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# Photoelectrochemical oxidation of a turn-on fluorescent probe mediated by a surface Mn<sup>II</sup> catalyst covalently attached to TiO<sub>2</sub> nanoparticles



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#### ABSTRACT

A manganese complex covalently attached to a  $TiO_2$  electrode via a light-absorbing organic linker (L) was used in the photooxidation of 2',7'-dihydrodichlorofluorescein (H<sub>2</sub>DCF). Significant and sustained photocurrent was observed upon visible-light illumination of the fully assembled anode in the presence of the substrate. The two-electron, two-proton oxidation of H<sub>2</sub>DCF yields the fluorescent compound, 2',7'dichlorofluorescein (DCF). Our studies suggest that the Mn<sup>II</sup>-L-TiO<sub>2</sub> architecture is an effective photoanode for multielectron chemistry, as production of DCF under visible-light illumination exceeds yields observed for bare TiO<sub>2</sub> as well as  $Zn^{II}$ -L-TiO<sub>2</sub> anodes. The turn-on fluorescent behavior of H<sub>2</sub>DCF upon oxidation makes it an excellent substrate for the study of new photoanodes. The high fluorescence quantum yield of DCF allows for nanomolar sensitivity and real-time monitoring of substrate oxidation.

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#### 1. Introduction

Photochemical and photoelectrochemical reactions are sustainable approaches for carrying out chemical transformations [1–3]. Nature has provided key inspirations for the fabrication of artificial photosynthetic assemblies from earth-abundant materials [4,5]. Surface sensitization of semiconductors, such as titanium dioxide (TiO<sub>2</sub>), has been extensively studied as an effective way to mediate light harvesting and subsequent charge transfer. Dye-sensitized solar cells (DSSCs) are successful examples of photoelectrochemical devices utilizing semiconductor surface sensitization for the conversion of solar energy to electricity [6–8]. Following the design of DSSCs, dye-sensitized photoelectrochemical cells have been prepared by adsorbing catalysts in addition to light-harvesting dyes onto TiO<sub>2</sub> surfaces for light-driven chemical transformations relevant to fuel production [9-11]. Recently, several overall solar water splitting systems have been prepared by coupling water-oxidation catalysts to a DSSC [12-14]. Many artificial photosynthetic assemblies feature costly transition metals such as ruthenium and iridium for light harvesting and/or catalysis [15-18]. The construction of artificial photosynthetic cells from inexpensive materials is critical to the implementation of these devices on a large scale [19]. Our recent work has focused on pure organic molecules as chromophoric linkers that facilitate the immobilization of manganese-based molecular catalysts on TiO<sub>2</sub> surfaces [20-23]. This present study employs a synthetic organic linker molecule (L) containing an acetylacetonate (acac) moiety [20-24] for surface immobilization and a terpyridine (terpy) ligand for Mn<sup>II</sup> complexation. Fig 1a shows the structure of a molecular Mn<sup>II</sup> catalyst immobilized on the surface of a TiO<sub>2</sub> nanoparticle (NP). Our previous studies have demonstrated that surface sensitization with L effectively extends the absorption edges of TiO<sub>2</sub> NPs to the visible-light region [20,21]. Studies using time-resolved terahertz spectroscopy and computational modeling showed that ultrafast interfacial electron injection from the linker to TiO<sub>2</sub> occurs on a sub-picosecond timescale upon 400 nm excitation [20]. Furthermore, the surface sensitization with L is robust under aqueous and oxidative conditions [20]. In addition, a dimeric Mn<sup>III,IV</sup> water-oxidation catalyst was successfully assembled on the surfaces of TiO<sub>2</sub> NPs containing covalent attachments via this linker molecule [21].

Necessary for the advancement of low-cost photoelectrosynthetic cells is the development of effective means to evaluate device performance. In the case of artificial photosynthetic cells, oxygen generation is typically measured by electrochemical or fluorescence methods and often requires micromolar changes in concentration to be observed. The splitting of water remains difficult for many devices, due to the high thermodynamic (2.46 eV/ molecule  $H_2O$ ) and kinetic (4H<sup>+</sup>, 4e<sup>-</sup>) demands of the reaction. One strategy to study these systems is to provide an alternative substrate that is both easier to oxidize and involves fewer protons and electrons. However, quantification, particularly in real time, can be challenging. For example, 2-propanol is an attractive

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**Fig. 1.** (a) The structure of a molecular  $Mn^{II}$  catalyst attached to a TiO<sub>2</sub> surface via a terpy-acac ligand (L), and (b) the schematic of a photoelectrochemical cell containing a light-absorbing linker and a  $Mn^{II}$  catalyst.

substrate, as its conversion to acetone and hydrogen involves two protons and two electrons and is endergonic by 0.64 eV. Its detection from a photoelectrosynthetic cell was previously achieved by Meyer et al. [17]. In these experiments, a ruthenium-based photoanode was used to drive oxidation in neat 2-propanol, and acetone was detected by GC–MS. However, photolysis was conducted for over 12 h before analysis. These requirements limit this method for the quantification of photoelectrosynthetic performance, particularly in the case of molecular catalysts and dyes, which are often not stable over long time periods and often desorb or decompose to form metal oxides.

The need for more efficient methods to quantify photoanode performance led us to explore substrates that could be detected with high sensitivity during photolysis. A turn-on fluorescent probe for oxidation is a particularly attractive solution. Fluorescent molecules offer exceptionally low limits of detection and have been employed in sensing applications in a variety of systems. In particular, the compound 2',7'-dihydrodichlorofluorescein (H<sub>2</sub>DCF) has been used extensively as a probe for oxidative stress in biological applications, due to its well-understood and well-behaved chemical reactivity [25–28]. Under oxidative conditions with a metal catalyst, H<sub>2</sub>DCF undergoes two-electron, two-proton oxidation to form 2',7'-dichlorofluorescein (Scheme 1). While H<sub>2</sub>DCF is non-luminescent, DCF is strongly fluorescent and can be detected at sub-picomolar concentrations.

In the present study, H<sub>2</sub>DCF was used to probe the effectiveness of a photoelectrochemical cell featuring organic chromophores with molecular Mn<sup>II</sup> catalysts adsorbed onto TiO<sub>2</sub> (Fig. 1). Mn<sup>II</sup>treated **L**-TiO<sub>2</sub> photoanodes were able to oxidize H<sub>2</sub>DCF to DCF following illumination with visible light. Sustained photocurrents observed with 2-propanol using Mn<sup>II</sup>-**L**-TiO<sub>2</sub> photoanodes match those observed during H<sub>2</sub>DCF oxidation, suggesting that 2-propanol may be photoelectrochemically oxidized. This study shows photoelectrochemical transformations can be mediated by surface immobilized Mn<sup>II</sup> catalysts and also demonstrates the utility of H<sub>2</sub>DCF as a turn-on fluorescent substrate for the study of photoelectrosynthetic cells.



