decrease of Chla⁺ yield with addition of UQ beyond the maximum Chla⁺ yield as due to excited singlet quenching by UQ.

Our results suggest that at least some Chla⁺ can be formed by direct photoexcitation without the intervention of an electron acceptor. With blue-light irradiation with a maximum energy of 3.8 eV this seems to be a one-photon process on the basis of the light intensity measurements of Figure 4. With red-light irradiation with a maximum energy of 2.1 eV two photons must be involved, and it seems probable that the triplet state is an intermediate. The light intensity measurements of Figure 4 do support a biphotonic mechanism, but the statistics are only marginally convincing.

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Registry No. Chl⁺, 11060-77-8; DPPC, 2797-68-4; MV, 1910-42-5; PBQ, 106-51-4; p-TCBQ, 118-75-2; TBB, 636-28-2; p-TBBQ, 488-48-2; NaNO₃, 7631-99-4; SmCl₃, 10361-82-7; Cd(Ac)₂, 543-90-8; potassium ferricyanide, 13746-66-2.

Mössbauer Study of the Kinetics of Fe³⁺ Photoreduction on TiO₂ Semiconductor Powders

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The kinetics of the photoreduction of Fe^{3+} to Fe^{2+} via illuminated TiO_2 particles suspended in ferric chloride electrolyte has been studied by ⁵⁷Fe Mössbauer spectroscopy. The semiconductor powder-liquid electrolyte slurry was quench-frozen after specific illumination periods to generate samples amenable to Mössbauer spectroscopy. The rates and equilibrium conversion of Fe^{3+} reduction were obtained for five TiO₂ particle-electrolyte systems: (1) intrinsic anatase powder; (2) intrinsic rutile powder; (3) intrinsic anatase powder with a facile hole acceptor added to the electrolyte; (4) reduced, n-type anatase; and (5) platinized, n-type anatase powder. A simple kinetic model, based on competition between the forward reduction of Fe^{3+} and the back oxidation of Fe²⁺, and controlled by semiconductor band/redox couple energetics, is able to account for the observed differences in Fe³⁺ photoreduction for the five systems.

Introduction

Photoelectrochemical systems based on semiconductor particles and colloids have received considerable attention in recent years.¹⁻¹⁵ Much of this work is qualitative; quantitative information concerning the kinetics of charge transfer at illuminated semiconductor-electrolyte interfaces has been based exclusively on pulsed laser experiments operating in the nanosecond to microsecond regime.¹⁶⁻²³ In the experiments reported here, kinetic data over long time scales (minutes to hours) have been obtained by Mössbauer spectroscopy of iron ions in frozen electrolytes.

Mössbauer spectroscopy is used to monitor the charge states of the ions in solution as a function of the illumination time of the suspended semiconductor particles. The electrolyte solution is quench-frozen in liquid nitrogen after each illumination period in order to obtain a Mössbauer spectrum; the time rate of change of the oxidation state of the iron ions can thus be followed. An important advantage of Mössbauer spectroscopy is that it allows in-situ determination of the relative amounts of Fe²⁺ and Fe³⁺ and it is not affected by other non-iron-containing redox species in the solution. This is especially important for cases where other redox species are added to the system to influence the chargetransfer process.

In the present work studies are made of titanium dioxide particles suspended in ferric chloride electrolyte and illuminated with white light from a xenon lamp; both anatase and rutile crystal forms of TiO_2 are studied. The kinetics of electron transfer from TiO_2 to Fe^{3+} are determined, as well as the effects of a hole acceptor, platinization, and TiO_2 doping by reduction.

Experimental Procedures

Sample Preparation and Illumination. The ferric chloride solution was prepared by dissolving Fe_2O_3 (95% ⁵⁷Fe enriched)

in boiling 8 N HCl, and then adding H₂O to produce a final Fe³⁺ ion concentration of 0.014 M. Other redox species, such as the facile hole acceptor sodium acetate, were added to the solution in some experiments.

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Figure 1. Mössbauer spectra of frozen electrolyte solutions containing iron ions and titanium dioxide (anatase) powders after various illumination times. The solid lines are least-squares fit as described in the text. Zero velocity corresponds to the center of the α -Fe calibration spectrum.

