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Anchored Oxo-Bridged Bimetallic Complexes, $(\text{SiO})_3\text{—Ti—O—Fe}(\text{corrole})$, on Silica Mesopores as Multi-Electron-Transfer Photosystems

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The anchored molecular multielectron transfer (MET) complex, $(\text{SiO})_3\text{—Ti—O—Fe}(\text{tpfc})$ (tpfc = 5,10,15-tris(pentafluorophenyl) corrole), composed of an Fe-centered corrole and a single-site TiO_4 charge-transfer (CT) chromophore, has been synthesized on the pore surface of mesoporous silica. The diffuse reflectance (DR) UV–vis and Fe K-edge X-ray absorption near edge structure (XANES) measurements showed that the anchored complex has an oxo-bridged $\text{Ti}^{\text{IV}}\text{—O—Fe}^{\text{IV}}$ bimetallic linkage between the Fe-centered corrole and the TiO_4 chromophore. Photoexcitation of the $\text{Ti}^{\text{IV}}\text{—O}^{\text{II}} \rightarrow \text{Ti}^{\text{III}}\text{—O}^{\text{I}}$ ligand to metal CT in the anchored complex in the presence of CO_2 and H_2O provided the adsorbed HCOOH and $\text{HO}\cdot$ (and/or $\text{SiO}\cdot$) as reaction products. Fe-centered corroles have a unique ability that they can accommodate multiple electrons at the single Fe center and initiate the two-electron reduction of CO_2 when the Fe center is reduced from 4+ to 1+. Therefore, the formation of adsorbed HCOOH demonstrates that the stepwise reduction of the centered Fe from 4+ to 1+ is accomplished by the sequential photoinduced CT through the confined Ti—O—Fe bimetallic linkages.

1. Introduction

Multielectron transfer (MET) catalysts have the ability to accommodate and transfer multiple electrons to reaction substrates at one time. In biological systems, metalloenzymes embedded into protein scaffolds are known to undergo the MET processes,¹ in such as oxygen reduction, water oxidation, nitrogen fixation, and sulfate reduction, and enable chemical reactions to proceed without forming radical intermediates. These abilities are distinct from sequential-redox processes composed of several individual one-electron redox steps in equilibrium. However, underlying principles of how multiple electrons participate in a reaction at one time remained unsolved. The recently developed electron transfer theory by Tributsch et al.^{1,2} predicts the involvement of the self-organized flow of electrons in the MET process, making this system a theoretically and chemically intriguing research topic.

Synthetic organometallic complexes, on the one hand, that can undergo MET processes have been studied extensively not only from the point of view of basic researches for MET mechanisms but also for their practical application in biosensors,³ bioelectronics,⁴ electro-catalysts,⁵ homogeneous⁶ and/or heterogeneous⁷ molecular catalysts, among others. A number of molecular MET assemblies have been synthesized, but there are relatively few examples of systems which are directly coupled to molecular CT chromophores and operate under light irradiation.⁸ Specifically, for the heterogeneous molecular MET systems, all are driven either by adding strong reducing and oxidizing reagents into solution or electrochemical redox reactions,⁷ in which the activation process of the MET complexes relies on random collision processes between the

complexes and the reagents added, except for the one reported system in which the photoinduced MET process occurs through the grafted heme on polycrystalline TiO_2 particles.⁹ Such a heterogeneous photosystem is important as a building block for constructing photosynthetic assemblies, especially when a target reactant is a very stable substrate and the spatial separation of oxidizing from reducing sites is required. One of the main obstacles toward this is the difficulty of rational design and synthesis of grafted MET photosystems on the surface of inorganic solid supports.

On the basis of these considerations, the objective of this study is to explore a synthetic strategy to anchor the molecular MET catalyst to the single-metal CT chromophore, whose activation processes are directly controlled by light irradiation, as depicted in Figure 1 A. The Fe-centered corrole, used in the present work as a MET complex, is an established homogeneous CO_2 and O_2 reduction catalyst¹⁰ and has the ability to store multiple electrons at a centered single Fe with a corresponding change in its redox states from 4+ to 1+.^{10a} Our approach involved the construction of an oxo-bridged Ti—O—Fe bimetallic linkage as a CT moiety between the active metal center of a MET catalyst and a single-metal CT chromophore on the inner surface of mesoporous silica (proposed photoinduced MET processes are shown in Figure 1B). The grafting procedures of single metal centers on silica surfaces are well established,¹¹ and subsequently constructed oxo-bridged bimetallic complexes have recently been shown as a new class of CT moieties having a flexible choice of metal combinations.^{12–14} Various metal combinations of oxo-bridged bimetallic assemblies (Zr/Cu , Ti/Cu , Ti/Sn , Ti/Co , Ti/Ce , Ti/Fe , Ti/Cr), thus having various optical and redox properties, have been synthesized on the surface of mesoporous silica.^{12–14} The present approach, therefore, has an advantage for the rational design and synthesis of anchored molecular MET photosystems. In this paper, we report the synthetic route and spectroscopic characterization of the

