

Preferential Direction of Electron Transfers at a Dye–Metal Oxide Interface with an Insulating Fluorinated Self-Assembled Monolayer and MgO

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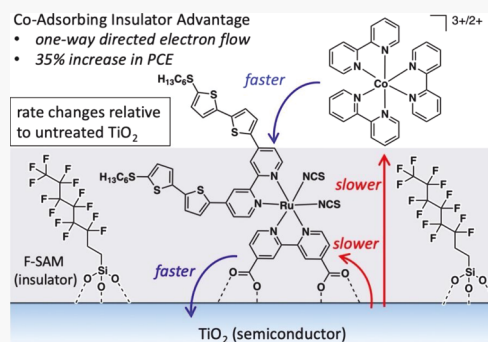
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ABSTRACT: Slowing undesirable electron transfer reactions at metal oxide–dye interfaces is important for many technologies. In particular, after an interfacial photoinduced charge separation event at a metal oxide–dye interface, it is critically important to limit the rate of electron transfer reactions back to sensitizers and to limit electron transfer reactions between the electrolyte and the metal oxide. Ruthenium-based dyes at metal oxide interfaces are widely used in many fields; however, these dyes often have poor surface insulation resulting in fast recombination kinetics with transition metal-based redox shuttles (RSs) in an electrolyte. This work explores two semiconductor surface modification strategies designed to minimize recombination events of electrons in TiO₂ with oxidized RSs using a fluorinated siloxane insulator (PFTS) and a metal oxide insulator (MgO) with a well-known Ru dye, **B11**. Additionally, the influence of these treatments on the rate and duration of photoinduced interfacial charge separation at the TiO₂–dye interface was examined. The TiO₂–dye–RS systems were studied via dye-sensitized solar cell current–voltage curve, incident photon-to-current conversion efficiency, small modulated photovoltage transient, time-correlated single-photon counting, and transient absorption spectroscopy measurements. MgO was found to decrease the rate of the electron transfer reaction from the metal oxide to the electrolyte, decrease the rate of the electron transfer reaction to the oxidized dye from TiO₂, increase the electron transfer reaction rate from a reduced RS to an oxidized dye, and decrease the electron injection rate from the photoexcited dye to TiO₂. Interestingly, 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (PFTS) was found to desirably improve these rates relative to MgO or untreated TiO₂. A model based on electrostatic interactions is presented to explain the exceptional behavior of PFTS with density functional theory computational analysis of PFTS supporting this model.



INTRODUCTION

Dye-sensitized solar cells (DSCs) offer a convenient way to analyze interfacial electron transfer reactions within a well-understood framework.^{1–13} In general, DSCs are continuing to attract intense research interest because of the ability to use these devices as building-integrated photovoltaics,^{6,14–17} a relatively low production cost compared to many inorganic technologies,^{6,14,18,19} high performance in low-light environments such as those commonly used for consumer electronics,^{20–22} and a continuous rise of power conversion efficiencies (PCEs).^{23–27} PCEs as high as 14.3% for organic dye-based devices have been demonstrated,²⁴ which have surpassed the highest PCEs of the traditionally dominant ruthenium-based sensitizers at approximately 11.9%.²⁸

n-Type DSCs operate by photoexcitation of a sensitizer followed by an interfacial electron transfer reaction at a metal oxide interface (injection, Figure 1). The electron then traverses an external circuit to a counter electrode and is collected by a redox shuttle (RS). The RS then returns the electron to the oxidized dye (regeneration) to complete the

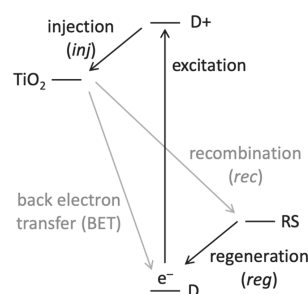
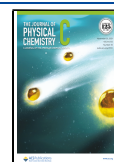


Figure 1. Illustration of the desired (black) and undesired (gray) electron transfer pathways with nomenclature listed beside each arrow.

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circuit. Two nonproductive competing pathways are (1) electron transfer from TiO_2 to the oxidized dye after electron injection (back electron transfer, BET) and (2) transfer of electrons in TiO_2 to the electrolyte (recombination).

The higher performance of organic sensitizers relative to metal-based dyes is due in part to organic sensitizers being more easily engineered to give slower recombination rates in many cases. This allows for the use of positively charged one-electron RSs with organic sensitizers that would otherwise have PCE inhibitive fast recombination rates with metal-based dyes.^{29–33} The highest-efficiency ruthenium sensitizers with I_3^-/I^- often rely on ligands such as thiocyanate (NCS^-) which are not easily amenable to the introduction of long-alkyl-chain groups often used to slow recombination rates with one-electron RSs.^{1,34–37} A popular strategy to overcome this limitation is through the molecular engineering of ruthenium sensitizers without NCS^- ligands for better semiconductor surface protection which has improved the PCE of ruthenium sensitizers to above 9% with cobalt-based RSs.^{37–43} However, these approaches have generally resulted in blue-shifted absorption spectra, which has limited these sensitizers from reaching the high photocurrent values traditionally associated with ruthenium dyes.^{28,44,45} An alternative approach to the re-engineering of ruthenium sensitizers to be compatible with transition metal-based RSs is the use of surface insulation strategies that are irrespective of the sensitizer structure.^{46–55} Strategies working irrespective of the sensitizer structure are particularly attractive as they reduce synthetically difficult dye design demands and could allow for the use of existing, broadly absorbing dyes such as **B11** with transition metal-based RSs such as $[\text{Co}(\text{bpy})_3]^{3+/2+}$ (Figure 2).⁵⁶ Through kinetic

noncovalent bonding or electrolyte adhesion to the TiO_2 surface).^{49,61–64} This study seeks to compare these two approaches using a transition metal-based RS ($[\text{Co}(\text{bpy})_3]^{3+/2+}$) used widely in high performing devices and a ruthenium sensitizer (**B11**) that is one of the highest PCE ruthenium dyes known using I_3^-/I^- (Figure 3).⁵⁶ Notably, with the MgO insulating approach, significant effects on the rates of the injection, BET reaction, and recombination reactions are expected because each of these electron transfers crosses the insulating barrier. With the F-SAM approach, only the recombination reactions would have to cross the insulating barrier while the remaining electron transfer reactions would not have to directly cross the insulating barrier. The majority of the prior studies on these two insulating approaches focus on monitoring recombination rates typically with ruthenium-based sensitizers and the iodide/triiodide RS through light-modulated voltage techniques or electrochemical impedance spectroscopy (see Table S1 for a more detailed analysis of prior studies that were referenced above). A common observation in these studies is a reduction in charge recombination rates. The study of ruthenium-based sensitizers with cobalt RSs to analyze regeneration rates and injection rates in the presence of insulator functionality at the TiO_2 surface is understudied and a focus of this work. Combining ruthenium photosensitizers with a cobalt RS and comparing F-SAM to MgO while studying electron transfer reactions via transient absorption spectroscopy (TAS) and time-correlated single-photon counting (TCSPC) is a new approach to the best of our knowledge. Additionally, the BET reaction and recombination reaction are also studied in this work to give a more complete picture of how these insulating approaches are affecting the four primary electron transfer reactions in the DSC device.