Both the rutile and anatase crystal forms of TiO_2 were studied. In addition to these intrinsic powders, reduced (n-type) anatase, platinized anatase, and platinized, n-type anatase were also studied. The formation of n-type anatase was accomplished by heating the TiO_2 in an inert environment at 650 °C for 6 h to produce oxygen vacancies. Platinization was done according to a process reported by Kraeutler and Bard.¹³

The samples were prepared by putting 20 mg of TiO₂ in an annular Plexiglass sample disk, cementing on a 140- μ m-thick glass cover slip, and then filling it with the FeCl₃ solution. The electrolyte volume of each sample disk was about 0.6 cm⁻³ (16 mm diameter × 3.2 mm thick).

The samples were illuminated by an OSRAM 900-W xenon lamp through the glass cover slip. The intensity for each sample, as measured by a thermopile, was 59 mW/cm², with an infrared filter in place. To keep the TiO₂ particles suspended and to ensure illumination of all electrolyte and powder, the sample disks were mechanically shaken while under illumination.

Since Mössbauer spectroscopy requires the sample to be in the solid state, the FeCl₃–TiO₂ suspensions were quick-frozen in their sample cells in liquid nitrogen immediately after the illumination period. Immediate freezing also prevented possible back oxidation of the photoproduced Fe^{2+} . The samples were kept frozen and their temperature controlled during spectrum accumulation by a liquid nitrogen cold-finger apparatus. A fresh sample was prepared for each illumination and Mössbauer measurement.

Mössbauer Measurements. Each absorption spectrum was obtained with a conventional constant acceleration spectrometer by using a 15-mCi ⁵⁷Co:Rh source. The absolute velocity scale was determined by calibrating the spectrometer periodically with the six-line spectrum of metallic iron. Each spectrum was least-squares computer-fitted with a superposition of Lorentzian resonance lines. Figure 1 shows a typical series of spectra as a function of illumination time, and the types of fits used. Prior to illumination the spectrum was typical of a frozen solution containing only Fe³⁺ ions; magnetic hyperfine interactions produce a spectrum that is a superposition of a very broad resonance and a relatively sharp resonance.²⁴ The velocity range was chosen sufficiently large $(\pm 10 \text{ mm/s})$ to include all magnetic resonance peaks due to high-spin Fe³⁺ ions. The magnetically broadened resonance (Figure 1) was fitted here by a single broad Lorentzian line, and the resonance area obtained by integrating only that portion of the Lorentzian in the range from -10 to +10 mm/s.

TABLE I: Mössbauer Spectral Parameters from the Fe^{3+} and Fe^{2+} Species in Frozen Solution at 150 K^a

species	δ, mm/s	Γ, mm/s	Δ , mm/s	
Fe ³⁺ (sharp)	0.48	0.70	0	
Fe ³⁺ (broad)	0.5	18	0	
Fe ²⁺	1.35	0.31	2.98	

 ${}^{a}\delta$ is the isomer shift relative to α -Fe at 298 K. Γ is the full line width at half-maximum. Δ is the quadrupole splitting.



Figure 2. Mössbauer spectra of frozen solutions containing iron ions and the various powders indicated. The illumination times were as follows: anatase, 60 min; rutile, 60 min; anatase + hole acceptor (Na acetate), 300 min; n-type anatase, 120 min. The solid lines are least-squares fits as described in the text. Zero velocity corresponds to the center of the α -Fe calibration spectrum.

An experimental procedure was developed which minimized the amount of the broad magnetic component in each experiment: after the sample was quick-frozen and mounted in the cold-finger apparatus, it was allowed to warm to about 195 K and then cooled back to about 150 K; the spectrum was then accumulated at the latter temperature. This "anneal" process produces a glass-to-crystal phase transition in the ice matrix,²⁵ and the magnetic hyperfine interactions producing the broad component for Fe³⁺ are significantly reduced in the new phase. This procedure reduced the resonance area of the broad component by at least a factor of two. However, as seen in Figure 1, the spectra still contained significant amounts of the broad component (20–50% of the total resonance area depending upon the experiment) and therfore had to be carefully treated in the analysis.

The high-spin Fe^{2+} produced by illumination is readily identified by its large quadrupole doublet; this is seen in Figure 1 after 60and 300-min illumination. Only one line of the doublet is clearly resolved after 15-min illumination and the total resonance of the Fe^{2+} in this type of case was obtained by simply doubling the area of the resolved line.