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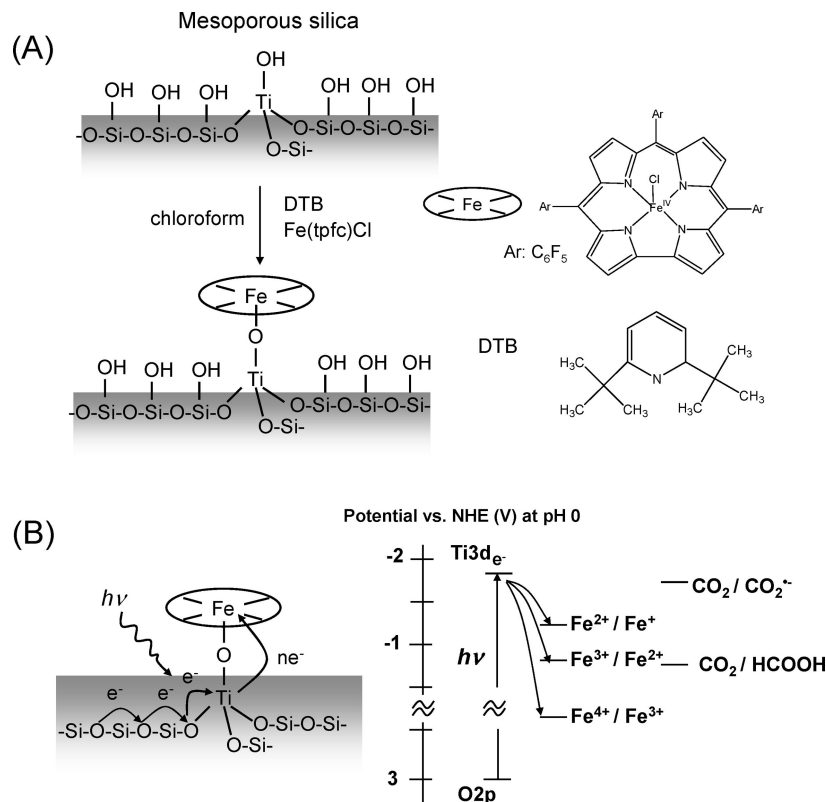


Figure 1. (A) Schematic illustration of the site-specific anchoring of iron-centered corroles on pre-grafted, single Ti^{IV}O₄ centers inside the pores of mesoporous silica. (B) The proposed photoinduced processes occurring at anchored Ti—O—Fe(tpfc) bimetallic complexes under photoexcitation of the framework oxygen to Ti^{IV} charge transfer band, and the energy level diagrams of the related species of the photochemical CO₂ reductions. The energy levels of the Fe species were determined from the reported electrochemical data^{10a} of Fe centered corroles dissolved in acetonitrile solution.

anchored oxo-bridged (SiO)₃—Ti—O—Fe(tpfc) bimetallic complex on silica mesopores and its capability to undergo MET processes under light irradiation through the metal-to-metal charge-transfer (MMCT) from the photoexcited Ti to the Fe center. We also discuss the applicability of the present strategy to construct all-inorganic molecular MET photosystems.

2. Experimental Procedures

A. Synthesis. Siliceous SBA-15 sieve having 2D hexagonal pores structure with a diameter of approximately 90 Å was used as a synthetic platform for anchored MET complexes. The synthesis of (SiO)₃—Ti—OH centers within the pore of SBA-15 (Ti/Si ratio is 0.02) was conducted using the titanocene dichloride (Cp₂TiCl₂) method described in previous work.^{11,13} Briefly, 500 mg of dehydrated SBA-15 powder and 42.5 mg of Cp₂TiCl₂ (Aldrich) were added inside a Schlenk tube and evacuated for 1 h at room temperature. Subsequently, 25 mL of dry chloroform (Aldrich) was added, and the resultant mixture was stirred for 1 h to ensure complete dissolution and diffusion of Cp₂TiCl₂ into the pores of SBA-15. A 0.6 mL quantity of TEA (triethylamine, Aldrich) was added to the above mixture, and the reaction was continued under stirring for 12 h. A pale yellow powder was recovered by filtration, washed, dried at room temperature, and finally calcinated at 550 °C in air for 10 h to remove the CP ligands of grafted Cp₂TiCl₂. The formation of tetrahedrally coordinated single TiO₄ sites was confirmed by UV–vis absorption and Ti K-edge X-ray absorption measurements.¹³ The Ti grafted SBA-15 samples thus obtained hereafter will be referred as to Ti-SBA-15.

