Supporting Information for

Diazo Coupling for Surface Attachment of Small Molecules to TiO₂ Nanoparticles

Jennifer L. Troiano, Gongfang Hu, Robert H. Crabtree* and Gary W. Brudvig*

Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States and Yale Energy Sciences Institute, Yale University, West Haven, Connecticut 06516, United States

Corresponding Authors

Robert H. Crabtree	Phone: 203-200-8936	robert.crabtree@yale.edu
Gary W. Brudvig	Phone: 203-432-5202	gary.brudvig@yale.edu

Materials. All materials were purchased from Aldrich or Alfa-Aesar and used without further purification unless otherwise noted. *p*-Aminophenyltrimethoxysilane, 90% purity, was purchased from Gelest. Ti-Nanoxide T/SP paste was purchased from solaronix. The particles are anatase and 15–20 nm. Anhydrous acetonitrile was purified with a Solvent Dispensing System. Triethanolamine was dried with Linde type 4A molecular sieves for 24 h at room temperature in the dark.¹ CDCl₃ was passed through a short pipette column of basic alumina before adding to samples to remove residual acid and water. Millipore water was used in all cases.

Instrumentation. UV-visible absorption spectra were collected using a Shimadzu UV-2600 spectrophotometer. ¹H NMR data were collected using an Agilent 400 MHz NMR instrument, and referenced to the residual ¹H resonances (7.26 ppm for CDCl₃). X-ray photoelectron spectroscopic measurements were performed using a PHI VersaProbe II Scanning XPS Microprobe. A Hitachi SU-70 analytical scanning microscope was used for Scanning Electron Microscopy (SEM) measurements. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic measurements were performed using an Agilent Technologies Cary 600 series FTIR spectrometer and a PIKE technologies GladiATR. A Bruker Dektak XT stylus profilometer was used to measure TiO₂ film thicknesses. All sonication procedures were carried out with a benchtop sonicator.

TiO₂ Thin Film Preparation. Plain glass microscope slides were first cleaned *via* sequential sonication steps in water, acetone, isopropanol, and ethanol for 15 minutes each. The slides were then blown dry with N₂. One layer of TiO₂ was doctor bladed onto the clean glass slide using the commercial Ti-Nanoxide paste and one layer of Scotch[®] MagicTM Tape as the barrier. To complete the thin film preparation, the samples were thermally annealed in a box oven by heating from 25 to 370 °C at a rate of 180 °C/h, holding at 370 °C for 10 min, followed by heating to 480 °C at a rate of 180 °C/h, holding at 480 °C for 30 min, and finally cooling to room temperature. The resulting thickness of the films was ~4 μ m as determined by profilometry. In order to obtain SEM images without significant charging, samples were also made on conductive fluorine doped tin oxide (FTO) coated glass slides. These samples were prepared in exactly the same manner as the samples on plain glass slides.

Synthesis of 4-aminophenylsilatrane (APSil). Following a reported method² with modifications, the received *p*-aminophenyltrimethoxysilane was recrystallized at -20 °C overnight in anhydrous acetonitrile under inert atmosphere to afford a while solid. *[Note: this is necessary to achieve a moderate yield.]* The resulting sample (1.08 g, 5.00 mmol, 1.0 equiv) was charged into a Schlenk flask along with a stir bar. The Schlenk flask was evacuated under high vacuum for 5 min, and then purged with N₂. Dried triethanolamine¹ (0.76 g, 0.68 mL, 5.1 mmol, 1.02 equiv) was added to the Schlenk flask *via* a syringe. The resulting mixture was stirred at 110 °C for 4 h under N₂, and allowed to cool to room temperature. Produced methanol was removed with a rotavapor. The solid residue was passed through a pad of silica gel (CH₂Cl₂/CH₃CN = 1:2). The eluate was concentrated and recrystallized at -20 °C overnight with anhydrous acetonitrile. The emerging solid was filtered and dried *in vacuo* to afford a light brown solid (1.10 g, 81%): ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.65 (d, *J* = 8.0 Hz, 2H, Ar-H), 3.89 (t, *J* = 6.1 Hz, 6H, O-CH₂), 3.55 (br, s, 2H, NH₂), 2.90 (t, *J* = 5.9 Hz, 6H, N-CH₂). Characterization data are comparable to those reported in the literature.^{2,3}