The fractional amount of Fe^{2+} was obtained from the ratio of the Fe^{2+} resonance area to the total resonance area comprised of the Fe^{2+} doublet, the sharp Fe^{3+} singlet, and the very broad Fe^{3+} resonance between ± 10 mm/s. This procedure assumes identical recoilless fractions for the Fe ions in the three sites. Average spectral parameters for these components are listed in Table I.

Results

Kinetic data on the photoreduction of Fe^{3+} by TiO_2 powders were obtained by illuminating the TiO_2/Fe^{3+} samples for specific periods of time, then quench-freezing the sample, and obtaining

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Figure 3. Fe^{2+} concentration vs. time of illumination for five series of runs. Typical uncertainties based on the computer deconvolutions of the Mössbauer spectra are indicated for each series. The uncertainty for the anatase and hole acceptor series is larger because of increased broad Fe^{3+} resonance which has a larger associated uncertainty. The solid and dashed lines are fits of the rate equation as described in the text.

Mössbauer spectra. Figure 1 shows typical spectra demonstrating the formation of Fe^{2+} as a function of illumination time in the presence of anatase powder; Figure 2 compares Fe^{2+} production with various types of TiO₂ powders and electrolytes.

The kinetic data were analyzed by assuming first-order rate expressions for the forward photoreduction and the reverse oxidation processes:

$$dC^{3+}/dt = -k_eC^{3+} + k_hC^{2+}$$
(1)

where C^{3+} is the fractional concentration of Fe³⁺, C^{2+} is the fractional concentration of Fe²⁺, k_e is the forward rate constant for Fe³⁺ reduction by electrons, and k_h is the reverse rate constant for Fe²⁺ oxidation by holes. This expression is based on a constant photon flux and a constant weight of TiO₂ and electrolyte volume for each experiment; therefore, the first-order rate constants are only relative values for the experimental conditions chosen here. Since $C^{2+} + C^{3+} = 1$, then

$$dC^{3+}/dt = -k_eC^{3+} + k_h(1 - C^{3+})$$
(2)

A steady-state concentration of ferric ion (C_{∞}^{3+}) is reached such that $dC^{3+}/dt = 0$; hence

$$C_{\infty}^{3+} = \frac{k_{\rm h}}{k_{\rm e} + k_{\rm h}} \tag{3}$$

Integration of eq 2 and substitution of eq 3 yields

$$C^{2+} = C_{\infty}^{2+} (1 - e^{-(k_{\rm e} + k_{\rm h})t})$$
(4)

where C_{∞}^{2+} is the concentration of Fe²⁺ at long times, when steady state is reached.

Figure 3 summarizes all of the data on the kinetics of Fe^{2+} formation from five series of spectra. The top of the figure compares anatase to rutile. The solid lines are fits of the data to eq 4. The results for anatase and rutile are

$$C^{2+}(\text{anatase}) = 0.20(1 - e^{-0.021t})$$
 (5)

$$C^{2+}(\text{rutile}) = 0.11(1 - e^{-0.012t})$$
 (6)

TABLE II: Summary of Fits of Kinetic Data to Eq 1

experiment	C_{β}^{2+}	$10^3 k_e, \ min^{-1}$	$\frac{10^3 k_{\rm h}}{{\rm min}^{-1}}$
unreduced anatase	$0.20 \ (0.02)^a$	4 (1)	17 (4)
unreduced rutile	0.11 (0.02)	1.3 (0.7) 2.1 $(1.1)^{b}$	11 (6) 17 (9)
unreduced anatase plus hole acceptor (sodium acetate)	0.40 (0.15)	4 (2)	6 (4)
reduced, n-type anatase	0.10 (0.02)	5 (3)	50 (30)
n-type anatase with platinum	0.40 (0.20)	2 (1)	2 (1)

^aUncertainties in values are indicated in parentheses. ^bDashed line in Figure 3.