The Fe^{IV}(tpfc)Cl (tpfc = 5,10,15-tris (pentafluorophenyl) corrole) was synthesized according to published procedures,¹⁵

and purified by chromatography using silica gel with eluent of hexane/CH₂Cl₂ = 3:1 for H₃(tpfc) and diethyl ether for Fe(tpfc)Cl.¹⁵ Characterization of H₃(tpfc) and subsequently obtained Fe(tpfc)Cl were made using ¹H NMR, MALDI-TOF mass, and UV–vis absorption spectroscopy. ([H₃(tpfc)]); ¹H NMR (CDCl₃): δ = 9.12 (d, 2 H), 8.78 (d, 2H), 8.59 (d, 4H); UV/vis (CH₂Cl₂): λ_{max}: 409, 563, 604 nm; MS: *m/z*: 797.1. [Fe(tpfc)Cl]; ¹H NMR (CDCl₃): δ = −2.63 (s, 2 H), −11.06 (s, 2H), −34.47 (s, 2H); UV/vis (CH₂Cl₂): λ_{max}: 370, 396 nm; MS (DCI[−]): *m/z*: 848.7).

The anchoring of Fe^{IV}(tpfc)Cl onto the (SiO)₃—Ti—OH centers of Ti-SBA-15 was conducted according to the procedures reported in our previous study.¹³ A 17.8 mg quantity of Fe(tpfc)Cl was dehydrated inside a Shlenck tube at room temperature for 30 min. This was then dissolved in 10 mL of anhydrous chloroform containing 38 μL of 2,6-ditert-butylpyridine (DTB, Aldrich). Separately, using another Shlenck tube, 100 mg of Ti-SBA-15 powder was dehydrated under vacuum at 150 °C for 5 h. The powder was cooled to room temperature, and then the above mixture (DTB-chloroform) was added and stirred for 3 h at room temperature. The resultant brown suspension was filtered, washed with 20 mL of dry chloroform two times under N₂ atmosphere, and dried under dynamic vacuum at room temperature for 12 h. As a comparison, grafting of Fe(tpfc)Cl onto the pores of SBA-15 having no Ti center was conducted using the same procedure as above. The resultant samples with and without Ti center will be referred to hereafter as Fe(C)/Ti-SBA-15 and Fe(C)-SBA-15, respectively. All the chemicals used in this work were used as received.

B. Spectroscopic Characterizations. The optical spectra of grafted Fe(tpfc)Cl complexes on Ti-SBA-15 were measured in

diffuse reflectance (DR) mode using a UV-vis spectrometer (MPC-2200, SHIMADZU). For DR measurements, a silica sample (ca. 10 mg) was pressed into a self-sustaining wafer of 13 mm in diameter and introduced into an in-house constructed vacuum cell equipped with a quartz window. The cell allowed us to evacuate and introduce the controlled reaction gases. The X-ray absorption near edge structure (XANES) measurements were performed at the undulator beamline (BL39XU) at SPring-8. A diamond (111) double-crystal was employed as the monochromator, and the higher-order harmonics were suppressed using a flat Pt-coated mirror. For the standard samples, the XANES spectra were measured using transmission mode, while the fluorescence mode was employed for the measurements of the Fe(C)/Ti-SBA-15 samples because of the low Fe density. For the Fe K edge spectra, all data were normalized by the intensity at 7200 eV.¹⁶

C. Photochemical Reactions. Ten milligrams of Fe(C)/Ti-SBA-15 powder was pressed into a self-supporting wafer (13 mm in diameter). The wafer was then mounted in a transmission infrared vacuum cell (volume; 4.6 cm³) equipped with CaF₂ windows. The IR cell was evacuated using a rotary pump (<1 mmTorr) for 1 h at room temperature prior to the reaction. The reaction gas was then loaded into the IR cell from the gas handling system. The photochemical reaction was conducted at room temperature, using a 1000 W Xe lamp, equipped with a monochromator. Monochromatic light at 340 nm with the bandwidth of 10 nm was used to irradiate the wafers. The light intensity was adjusted to 40 mW cm⁻² with neutral density filters. After the photoirradiation, the IR cell was placed in the sample chamber of an FTIR spectrometer (IRPrestige-21, SHIMADZU) with a deuterated triglycine sulfate (DTGS) detector. Before the measurements, the sample chamber was purged with dry N₂ at flow rate of 15 L/min, and the IR cell was kept in the dark for about 90 min. The IR intensity (*I*) versus wavelength was obtained by averaging 200 scans at a resolution of 2 cm⁻¹, with a processing time of 3 min for one spectrum. All IR absorption spectra were obtained in the form of absorbance, log(*I*₀/*I*), using a spectrum taken before irradiation as a reference (*I*₀).

