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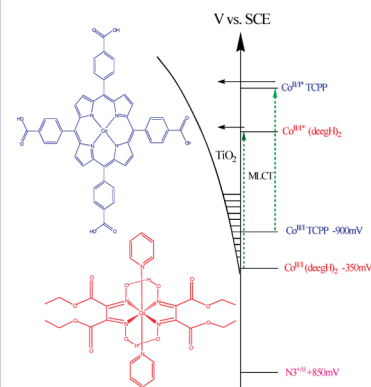
# Sensitization of TiO<sub>2</sub> by the MLCT Excited State of Co<sup>I</sup> Coordination Compounds

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**ABSTRACT** Co<sup>I</sup> coordination compounds, based on porphyrin or glyoxime ligands, anchored to TiO<sub>2</sub> nanocrystallites interconnected in a mesoporous thin film were found to efficiently inject electrons into TiO<sub>2</sub> when excited with visible or near-infrared light. When a cobalt metalloporphyrin sensitizer was employed, electron injection was rapid and led to a long-lived (millisecond time scale) charge-separated state whose recombination kinetics were nonexponential but were first order in the concentration of TiO<sub>2</sub> electrons. The MLCT excited state was found to inject electrons more efficiently than the  $\pi \rightarrow \pi^*$  excited state of the porphyrin, even though unfilled d orbitals were present. These findings provide an earth-abundant metal to use in coordination compounds for sensitization of wide-band-gap semiconductor nanoparticles, especially those whose conduction band edges are generally closer to the vacuum level.

**SECTION** Energy Conversion and Storage



Dye-sensitized solar cells represent an intriguing alternative to traditional silicon-based technologies, yet the most efficient cells employ ruthenium–polypyridyl compounds as sensitizers.<sup>1,2</sup> Efforts to replace the metal center with iron have been frustrated by rapid deactivation of metal-to-ligand charge-transfer (MLCT) excited states via ligand-field (LF) states<sup>3</sup> that lower the yield of excited-state injection into the semiconductor.<sup>4</sup> In an effort to identify an alternative first-row transition metal, we report here that the MLCT excited states of Co<sup>I</sup> (d<sup>8</sup>) coordination compounds sensitize TiO<sub>2</sub> to visible and even near-infrared light. Although the Co<sup>III/I</sup> reduction potentials of these specific compounds were not appropriate for application in present dye-sensitized solar cells, the data provide fundamentally new insights into injection from excited states with different parentage as well as interfacial charge recombination with low thermodynamic driving force in the presence of trapped electrons.

The mesoporous, nanocrystalline (anatase) TiO<sub>2</sub> thin films were prepared as previously described.<sup>5</sup> The films were placed in millimolar solutions of Co(TCPP)Cl in DMSO, where TCPP is *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, that resulted in surface coverages of  $(1-4) \times 10^{-9}$  mol/cm<sup>2</sup>, abbreviated Co<sup>III</sup>/TiO<sub>2</sub>. The thin films were rinsed and immersed in argon-saturated 100 mM TBAClO<sub>4</sub>/CH<sub>3</sub>CN electrolyte with 0.2% v/v pyridine, and the Fermi level of the TiO<sub>2</sub> was potentiostatically controlled (versus SCE). Figure 1a shows the absorption spectrum of such a film in the presence of 25 mM pyridine with Co in the (III), (II), and (I) formal oxidation states as well as that of trapped TiO<sub>2</sub> electrons, TiO<sub>2</sub><sup>-</sup>(e<sup>-</sup>)s. Comparative spectroelectrochemical studies on ZrO<sub>2</sub> thin films were consistent with this data and revealed no evidence for direct Co<sup>I</sup> to TiO<sub>2</sub> charge-transfer bands. The formal reduction potentials were taken as the potential

where a 50:50 mixture of the two redox states were present upon forward bias,  $E^{\circ}(\text{Co}^{\text{III/II}}) \approx -480$  mV,  $E^{\circ}(\text{Co}^{\text{II/I}}) \approx -900$  mV. The Co<sup>III/I</sup> couple was reversible, while the Co<sup>III/II</sup> couple was influenced by charge rectification at the TiO<sub>2</sub> interface.