**Scheme 1.** Two-proton, two-electron oxidation of 2',7'-dihdyrodichlorofluorescein (H<sub>2</sub>DCF) yields 2',7'-dichlorofluorescein (DCF).

# 2. Materials and methods

# 2.1. Synthetic procedures

#### 2.1.1. General

2-Acetyl pyridine, 2,4-pentadione, and iodine (ACS grade, Acros Organics) were purchased from Fischer Scientific. 1-Ethyl-3-(3dimethylaminopropyl)carbodiimide hydrochloride (EDC) was obtained from Bachem, 4-dimethylaminopyridine (DMAP) on polystyrene beads (3 mmol DMAP/g) from Santa Cruz Biotechnology, and 200 proof ethanol from Decon Laboratories Inc. Palladium on carbon (5% Pd by weight), cesium carbonate, and copper(I) iodide (99.9%) were obtained from Strem Chemicals. 2',7'-Dichlorofluorescein was purchased from Sigma-Aldrich. Silica gel (SiliaFlash F60, 0.040-0.063 mm) was purchased from SiliCycle Inc., and Celite 545 from EMD Chemicals. The remaining chemicals and solvents (ACS grade) were obtained from VWR. Dichloromethane was dried on an activated alumina column (Innovative Technology Inc. solvent purification system). Copper iodide was purified according to a literature procedure just before use [29]. All the other solvents and chemicals were used as received and without further purification. NMR spectra were recorded on an Agilent 400 MR spectrometer operating an Oxford AS400 magnet or a Varian 300 MR spectrometer. Chemical shifts are reported in ppm, relative to tetramethylsilane (CDCl<sub>3</sub>) or to the residual solvent peak (CD<sub>3</sub>CN. DMSO- $d_6$ , CD<sub>3</sub>OD).

# 2.1.2. Synthesis of (E)-3-(4-nitrophenyl)-1-(pyridin-2-yl)prop-2-en-1one (1)

This compound was prepared following the procedure reported by Das *et al.* with minor modification [30]. A 250-mL round-bottom flask was charged with 2.4 g of 2-acetylpyridine (19.8 mmol), 3 g of 4-nitrobenzaldehyde (19.8 mmol), and 40 mL of methanol. After cooling the mixture to 0 °C, a solution of 1.15 g of potassium hydroxide (19.8 mmol) dissolved in 7.5 mL of mQ water was added dropwise to the medium. The mixture was stirred at 0 °C for 30 min and further stirred at room temperature for 12 h, during which time a solid precipitated. The precipitate was collected by vacuum filtration and washed with cold methanol (3 × 50 mL). The crude solid was dissolved in the minimum volume of warm chloroform (ca. 10 mL) and recrystallized by slow diffusion of methanol (~90 mL) at 4 °C, to give **1** as light yellow crystals. Yield: 2.65 g (11 mM, 56%). <sup>1</sup>H NMR spectrum was in good agreement with the data previously reported in the literature [30].

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): 8.78–8.72 (m, 1H), 8.43 (d, J = 16.1 Hz, 1H), 8.33–8.23 (m, 2H), 8.20 (dd,  $J_1 = 7.9$  Hz,  $J_2 = 0.9$  Hz, 1H), 7.98–7.81 (m, 4H), 7.53 (ddd,  $J_1 = 7.6$  Hz,  $J_2 = 4.7$  Hz,  $J_3 = 1.2$  Hz, 1H).

# 2.1.3. Synthesis of 1-(2-oxo-2-(pyridin-2-yl)ethyl)pyridinium iodide (2)

This compound was prepared following the procedure reported by Das et al. with minor modification [30]. To a 50-mL round-bottom flask, 3.0 g of 2-acetylpyridine (24.7 mmol), 6.2 g of iodine (24.7 mmol), and 14 mL of pyridine were added. The mixture was purged with Argon for 15 min then refluxed under argon until the medium crystallized ( $\sim$ 30 min). After cooling down the reaction mixture to room temperature, the crude solid was dissolved in acetonitrile (100 mL), and 20 mL of silica was added. The solvent was evaporated under reduced pressure, and the resulting coated silica was loaded on a silica short plug (SiO<sub>2</sub>, acetonitrile). The desired compound was eluted with acetonitrile (second compound eluted). Recrystallization from boiling ethanol yielded **2** as offwhite crystals. Yield: 6.4 g (19.6 mmol, 79%). <sup>1</sup>H NMR spectrum was in good agreement with the data previously reported in the literature [30].

<sup>1</sup>**H** NMR (400 MHz, CD<sub>3</sub>CN): 8.75 (s, 2H), 8.75–8.72 (m, 2H), 8.69 (d, J = 8.0 Hz, 2H), 8.37 (d, J = 8.8 Hz, 2H), 8.05 (td,  $J_1 = 7.7$  Hz,  $J_2 = 1.8$  Hz, 2H), 7.39 (ddd,  $J_1 = 7.4$  Hz,  $J_2 = 4.8$  Hz,  $J_3 = 1.1$  Hz, 2H).

#### 2.1.4. Synthesis of 4'-(4-nitrophenyl)-2,2':6',2"-terpyridine (3)

This compound was prepared following the procedure reported by Das et al. with minor modification [30]. A 250-mL round-bottom flask was charged with 2.2 g of **1** (6.7 mmol), 1.7 g of **2** (6.7 mmol), 3.6 g of ammonium acetate (46.8 mmol), and 100 mL of methanol. The mixture was purged with argon for 15 min then refluxed under argon for 4 h, during which time an off-white solid precipitated. After cooling down the mixture to room temperature, the precipitate was collected by vacuum filtration and washed with cold methanol ( $3 \times 50$  mL) to give the desired nitrophenyl terpyridine **3** as a white solid. Yield: 1.85 g (5.2 mmol, 78%). <sup>1</sup>H NMR spectrum was in good agreement with the data previously reported in the literature [30].

<sup>1</sup>**H NMR** (400 MHz, DMSO- $d_6$ ): 8.71 (ddd,  $J_1 = 4.8$  Hz,  $J_2 = 1.8$  Hz,  $J_3 = 0.9$  Hz, 2H), 8.67 (s, 2H), 8.60 (td,  $J_1 = 8.0$  Hz,  $J_2 = 1.0$  Hz, 2H), 8.35–8.31 (m, 2H), 8.14–8.10 (m, 2H), 8.02–7.97 (m, 2H), 7.49 (ddd,  $J_1 = 7.5$  Hz,  $J_2 = 4.8$  Hz,  $J_3 = 1.2$  Hz, 2H).