3. Results and Discussion

The synthetic scheme for anchoring the Fe^{IV}(tpfc)Cl complexes onto single Ti centers of Ti-SBA-15 is depicted in Figure 1 A. The Fe(tpfc)Cl complex, which is an established two electron reduction CO₂ MET catalyst,^{10a} has a labile chloride ligand at an axial site of the Fe center.¹³ To achieve selective anchoring of the Fe(tpfc)Cl complex to the pre-grafted single Ti centers (TiOH/SiOH = 0.05), the reaction was conducted in a chloroform solvent containing the weak base DTB (p*K*_a = 3.58) having steric hindrance. Our previous study,¹³ using FeCl₂·(H₂O)₄ and FeCl₃ as model iron complexes with a labile chloride ligand, has shown that DTB works as a selective activator of Ti—OH groups and provides the anchored Ti—O—Fe bimetallic complexes with high yield,¹³ in which the formation of oxo-bridged moieties was directly confirmed by Fourier transform IR spectroscopy. Since the Ti—OH group has stronger Bronsted acid than the Si—OH groups, the weak base DTB leads to the selective deprotonation reaction of Ti—OH groups on the silica surfaces. The resultant Ti—O⁻ has a strong nucleophilic character, thereby producing the oxo-bridged Ti—O—Fe(tpfc) bimetallic complexes via nucleophilic substitutional reaction of Ti—O⁻ to Fe^{IV}(tpfc)Cl complexes. The choice of chloroform as a solvent, instead of toluene as used in our previous work,¹³ is for preventing the axial chloride ligand of

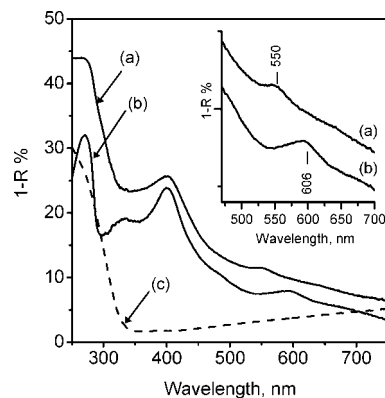


Figure 2. DR UV-vis spectrum of a pressed wafer of (a) Fe(C)/Ti-SBA-15 and (b) Fe(C)-SBA-15 powder under vacuum, with an expanded view of the Q-band absorption region (inset). (c) DR UV-vis spectrum of Ti-SBA-15.

Fe^{IV}(tpfc)Cl from being detached before reacting with the nucleophilic Ti—O⁻ group, which otherwise causes the non-selective grafting of Fe(tpfc) both onto Ti—OH and Si—OH sites. The comparison of the UV-vis absorbance spectra of Fe(tpfc)Cl dissolved in either chloroform or toluene showed the partial loss of a chloride ligand in toluene. These reflect the unstable character of Fe(tpfc)Cl in toluene and are similar to the reported observation that a chloride ligand of Fe(tpfc)Cl is highly labile in benzene.^{15b}

The reaction of Fe(tpfc)Cl with (SiO)₃—Ti—OH centers was then conducted in chloroform, and the DR UV-vis spectrum of the resultant solid product was measured under vacuum in the form of a pressed wafer (Figure 2, trace a). The intense absorption below 350 nm is assigned to the LMCT (ligand-to-metal charge-transfer) band from the framework oxygen to the Ti center of anchored (SiO)₃—Ti—O—Fe(tpfc) complexes. The Soret band was resolved at 401 nm, and there was a large blue-shift in the Q-band compared to the Fe(tpfc)Cl in chloroform, that is, the Q-band at 606 nm for Fe^{IV}(tpfc)Cl in chloroform solution (spectrum was not shown here) was shifted to 550 nm upon reaction with the (SiO)₃—Ti—OH centers. In contrast, no blue-shift in the Q-band was observed when the Fe(tpfc)Cl was grafted onto the SBA-15 lacking Ti centers (Figure 2, trace b), indicating the presence of a physically adsorbed Fe-centered corrole on the silica surface. Since the d electrons of the Fe center participate in the $\pi\pi^*$ transitions largely localized on the corrole macrocycles,¹⁷ the peak position of the Q-band reflects the coordination environment of the centered Fe.¹⁸ The observed large shift in the Q-band is, therefore, an indication of the ligand substitution at the centered Fe from Cl⁻ to Ti—O⁻ and the resulting formation of oxo-bridged Ti—O—Fe linkages on the surface of mesoporous silica, as depicted in Figure 1 A.