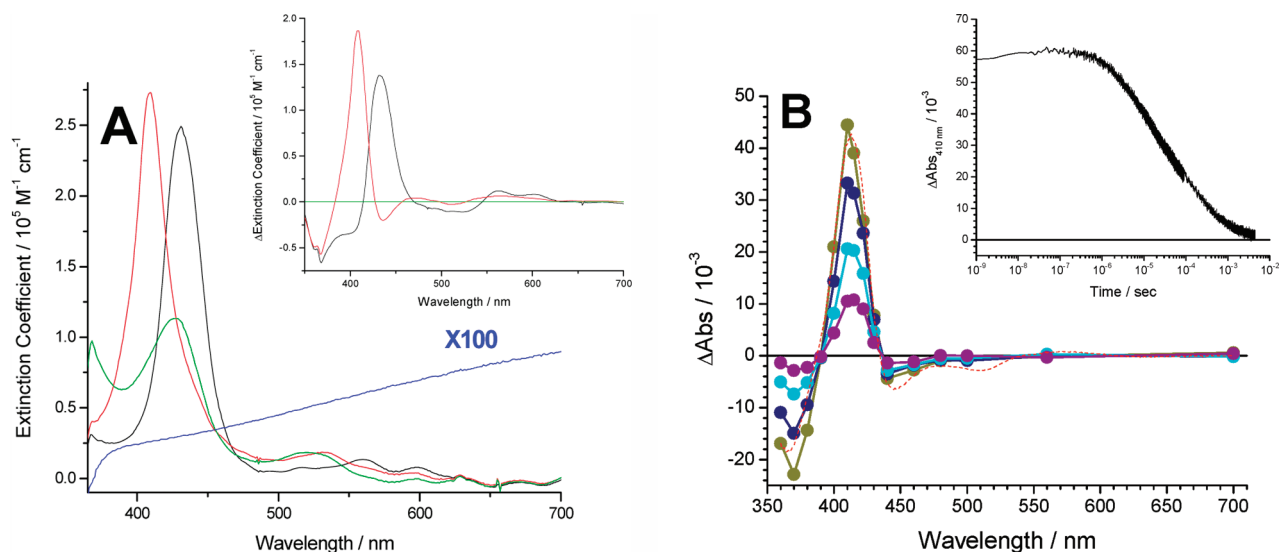
Nanosecond 532 nm laser excitation of Co<sup>I</sup>/TiO<sub>2</sub> led to the prompt appearance of an absorption spectrum consistent with an interfacial charge-separated state, comprised of an injected electron in TiO<sub>2</sub> and an oxidized sensitizer, abbreviated Co<sup>II</sup>/TiO<sub>2</sub>(e<sup>-</sup>) (Figure 1b). The inset shows that injection was complete within 100 ns while Co<sup>II</sup>/TiO<sub>2</sub>(e<sup>-</sup>) → Co<sup>I</sup>/TiO<sub>2</sub> recombination was well-described by the Kohlrausch–Williams–Watts (KWW) kinetic model,  $\Delta A = \Delta A_0 \exp[-(k_{\text{KWW}}t)^{\beta}]$ , where  $k_{\text{KWW}}^{-1}$  is a characteristic lifetime and  $\beta$  is inversely related to the width of an underlying Lévy distribution of rate constants.<sup>6,7</sup> In the absence of pyridine, rapid injection was again observed, but the recombination rate increased. The MLCT excited state was not observed by transient absorption in solution (Co<sup>I</sup> generated via chemical reductant) nor immobilized on an insulating ZrO<sub>2</sub> surface, implying  $\tau < 10$  ns. Further evidence that the absorption features resulted from rapid excited-state electron injection was garnered by time-resolved photocurrent measurements, where a transient anodic signal (< 100 ms) and immediate cathodic rebound was observed after pulsed excitation. As redox mediators were absent, the photocurrents could not be sustained under steady-state illumination.

A convenient method for maintaining the Co<sup>I</sup> formal oxidation state was with an applied bias. However, it was difficult to ensure that this state was present without a significant