#### 2.1.5. Synthesis of 4'-(4-aminophenyl)-2,2':6',2"-terpyridine (4)

This compound was prepared following the procedure reported by Das et al. with minor modification [30]. In a 500-mL round-bottom flask, 0.95 g of nitrophenyl terpyridine 3 (2.7 mmol), 250 mg of palladium on carbon (5% Pd-loading), and 200 mL of absolute ethanol were added. The resulting suspension was purged with argon for 15 min and brought to reflux under argon. 3.4 mL of hydrazine monohydrate (3.5 g, 70 mmol) was added, and the mixture further refluxed under argon for 2 h, during which time the nitrophenyl terpyridine 3 dissolved completely. After cooling down the medium to room temperature, the catalyst was removed by vacuum filtration over a Celite short plug and washed with dichloromethane  $(3 \times 100 \text{ mL})$ . The filtrate was concentrated under reduced pressure until white needles started to crystallize out of the medium ( $\sim$ 75 mL). The saturated solution was then stored at 4 °C overnight. The grown crystals were recovered by vacuum filtration and washed with cold ethanol ( $3 \times 50$  mL). The aminophenyl terpyridine **4** was obtained as white needles. Yield: 547 mg (1.7 mmol, 63%). <sup>1</sup>H NMR spectrum was in good agreement with the data previously reported in the literature [30].

<sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>): 8.73 (ddd,  $J_1 = 4.8$  Hz,  $J_2 = 1.8$  Hz,  $J_3 = 0.9$  Hz, 2H), 8.63 (td,  $J_1 = 8.0$  Hz,  $J_2 = 1.0$  Hz, 2H), 8.61 (s, 2H), 8.02–7.98 (m, 2H), 7.69–7.63 (m, 2H), 7.49 (ddd,  $J_1 = 7.5$  Hz,  $J_2 = 4.8$  Hz,  $J_3 = 1.2$  Hz, 2H), 6.74–6.71 (m, 2H), 5.60 (s, 2H).

#### 2.1.6. Synthesis of 3-[4-Benzoic acid]pentane-2,4-dione (5)

This compound was prepared following the procedure reported by Jiang et al. with minor modification [31]. In a 100-mL Schlenk tube, 1.0 g of 4-iodobenzoic acid (4.0 mmol), 90 mg of L-proline (0.78 mmol), 3.3 g of cesium carbonate (10.1 mmol), and 15 mL of anhydrous dimethylsulfoxide were added. The suspension was purged with argon for 30 min, and 1.5 mL of 2,4-pentadione (1.2 g, 12 mmol) was added. The mixture was further purged with argon for 5 min, and 75 mg of freshly recrystallized copper iodide (0.4 mmol) was added. The mixture was stirred at 85 °C under argon for 12 h. After cooling down to room temperature, the reaction mixture was poured into 100 mL of water. The aqueous phase was washed with ethyl acetate (3 × 50 mL, discarded). The pH of the aqueous phase was then adjusted to pH ~ 2 with the slow addition of 12 M hydrochloric acid, and the medium was further extracted with ethyl acetate (3 × 50 mL). The latter organic layers were combined, dried over sodium sulfate, and filtered, and the solvent was evaporated under reduced pressure. Column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–1% MeOH) was conducted. Due to the very small difference in polarity between the staring material (traces), the desired compound, and a degradation product, small fractions were collected and the purity of each fraction was determined using <sup>1</sup>H NMR. Combination of the pure fractions gave the *p*-carboxy-phenyl acac **5** as an off-white solid. Yield: 205 mg (0.93 mmol, 23%). The low yield reported here is due to important loss of the material during the column chromatography purification step. Furthermore, due to its thermal instability, compound **5** was strictly stored at -20 °C. <sup>1</sup>H NMR spectrum was in good agreement with the data previously reported in the literature [20,31].

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): 16.73 (s, 1H), 8.16–8.13 (m, 2H), 7.35–7.31 (m, 2H), 1.91 (s, 6H).

## 2.1.7. Synthesis of 4'-(N-(4-(2,4-dioxopentan-3-

### yl)phenyl)benamide)2,2':6',2"-terpyridine (L)

This compound was prepared following the procedure reported by McNamara et al. with minor modification [20]. A 100-mL Schlenk tube was charged with 143 mg of *p*-carboxyphenyl acac **5** (0.65 mmol), 435 mg of DMAP on beads (3 mmol/g, 1.3 mmol), 126 mg of EDC (0.66 mmol), and 10 mL of dry dichloromethane. The mixture was stirred at 0 °C for 15 min under argon. A solution of 177 mg of aminophenylterpyridine 4 (0.55 mmol) in 4 mL of dry DMF was added, and the reaction mixture was allowed to be stirred at room temperature under argon. The progression of the reaction was monitored by <sup>1</sup>H NMR. After 12 h at room temperature, a conversion of 60% was reached, and no further evolution could be observed. A solution of 100 mg of 5 (0.45 mmol) activated with 98 mg of EDC (0.51 mmol) in 2 mL of dry dichloromethane was added to the reaction mixture, and the medium was further stirred at room temperature, under argon, for 12 h. <sup>1</sup>H NMR analysis indicated that the conversion then reached 85%. A second aliquot of 100 mg of 5 (0.45 mmol) activated with 98 mg of EDC (0.51 mmol) in 2 mL of drv dichloromethane was added to the reaction mixture. and the medium was further stirred at room temperature for 12 h after which time no traces of the starting aminophenylterpyridine 4 could be observed by <sup>1</sup>H NMR. The reaction mixture was filtered, and the beads washed thoroughly with 50 mL of dichloromethane. The combined organic phases were extracted with water  $(5 \times 50 \text{ mL})$ , NaHCO<sub>3</sub> (5% aqueous,  $1 \times 50 \text{ mL})$ , and saturated NH<sub>4-</sub> Cl (1  $\times$  50 mL). The organic layer was collected, dried over sodium sulfate, filtered, and the solvent was evaporated. Successive recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-hexanes and CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether yielded the desired ligand L as a white solid. Yield: 65 mg (0.12 mmol, 22%). Due to the thermal instability of L, this compound was strictly stored at -20 °C. <sup>1</sup>H NMR spectrum was in good agreement with the data previously reported in the literature [20].

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): 16.72 (s, 1H), 8.75 (s, 2H), 8.74 (ddd,  $J_1 = 4.8$  Hz,  $J_2 = 1.8$  Hz,  $J_3 = 0.9$  Hz, 2H), 8.68 (td,  $J_1 = 8.0$  Hz,  $J_2 = 1.0$  Hz, 2H), 7.99–7.93 (m, 5H), 7.91–7.87 (m, 2H), 7.85–7.82 (m, 2H), 7.38–7.34 (m, 4H), 1.92 (s, 6H).