METHODS

General Information. All commercial materials were used as received unless otherwise noted. **B11** was purchased from Dyenamo and purified with Sephadex LH-20 twice with methanol as the eluent before any studies were conducted.⁶⁵ Sephadex LH-20 was purchased from GE Healthcare Life Sciences. **N719** was purchased from Solaronix. PFOS was purchased from Ark Pharm. $\text{Mg}(\text{OMe})_2$ was purchased from Aldrich. $[\text{Co}(\text{bpy})_3]^{3+/2+}$ was prepared following literature procedures.⁶⁶ FTO was purchased from Hartford Glass Company, Indiana, USA. Absorption spectroscopy was conducted with a Cary 5000 UV–vis–NIR spectrophotometer.

DSC Device Fabrication. DSC devices were fabricated and characterized as previously reported with identical equipment to that previously reported.⁶⁷ The active-layer TiO_2 (nanoparticle size 28–31 nm, Dyenamo, DN-GPS-30TS) film thickness was 5 μm . Sensitized TiO_2 films were prepared by immersion in a room-temperature dye solution for 4 h. Dye uptake was found to be near complete at 3 h with modest changes after 3 h (Figure S4). The **B11** solution is 0.3 mM dye concentration in equal parts acetonitrile, *tert*-butyl alcohol, and DMSO with chenodeoxycholic acid (CDCA) added as a coadsorbent at a concentration of 20 mM. Notably, the CDCA additive was found to be important for F-SAM-based device performances, which indicates that both additives are beneficial similar to the observations of Wooh et al. (Table S4 and Figures S22 and S23).⁶¹ The **N719** solution is 0.3 mM dye concentration in ethanol. The $[\text{Co}(\text{bpy})_3]^{3+/2+}$ electrolyte

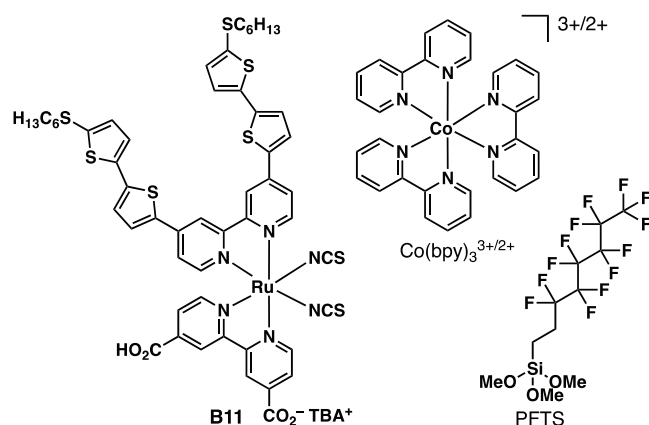


Figure 2. Structures of **B11** (where TBA is tetrabutylammonium), $[\text{Co}(\text{bpy})_3]^{3+/2+}$, and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrimethoxysilane (PFTS).

improvements such as slowing recombination and BET rates, there is potential to enhance the performance of a broadly absorbing **B11**/ $[\text{Co}(\text{bpy})_3]^{3+/2+}$ system to have wide applicability for many dye-sensitized applications.

The use of insulating metal oxides such as MgO and Al_2O_3 between the dye and semiconductor to reduce recombination rates has been an active area of research within the DSC field.^{46,49,50,53–55,57–60} More recently, fluorinated molecules with silyl anchors have been employed as fluorinated self-assembled monolayers (F-SAMs) that coadsorb to the semiconductor in the presence of dyes to reduce recombination sites and lower surface tension (i.e., give a reduction in

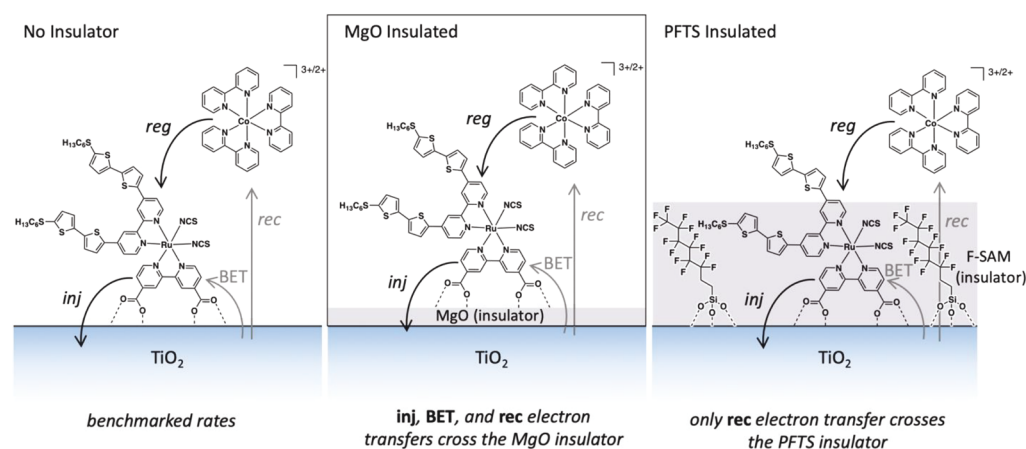


Figure 3. Added insulation strategies being probed in this work compared to the case of no-added insulators. Arrows represent electron transfer reactions with black arrows representing productive electron transfer reactions and gray arrows representing nondesirable electron transfer reactions.

was composed of a saturated solution of near 0.25 M Co^{2+} , 0.05 M Co^{3+} , 0.1 M LiTFSI (TFSI = bis-(trifluoromethanesulfonyl)imide), and 0.5 M TBP (TBP = 4-*tert*-butylpyridine) in acetonitrile. The PFTS treatment was applied as previously described.⁶⁷

MgO Film Formation. A 6 mL solution of the desired concentration of $\text{Mg}(\text{OMe})_2$ was prepared in methanol. Before sensitization, the TiO_2 electrodes were dipped in the MgO solution in the dark for 30 min. After 30 min, the electrodes are rinsed with methanol and dried in a furnace for 1 h at 500 °C. The electrodes are allowed to cool to room temperature and sensitized as described. This is very similar to the procedure previously reported in the literature that results in thicknesses on the order of 1 nm.⁵⁴

TCSPC Measurements. Emission lifetime curves were obtained using the 485 nm line of an LDH series 485B pulsed diode laser (pulse width approx. 100 ps) as the excitation source, and emission was detected using a PicoQuant PDM series single-photon avalanche diode (time resolution approx. 50 ps) and a TimeHarp 260 time-correlated single-photon counter (25 ps resolution). Time-resolved emission measurements were monitored with a 650 nm longpass filter and averaged over three kinetic measurements. Time-resolved emission kinetics were best modeled by a single-exponential function.