To confirm the above assignment, we conducted the following two experiments: (1) grafting Fe(tpfc)Cl onto polycrystalline TiO₂ (anatase) nanoparticles instead of Ti-SBA-15, whose surfaces are covered with abundant OH groups coordinated with the surface Ti sites, and (2) exposing CH₃OH(g) to the Fe(tpfc)Cl complexes. Since the OH group of CH₃OH(g) has an acidity similar to the Ti—OH group, a ligand exchange reaction between an axial Cl and CH₃OH, followed by the blue-shift in the Q-band is anticipated. For the Fe(tpfc)Cl—TiO₂ experiment (1), the blue-shift in the Q-band from 606 to 550 nm was observed upon grafting the Fe(tpfc)Cl onto TiO₂ surfaces, as expected (Figure 3). This is the same behavior as exhibited when the Fe(tpfc)Cl is grafted onto Ti-SBA-15 (Figure 2, trace a). Since no shift in the Q-bands was observed if the

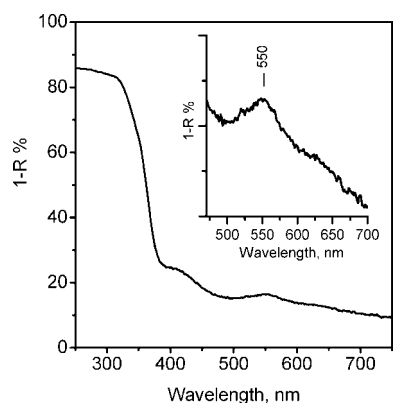


Figure 3. DR UV-vis spectrum of a pressed wafer of TiO₂ (anatase) powder after grafting the Fe(tpfc)Cl complexes in chloroform, with an expanded view of the Q-band absorption region (inset).

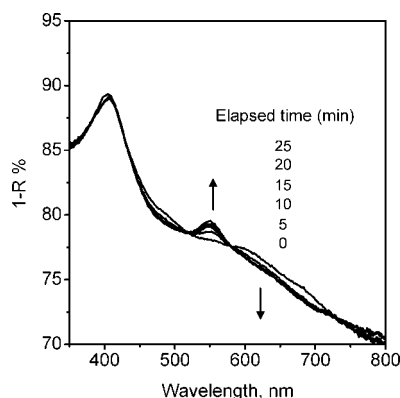


Figure 4. Time course of the DR UV-vis spectrum for a pressed wafer of Fe(C)-SBA-15 in the presence of CH₃OH(g) (70 Torr). Spectra were recorded at 0, 5, 10, 15, 20, 25, 30 min after the introduction of CH₃OH(g) into the DR UV-vis cell. Arrows in the figure indicate the direction of spectral changes with time.

SBA-15 supports lack Ti centers (Figure 2, trace b), this result confirms that the blue-shift in the Q-band is due to the formation of oxo-bridged Ti—O—Fe bimetallic moieties.

The identical shift of the Q-band and the isosbestic behavior between the band at 550 and the 606 nm was seen in the CH₃OH(g) exposure experiment (2). Upon introducing 70 Torr of CH₃OH(g) into the DR UV-vis cells, in which the pressed wafer of Fe(C)-SBA-15 powder was mounted, the broadband centered around 606 nm decreased in intensity, whereas a band at 556 nm appeared (Figure 4). This small change appeared to increase with time, and clear isosbestic behavior was observed. No change in the spectrum was observed after subsequent evacuation of the sample, indicating clearly that the strong coordination of CH₃OH to the centered Fe is the reason for the blue-shift in the Q-band. All the spectroscopic data are consistent with the aforementioned assignments and support the occurrence of the nucleophilic ligand substitution reaction depicted in Figure 1 A. It can thus be concluded that the reaction of Fe(tpfc)Cl complexes with nucleophilic Ti—O[−] groups provides the oxo-bridged Ti—O—Fe linkages between the Fe-centered corrole and the single Ti chromophore inside the pore of SBA-15.

The Fe K-edge XANES spectrum of Fe(C)/Ti-SBA-15 was measured in the form of a pressed wafer. As reference compounds, that of Fe(C)-SBA-15 before and after exposed with CH₃OH(g) (70 Torr), and also α-Fe₂O₃ (distorted *O_h* symmetry) were measured, and their expanded view of the 1s → 3d pre-edge region is shown in Figure 5, trace b, c, and d, respectively. All spectra were normalized by the intensity at 7200 eV.¹⁶ It