#### 2.1.8. Synthesis of 2',7'-Dihydrodichlorofluorescein (H<sub>2</sub>DCF)

The compound was prepared following a modification of the procedure reported by Brandt and Keston [32]. To a 250-mL round-bottom flask, 1 g of 2',7'-dichlorofluorescein (2.5 mmol) was added to 40 mL of MeOH. The flask was heated to reflux and 20 mL glacial HOAc was added. Zinc dust was added to the solution in five 0.6 g portions over 10 min. The solution was filtered to remove the solid, the filtrate was returned to reflux, five additional 0.6 g portions of zinc dust were added, and the solution was heated at reflux for an additional 1 h, during which time the solution became colorless. Following reflux, the solution was filtered and allowed to cool. To the filtrate, 300 mL DI H<sub>2</sub>O was added, forming

an off-white precipitate. The product was removed by filtration, washed with  $H_2O$  and hexanes, and placed under vacuum in the dark to dry. The compound was stored at -20 °C in the dark until use. Yield: 780 mg (1.9 mmol, 78%).

1H NMR (300 MHz, CD3OD): 6.17 (1H, s), 6.67 (2H, s), 6.92 (2H, s), 6.98 (dd, J1 = 8 Hz, J2 = 0.8 Hz, 1H), 7.26 (td, J1 = 7.5 Hz, J2 = 0.8 Hz, 1H), 7.37 (td, J1 = 7.5 Hz, J2 = 0.8 Hz, 1H), 7.87 (dd, J1 = 8 Hz, J2 = 1 Hz, 1H).

#### 2.2. Preparation of TiO<sub>2</sub> electrodes

A commercially available TiO<sub>2</sub> sample, P25, was used as received from Evonik. The P25 TiO<sub>2</sub> consists of ~85% anatase and ~15% rutile with a specific surface area of 50 m<sup>2</sup>/g [33]. Electrodes were made from fluorine-doped tin oxide conducting glasses (FTO, Hartford Glass Co., Inc.), which were coated with TiO<sub>2</sub> NPs (dimension 1 cm  $\times$  1 cm, thickness ~20  $\mu$ m) by doctor-blading [34]. The TiO<sub>2</sub> electrodes were dried at room temperature and further sintered at 450 °C for 2 h (ramp rate 5 °C/min).

#### 2.3. Surface sensitization of TiO<sub>2</sub> electrodes

Surface sensitization of the TiO<sub>2</sub> electrodes was accomplished by soaking the electrodes in a solution of 1 mM **L** in dichloromethane at room temperature for 18 h. The sensitized TiO<sub>2</sub> electrodes were then washed with dichloromethane and dried at room temperature (denoted "L–TiO<sub>2</sub>"). The surface Mn<sup>II</sup> or Zn<sup>II</sup> complex, shown in Fig. 1a, was prepared by soaking a sensitized TiO<sub>2</sub> electrode in a solution of 2 mM Mn(OAc)<sub>2</sub> or Zn(OAc)<sub>2</sub> for 3 h at room temperature. The surface complex, denoted "Mn<sup>II</sup>–L–TiO<sub>2</sub>" or "Zn<sup>II</sup>–L–TiO<sub>2</sub>," was always prepared and washed with mQ water immediately before photoelectrochemical studies.

#### 2.4. Characterization of TiO<sub>2</sub> electrodes

Optical spectra of bare and sensitized  $TiO_2$  NPs were collected on a Varian Cary 3 spectrophotometer in diffuse reflectance geometry.

#### 2.5. EPR studies

Perpendicular-mode EPR spectra were recorded on an X-band Bruker Biospin/ELEXSYS E500 spectrometer equipped with a SHQ cavity and an Oxford ESR-900 liquid helium cryostat. Spectra were collected at 6 K on powdered samples sealed in capillary tubes placed in 5 mm OD quartz EPR tubes containing 60/40 toluene/ace-tone which forms a transparent glass for efficient illumination of the sample and allows efficient heat transfer to prevent heating of the sample during illumination [20]. Samples were illuminated in the cryostat at 6 K with white light from a Fiber-Lite Series 180 illuminator (Dolan-Jenner Industries, Inc., intensity 60 mW/ cm<sup>2</sup>) equipped with a fiber optic light guide, which only transmits light with wavelengths greater than 425 nm [21]. Spectra were recorded with the following settings: modulation amplitude = 10 G, modulation frequency = 100 kHz, microwave power = 0.05 mW, and microwave frequency = 9.357 GHz.

#### 2.6. Photoelectrochemical studies

Photoelectrochemical measurements were made on an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat using a homebuilt PEC cell (Fig. S1). A platinum wire was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode (NHE vs. Ag/AgCl: +199 mV). A bias potential of 500 mV vs. NHE was used for all measurements. This value was set to match the open circuit potential of the Mn<sup>II</sup>–L–TiO<sub>2</sub>

cells. Experiments were carried out in aqueous solutions containing pH 4.5, 0.05 M NaOAc as the supporting electrolyte and either 20  $\mu$ M H<sub>2</sub>DCF in 2% MeCN solution or 1% v/v isopropanol as the substrate. For measurements using H<sub>2</sub>DCF, 50  $\mu$ L aliquots were removed from the electrolysis cell at regular intervals (0, 2, 5, and 8 min following illumination) and diluted to 4.5 mL with 10 mM pH 4.5 acetate buffer. Stock solutions of H<sub>2</sub>DCF were stored over ice in the dark until use and showed no evidence of oxidation during the day's experiments. Illumination of the sample was performed using a 250 W Xe arc lamp with a water IR filter and a 420 nm long-pass filter.

#### 2.7. Fluorescence studies

Uncorrected emission spectra were collecting using a Jobin Yvon Horiba Fluorolog-3-11. Sample excitation was achieved via a 450-W xenon arc lamp with a monochromator providing wavelength selection. Samples were excited at 500 nm, and emission spectra were recorded between 510 and 700 nm. Slits of 2 nm bandpass were used for excitation and emission.

#### 3. Results and discussion

# 3.1. Characterization of Mn<sup>II</sup>-L-TiO<sub>2</sub> anodes

While pure TiO<sub>2</sub> NPs are white, the sensitized  $L-TiO_2$  samples have a yellowish color, suggesting that the surface sensitization extends the absorption edge of pure TiO<sub>2</sub> NPs to the visible-light region. The optical absorption features of bare and sensitized TiO<sub>2</sub> NPs are shown in Fig. 2. The spectrum confirms that the pure TiO<sub>2</sub> material used in this study does not absorb much visible light. This is due to the fact that TiO<sub>2</sub> is a wide bandgap semiconductor (typical bandgap energies are 3.2 eV for the anatase phase and 3.0 eV for the rutile phase) [35]. While free L possesses no absorption bands in the visible region (Fig. S2), it can be seen from the spectrum that the sensitized  $L-TiO_2$  has increased absorption in the blue region. The appearance of new visible bands suggests that L is a Type II dye, where electron injection occurs directly from the highest occupied molecular orbital of L to the conduction band of TiO<sub>2</sub>.