TAS Electrode Fabrication. The electrodes were composed of a 3 μm mesoporous TiO_2 layer (particle size 30 nm, Dyenamo, DN-GPS-30TS) with no scattering layer added. The dye- TiO_2 film preparation is as described above in the DSC section. Once the dyed-film was removed from the dyeing solution and rinsed, the electrode was partially sealed with a precut semicircle (about 75% of a complete circle) of 25 μm -thick hot melt film (Surlyn, Solaronix, “Meltonix 1170–25”) and a thin glass cover slip by heating the system at 130 °C under 0.1 psi pressure for 30 s. Devices were completed by filling the cells with electrolyte solution by injecting it into the open portion of the coverslip with a microsyringe. The device is then sealed with a light-cured adhesive (PermaBond UV6231) and curing under 450 nm light for 45 s with the active area shielded from light.

Transient Absorption Measurements. Time-resolved absorption spectra were collected using an Edinburgh LP980 optical system. Excitation light of 532 nm (<2 mJ/pulse; 6 ns

pulswidth) was provided by a Continuum Surelite pulsed Nd:YAG laser equipped with a doubling crystal, and the probe source was a 150 W pulsed xenon arc lamp. TiO_2 electrodes of 3 μm thickness were used for the transient absorption measurements. The devices were positioned at a 45° angle relative to the pump and probe sources to maximize overlap and direct scattered light away from the entrance slit to the monochromator.

Computational Approach. Molecules were drawn in ChemDraw (19.1.0.5) and saved as an MDL Molfile. These geometries were then optimized with the MMFF94 force field via Avogadro (1.2.0). Accurate geometry optimizations were then performed with density functional theory (DFT) using Gaussian16 at the B3LYP/6-311G(d,p) level of theory.⁶⁸

RESULTS AND DISCUSSION

DSC devices with **B11** as the dye and $[\text{Co}(\text{bpy})_3]^{3+/2+}$ as the RS were fabricated by treating TiO_2 -dye electrodes with varying concentrations of a F-SAM-generating reagent, 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (PFTS, Figures 2, 4, and 5, Table 1). In the absence of PFTS, the **B11**/ $[\text{Co}(\text{bpy})_3]^{3+/2+}$ RS DSC device gives a baseline PCE of 5.7% according to the equation $\text{PCE} = (J_{\text{SC}} \times V_{\text{OC}} \times FF)/I_0$, where J_{SC} is the short-circuit current density, V_{OC} is the open circuit voltage, FF is the fill factor, and I_0 is the incident photon intensity set to 1 sun for these studies (Table 1, entry 1; Figure 4). Upon submerging the TiO_2 -**B11** sensitized electrode into a 0.0125 M PFTS solution in hexanes for 90 min at 30 °C and then assembling the DSC device, the PCE increased to 6.3% primarily because of an increase in V_{OC} from 717 to 752 mV (Table 1, entry 2; Figure 4). The increase in photovoltage is likely due to a reduction in the recombination of electrons at

the TiO_2 surface with $[\text{Co}(\text{bpy})_3]^{3+}$ and is further discussed below. A modest increase in J_{SC} is also noted from 11.7 to 11.9 mA/cm^2 . Increasing the PFTS solution concentration to 0.025 M further increased the V_{OC} to 779 mV and gave a significant increase in J_{SC} to 13.5 mA/cm^2 for a PCE of 7.7% (Table 1, entry 3). The observed PCE value corresponds to a 35% increase in PCE over the no-PFTS device. The increase in J_{SC} is apparent from the IPCE measurement which shows an increased height throughout the spectrum with a higher peak IPCE value at 70% versus 60% for the no-PFTS device (Figure 4). The increase in J_{SC} may be due to the reduction of surface

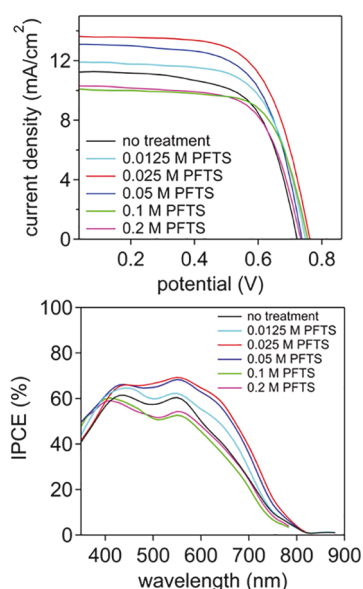


Figure 4. Current density–voltage (J – V) curves (top) and incident photon-to-current conversion efficiency (IPCE) curves (bottom) for varying PFTS concentrations on **B11**/[Co(bpy)₃]^{3+/2+} DSC device performances.

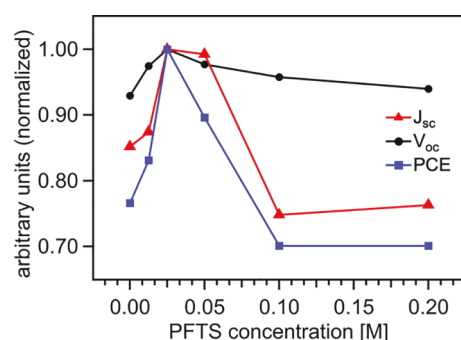


Figure 5. Changes in photovoltage, photocurrent, and PCE with respect to PFTS concentration. All values are normalized to the highest performing cell values.