TiO₂ Thin Film Sensitization. TiO₂ thin films were sensitized with APSil prior to diazo coupling using a previously reported method.⁴ 2 mM solutions of APSil in acetonitrile were used as the sensitization solutions. Mild sonication was needed to fully dissolve the APSil. The thin film, having an approximate geometric surface area of 0.5 cm², was placed in a vial with 2.5 mL of the sensitization solution. The vial was heated to 70 °C under a N₂ atmosphere, and kept in the dark for ~20 h. Post sensitization, the sample was removed from the solution and rinsed three times with anhydrous acetonitrile. The samples were stored in a dark location at room temperature.

The Method for Diazo Coupling Reactions.

Surface-Bound 1-(phenyldiazenyl)naphthalen-2-ol. 5 mL of 0.1 M citrate buffer solution (pH 3) was placed in a 10 mL vial and cooled to ~0 °C using an ice bath. The glass slide with **TiO₂-APSil** was submerged in the solution and left to cool for 10 min. 1 mL of a 1 M NaNO₂ (aq) was added dropwise to the reaction mixture containing **TiO₂-APSil**. **TiO₂-APSil** was left in this reaction mixture at ~0 °C for 1 h. 2-naphthol (36 mg, 0.25 mmol) was first ground in a mortar and pestle, and treated with 5 mL of a 0.1 M carbonate buffer solution (pH 10). The mixture was sonicated until a homogeneous solution formed, affording a 50 mM 2-naphthol solution in the carbonate buffer. The 2-naphthol solution was placed in a 10 mL vial and cooled to ~0 °C using an ice bath. The glass slide with **TiO₂-APSil** was removed from the citrate buffer solution and immediately placed in the 2-naphthol solution. The reaction mixture was left to sit for 2 hours, maintained at ~0 °C. The slide was then rinsed three times with anhydrous acetonitrile to ensure all the unreacted 2-naphthol was removed from the surface prior to characterization. The samples were left under ambient conditions to fully dry before any measurements were taken.

Surface-Bound (phenyldiazenyl)aniline: The same procedure as above was carried out, but 2-naphthol was replaced with aniline. No grinding or sonication was needed.

Surface-Bound (phenyldiazenyl)phenol: The same procedure as above was carried out, but 2-naphthol was replaced with phenol. No grinding or sonication was needed.

FTIR Measurements. In order to achieve a big enough signal, the bare and sensitized thin films were removed from the glass surface prior to measurement. This was done with a toothpick.

A surface area of about 0.5 cm^2 was removed and the resulting powder was pressed onto the crystal and clamped down using the adjustable arm to obtain good surface contact. Measurements were taken with a spectral resolution of 1 cm^{-1} and 200 scans.

Determination of Surface Loading. Surface loading was calculated using UV-visible spectroscopic measurements. This was carried out through a well-reported⁵ method using the formula,

$$\Gamma(mol \cdot cm^{-2}) = \frac{A(\lambda)}{1000 \times \varepsilon}$$
(eq. S1)

where $A(\lambda)$ is the absorbance at wavelength λ , and ε is the molar absorptivity at wavelength λ . Molecular 1-(phenyldiazenyl)naphthalen-2-ol (1) has a molar absorptivity of 14,500 M⁻¹·cm⁻¹ at 480 nm which was used along with the corrected absorbance to calculate the loading number.⁶ The corrected absorbance of **TiO₂-1** was determined by subtracting the measured absorbance of **TiO₂-1** Bare at 480 nm from the measured absorbance of **TiO₂-1** at this wavelength. In order to report this value in terms of thin film volume rather than thin film area, we divided the surface loading by the thickness of the TiO₂ thin film. The thickness, determined by profilometry, was 4 µm.



Figure S1. X-ray photoelectron spectra of a) TiO₂-Bare and b) TiO₂-APSil showing the N 1s peak at 399.7 eV.



Figure S2. UV-visible spectroscopy of TiO_2-1 (red) and TiO_2-1 after subsequent diazo coupling reactions under the same conditions (blue).



Figure S3. SEM images of a) TiO₂-Bare, b) TiO₂-APSil, and c) TiO₂-1 revealing surface morphology.

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