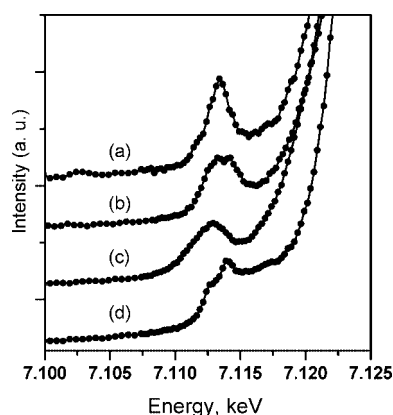


Figure 5. 1s → 3d pre-edge region Fe K-edge XANES spectra of (a) Fe(C)/Ti-SBA-15. Spectra of Fe(C)-SBA-15 before (b) and after (c) exposed with CH₃OH(g) (70 Torr), and α-Fe₂O₃ (distorted *O_h* symmetry) (d) are also depicted. The Fe K-edge spectra were normalized by the intensity at 7200 eV.¹⁶

can be seen that the Fe(C)/Ti-SBA-15 (trace a) has one sharp peak at 7113.5 eV and its intensity in area was stronger than that for the octahedral Fe compound of α-Fe₂O₃ (trace d). Such a sharp, pre-edge feature of Fe(C)/Ti-SBA-15 has been seen for iron complexes with five-coordinated square pyramidal geometry (*C_{4v}*),¹⁹ and has been assigned to the 1s → (3d + 4p) electronic dipole transition.¹⁸ In contrast, a weaker pre-edge band was observed for the Fe(C)-SBA-15 samples when centered-Fe was exposed with CH₃OH(g) (trace c, in Figure 5). The 1s → 3d electric dipole transition is forbidden for the Fe centers with central symmetry. However, there is an increase in a peak intensity if central symmetry of the Fe center is lost because of the appearance of the allowed 1s → (3d + 4p) transition.¹⁹ Therefore, the weaker pre-edge intensity for centered Fe exposed to CH₃OH(g) implies that the axial sites of Fe are both occupied with the coordinated CH₃OH, in accordance with the aforementioned discussion in Figure 4 that the shift of the Q-band is due to the coordination of CH₃OH(g) to the centered Fe. In addition, a shift of the peak position was also confirmed for the Fe(C)-SBA-15 samples before and after being exposed with CH₃OH(g) (trace b and c in Figure 5). Since the shift of the 1s → 3d pre-edge peak reflects the change of coordination environments of the centered Fe, this also provides the support that the axial coordination sites of Fe are occupied with the coordinated CH₃OH.

The capability of the oxo-bridged Ti—O—Fe bimetallic linkage to mediate a charge transfer from the photoexcited Ti center to the centered Fe was examined. We employed the carbon monoxide (CO) binding property for the Fe(C)/Ti-SBA-15 sample under photoexcitation of the LMCT band from the framework oxygen to the Ti center, since it was reported that CO binds to the Fe corrole when the centered Fe^{IV} is reduced to Fe^{II}.^{10a}



The CO-coordinated Fe^{II}-corrole is a stable compound under an ambient condition,^{10a} allowing us to confirm whether the photochemical reduction of the centered Fe^{IV} occurs on Fe(C)/Ti-SBA-15 or not. Figure 6a shows the DR UV-vis absorption spectrum of a pressed wafer of Fe(C)/Ti-SBA-15 after photoexcitation of Ti^{IV}—O^{II} → Ti^{III}—O^I LMCT using a monochromatic light at a wavelength of 320 nm for 30 min in the presence of CO (750 Torr) and H₂O (10 Torr). The absorption spectra of Fe(C)/Ti-SBA-15 before irradiation was also shown in trace (b).

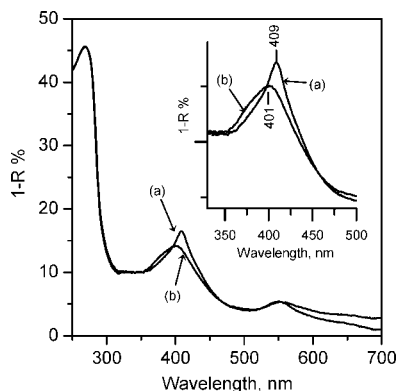


Figure 6. DR UV-vis spectra of a pressed wafer of Fe(C)/Ti-SBA-15 before (b) and after (a) irradiation for 30 min in the presence of CO (750 Torr) and H₂O (10 Torr) with an expanded view of the Soret band region (inset).

Comparison of trace (a) and (b) shows that irradiation caused a clear red-shift of the Soret band from 401 to 409 nm with the band being sharper and more intense. This is in harmony with the reported spectral change in the Soret band region for the CO-coordinated Fe^{II}-corrole.^{10a} We confirmed that no change in spectra was observed when the sample was irradiated for 30 min in the absence of CO. Therefore, these results confirm the photochemical formation of the [(CO)Fe^{II}(tpfc)] in the (SiO)₃-Ti-O-Fe(tpfc) complex.