Table 1. Effect of Varying PFTS Concentrations on **B11**/[Co(Bpy)₃]^{3+/2+} DSC Device Performance^a

entry	PFTS	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)
1	none	717 ± 12	11.7 ± 0.8	0.66 ± 0.05	5.7 ± 0.2
2	0.0125 M	752 ± 8	11.9 ± 0.1	0.68 ± 0.01	6.3 ± 0.1
3	0.025 M	779 ± 7	13.5 ± 0.4	0.70 ± 0.01	7.7 ± 0.3
4	0.05 M	760 ± 19	13.0 ± 0.7	0.68 ± 0.03	6.8 ± 0.2
5	0.1 M	748 ± 45	9.9 ± 0.5	0.71 ± 0.01	5.3 ± 0.2
6	0.2 M	732 ± 11	10.3 ± 0.4	0.70 ± 0.00	5.4 ± 0.3

^aEach entry is an average of at least five devices.

tension (defined above) allowing for a faster flowing electrolyte in addition to slowing recombination, slowing BET, or increasing injection efficiencies (see the discussion below).⁶¹ Increasing the PFTS solution concentration further gave lower V_{OC} , J_{SC} , and PCE values relative to the 0.025 M treatment (Table 1, entries 4–6; Figure 5). Surface absorption curves were taken with **B11** on TiO₂, **B11** on MgO-treated TiO₂ (discussed below), and **B11** on PFTS-treated TiO₂ to evaluate relative dye loadings (Figure S1). **B11** on TiO₂ and **B11** on

MgO-treated TiO₂ films show similar film absorbances with no appreciable change. However, upon PFTS treatment (0.025 M), a 40% reduction in film absorption is observed. Upon analyzing the PFTS treatment solution after the film is submerged, no significant absorption is found in the liquid layer corresponding to **B11** which suggests that the dye is not desorbing from the surface (Figure S2). Increasing the concentration of PFTS correlates to decreasing film absorption (Figure S3), which could be due to a difference in the dielectric environment around **B11** being induced by PFTS. Analogous device data were also obtained for an additional ruthenium-based sensitizer, **N719** (Figures S5–S7; Table S2). A similar trend for **N719** devices was observed which indicates that this approach is likely general because two ruthenium-based sensitizers with significantly different structures demonstrated an increase in PCE values at low PFTS solution concentrations when compared to no-PFTS devices and devices prepared with higher PFTS solution concentrations (Figures S3 and S4 and Table S1). Additionally, F-SAM treatments with three different fluorinated materials varying the number of perfluorinated carbons were also analyzed in DSC devices with longer chain lengths favoring higher V_{OC} values (Table S3; Figures S20 and S21). The highest photocurrent is observed at the intermediate chain length. These chain length-dependent trends are discussed with regard to the kinetics of electron transfer reactions below; however, the PFTS treatment is consistently used for the remaining comparative studies.

Devices with no PFTS, 0.025 M PFTS, and 0.05 M PFTS were probed further to better understand the role of PFTS in electron lifetimes with small modulated photovoltage transient (SMPVT) measurements (Figure 6).^{8,9} The three concen-

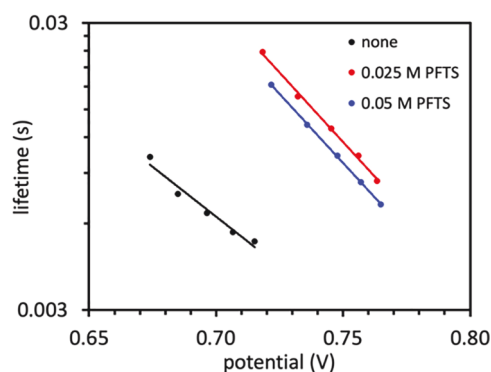


Figure 6. SMPVT measurement with **B11**/[Co(bpy)₃]^{3+/2+} DSC devices with varying concentrations of PFTS.

trations were selected with no PFTS being the baseline measurement, 0.025 M PFTS being the peak PCE conditions, and 0.05 M PFTS showing a decline in device performance. SMPVT data correlate with the photovoltage trend observed via J – V curve measurements with electron lifetime in TiO₂ increasing as follows: no PFTS < 0.05 M PFTS < 0.025 M PFTS (Figure 6). These data suggest that recombination in the DSC device decreases initially as PFTS is added and then begins to increase modestly as a larger amount of PFTS is added to the TiO₂ surface. The reason for the modest increase in recombination rates at higher PFTS loading is not apparent from the SMPVT measurements because increased amounts of PFTS would presumably serve to better block TiO₂ surface sites.

Table 2. Effect of Varying $\text{Mg}(\text{OMe})_2$ Concentrations on $\text{B11}/[\text{Co}(\text{bpy})_3]^{3+/2+}$ Device Performances^a

entry	$\text{Mg}(\text{OMe})_2$ (conc.)	PFTS	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF	PCE (%)
1	none	none	717	11.7	0.66	5.7
2	0.001 M	none	773	13.2	0.68	6.9
3	0.005 M	none	764	12.2	0.61	5.7
4	0.01 M	none	809	8.3	0.71	4.9
5	0.05 M	none	841	7.2	0.74	4.6
6	0.1 M	none	859	7.9	0.76	5.2
7	0.15 M	none	836	6.8	0.75	4.3
8	0.001 M	0.0125 M	758	10.9	0.63	5.3
9	0.001 M	0.025 M	764	11.6	0.71	6.5
10	0.001 M	0.05 M	809	11.6	0.70	6.6
11	0.001 M	0.1 M	782	13.5	0.49	5.3

^aEach entry is an average of at least two devices with a PCE standard deviation of $\leq \pm 0.3$.

MgO as an outer shell surface insulating approach to the TiO_2 nanoparticles was analyzed by applying an MgO layer from a solution of varying concentrations of $\text{Mg}(\text{OMe})_2$ in methanol at room temperature for 30 min to nonstained TiO_2 films. These films were prepared as previously described in the literature.^{53,54} Films were rinsed with MeOH and heated to 500 °C before staining the MgO -insulated electrode surface with the sensitizer. This approach shows an increase in PCE for the lowest concentration applied (0.001 M $\text{Mg}(\text{OMe})_2$) relative to the untreated surface (5.7 versus 6.9%, Table 2, Figures S8 and S9). A smaller peak PCE performance is observed with the MgO treatment compared to the PFTS treatment approach (6.9 versus 7.7%). The increase in PCE when MgO is used compared to non- MgO -treated films is due to an increase in both V_{OC} (717 versus 773 mV) and J_{SC} (11.7 versus 13.2 mA/cm²) for the MgO -treated surface because of a lowering of the recombination rate which is supported by SMPVT measurements that demonstrate an increase in electron lifetimes when MgO is applied (Figure S10). Attempts to further lower the $\text{Mg}(\text{OMe})_2$ concentration beyond 0.001 M led to aberrant results with low reproducibility. Addition of higher amounts of MgO led to lower performing devices because of a rapid loss in J_{SC} that was partially offset by the continually rising V_{OC} values (Table 2, entries 3–7). Notably, attempts to combine the two surface treatment approaches (MgO and PFTS) did not lead to a combined performance enhancement in the DSC devices compared to either of the individual treatments (Table 2, entries 8–11). The effects of MgO and PFTS on electron transfer kinetics (electron injection, BET, and regeneration) were further probed with TCSPC and TAS.

