodynamically favorable. Another possible pathway to the exact same binding mode is the possibility of a hydroxide adsorbed on a Ti surface site, that nucleophilically attacks the boron, expelling a fluoride and releasing its proton, leading to the exact same binding mode. The high thermodynamical favorability of this adsorption of 1 is the reason we simulate the  $1/TiO_2$  system with this specific binding, that would also explain the strong boron-surface attachment.



**Figure S28.** Switch of adsorption mode of  $1/\text{TiO}_2$  over the course of the NVT equilibration. Initially, 1 is attached via the boron on a step oxygen (a). During the nuclear dynamics, the step oxygen gets plucked out of the surface, releasing an oxygen vacancy while attaching 1 via a boron-oxygen-titanium bridge on the anatase surface.

# Hückel parameter optimization

The versatility of the Extended Hückel (EH) based Hamiltonian is, apart from its low computational cost, the ability to optimize the parameters, such that the energy differences of the frontier orbital levels reproduce higher level methods or experiments. GFN-xTB based geometries of the dyes in their neutral form (before dissociative adsorption on the anatase surface) were used to obtain energies and orbitals using the standard Hückel parameters. Figure S29 shows the density of states (DOS) of the anatase (101) model and the two dyes **1** and **2** obtained with standard Hückel parameters. As can be seen, using standard parameters, the LUMO levels of both dyes fall within the TiO<sub>2</sub> band gap, contrary to experiment. We therefore optimize the parameters so that the HOMO and LUMO levels have the correct relative energy in comparison to the anatase conduction band edge (CBE).



Figure S29. DOS of TiO<sub>2</sub> (black), 1 (red), and 2 (blue) using the standard EH parameters on GFN-xTB optimized geometries. The CBE of the TiO<sub>2</sub> and the HOMO and LUMO of 1 and 2 are marked. Note that the LUMOs of 1 and 2 are in the band gap of TiO<sub>2</sub>.

Table S4 gives the experimental values for the CBE of  $TiO_2$  as derived in the main manuscript and the HOMO and LUMO levels derived from the experimental oxidation potential and  $E_{0-0}$  energies for **1** and **2** (compare also Figure 2 in the main manuscript). This is given in potential vs NHE as well as energy. Using the energy of the CB edge of anatase, we determined the relative energy of the other levels. As can be seen in Figure S29, the CBE of anatase in our model system using standard Hückel parameters is -9.87 eV. This is the energy we will use as reference to optimize the Hückel parameters for **1** and **2**. The target values were obtained by adding the relative energies of each respective energy level to the -9.87 eV of the CBE (Table S4). The last column of Table S4 gives the energies obtained by EH for TiO<sub>2</sub>, **1**, and **2** with optimized parameters.

Table S4. Experimental potential, energy and relative energy vs the CBE of TiO2 for relevant electronic states in TiO2,
1 and 2, as well energies obtained with standard EH parameters, the target values obtained from experiment used for
optimization and the resulting energies when using the optimized EH parameters.

		$\begin{array}{c} \text{Potential} \\ V_{\text{NHE}} \end{array}$	Energy (exp)	Relative energy vs.	Standard EH	Target (-5.87 eV)	Optimized EH
				CDE	parameters		parameters
TiO <sub>2</sub>	CBE	-0.57 V	-4.00 eV	0.00 eV	-9.87 eV	-9.87 eV	-9.87 eV
1	НОМО	1.76 V	-6.33 eV	-2.33 eV	-11.79 eV	-12.20 eV	-12.20 eV
	LUMO	-0.67 V	-3.90 eV	+0.10 eV	-10.12 eV	-9.77 eV	-9.77 eV
2	НОМО	1.51 V	-6.08 eV	-2.08 eV	-11.61 eV	-11.95 eV	-11.93 eV
	LUMO	-0.87 V	-3.70 eV	+0.30 eV	-10.08 eV	-9.57 eV	-9.55 eV

The optimization procedure itself was performed using a genetic algorithm to reduce the effect of a cost function and is described in more detail elsewhere.<sup>3</sup> Figure S30 shows the new DOS of anatase (101),  $\mathbf{1}$ , and  $\mathbf{2}$  with optimized parameters.



Figure S30. DOS of TiO<sub>2</sub> (black), 1 (red), and 2 (blue) using the optimized EH parameters on GFN-xTB optimized geometries. The CBE of the TiO<sub>2</sub> and the HOMO and LUMO of 1 and 2 are marked. Note that the LUMO of 1 and 2 are now within the CBE of TiO<sub>2</sub>, allowing for injection.