Thus, for anatase, since $(k_h + k_e) = 0.021 \text{ min}^{-1}$, and $k_h/(k_h + k_e) = 0.8$, $k_e = 0.004 \text{ min}^{-1}$ and $k_h = 0.017 \text{ min}^{-1}$. For rutile, $(k_h + k_e) = 0.012 \text{ min}^{-1}$, $k_h/(k_h + k_e) = 0.89$, and $k_e = 0.0013 \text{ min}^{-1}$, $k_h = 0.011 \text{ min}^{-1}$. If it is assumed that the rates for hole oxidation for anatase and rutile are equal because the positions of the valence band edges are approximately equal, and thus one fixes the rate constant for hole oxidation (k_h) for both anatase and rutile to be equal to $k_h = 0.017 \text{ min}^{-1}$, then k_e for rutile becomes $k_e = 0.0021 \text{ min}^{-1}$. This fit for the rutile data is shown in Figure 3 as the dashed line. However, the data are not sufficiently precise to distinguish between the two fits.

The scatter in the data is due in part to the uncertainty in the area of the broad Fe^{3+} resonance, in part to the procedure of preparing a fresh sample for each run, and in part to factors not yet understood. For example, in the rutile data two samples showed about 7% Fe^{2+} after 30-min illumination, whereas a third showed no evidence of Fe^{2+} . This may be due to variations in the oxygen content of the electrolyte, which inhibits Fe^{3+} reduction. We have found in recent experiments on CdS particles that the scatter can be reduced substantially by using the same sample repeatedly, rather than by preparing a fresh sample for each time period. That is, a given sample is illuminated for a time period, requenched, melted, illuminated for the next time period, requenched, measured, remelted, etc. The rate constants determined by this procedure have much less error; this work will be reported separately in a future publication.

The curves in the lower half of Figure 3 show the data and theoretical fits (again using eq 4) for anatase in the presence of an efficient hole acceptor (sodium acetate), for reduced (n-type) anatase, and for n-type anatase with platinum deposited on the surface.

The results for all types of samples are summarized in Table II; estimates of the uncertainty in the direct and derived experimental values are indicated in parentheses. The results show that k_e for anatase is about two to three times that for rutile. Also, compared to intrinsic anatase the presence of the hole acceptor decreases k_h by about a factor of 3; for n-type anatase k_h is increased by about a factor of 3. Finally, for platinized n-type anatase, the rate constants for electron injection (k_e) and hole injection (k_h) are both decreased by factors of about 2 and 8, respectively, compared to unreduced anatase.

Discussion

Illumination of a semiconductor in contact with an electrolyte produces electron-hole pairs that can more readily separate if an electric field (depletion layer) exists at the semiconductor-electrolyte interface. The separated electrons and holes can drive reduction and oxidation reactions, respectively, at the surface to produce an overall net chemical reaction in the electrolyte. This process is enhanced when an ohmic metal contact to the semiconductor provides a facile and energetically favorable pathway for the removal of the majority carriers from the semiconductor; the minority carriers are also removed with the assistance of the electric field (see Figure 4a).

In semiconductors with very low carrier concentrations, the electric field is relatively small, but electron-hole pair separation can still occur if carrier diffusion to the surface is fast compared to electron-hole recombination, and preferential trapping or reaction of electrons or holes occurs at the semiconductor surface





Figure 4. Schematic diagrams of energetics associated with semiconductor particles in electrolytes having redox couples A/A^- and B/B^+ : (a) n-type particle partially coated with a metal which forms an ohmic contact; (b) intrinsic semiconductor particle without metal contact on the surface.

semiconductor

(see Figure 4b). This is the situation with nonreduced (intrinsic), insulating TiO_2 powders. Because of the low doping density and small electric field at the surface, the conduction and valence bands are relatively flat. Photogenerated electrons and holes can both be injected into the solution, but the process is not very efficient without ohmic contacts and significant electric fields in the depletion region.

In aqueous electrolyte containing FeCl₃, the injected holes initially will either oxidize H_2O to O_2 or Cl⁻ to Cl₂; both of these reactions involve multiple electron transfer and are thus kinetically slow. On the other hand, the injected electrons will easily reduce Fe³⁺ to Fe²⁺, a relatively fast one-electron reaction. This reaction also proceeds preferentially compared to the multistep reduction of H⁺ to H₂. As the concentration of Fe²⁺ builds up in the electrolyte, it can also compete for photogenerated holes, and reverse the forward Fe³⁺ reduction reaction (as assumed in eq 1). Thus, the conversion of Fe³⁺ to Fe²⁺ is controlled by the competing and rate-limiting processes of hole oxidation; this kinetic picture is shown in Figure 5a.