The excited-state dynamics of **B11** were probed using steady-state and time-resolved emission spectroscopy (Figure 7 and Table 3). Time-resolved emission experiments were performed to evaluate the kinetics of electron injection based on different surface treatments (see the Experimental Section for spectroscopy equipment details). Excited-state lifetimes were measured for **B11** anchored on an insulating zirconium oxide (ZrO_2) film, a TiO_2 film, a TiO_2 film with a MgO surface treatment prepared from a 0.001 M $\text{Mg}(\text{OMe})_2$ solution, and a TiO_2 film with a PFTS surface treatment prepared from a 0.025 M PFTS solution. All films were submerged in a 0.1 M LiTFSI solution in MeCN. Electron injection efficiencies (η_{eff}) were determined according to eq 1 where τ_{TiO_2} represents the approximate excited-state lifetime on TiO_2 and τ_{ZrO_2} represents the approximate excited-state lifetime on ZrO_2 .

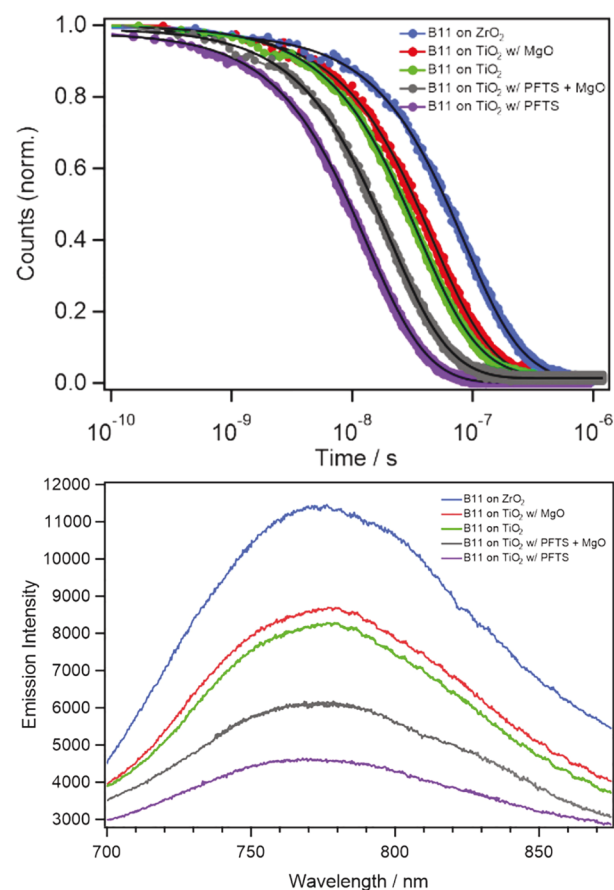


Figure 7. (A) Time-resolved emission decays of **B11** on ZrO_2 (blue), TiO_2 with no surface treatment (green), TiO_2 with a MgO surface treatment (red), TiO_2 with a PFTS surface treatment (purple), and TiO_2 with a combined PFTS and MgO surface treatment (gray). The acquisition time for each sample was 300 s with excitation at 485 nm. (B) Steady-state emission spectra of **B11** on insulating ZrO_2 and semiconducting TiO_2 collected at room temperature.

$$\eta_{\text{eff}} = \left[1 - \frac{\tau_{\text{TiO}_2}}{\tau_{\text{ZrO}_2}} \right] \times 100 \quad (1)$$

The excited-state lifetime measured for **B11** sensitized on ZrO_2 was used as a reference measurement because ZrO_2 is an insulator that prevents electron injection and allows for the monitoring of dye excited-state kinetics at a solid surface.^{69,70} The emission lifetime of **B11** on ZrO_2 was estimated to be

Table 3. Excited-State Emission Measurements for Insulating ZrO₂ and Semiconducting TiO₂ Films Sensitized with Dye B11

sample	τ (ns)	η_{eff} (%)
B11 on ZrO ₂	12.5	
B11 on TiO ₂	4.2	66
B11 on TiO ₂ w/MgO	5.2	58
B11 on TiO ₂ w/F-SAM	1.8	86
B11 on TiO ₂ w/MgO and F-SAM	2.5	80

12.5 ns, which is consistent with previously reported studies of the decay dynamics of Ru triplet excited states using ZrO₂ as a reference material under similar environmental conditions (Table 3; Figure 7).^{69,70} In contrast, the excited-state lifetime on TiO₂ is predicted to be significantly shorter because of emission quenching upon injection of an electron from the photoexcited dye to the TiO₂ conduction band (CB). For the TiO₂ electrode without a surface treatment, the emission lifetime of B11 was found to be 4.2 ns which corresponds to a η_{eff} of 66%. This is notably shorter than the lifetime measured on ZrO₂ and is assigned to quenching of the B11 triplet excited state by electron injection. Steady-state emission measurements of the TiO₂-B11 film show a quenching of the emission intensity relative to ZrO₂-B11 films as expected (Figure 7). With the addition of an MgO surface insulating treatment between TiO₂ and B11, the excited-state lifetime was observed to increase to 5.2 ns, which decreased η_{eff} from 66 to 58% when TiO₂ films and MgO-treated TiO₂ films were compared (Table 3). This suggests that the presence of a thin insulating layer between TiO₂ and the dye results in a decrease in injection quantum yields from the photoexcited dye. Interestingly, when PFTS was used as a surface treatment, the emission lifetime of B11 on TiO₂ decreased to 1.8 ns, which improved η_{eff} from 66 to 86%. This result suggests that the PFTS surface treatment not only acts as an insulating layer, but may also introduce a method for improving charge transfer efficiency from photoexcited dyes to TiO₂. Upon analyzing F-SAM materials with various numbers of perfluorinated carbons, an injection efficiency trend is observed with $4 < 6 < 8$ perfluorinated carbons on the F-SAM reagent giving devices ranging from 85 to 87% injection efficiency (Figures S32 and S33; Table S6). Notably, combining the MgO and PFTS treatments leads to injection efficiencies between MgO only- and PFTS only-treated films (Figures S32 and S33; Table S6).