Previous studies using time-resolved terahertz spectroscopy demonstrated that ultrafast interfacial electron injection from the linker to the  $TiO_2$  conduction band occurs upon visible-light excitation [20]. Changes in the EPR spectra of bare  $TiO_2$  and **L**– $TiO_2$  NPs upon photoexcitation with visible light (>425 nm) are shown in Fig. 3. No significant change was observed in the EPR spectrum



**Fig. 2.** UV-visible spectra of bare  $TiO_2$  NPs (black, dotted), **L** $-TiO_2$  (red, dashed) and  $Mn^{II}$ –**L** $-TiO_2$  (red, solid). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** EPR spectra of (a) bare  $TiO_2$  NPs and (b) sensitized  $L-TiO_2$  upon visible-light illumination. Corresponding dark spectra were subtracted. The g values of organic radicals and trapped electrons are labeled in the figure. The spectra were collected in the dark at 6 K.

of pure  $TiO_2$  NPs upon the visible-light illumination. This is consistent with the observation that bare  $TiO_2$  does not absorb (and therefore cannot be activated with) visible light.

Visible-light photoexcitation of **L**-TiO<sub>2</sub> leads to the formation of Ti<sup>III</sup> sites and organic radicals, as indicated by the corresponding EPR signals shown in Fig. 3b. The Ti<sup>III</sup> signals at *g* = 1.990 and 1.974 are characteristic of lattice-trapped electrons in the anatase and rutile phases, respectively [35,36]. This is consistent with the fact that the P25 TiO<sub>2</sub> material used in this study contains ~85% anatase and ~15% rutile nanoparticles. Since no significant Ti<sup>III</sup> signal was observed in the spectrum of pure TiO<sub>2</sub> NPs upon visible-light illumination (Fig. 3a), the trapped electrons must originate from the chromophoric linker **L**. The organic radical signal at *g* = 2.003 is attributable to photogenerated holes located in the linker molecules. This observation is consistent with the injection of photoexcited electrons from the linker molecules to the TiO<sub>2</sub> nanoparticles.

The behavior of  $Mn^{II}$ –**L**–TiO<sub>2</sub> following visible-light excitation in the absence of substrate was examined using EPR spectroscopy (Fig. 4) [20]. Illumination of  $Mn^{II}$ –**L**–TiO<sub>2</sub> nanoparticles results in decay of  $Mn^{II}$  signal, consistent with the formation of an EPR-silent  $Mn^{III}$  state. No  $Mn^{IV}$  species or multinuclear species were detected. When the light is turned off, the  $Mn^{II}$  signal returns to baseline after ~100 s. The decay and rise of the EPR signal follow biexponential behavior,

$$EPR = A_1 e^{-k^{(+)}t} + A_2 e^{-k^{(-)}t} + A_0$$
(1)

with rate constants  $k^{(+)}$  and  $k^{(-)}$  and amplitudes  $A_1$ ,  $A_2$  and  $A_0$ , given in Table 1.

The biexponential decay and rise are consistent with a threestate model, described in Fig. 5, where [3] represents a state in which Mn has been oxidized to  $Mn^{III}$ , while [1,2] represent a charge-separated state generated by photoexcitation. A detailed description of the derivation of Eq. (1) giving the biexponential behavior of this kinetic model is presented in the Supplementary information.

### 3.2. Photoelectrochemical oxidation of H<sub>2</sub>DCF

The present work focuses on the photoelectrochemical properties of the surface molecular complex using H<sub>2</sub>DCF as the substrate. Visible-light illumination ( $\lambda > 420$  nm) of Mn<sup>II</sup>–L–TiO<sub>2</sub> with H<sub>2</sub>DCF led to photocurrent that rose slowly over time before reaching a maximum current density of ~5.5  $\mu$ A/cm<sup>2</sup> after ~5 min before holding relatively constant (Fig. 6a). Zn<sup>II</sup>–L–TiO<sub>2</sub> anodes were also



**Fig. 4.** (Top) Steady-state EPR spectrum of  $Mn^{II}$ –L– $TiO_2$  NPs at 6 K in solvent before (black) and after (red) visible-light illumination. (Bottom) EPR signal at 3086 G during illumination. Overall decay of  $Mn^{II}$  signal was ~10%. Up and down arrows indicate times when the light was turned on and off, respectively. Biexponential fitted curves with parameters given in Table 1, shown in red and blue for light on and light off, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.** Schematic of the slow kinetics monitored by EPR, after the initial preequilibrium established by ultrafast injection and recombination, upon turning the light on.

prepared and tested. As  $Zn^{II}$  cannot be oxidized by  $L^+$ ,  $Zn^{II}-L-TiO_2$ anodes are not expected to catalyze  $H_2DCF$  oxidation as efficiently as their  $Mn^{II}$  counterparts. Illumination of  $Zn^{II}-L-TiO_2$  leads to an immediate spike in current, followed by exponential decay



**Fig. 6.** Photoelectrochemical response of (a)  $Mn^{II}$ –**L**–TiO<sub>2</sub>, (b)  $Zn^{II}$ –**L**–TiO<sub>2</sub>, and (c) bare TiO<sub>2</sub> upon visible light ( $\lambda > 420$  nm) illumination in 20  $\mu$ M solutions of H<sub>2</sub>DCF. Up and down arrows indicate times when the light was turned on and off, respectively.

(Fig. 6b). Interestingly, the current passed by  $Zn^{II}$  anodes exceeds that of  $Mn^{II}$  over the timescale of the experiment. Bare  $TiO_2$  anodes showed a stable photocurrent of  ${\sim}2~\mu\text{A/cm}^2$  under illumination (Fig. 6c).

Curiously, illumination of Mn<sup>II</sup>–L–TiO<sub>2</sub> results in no immediate photoresponse, and current does not begin to rise until roughly 100 s after illumination. The delayed photoelectrochemical behavior suggests that illumination leads to some change in Mn<sup>II</sup>-L-TiO<sub>2</sub> that allows for greater injection. Repeated "on-off" cycles of Mn<sup>II</sup>–L–TiO<sub>2</sub> after the first illumination result in immediate photoresponse suggesting whatever is formed initially on the surface persists for some time (Fig. S3). Based on the immediate response of Zn<sup>II</sup>–L–TiO<sub>2</sub> anodes, it is clear that Mn<sup>II</sup> must play some role in delaying the buildup in photocurrent. Terahertz spectroscopy measurements conducted on L-TiO<sub>2</sub> and Mn<sup>II</sup>-L-TiO<sub>2</sub> shows that each injects with equal efficiency when excited at 410 nm [20]. This is consistent with L being a Type II dye. However, this experiment observed the first 10 ps following excitation. It is possible that Mn<sup>II</sup> quenches the immediate charge-transfer state,  $Mn^{II} - L^{+} - TiO_2^{-}$ , over longer timescales. Indeed, THz amplitude does begin to



**Fig. 7.** Concentration of DCF taken from aliquots of 20  $\mu$ M solutions of H<sub>2</sub>DCF solutions undergoing visible-light photoelectrolysis using Mn<sup>II</sup>–L–TiO<sub>2</sub> (red circles) or Zn<sup>II</sup>–L–TiO<sub>2</sub> (blue squares) anodes. Calculated from fluorescence intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

decrease over the 10 ps timescale when compared to a control dye [20]. Over time, the population of  $Mn^{III}-L-TiO_2$ , which is not quenched, builds, and photocurrent is observed. Such behavior implies that each  $Mn^{II}-L-TiO_2$  complex undergoes two successive photochemical oxidations under catalytic conditions. However, the exact mechanism for this behavior cannot presently be determined and is a subject of further investigation.