The data indicate that for anatase the steady-state Fe^{2+} concentration under illumination is about twice that produced by rutile (20% vs. 11%), and the forward rate constant (k_e) for Fe^{3+} reduction is about two or three times greater for anatase than for rutile. These results can be explained by the larger band gap for anatase (3.2 eV vs. 3.0 eV for rutile) which leads to a higher lying (i.e., more negative on the electrochemical scale) conduction band edge;¹³ the valence band edge is about the same for both crystal phases. This, in turn, permits more facile electron transfer to the electrolyte. Previous work¹³ on the photoactivity of TiO₂ powders also showed that anatase is more photoactive than rutile.

The data also show that addition of an efficient hole acceptor to the solution will enhance electron injection. Thus addition of acetate ion, a species more easily oxidized than H_2O , results in enhanced Fe^{3+} reduction (see Table II and Figure 3). This is reflected by the lower k_h for anatase in the presence of sodium acetate, and the higher steady-state conversion of Fe^{3+} to Fe^{2+} . This result is consistent with hole oxidation being the rate-controlling step in the overall kinetics. Enhanced hole oxidation



Figure 5. Schematic diagrams of energetics associated with TiO_2 particles in electrolytes: (a) shows competition of Fe^{3+}/Fe^{2+} and H_2O/O_2 redox couples for photogenerated holes; (b) shows effect of band bending in reduced, n-type TiO_2 particles on photooxidation of B (enhanced oxidation rate relative to Figure 4b) and photoreduction of A (retarded reduction rate relative to Figure 4b).

through addition of acetate ion results in enhanced electron injection and Fe^{3+} reduction since charge neutrality must be maintained in the semiconductor powder.

The model for small particles of pure rutile and anatase suspended in solution assumes that they have flat bands since the carrier concentration is very low. For reduced, n-type anatase, the carrier concentration is much higher and a significant depletion layer exists causing bent bands and a potential barrier for electron injection. For these band energetics the minority carriers (holes) are easily injected into the solution, while the majority carriers (electrons) are inhibited by the field (see Figure 5b). In conducting particles with no second metal phase producing an ohmic contact, the majority electrons cannot readily escape. Hence, electron injection from the n-type doped semiconductor powders is expected to be slow.

This type of behavior is consistent with the observations for doped anatase. As shown in Figure 3 and Table II the steady-state reduction level of Fe^{3+} with doped anatase is much lower than that for pure anatase, and k_h is about three times higher. These results strongly support the idea that a strong depletion region exists in the reduced small particles and that it inhibits electron injection and enhances hole injection.

Figure 3 and Table II also present data for reduced (n-type) anatase onto which platinum had been deposited. As seen in Table II, the effect of platinum is to reduce k_e and k_h relative to the n-type anatase by factors of about 2 and 8, respectively. These results can be explained by the catalytic effect of platinum on the kinetics of the competing H₂O oxidation reaction and the H₂ evolution reaction. Platinum will enhance the kinetics of H₂O oxidation compared to Fe²⁺ oxidation; this will decrease the rate of the back oxidation of photoreduced Fe²⁺. Platinum will also enhance the rate of H⁺ reduction to H₂. However, since photoreduction is inhibited by the band bending in n-type anatase, the catalytic effect of Pt on H₂ evolution vs. Fe³⁺ reduction is not expected to be as great as for the relative rates of hole oxidation of H₂O vs. Fe²⁺.

Platinum is not expected to form an ohmic contact with TiO_2 because the work function of Pt is below the Fermi level of TiO_2 ; therefore the potential barrier for electron transfer to the elec-

trolyte exists both at the bare TiO_2 surface and at the platinum sites. This barrier limits the kinetics of electron injection into the electrolyte as discussed above.

The influence of particle size and surface area on the relative kinetics of photoreduction was not studied in detail. Electron micrographs showed that the anatase particles were uniformly less than about 1 μ m in diameter, whereas the rutile particles had a broad distribution of particle sizes, up to about 20 μ m in diameter. The surface areas of the anatase and rutile powders were not determined; however, previous work²⁶ on anatase and rutile powders with the same surface area showed that anatase was more photoactive and that the photoactivity of rutile relative to anatase was not sensitive to surface area.