Next, TAS was used to probe the rate of BET to the dye and the rate of regeneration of the ground-state dye from [Co(bpy)₃]²⁺ after photoinduced interfacial charge separation.

Following photoexcitation of B11, electrons are injected into the CB of TiO₂, which produces an oxidized B11 dye and reduced TiO₂. When measuring device kinetics on a microsecond timescale, electron injection is assumed to be completed, and therefore, the main signal observed can be attributed to the oxidized dye. Figure 8 shows the transient absorption spectrum of a TiO₂-B11 sensitized film, which consists of a negative absorption band that corresponds to the ground-state bleach region and a positive, lower energy, absorption band that corresponds to the absorption spectrum of oxidized B11. Time-resolved absorption measurements were monitored in the oxidized B11 absorption region to analyze the effects of the two surface treatments on regeneration and BET reactions. The transient absorption kinetics were monitored at a constant wavelength (750 nm) near the maxima of the oxidized B11 absorption signal despite some modest drift in the observed absolute maxima value of the broad oxidized B11 absorption signal.

Transient decays were nonexponential in nature and well described by a Kohlrausch–Williams–Watts^{69–76} stretched exponential function according to eq 2,

$$\Delta OD(t) = \Delta OD_{t=0} e^{-\left(\frac{t}{\tau_{\text{KWW}}}\right)^\beta} \quad (2)$$

where $\Delta OD_{t=0}$ is equal to the signal magnitude at time zero and β is the stretching parameter, which is inversely related to the width of the underlying Lévy distribution of rate constants and ranges in value from 0 to 1. Correlation between the calculated lifetime constant and the stretching parameter can lead to significantly different distributions of the underlying rate constants that fit the kinetics objectively well.² To ensure the most appropriate fits, time constants and β values chosen to normalize the transient absorption kinetics were sampled from a range of values and assigned on the basis of best fit and minimal error. The average lifetime can be calculated from these fitting parameters using a gamma function distribution of β^{-1} (eqs 3 and 4),

$$\Gamma(x) = \int_0^\infty u^{(x-1)} e^{-u} du \quad (3)$$

$$\tau_{\text{obs}} = \tau \Gamma\left(\frac{1}{\beta}\right) \quad (4)$$

where Γ denotes the gamma function distribution and u is the integrand $\beta^\alpha \times \Gamma(x)^{-1}$. The parameter α is known as the shape parameter and it defines the shape of the distribution and β is the inverse scale (or stretch) parameter that defines the width

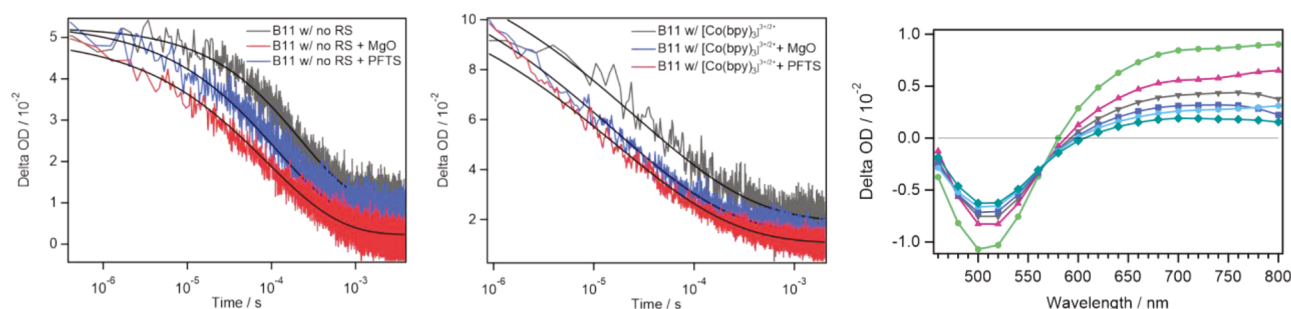
**Figure 8.** Transient absorption kinetics in the logarithmic scale monitoring the rate of: (left) the BET reaction and (middle) the regeneration reaction for: a TiO₂-B11 sensitized film, a TiO₂-B11 sensitized film with an MgO surface treatment, and a TiO₂-B11 sensitized film with a PFTS surface treatment. (Right) Transient absorption difference spectra for a TiO₂-B11 sensitized film with a PFTS surface treatment.

Table 4. Summary of Kinetic Data Obtained for B11 Devices^a

sample	$\tau_{\text{KWW}} (\mu\text{s})$	β	Γ	$\tau_{\text{obs}} (\mu\text{s})$	$\kappa_{\text{obs}} (\text{s}^{-1})$	$\Phi (\%)$
B11	70.2	0.50	1.0	150	6.70×10^3	
B11/[Co(bpy) ₃] ^{3+/2+}	13.6	0.35	1.3	68.0	1.50×10^4	70
B11/MgO	90.2	0.50	1.0	180	5.30×10^3	
B11/MgO/[Co(bpy) ₃] ^{3+/2+}	0.55	0.32	2.3	4.0	2.50×10^5	98
B11/PFTS	98.0	0.50	1.0	200	5.00×10^3	
B11/PFTS/[Co(bpy) ₃] ^{3+/2+}	0.58	0.32	2.3	4.2	2.40×10^5	98

^aBET kinetics were measured with an electrolyte containing 0.1 M LiTFSI and 0.5 M TBP in MeCN. Regeneration kinetics were measured with an electrolyte containing 0.25 M Co²⁺, 0.05 M Co³⁺, 0.1 M LiTFSI, and 0.5 M TBP in MeCN. All TAS measurements were taken under open-circuit conditions, with the pump power = <2.0 mJ/pulse and the probe wavelength set to 750 nm.

of the distribution. This mean lifetime can then be used to calculate the observed rate values obtained in the absence, k_{BE} , and presence, k_{reg} , of a redox-active species (eq 5). The regeneration efficiency is then calculated using eq 6.

$$k_{\text{obs}, i} = \frac{1}{\tau_{\text{obs}, i}} \quad (5)$$

$$\varphi_{\text{reg}} = \frac{k_{\text{reg}}}{k_{\text{reg}} + k_{\text{BE}}} \times 100 \quad (6)$$

We stress that assigning absolute regeneration efficiencies is challenging with several approaches noted in the literature in addition to the commonly used approach above.^{77–80} We note that this comparison likely overestimates the absolute regeneration efficiency as has been noted in the literature, but this method does allow for a simple comparison of regeneration efficiencies within this study.⁷⁹