We have then examined the photochemical MET process for Fe(C)/Ti-SBA-15 by using the gas-phase photochemical reduction of CO₂. The pressed wafer of 10 mg of Fe(C)/Ti-SBA-15 powder was mounted onto the transmission FTIR cell. Subsequently, the sample was exposed to a mixture of CO₂ (750 Torr) and H₂O (10 Torr), and the LMCT band from the framework oxygen to the Ti center was excited using a monochromatic light at a wavelength of 340 nm. Differences in FTIR spectra before and after irradiation (trace (a) and (b) in Figure 7 A) shows the appearance of new absorption band peaks at 2977, 1707, and 1374 cm⁻¹. These three bands increased in intensity with irradiation time, and showed the same time profiles with each other (Figure 7 B). These bands are characteristic for the ν(CH), ν(C=O), and δ(COH) of carboxylic acids and are consistent with those HCOOH species adsorbed on silica surfaces. No peaks were observed at 2977, 1707, and 1374 cm⁻¹ when the light irradiation was conducted to the Fe corroles lacking Ti centers and also the Ti-SBA-15 sample lacking Fe corroles.

The possible side reactions of self-oxidative decomposition of the (SiO)₃-Ti-O-Fe(tpfc) complex was then investigated. The light-irradiation of the Fe(C)/Ti-SBA-15 sample in the absence of CO₂(g), that is, 750 Torr of N₂ and 10 Torr of H₂O, gave much weaker positive- and negative-going bands in the spectral region from 3100 to 1300 cm⁻¹, whereas no peaks corresponding to the adsorbed HCOOH species at 2977, 1707, and 1374 cm⁻¹ were observed (trace (c) of Figure 7A). These results exclude the involvement of self-oxidation processes in the formation of the 2977, 1707, and 1374-cm⁻¹ bands resolved in Figure 7A, trace (a) and (b), and provide evidence that they are the reaction products formed by the photochemical reduction of CO₂ at the Fe sites of anchored (SiO)₃-Ti-O-Fe(tpfc) complexes.

The photogenerated holes, on the other hand, react with H₂O and Si-OH inside the pores by virtue of hole-hopping along the framework oxygen^{8d,e} of mesoporous silica. With the oxygen isotopic labeling experiment using the reaction gas containing H₂¹⁸O (10 Torr) and C¹⁶O₂ (750 Torr), the shift of ν(C=O) band

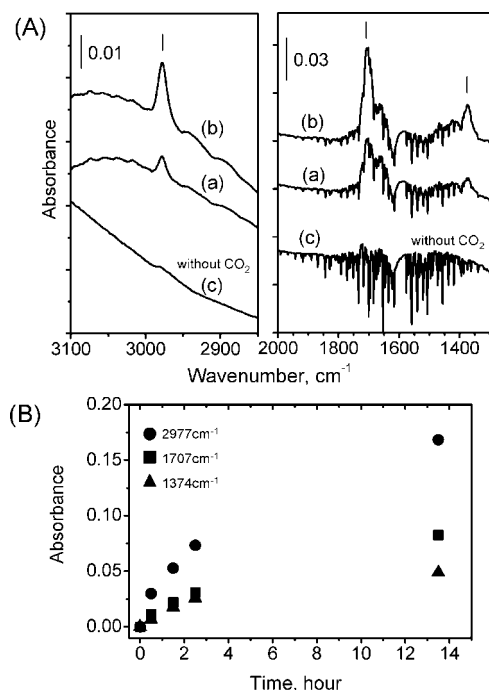
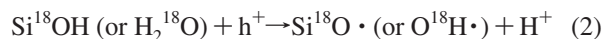


Figure 7. (A) Difference FTIR spectra (wavenumber region from 3100 to 2850, and 2000 to 1300 cm⁻¹) before and after irradiation of a pressed wafer of Fe(C)/Ti-SBA-15 sample in the presence of CO₂ (750 Torr) and H₂O (10 Torr) as a function of the light-irradiation time: (a) and (b), 30 min and 90 min, respectively. Trace (c) shows the difference FTIR spectra when the Fe(C)/Ti-SBA-15 sample was irradiated for 30 min in the presence of N₂ (750 Torr) and H₂O (10 Torr). (B) The band intensities at 2977, 1707, and 1374 cm⁻¹ in the presence of CO₂ and H₂O as a function of light-irradiation.

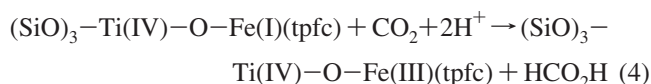
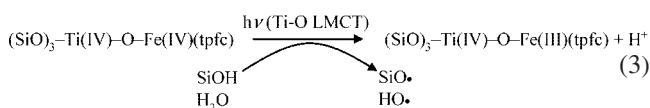
of adsorbed HCOOH from 1707 to 1700 cm⁻¹ was confirmed. The oxygen isotopic scrambling reaction requires the involvement of radical oxygen species.²⁰ Molecular H₂¹⁸O does not induce the scrambling reactions.²⁰ Therefore, the incorporation of ¹⁸O into HCOOH reflects the formation of Si¹⁸O• and ¹⁸OH• radicals via reactions of photogenerated holes with Si-¹⁸OH and H₂¹⁸O.



