

## Dye-Sensitized Solar Cell Redox Shuttles

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### Supporting Information

#### Experimental

A blocking layer of TiO<sub>2</sub> was deposited on cleaned fluorine doped tin oxide, FTO, coated glass (Hartford glass) via ALD using 500 cycles of titanium isopropoxide (Aldrich) and water as precursors at 225 °C with a Savannah 100 instrument (Cambridge Nanotech Inc.). A transparent TiO<sub>2</sub> nanoparticle layer was prepared by doctor blading a paste of 20 nm TiO<sub>2</sub> nanoparticles (DSL 18NR-T, Dyesol) one scotch tape thickness on the FTO substrate. After relaxing the transparent layer at 100 °C for 10 minutes a scattering TiO<sub>2</sub> nanoparticle layer was prepared by doctor blading a paste of 400 nm TiO<sub>2</sub> nanoparticles (DSL 18NR-AO). The resulting electrodes were annealed by heating in air to 325 °C for 5 minutes, 375 °C for 5 minutes, 450 °C for 5 minutes, and 500 °C for 15 minutes. A single layer of Al<sub>2</sub>O<sub>3</sub> was additionally deposited using one cycle of trimethylaluminum (Aldrich) and water as precursors at 250 °C after removing from the furnace and cooling to 100 °C. Pulse times of 0.015 s and exposure times of 10 s were used for both precursors. The electrodes were then annealed at 500 °C in air for 30 minutes. The resulting electrodes were allowed to cool to 100 °C before being added to a solution of 0.5 mM [Ru(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub>] (Dyesol, B4 dye) in ethanol. After 20-24 hours they were removed and rinsed briefly with acetonitrile. TiO<sub>2</sub> film thickness was measured using a Dektak3 Surface Profiler to be 12 μm.

Sandwich DSSCs were fabricated by sandwiching a  $\sim 25\mu\text{m}$  thick Surlyn frame (Solaronix) between the photoanode and a platinized FTO electrode with light pressure applied at  $140\text{ }^\circ\text{C}$  to seal the cell. Electrical contact was achieved using copper wire and silver epoxy after scratching through the  $\text{TiO}_2$  blocking layer with sand paper. Electrolyte was loaded through a hole in the counter electrode. The electrolyte contained  $0.1\text{ M LiClO}_4$ ,  $0.2\text{ M 4-tert-butylpyridine}$ , and  $0.22\text{ M [Co}(t\text{-Bu}_2\text{bpy})_3\text{](PF}_6\text{)}$  in acetonitrile. Sufficient  $\text{NOBF}_4$  was added from a stock solution to oxidize  $20\text{ mM}$  of the cobalt. DSSCs were aged a minimum of 24 hours before measurements were taken.

Photoelectrochemical measurements were performed with an Autolab PGSTAT 126N potentiostat interfaced with a Xe Arc Lamp. An AM 1.5 solar filter and neutral density filters were used to simulate sunlight at  $100\text{ mW cm}^{-2}$ .