If the dye-sensitized device contains an electrolyte void of a redox-active species, the oxidized B11 will undergo BET from the reduced TiO₂. The rate of this BET reaction, k_{BE} , can be determined from the time-resolved absorption profile of a sample without a RS present. If a RS is present in the electrolyte, the neutral B11 ground-state dye can be formed by either BET with reduced TiO₂ or by the regeneration reaction with the RS. In this case, the term “neutral” is the initial dye prior to photoinduced electron transfer not the absolute charge state of the complex. Efficient dye regeneration (φ_{reg}) requires that the rate of the reduction of the oxidized dye by the RS (k_{reg}) is sufficiently fast to effectively compete with the BET reaction rate (k_{BE}). When regeneration is efficient, the absorption-time profile is dominated by the regeneration reaction and the corresponding rate constant, k_{reg} , is representative of the rate of neutral dye regeneration by the RS.⁸¹

In all cases examined, the rate of the dye cation decay is observably faster for devices containing the [Co(bpy)₃]^{3+/2+} RS than for the RS-free devices, which suggests that the rate of dye regeneration is sufficiently competitive with the rate of the BET reaction irrespective of surface treatment (Figure 8 and Table 4). Without a surface treatment,

the rate of oxidized dye consumption is an order of magnitude faster in the presence of [Co(bpy)₃]^{3+/2+} at $1.50 \times 10^4 \text{ s}^{-1}$ versus $6.70 \times 10^3 \text{ s}^{-1}$ in the absence of the RS. This leads to a dye regeneration efficiency of 70% according to eq 6. Comparatively, the use of an insulating MgO surface treatment leads to a dye cation consumption rate of $5.30 \times 10^3 \text{ s}^{-1}$ with no RS present, which is modestly slower than the interfacial charge-separated lifetime in the absence of MgO. The electron transfer reaction from [Co(bpy)₃]^{3+/2+} is surprisingly faster in

the presence of an MgO treatment when compared to the no-treatment system ($2.50 \times 10^5 \text{ s}^{-1}$ vs $1.50 \times 10^4 \text{ s}^{-1}$). Thus, the faster regeneration reaction rate in the presence of an MgO surface treatment leads to a significant increase in the overall regeneration efficiency (98%). Concerning electron transfer reactions across the TiO₂|MgO|B11 interfaces, MgO primarily affects the rate of the regeneration reaction (beneficially) and electron injection reaction (detrimentally). A similar, yet more dramatic regenerative effect was observed when a PFTS surface treatment was applied. Addition of PFTS led to a BET reaction rate of $5.00 \times 10^3 \text{ s}^{-1}$, which is slower than that observed for untreated TiO₂ devices or MgO-treated devices. Additionally, F-SAM materials with a lower number of perfluorinated carbons led to slower BET rates (Figures S28, S29, and S31; Table S5). The PFTS findings coupled with emission lifetime studies show a dramatic increase in both the rate and duration of charge separation at TiO₂–dye interfaces as is desired for many dye-sensitized applications with a coadsorbent adjacent to the dye rather than between the dye and the metal oxide. Notably, addition of a PFTS surface treatment also increases the rate of the electron transfer reaction from [Co(bpy)₃]^{3+/2+} to the oxidized dye relative to untreated TiO₂ films, and the overall regeneration efficiency is improved to 98 versus 70% for untreated TiO₂. The reason for the increase in the rate of electron transfer from [Co(bpy)₃]²⁺ to the oxidized dye when the F-SAM is used is not directly obvious but may have to do the installation of a fluorine phase at the TiO₂–dye surface that allows for faster electrolyte diffusion across the TiO₂–dye surface because of a reduction in attractive noncovalent interactions. An increased diffusion rate would allow for an increased rate of collision between the dye cation and the reducing RS for an overall faster regeneration. Importantly, the directional charge transfer control imparted by PFTS (faster injection, faster regeneration, slower BET, and slower recombination) is important for achieving efficient and prolonged charge separation durations. Notably, combining PFTS with MgO did not significantly improve the electron transfer reactions further when compared to PFTS-treated devices (Figure S30; Table S5).

Based on the first-principles model shown in Figure 3, the rate of recombination was expected to be perturbed for both surface treatment approaches as is observed in Figure 9. The lifetime of electrons in TiO₂ was found to go up for both MgO and PFTS, with PFTS showing a modestly longer electron lifetime (slowed recombination) based on SMPVT measurements at open circuit potentials. No significant effect on regeneration was predicted based on the first-principles model; however, much faster regeneration is observed via TAS when MgO or PFTS is used. Only MgO is predicted to have a significant effect on electron injection rates and BET reaction

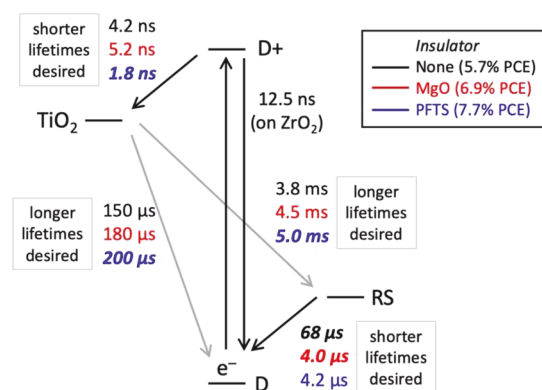


Figure 9. Diagram of electron lifetimes for each electron transfer reaction with and without an added insulator (no insulator = black; MgO = red; and PFTS = blue). The most desirable value is in bold and italics for each electron transfer reaction. The PCE obtained with each condition is shown in the legend.

rates based on the first-principles model. Surprisingly, both electron injection and BET reaction rates were affected to a larger degree by the PFTS insulator than MgO. The lifetime of electrons in the dye excited state was shortened by more than 2 $\times$ (indicative of faster electron injection via TCSPC studies) with PFTS when compared with MgO. Similarly, the lifetime of electrons in TiO_2 in the presence of the oxidized dye as the only oxidizing species shows a longer electron lifetime for the PFTS-treated electrode than MgO (slower BET reaction rate for PFTS systems). Combined, this shows that as expected PFTS slows the detrimental recombination reaction, while unexpectedly increasing the rate of the desirable electron injection reaction, unexpectedly increasing the rate of the regeneration reaction, and slowing the rate of the detrimental BET reaction. Thus, desirable electron transfer reaction events are favored herein with faster photoinduced charge separation and prolonged charge separation. This one-way valved or gated

electron flow behavior induced by PFTS is highly desirable and has led to a 35% increase in PCE (5.7% without PFTS, 7.7% with PFTS) with the $B11/[Co(bpy)_3]^{3+/2+}$ DSC devices studied here with all other components being held constant.