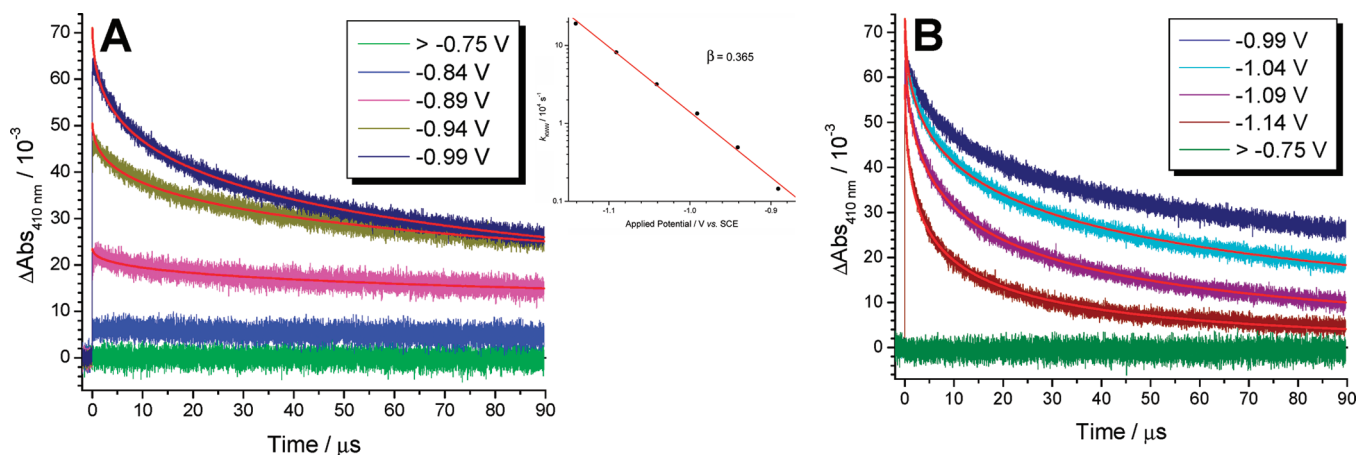
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**Figure 1.** (A) Absorption spectra for a Co/TiO<sub>2</sub> thin-film electrode in the formal oxidation states of Co<sup>III</sup> (black), Co<sup>II</sup> (red), and Co<sup>I</sup> (green) obtained via spectroelectrochemistry, where TiO<sub>2</sub>(e<sup>-</sup>) absorption features, shown for an unsensitized TiO<sub>2</sub> thin film (blue), were removed from the Co<sup>I</sup> spectrum. The inset displays the same spectra but referenced to the Co<sup>I</sup>/TiO<sub>2</sub> spectrum. (B) Transient absorption difference spectra for Co<sup>I</sup>/TiO<sub>2</sub> measured after pulsed 532 nm laser excitation at delay times of 20 ns (brown), 500 ns (dark blue), 5.0 μs (light blue), and 60 μs (purple). Overlaid as a red dashed line is the (Co<sup>II</sup>–Co<sup>I</sup>) difference spectrum from the inset in panel A. The inset depicts the absorption change observed at 410 nm.

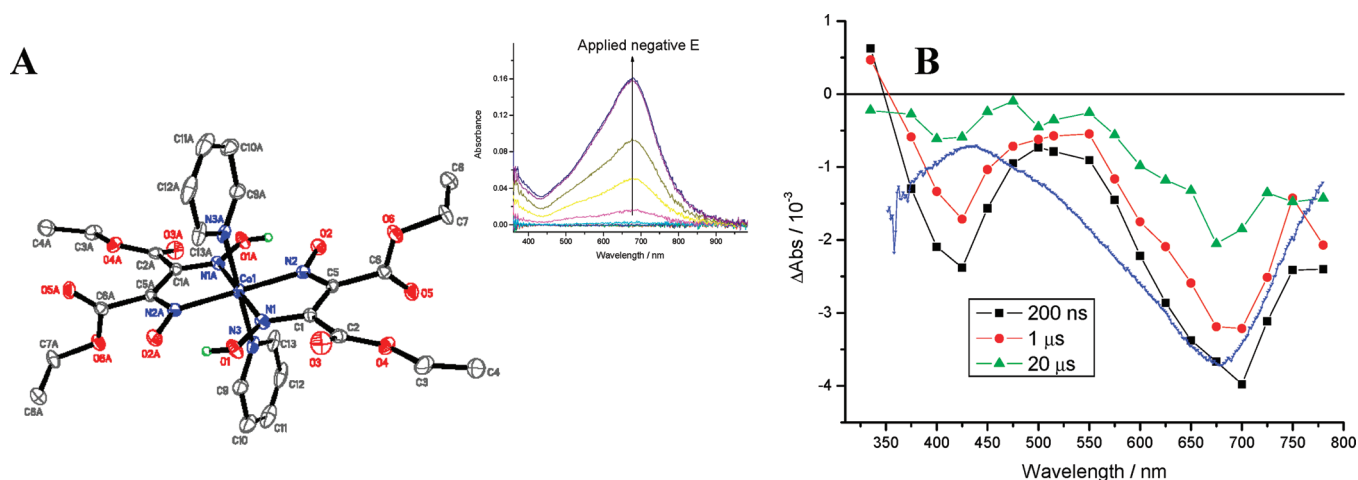


**Figure 2.** (A, B) Transient absorption changes at 410 nm after pulsed 532 nm excitation of the sample from Figure 1 at the indicated applied potentials. Overlaid are fits to the KWW model with  $\beta = 0.365(2)$ . The inset illustrates the logarithmic dependence between applied bias and the extracted rate constants as is apparent by the linear fit.