During photoelectrolysis, the luminescence intensity of the solutions increased noticeably, indicative of formation of DCF. The integrated intensity of the spectra increases over time for both  $Mn^{II}$ –L–TiO<sub>2</sub> and  $Zn^{II}$ –L–TiO<sub>2</sub> (Fig. 7).  $Mn^{II}$  anodes showed greater increases in fluorescence intensity than those of  $Zn^{II}$ . Importantly, samples from  $Mn^{II}$  anodes show minimal changes in intensity over the first two minutes (where the observed photocurrent is minimal). Measurements conducted on  $Mn^{II}$ –L–TiO<sub>2</sub> electrodes with an applied potential in the dark showed no buildup of product, while illumination of  $Mn^{II}$ –L–TiO<sub>2</sub> slides disconnected from the circuit showed moderate increases in fluorescence intensity. Photolysis of H<sub>2</sub>DCF solutions in the absence of any electrodes resulted in negligible changes in fluorescence intensity (Fig. S4).

Two possible mechanisms for Mn-mediated photooxidation of  $H_2DCF$  are presented in Scheme 2. Light absorption leads to electron transfer to TiO<sub>2</sub> to form a Mn<sup>III</sup> state (A1), followed by a subsequent photoinduced electron transfer to form a Mn<sup>IV</sup> species (A2). Mn<sup>IV</sup> then catalyzes the two-electron, two-proton oxidation of  $H_2DCF$  to DCF (A3). Alternatively, following one-electron oxidation to Mn<sup>III</sup> (B1), the metal center may oxidize  $H_2DCF$  by one electron, generating the radical cation  $H_2DCF^{+}$ . (B2). This species may be oxidized by an additional equivalent of Mn<sup>III</sup> (B3). Alternatively, due to its instability,  $H_2DCF^{+}$  may be oxidized to DCF by dissolved oxygen or disproportionate to form  $H_2DCF$  and DCF.

The ability of  $Zn^{II}$  anodes to photooxidize  $H_2DCF$ , albeit at decreased efficiency, is not unexpected. In these  $M^{II}$ –L–TiO<sub>2</sub> anodes, electron injection from L generates the organic radical L<sup>+</sup>. For  $Mn^{II}$ –L–TiO<sub>2</sub>, L<sup>+</sup> rapidly oxidizes  $Mn^{II}$  to  $Mn^{III}$ , which goes on to drive catalysis. Conversely, L<sup>+</sup> is incapable of oxidizing  $Zn^{II}$ . However, it may be able to oxidize  $H_2DCF$  directly, and catalysis at  $Zn^{II}$ –L–TiO<sub>2</sub> electrodes may operate in this fashion. Further, when L–TiO<sub>2</sub> anodes were tested, photocurrents and oxidation yields similar to those of  $Zn^{II}$ –L–TiO<sub>2</sub> were observed. The decay in photocurrent following illumination, as well as the lower efficiency of substrate oxidation, suggests that, in the absence of a

(A1) 
$$Mn^{II}-L-TiO_2 \xrightarrow{hv} Mn^{III}-L-TiO_2$$
  
(A2)  $Mn^{III}-L-TiO_2 \xrightarrow{hv} Mn^{IV}-L-TiO_2$   
(A3)  $Mn^{IV}-L-TiO_2 + H_2DCF \longrightarrow Mn^{II}-L-TiO_2 + DCF + 2 H^+$   
(B1)  $Mn^{II}-L-TiO_2 \xrightarrow{hv} Mn^{III}-L-TiO_2$   
(B2)  $Mn^{III}-L-TiO_2 + H_2DCF \xrightarrow{mv} Mn^{II}-L-TiO_2 + H_2DCF^{++}$   
(B3)  $Mn^{III}-L-TiO_2 + H_2DCF^{++} \longrightarrow Mn^{II}-L-TiO_2 + DCF + 2H^+$ 

**Scheme 2.** Oxidation of H<sub>2</sub>DCF at Mn<sup>II</sup>–L–TiO<sub>2</sub> electrodes.

catalytically-active metal, photolysis leads to degradation of **L**. On the other hand, when  $Mn^{II}$  is added to **L**-TiO<sub>2</sub>, illumination ultimately leads to stable photocurrent, suggesting oxidation of  $Mn^{II}$  stabilizes the anode by regenerating **L**.

The fluorescence intensity increase observed during photolysis of bare TiO<sub>2</sub> anodes may be a result of sensitization of the surface by H<sub>2</sub>DCF, which is capable of adsorbing onto TiO<sub>2</sub> surfaces through their carboxylic or phenolic groups. Following adsorption, illumination leads to electron injection from H<sub>2</sub>DCF [37–39]. Consistent with this mechanism, TiO<sub>2</sub> anodes illuminated with visible light ( $\lambda > 420$  nm) show no photoresponse in the absence of H<sub>2</sub>DCF, whereas sustained current of 2  $\mu$ A is observed when 20  $\mu$ M H<sub>2</sub>DCF is added to the solution (Fig. 6c). Surface passivation of TiO<sub>2</sub> by **L** likely prevents adsorption of H<sub>2</sub>DCF in the other systems examined.

The Faradaic efficiencies of the photoelectrochemical reaction were calculated for  $Mn^{II}$ –L– $TiO_2$  and  $Zn^{II}$ –L– $TiO_2$  anodes. Following 8 min of photolysis, a Faradaic yield 290% was recorded for production of DCF using  $Mn^{II}$ –L– $TiO_2$  and 30% for  $Zn^{II}$ –L– $TiO_2$ . Importantly, the yield of DCF featuring  $Mn^{II}$  anodes is ~10× higher than those of  $Zn^{II}$ , demonstrating the importance of  $Mn^{II}$  centers in mediating catalysis. The low yield from  $Zn^{II}$ –L– $TiO_2$  anodes is a result of both decreased production of DCF as well as increased photocurrent. Importantly,  $Zn^{II}$ –L– $TiO_2$  anodes, despite their higher photocurrents, showed less catalytic activity than their  $Mn^{II}$ counterparts. The fluorescence results conclusively show that the higher photocurrents observed for  $Zn^{II}$  anodes do not correlate with enhanced performance. This observation underscores the necessity to probe product formation in photoelectrosynthesis experiments.