A plausible model which explains the unexpected behavior observed in PFTS-treated systems with regard to electron injection and the BET reaction is shown in Figure 10. The Mulliken charges (Figures S34 and S35) and molecular electrostatic potential (MEP) maps (Figures 10 and S36) of PFTS and the hydroxyl-terminated analogue 1H,1H,2H,2H-perfluorooctylsilanetriol were computationally analyzed via DFT at the B3LYP/6-311G (*d,p*) level of theory.^{82–84} The hydroxyl-terminated analogue is shown in Figure 10 because the OMe groups are anticipated to have hydrolyzed upon surface binding. The MEP surface map shows a region of negative electrostatic charge extending from the surface because of the fluorine atoms (red colored surface region, Figure 10). A region of positive electrostatic charge is observed near the silicon atom because of the hydrogen atoms at the two methylene groups attached to the silicon. This generates a layer of partial negative charge away from the TiO_2 surface and a region of partial positive charge near the TiO_2 surface. Upon photoexcitation of the dye, electron density is moved toward TiO_2 during the metal-to-ligand charge transfer event. This negative charge on the dye near the surface can be stabilized by the partial positive charge of the PFTS-treated surface near the TiO_2 . The remaining dye cation is located further away from the surface in the partial negative region of the PFTS-treated surface, serving to further stabilize the oxidized chromophore (Figure 10B). Upon electron injection, the negative charge is moved from the dye to TiO_2 which is stabilized by the partial positive charge from the PFTS-treated surface (Figure 10C). This presumably leads to more favorable charge injection and more favorable sustained charge separation duration because of electrostatic effects which results in surface treatment-induced rectification (Figure 10D). Electrostatic attraction of the

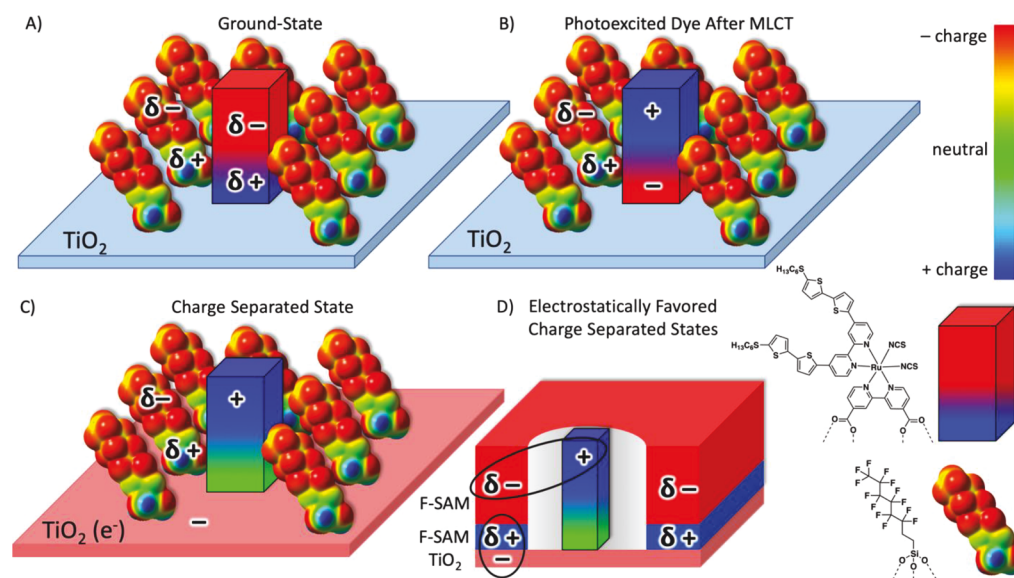


Figure 10. MEP maps of hydroxyl-terminated PFTS molecules surrounding B11 on a TiO_2 surface. (A) Ground-state partial charge configuration, (B) photoexcited MLCT state with electrostatically attracted partial charges on PFTS to the B11 molecule, (C) interfacial charge-separated state with an electron injected into TiO_2 and B11 cation electrostatically attracted to a PFTS molecule, and (D) general charge layer cartoon with PFTS (red and blue) surrounding a B11 cationic dye (blue and green). Note that the small blue region at the bottom of the perfluorinated molecules in the MEP surface map is representative of a hydrogen that may not be present upon surface binding.

negative charge from the fluorine atoms with the positively charged RS may also aid in an increased rate of ground-state dye regeneration by increasing the effective concentration of the RS near the film.

CONCLUSIONS

Two surface modification strategies, PFTS and MgO, were evaluated within DSC devices based on **B11** and $[\text{Co}(\text{bpy})_3]^{3+/2+}$. Initial studies show an improved device efficiency from 5.7 to 7.7% with the addition of a PFTS surface treatment, which suggests that desired electron transfer reaction pathways are improved with this F-SAM treatment. A similar, yet lesser effect is observed when MgO is used as a surface treatment. Additionally, SMPVT measurements reveal longer electron lifetimes when a PFTS surface treatment is applied, which indicates a slower rate of electron recombination between electrons in the TiO_2 CB with acceptors in the electrolyte. Emission lifetime studies on **B11**-sensitized films show reduced charge injection efficiency with an MgO treatment as expected from an insulating layer between the dye and TiO_2 . Interestingly, the introduction of a PFTS surface treatment results in a $> 2\times$ increase in the rate of charge injection. Nanosecond transient absorption studies show that the addition of an MgO or PFTS surface treatment results in a slower BET reaction from TiO_2 to the dye cation in comparison to devices without surface modification. Importantly, this study shows that electron transfer reaction rates can be preferentially accelerated in the desired forward direction (electron injection and regeneration) and preferentially slowed in the undesirable directions (BET and recombination) with the use of a coadsorbent insulating surface protection strategy which does not space the dye from the semiconductor. Intriguingly, a more efficient electron transfer reaction between the dye cation and an electron transfer reaction reagent ($[\text{Co}(\text{bpy})_3]^{3+/2+}$) in the electrolyte is observed to occur at the TiO_2 surface. This one-way electron transfer inducing approach also has broad application in areas such as dye-sensitized photoelectrochemical cells and dye-sensitized photodetectors. Future studies are aimed at evaluating the effect of alternative coadsorbents to further enhance these desirable effects.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c07981>.

Additional DSC device characterization, transient absorption studies, and computational results (PDF)

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Notes

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