concentration of TiO<sub>2</sub>(e<sup>-</sup>)s.<sup>8</sup> It was of interest to quantify recombination under conditions where there were few and excess electrons in TiO<sub>2</sub> as this corresponds approximately to short- and open-circuit conditions of an operational solar cell. Hence, an electrochemical bias dependence study was performed, Figure 2. There was no evidence for excited-state injection when the compound was in the formal oxidation state of 2. Had such injection occurred, a significant bleach at 410 nm would have occurred, contrary to the experimental result. However, as the Fermi level was raised to  $\sim -990$  mV, the excited-state injection yield increased with the Co<sup>I</sup> concentration, Figure 2a. As the Fermi level was raised further to  $-1100$  mV, the amplitude of the absorption change remained nearly constant, but faster TiO<sub>2</sub>(e<sup>-</sup>) + Co<sup>II</sup> charge

recombination was apparent, Figure 2b. The recombination kinetics at each bias were well-described by the KWW kinetic model with a fixed  $\beta = 0.365$ . The observed rate constants were logarithmically dependent on the applied bias, Figure 2b inset. Given the known exponential density of TiO<sub>2</sub> states,<sup>9,10</sup> this data indicates that recombination was first-order in TiO<sub>2</sub>(e<sup>-</sup>)s. At more negative applied biases, the initial amplitude began to decrease, behavior attributed to either a lower injection yield or rapid subnanosecond recombination.

In sharp contrast to the Ru<sup>II</sup> sensitizers optimized for solar cell applications where the driving force for charge recombination is large,  $|\Delta G| > \lambda \approx 1$  eV, the near coincidence of the potential for TiO<sub>2</sub> and Co<sup>II</sup> reduction, implies a small free-energy change,  $|\Delta G| \approx 0$ . Therefore, the charge-recombination



**Figure 3.** (A) The structure of  $\text{Co}^{\text{II}}(\text{deegH})_2(\text{Py})_2$  determined by X-ray diffraction at 110 K. The inset depicts absorption difference spectra recorded for  $\text{Co}(\text{deegH})_2(\text{Py})_2/\text{TiO}_2$  as the compound was reduced from  $\text{Co}^{\text{II}}$  to  $\text{Co}^{\text{I}}$ . (B) Absorption difference spectra measured at the indicated delay times after pulsed 532 nm laser excitation of a  $\text{Co}^{\text{I}}(\text{deegH})_2/\text{TiO}_2$  thin film immersed in  $\text{CH}_2\text{CN}$ . Overlaid in blue is a scaled version of the expected difference spectrum from the spectroelectrochemical data shown in the inset.

reactions are expected to occur in the Marcus normal region for these  $\text{Co}^{\text{I}}$  sensitizers and in the inverted region for the standard ruthenium sensitizers. Given the parabolic dependence of electron-transfer rate constants with the Gibbs free-energy change, it is reasonable that the observed rate constants for the reactions are nearly the same.<sup>11</sup>

The injection quantum yield for  $\text{Co}^{\text{I}}/\text{TiO}_2$  at  $-1.16$  V versus SCE was  $0.46 \pm 0.06$  of that measured for *cis*- $\text{Ru}(\text{dcb})_2(\text{NCS})_2/\text{TiO}_2$ , where dcb is 4,4'-(COOH)<sub>2</sub>-2,2'-bipyridine, with pulsed 532 nm light and was dependent on the excitation wavelength. These quantum yields were determined by a previously described comparative actinometry procedure using  $\text{N3}/\text{TiO}_2$  as the actinometer.<sup>12</sup> The yield decreased by about 1/4 when 436 or 369 nm light and matched numbers of absorbed photons were utilized, compared to 532 nm excitation. The  $\text{Co}^{\text{I}}$  absorptions at 436 or 369 nm are intraligand  $\pi \rightarrow \pi^*$  transitions to the lowest unoccupied molecular orbital (LUMO), whereas those at 532 nm have MLCT character, as previously assigned by magnetic circular dichroism in  $\text{Co}^{\text{I}}$  phthalocyanines.<sup>13</sup> Assuming  $D_{4h}$  symmetry, electric dipole selection rules require that this MLCT transition be to upper unoccupied molecular orbitals, that is, LUMO+1 and LUMO+2.<sup>14</sup> This implies that MLCT excitation creates a stronger reductant than Soret or Q-band intraligand  $\pi \rightarrow \pi^*$  excitation, behavior that may underlie the higher injection yield. It also suggests that the energy of the  $d_{x^2-y^2}$  LF state (b1 state) is above the  $\pi^*$  LUMO+*n*, states, thus allowing injection to be competitive with decay through LF states. Wavelength-dependent injection from molecular sensitizers is rare but has been observed with  $\text{Fe}^{\text{II}}$  compounds, although the injection yields were about a factor of 5 lower than those reported herein.<sup>3</sup>