The large Faradaic yield observed for Mn<sup>II</sup>-L-TiO<sub>2</sub> anodes is likely a result of a combination of factors. Faradaic yields may be pushed above 100% through the oxidation of H<sub>2</sub>DCF via one-electron oxidation at the anode. Specifically, as Mn<sup>III</sup> and Mn<sup>IV</sup> species are expected to exist at low concentrations under experimental conditions, formation of the  $H_2DCF^+$  radical may be oxidized to DCF in solution by dissolved oxygen. Further, in the absence of an electrochemical potential, illumination of Mn<sup>II</sup>-L-TiO<sub>2</sub> results in significant formation of DCF (Fig. S4), suggesting that these passivated TiO<sub>2</sub> surfaces may catalyze the oxidation of H<sub>2</sub>DCF without passing current. This reaction would be similar to Scheme 2, where electrons injected into TiO<sub>2</sub> would reduce protons or oxygen in solution instead of traveling to the counter electrode. Importantly, both of these mechanisms would apply equally to Zn<sup>II</sup>-L-TiO<sub>2</sub> anodes, and any difference in efficiency is a result of performance of the metal ion.

## 3.3. Photoelectrochemical oxidation of 2-propanol

Among possible substrates for photoelectrosynthetic cells, alcohols represent a potentially useful class of compounds. The conversion of alcohols to the corresponding aldehyde or ketone is



Scheme 3. Conversion of 2-propanol to acetone and hydrogen.

particularly attractive due to the lower kinetic and thermodynamic demands of the reaction. Alcohol oxidation is a two-electron, twoproton process (vs. four-electron four-proton for water splitting) and requires less energy. One of the more significant challenges to exploring alcohols as a substrate for photoelectrochemical cells is the difficulty to identify oxidation products from these solutions.

In order to evaluate the capability of  $Mn^{II}-L$ -TiO<sub>2</sub> anodes, 2propanol was used as a substrate. The balanced reaction for the splitting of 2-propanol is presented in Scheme 3. The overall reaction is endergonic by 0.64 eV.

Illumination of 2-propanol solutions with Mn<sup>II</sup>–L–TiO<sub>2</sub>, Zn<sup>II–</sup>–L–TiO<sub>2</sub>, and bare TiO<sub>2</sub> anodes resulted in observed photocurrents that were similar to those seen with H<sub>2</sub>DCF (Fig. 8). For Mn<sup>II–</sup>–L–TiO<sub>2</sub>, current rose gradually over several minutes, reaching ~5  $\mu$ A, before beginning to decay slowly over 1 h. Illumination of Zn<sup>II–</sup>L–TiO<sub>2</sub> resulted in a sharp spike in current, followed by gradual decay. Bare TiO<sub>2</sub> anodes showed no photoresponse.

The gradual decay in current observed for  $Mn^{II}-L-TiO_2$  anodes may be associated with instability of manganese coordination to the terpyridine moiety in the linker molecules on TiO<sub>2</sub>. During the photoelectrochemical process, some manganese coordination may be lost, releasing  $Mn^{II}$  and/or  $Mn^{III}$  ions into the aqueous phase. This reduces the amount of potential surface catalytic sites and subsequently leads to a decrease in photocurrent over longer times. The lack of response upon illumination of bare TiO<sub>2</sub> contrasts with the photoresponse of these anodes when H<sub>2</sub>DCF was employed as a substrate. This result is consistent with the hypothesis that H<sub>2</sub>DCF and/or DCF are able to adsorb onto bare TiO<sub>2</sub> surfaces and sensitize the electrode.

Following photolysis, several attempts were made to analyze reaction products for acetone. Neither ESI–MS analysis nor Brady's test resulted in positive identification. The inability to identify acetone is likely due to low turnover numbers as indicated by the relatively small photocurrents and subsequent low concentrations of the products generated during the photoelectrochemical reaction.

The experimental results indicate that surface manganese complexes are necessary to achieve stable photocurrent in the

**Fig. 8.** Photoelectrochemical response of  $Mn^{II}$ –**L**–TiO<sub>2</sub> (red),  $Zn^{II}$ –**L**–TiO<sub>2</sub> (blue), and bare TiO<sub>2</sub> (black) upon visible light ( $\lambda > 420$  nm) illumination of a 1% solution of 2propanol in 50 mM, pH 4.5 acetate buffer. Up and down arrows indicate times when the light was turned on and off, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



#### Table 1

Parameters of the biexponential fits to the time dependent EPR signals obtained with light on/off conditions, shown in Fig. 4 (botom).

Parameter	Light on	Light off
A <sub>1</sub>	241.8	-189.0
k <sup>(+)</sup>	$(14.1 \text{ s})^{-1}$	$(42.2 \text{ s})^{-1}$
A <sub>2</sub>	328.4	-456.2
$k^{(-)}$	$(3.0 \text{ s})^{-1}$	$(9.2 \text{ s})^{-1}$
A <sub>0</sub>	5220.9	5794.5
Corr. Coeff.	0.998	0.999
EMS rel. error	0.210	7.263

photoelectrochemical cell. Photogenerated Mn<sup>III</sup> or Mn<sup>IV</sup> complexes are the most probable active species for the oxidation of 2-propanol, although the exact mechanism is not clear based on this work. Important studies remain to improve the efficiency of the photoelectrochemical process and to gain better insight into the reaction mechanism of the Mn<sup>II</sup> catalysts.

#### 4. Concluding remarks

Electron donor–acceptor assemblies have been widely studied for solar energy conversion. In this study, a donor–acceptor assembly was prepared based on inexpensive materials. The assembly consists of a  $TiO_2$  nanoparticle as the electron acceptor, an organic linker to absorb visible light, and a manganese complex as the electron donor. This assembly was further incorporated into a photoelectrochemical cell for use in visible-light-driven chemical transformations.

H<sub>2</sub>DCF was found to be promising substrate for evaluation of the performance of anodes in photoelectrosynthetic cells. The high fluorescence quantum yield of the oxidized product offers subnanomolar limits of detection, providing greater sensitivity than traditional substrates. The large Faradaic yields suggest that chemical processes may drive further H<sub>2</sub>DCF oxidation following initial photoelectrochemical oxidation. Such processes serve to chemically amplify the signal and increase the sensitivity for the method. Non-electrochemical photocatalysis does increase the background signal; however, these signals are outpaced by photoelectrochemical oxidation and can be distinguished after only a few minutes of photolysis.

Significant photocurrent was observed using 2-propanol as the substrate. The surface manganese complex was found to sustain stable photocurrent; however, attempts at direct detection of acetone were unsuccessful, possibly due to low yields and higher limits of detection. Nevertheless, this work highlights the possibility of using inexpensive materials for solar to chemical energy conversion (see Fig. 1).