However, the parameters do not only affect the energies of the orbitals but might also change their spatial character. To make sure the order of orbitals and their spatial distribution is not changed dramatically, we compare the spatial distribution of the frontier orbitals of **1** and **2** using standard and optimized Hückel parameters, with DFT as reference (using Gaussian,<sup>4</sup> B3LYP<sup>5-6</sup>, with the LANL2DZ basis set<sup>7-8</sup>). As can be seen, the spatial form of the frontier orbitals remains the same as the reference method DFT.

	DFT	Extended Hückel
	Compound 1	
номо		We want
LUMO		- Contraction of the second se
	Comp	ound 2
номо	A CONTRACT OF A	WHAT I WANT
LUMO		

Table S5. Spatial distribution of the frontier orbitals of 1 and 2, obtained by DFT and the optimized EH parameters.

In Table S6, we give the final optimized parameters, color coded for the respective atoms they were used for.

name	Color in structure	Orbital type	Ionization Potential	ζ	Wolfsberg- Helmholtz parameter
H1	Black	S	-13.03399	1.470434	1.540723
B1	Brown	S	-15.21663	1.078406	1.680590
		р	-8.44388	1.291772	2.283668
C1	Black	S	-21.27384	1.426073	2.593424
		р	-11.56910	1.645315	2.184011
C2	Cyan	S	-21.30001	1.385126	2.584027
		р	-11.54055	1.643315	2.314259
C3	Green	S	-20.68581	1.387871	1.833588
		р	-11.71759	1.386452	1.389984
C4	Orange	S	-21.88976	1.815491	2.453569
		р	-10.47301	1.094237	0.918308
N1	Blue	S	-26.31013	1.821709	1.146832
		р	-12.95164	2.050255	1.651968
01	Red	S	-32.94503	1.851820	2.004068
		р	-15.67865	2.769459	2.620027
F1	Purple	S	-40.74085	2.311883	1.093578
<u> </u>		р	-17.53355	2.079223	1.708915

 Table S6. Optimized EH parameters and atom types used for 1 and 2.



Using these optimized parameters, we then performed the quantum dynamics with this optimized EH Hamiltonian.

# Nuclear Dynamics and quantum propagation

In Figure S31 we show the procedure to run the electron injection simulations schematically. After optimization of the model systems 1/TiO<sub>2</sub> and 2/TiO<sub>2</sub>, GFN-xTB<sup>2</sup> based molecular dynamics were performed using the dftb+ program.<sup>1</sup> Using a Nosé-Hoover chain,<sup>9</sup> equilibration runs in the NVT ensemble at 300 K were performed using a time step of 1 fs and a total simulation time of 5 ps. After this equilibration, simulations in the NVE ensemble were performed using a 0.1 fs time step to a total of 2.5 ps. This production run was cut into ten trajectories of 250 fs each, that was used for the quantum dynamics simulations of photoexcited electron using the AO-MO propagator.<sup>10</sup> The initial excitation was modelled by preparing the initial electron wave packet in the fragment HOMO of the dye molecule. After running the ten quantum dynamics trajectories, the obtained electron populations on all fragments were obtained. The population on the dye fragments were than averaged over all ten trajectories to obtain mean electron injection traces that could be used for estimating the electron injection rates.



**Figure S31.** Schematic of the simulation procedure. Nuclear dynamics were simulated using semi-empirical GFNxTB based molecular dynamics. After initial equilibration at 300 K in the NVT ensemble with a time step of 1 fs for a total of 5 ps, a production run in the NVE ensemble using a shorter 0.1 fs time step was performed for a total of 2.5 ps. This trajectory was cut into 10 trajectories of 250 fs each to be used in the quantum dynamics simulations of interfacial electron transfer. The resulting electron populations were then averaged over all ten trajectories to obtain a mean electron injection trace to estimate injection rates.

# 8. NMR Characterization



Figure S32. <sup>1</sup>H NMR of 1 in CDCl<sub>3</sub>.



Figure S33. <sup>19</sup>F NMR of 1 in CDCl<sub>3</sub>.



Figure S35. <sup>1</sup>H NMR of 2 in CD<sub>3</sub>OH.



Figure S36. <sup>19</sup>F NMR of 2 in CD<sub>3</sub>OH.



Figure S37. <sup>11</sup>B NMR of 2 in CD<sub>3</sub>OH.

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