To test the generality of  $\text{Co}^{\text{I}}$  MLCT sensitization, a cobalt–diglyoxime coordination compound was synthesized,  $\text{Co}^{\text{II}}(\text{deegH})_2(\text{Py})_2$ , where deegH<sub>2</sub> is diethylesterglyoxime (Figure 3a). When anchored to  $\text{TiO}_2$  and reduced to the  $\text{Co}^{\text{I}}$  state,  $E^\circ(\text{Co}^{\text{II}}/\text{Co}^{\text{I}}) \approx -350$  mV, a broad absorption band centered at 680 nm was observed with a reported extinction coefficient of  $\sim 8000 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>15,16</sup> A similar absorption band

has been observed in closely related  $\text{Co}^{\text{I}}$  glyoxime compounds and was attributed to low-lying MLCT excited states.<sup>17</sup> Pulsed 532 nm laser excitation into this transition led to an immediate bleach of the MLCT absorption band, Figure 3b. A simulated difference spectrum based on the assumption of  $\text{Co}^{\text{I}}$  excited-state injection to yield  $\text{Co}^{\text{II}}$  agreed well with the observed data and supports an excited-state injection mechanism as opposed to reductive quenching of the  $\text{Co}^{\text{I}}$  excited state and/or ligand loss photochemistry. Recombination occurred on a 100  $\mu\text{s}$  time scale. The same transient absorption spectra were observed when 683 nm light excitation was employed. The ground state absorption spectrum suggests that this compound will sensitize  $\text{TiO}_2$  beyond 900 nm. Furthermore, without the interfering and overlapping intraligand transitions found in metalloporphyrins, verification of MLCT sensitization by a  $\text{Co}^{\text{I}}$  coordination compound was realized.

In conclusion, pulsed-light excitation of  $\text{Co}^{\text{I}}$ -sensitized  $\text{TiO}_2$  thin films resulted in rapid MLCT excited-state electron injection into  $\text{TiO}_2$  ( $k_{\text{inj}} > 10^8 \text{ s}^{-1}$ ) to yield a  $\text{Co}^{\text{II}}/\text{TiO}_2(e^-)$  charge-separated state. Although the expected quenching by LF states was present when the cobalt was in the (III) and (II) formal oxidation states, such behavior was not dominant with  $\text{Co}(\text{I})$ , behavior shown to result from an underlying MLCT excited state. The lifetime of the  $\text{Co}^{\text{II}}/\text{TiO}_2(e^-)$  state was found to be linearly dependent on the concentration of  $\text{TiO}_2(e^-)$ s in the thin film. The charge-separated state lifetime could presumably be enhanced through the incorporation of a rigid rod spacer unit between the carboxylic acid groups and the  $\text{Co}(\text{I})$  center or through the addition of a blocking layer on the  $\text{TiO}_2$  surface.<sup>18–20</sup> Although second-row  $d^8$  coordination compounds based on  $\text{Pt}^{\text{II}}$  have recently been shown to sensitize  $\text{TiO}_2$  nanocrystallites,<sup>21,22</sup> the sensitization reported here is of potential practical importance as cobalt is an earth-abundant metal and the singly oxidized ( $d^7$ ) state is known to be sufficiently stable.<sup>23</sup> Closely related  $\text{Co}^{\text{II}}$  coordination compounds have in fact been utilized as redox mediators in dye-sensitized solar cells.<sup>24,25</sup> While  $\text{Co}^{\text{I}}$  compounds with appropriate energetics for regeneration by iodide may one day be exploited in practical dye-sensitized solar cells, these findings

may also restrict their application as semiconductor-anchored catalysts for solar fuel generation because excited-state injection may compete with hydrogen evolution or carbon dioxide reduction.

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