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2013.07.001.

#### References

- [1] V. Balzani, A. Credi, M. Venturi, ChemSusChem 1 (2008) 26-58.
- [2] I. McConnell, G. Li, G.W. Brudvig, Chem. Biol. 17 (2010) 434-447.
- [3] J.H. Alstrum-Acevedo, M.K. Brennaman, T.J. Meyer, Inorg. Chem. 44 (2005) 6802–6827.
- [4] M. Hambourger, G.F. Moore, D.M. Kramer, D. Gust, A.L. Moore, T.A. Moore, Coord. Chem. Rev. 38 (2009) 25–35.
- [5] J.P. McEvoy, G.W. Brudvig, Chem. Rev. 106 (2006) 4455-4483.
- [6] B. O'Regan, M. Grätzel, Nature 353 (1991) 737–740.
- [7] M. Grätzel, Nature 414 (2001) 338-344.
- [8] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110 (2010) 6595–6663.
- [9] Z. Chen, J.J. Concepcion, J.W. Jurss, T.J. Meyer, J. Am. Chem. Soc. 131 (2009) 15580–15581.
- [10] E. Reisner, D.J. Powell, C. Cavazza, J.C. Fontecilla-Camps, F.A. Armstrong, J. Am. Chem. Soc. 131 (2009) 18457–18466.
- [11] K.J. Young, L.A. Martini, R.L. Milot, R.C. Snoeberger III, V.S. Batista, C.A. Schmuttenmaer, R.H. Crabtree, G.W. Brudvig, Coord. Chem. Rev. 256 (2012) 2503–2520.
- [12] W.J. Youngblood, S.-H.A. Lee, Y. Kobayashi, E.A. Hernandez-Pagan, P.G. Hoertz, T.A. Moore, A.L. Moore, D. Gust, T.E. Mallouk, J. Am. Chem. Soc. 131 (2009) 926–927.
- [13] R. Brimblecombe, G.F. Swiegers, G.C. Dismukes, L. Spiccia, Angew. Chem. Int. Ed. Engl. 47 (2008) 7335–7338.
- [14] Y. Gao, X. Ding, J. Liu, L. Wang, Z. Lu, L. Li, L. Sun, J. Am. Chem. Soc. 135 (2013) 4219–4222.
- [15] L.A. Gallagher, S.A. Serron, X.G. Wen, B.J. Hornstein, D.M. Dattelbaum, J.R. Schoonover, T.J. Meyer, Inorg. Chem. 44 (2005) 2089–2097.
- [16] J.A. Moss, J.C. Yang, J.M. Stipkala, X. Wen, C.A. Bignozzi, G.J. Meyer, T.J. Meyer, Inorg. Chem. 43 (2004) 1784–1792.
- [17] J.A. Treadway, J.A. Moss, T.J. Meyer, Inorg. Chem. 38 (1999) 4386-4387.
- [18] G.F. Moore, J.D. Blakemore, R.L. Milot, J.F. Hull, H.-e. Song, L. Cai, C.A. Schmuttenmaer, R.H. Crabtree, G.W. Brudvig, Energy Environ. Sci. 4 (2011) 2389–2392.
- [19] H.B. Gray, Nat. Chem. 1 (2009) 7.
- [20] W.R. McNamara, R.C. Snoeberger, G. Li, J.M. Schleicher, C.W. Cady, M. Poyatos, C.A. Schmuttenmaer, R.H. Crabtree, G.W. Brudvig, V.S. Batista, J. Am. Chem. Soc. 130 (2008) 14329–14338.
- [21] G. Li, E.M. Sproviero, W.R. McNamara, R.C. Snoeberger, R.H. Crabtree, G.W. Brudvig, V.S. Batista, J. Phys. Chem. B 114 (2010) 14214–14222.
- [22] W.R. McNamara, R.C. Snoeberger, G. Li, C. Richter, L.J. Allen, R.L. Milot, C.A. Schmuttenmaer, R.H. Crabtree, G.W. Brudvig, V.S. Batista, Energy Environ. Sci. 2 (2009) 1173–1175.
- [23] W.R. McNamara, R.L. Milot, H.-e. Song, R.C. Snoeberger, V.S. Batista, C.A. Schmuttenmaer, G.W. Brudvig, R.H. Crabtree, Energy Environ. Sci. 3 (2010) 917–923.
- [24] T.A. Heimer, S.T. Darcangelis, F. Farzad, J.M. Stipkala, G.J. Meyer, Inorg. Chem. 35 (1996) 5319–5324.
- [25] C.P. LeBel, H. Ischiropoulos, S.C. Bondy, Chem. Res. Toxicol. 5 (1992) 227–231.
   [26] H. Possel, H. Noack, W. Augustin, G. Keilhoff, G. Wolf, FEBS Lett. 416 (1997)
- 175–178.
- [27] P.G. Gunasekar, A.G. Kanthasamy, J.L. Borowitz, G.E. Isom, J. Neurosci. Methods 61 (1995) 15–21.
- [28] E.W. Miller, S.X. Bian, C.J. Chang, J. Am. Chem. Soc. 129 (2007) 3458-3459.
- [29] R.K. Dieter, L.A. Silks, J.A. Fishpaugh, M.E. Kastner, J. Am. Chem. Soc. 107 (1985) 4679–4692.
- [30] S. Das, C.D. Incarvito, R.H. Crabtree, G.W. Brudvig, Science 312 (2006) 1941– 1943.
- [31] Y. Jiang, N. Wu, H. Wu, M. He, Synlett 2005 (2005) 2731-2734.
- [32] R. Brandt, A.S. Keston, Anal. Biochem. 11 (1965) 6-9.
- [33] G. Li, E.M. Sproviero, R.C. Snoeberger, N. Iguchi, J.D. Blakemore, R.H. Crabtree, G.W. Brudvig, V.S. Batista, Energy Environ. Sci. 2 (2009) 230–238.
- [34] G. Li, C. Richter, R.L. Milot, L. Cai, C.A. Schmuttenmaer, R.H. Crabtree, G.W. Brudvig, V.S. Batista, Dalton Trans. (2009) 10078–10085.
- [35] G. Li, K.A. Gray, Chem. Phys. 339 (2007) 173-187.
- [36] G. Li, N. Dimitrijevic, L. Chen, J. Nichols, T. Rajh, K.A. Gray, J. Am. Chem. Soc. 130 (2008) 5402–5403.
- [37] H. Gerischer, M.E. Michel-Beyerle, F. Rebentrost, H. Tributsch, Electrochim. Acta 13 (1968) 1509–1515.
- [38] G. Benkö, M. Hilgendorff, A.P. Yartsev, V. Sundström, J. Phys. Chem. B 105 (2001) 967–974.
- [39] M. Hilgendorff, V. Sundström, J. Phys. Chem. B 102 (1998) 10505-10514.