Conclusions

The kinetics of photoredox processes by small semiconductor particles suspended in liquids can be followed by using Mössbauer spectroscopy to monitor the charge state of Mössbauer ions in the solution as a function of time. This technique has the advantage of noninterference by other redox species in the solution that influence the charge-transfer process; however, the system must be quench-frozen after each illumination period to obtain a Mössbauer spectrum.

Results with Fe³⁺ and unreduced, intrinsic TiO₂ particles (~1 μ m diameter) in acid solutions show that anatase powder has a

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higher rate constant (~ 2 to 3×) for the photoreduction of Fe³⁺ than rutile powder. Complete conversion of Fe^{3+} to Fe^{2+} is prevented by a significant back oxidation of Fe²⁺ by holes in competition with H_2O oxidation. As a result, the equilibrium concentration of Fe²⁺ under illumination is 20% for anatase and 11% for rutile.

Addition of an efficient hole acceptor to the solution (e.g., sodium acetate) enhances the extent of Fe³⁺ photoreduction. This is because the hole acceptor competes more effectively for the photogenerated holes compared to H₂O, and this inhibits the back oxidation of Fe²⁺ by photogenerated holes.

Reduced, n-type anatase TiO_2 is less effective than nonreduced anatase for Fe³⁺ reduction. This effect is attributed to the larger electric field in the depletion layer and resultant potential barrier for electron transfer that arises in n-type semiconductors compared to intrinsic semiconductors.

Platinization of reduced, n-type anatase decreases the rate of both electron and hole injection to the Fe^{3+}/Fe^{2+} redox couple; the hole injection rate to Fe²⁺ is decreased more than the electron injection rate to Fe³⁺. These effects can be explained by the enhanced rate of parallel H₂O oxidation and reduction reactions produced by the presence of the platinum metal catalyst.

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Wavelength-Dependent Photochemical Reaction of Methylrhodium(III) Octaethylporphyrin. Studies on CH₃–Rh Bond Cleavage

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Methylrhodium(III) octaethylporphyrin, CH₃Rh(III)OEP, in degassed benzene solutions undergoes photochemical reaction to produce rhodium(II) octaethylporphyrin, Rh(II)OEP, which dimerizes to form [Rh(II)OEP]₂. The quantum yields, Φ_d , for the photodecomposition of CH₃Rh(III)OEP depend on the excitation wavelengths (λ): $\Phi_d = 0.22 \pm 0.02$ (410 nm < λ < 550 nm) and $\Phi_{\rm d}$ = 0.16 ± 0.02 (300 nm < λ < 410 nm) for degassed solutions, and $\Phi_{\rm d}$ = 0.038 ± 0.01 (410 nm < λ < 550 nm) and Φ_d = 0.16 ± 0.02 (300 nm < λ < 410 nm) for aerated solutions. Laser photolysis and phosphorescence studies reveal that the triplet state of CH₃Rh(III)OEP is not responsible for the photochemical reaction. Mechanisms for photochemical cleavage of the CH₃-Rh bond are discussed on the basis of (1) the quantum yields for the photodecomposition of CH₃Rh(III)OEP in aerated and degassed benzene solutions, (2) the wavelength and temperature dependence of the phosphorescence yields, and (3) the triplet yields obtained with 532- and 355-nm laser pulses.

Introduction

In contrast with organic molecules, metal complexes exhibit marked excitation wavelength dependence in photochemistry, i.e., the photoproducts and the quantum yields are strongly dependent on the properties of the electronic absorption bands excited.¹⁻⁶ The wavelength-dependent behavior of the metal complexes is regarded to originate from (1) the specific nature of the excited states and their energy relaxation processes arising from the interaction between metal d orbitals and ligand orbitals and (2) weaker bonds in the metal complexes compared to the covalent

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bonds of usual organic molecules. Recently, metal complexes have been extensively investigated for the purpose of their utilization as photosensitizers for solar energy conversion and storage.⁷⁻¹⁰ Therefore, studies on the energy relaxation processes of excited metal complexes are increasingly important both in the fundamental and applied research fields.

There have been a number of studies on the photocleavage of carbon-cobalt bonds in various cobalt complexes.¹¹⁻¹⁴ The present

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