The previous studies¹⁴ on photocatalytic CO₂ reduction using the Ti-containing meso- or micro-porous silica in the presence of H₂O as an electron donor shows the formation of trace amounts of dioxygen by a reaction of H₂O with photogenerated holes. We conducted the gas-phase product analysis using a quadrupole mass spectrometer, in which the reaction products formed inside the FTIR cell are vacuum-transferred into the MS ionization chamber after 20 h of light irradiation. However, we could not obtain the clear evidence for the generation of dioxygen as a reaction product of water oxidation within the detection limitation of O₂ by MS spectroscopy, being approximately 500 nmol, which corresponds to reaction turnover number (TON) of 30. The TON of HCOOH production was estimated to be 0.8 after 14 h of photoirradiation, with an assumption that all of the Fe-centered corrole grafted on Ti-SBA-15 works as a photoactive center by reacting with the (SiO)₃-Ti-OH CT chromophore.

The photoinduced processes occurring on the anchored (SiO)₃-Ti-O-Fe(tpfc) bimetallic complexes, shown in Figure 1 B, are proposed, together with the energy level diagram of related species. The energy levels of the Fe species were determined from the reported electrochemical data^{10a} for the Fe-

centered corroles dissolved in acetonitrile solution. The anchored $(\text{SiO})_3\text{—Ti—O—Fe(tpfc)}$ complexes have the five-coordinated square pyramidal geometry and an open site for CO_2 coordination at the axial position (Figure 5). Fe-centered corroles have an ability to accommodate multiple electrons at the iron center and initiate the two-electron reduction of CO_2 when the valency of the centered Fe becomes +1.^{10a} Therefore, it is considered that the formation of the two-electron CO_2 reduction product, adsorbed HCOOH , demonstrates that the stepwise activation of the Fe-centered corrole from 4+ to 1+ was accomplished by the sequential photoinduced CT processes through the confined Ti—O—Fe bimetallic linkage (Figure 1, and eqs 3 and 4).



The $[\text{Fe}^{\text{I}}(\text{tpfc})]$ in the $(\text{SiO})_3\text{—Ti—O—Fe(tpfc)}$ complex reacts with CO_2 and H^+ to produce HCO_2H and $[\text{Fe}^{\text{III}}(\text{tpfc})]$ (eq 4). The subsequent reduction of $[\text{Fe}^{\text{III}}(\text{tpfc})]$ to $[\text{Fe}^{\text{II}}(\text{tpfc})]$ by the photoexcited Ti^{III} species, which competes with the formation of $[\text{Fe}^{\text{IV}}(\text{tpfc})]$ by the reaction with the photogenerated hole ($\text{SiO}\cdot$ and/or $\text{OH}\cdot$), leads to the catalytic cycle of the two-electron CO_2 reduction process. The role of a Ti—O—Fe bimetallic linkage as a CT unit is consistent with the photochemical formation of the $[(\text{CO})\text{Fe}^{\text{II}}(\text{tpfc})]$ in the $(\text{SiO})_3\text{—Ti—O—Fe(tpfc)}$ complex (Figure 6, trace 1). This is also consistent with our previous reports¹³ on the construction of oxo-bridged Ti/Fe bimetallic CT complexes, in which the presence of a metal—metal interaction between a titanium and an iron via an oxygen linkage has been proven by the appearance of an MMCT band.¹³ It is to be noted here that one-electron redox potential of CO_2 to $\text{CO}_2^{\cdot-}$ ($E^0 = -1.9$ V vs NHE)¹⁸ is more negative than that of the $\text{Fe}^{2+}/\text{Fe}^+$ redox couple of the Fe centered corrole ($E^0 = -1.36$ V vs NHE)^{10a} (Figure 1 B). This indicates that the stepwise reduction of CO_2 via a formation of $\text{CO}_2^{\cdot-}$ radicals as an intermediate is energetically unfavorable. The formation of adsorbed HCOOH is thus attributable to the occurrence of a thermodynamically more favorable two-electron pathway, $\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{HCOOH}$ ($E^0 = -0.77$ V vs NHE),²¹ with the concomitant oxidation reaction of the centered Fe from +1 to +3 under light irradiation.

In this study, we have placed the emphasis on constructing the anchored heterogeneous MET complexes whose activation processes are controlled directly by light irradiation. The photochemical CO_2 reduction using the Fe-centered corroles was first reported by Fujita et al. in acetonitrile solution.^{10a} They employed the photochemically produced *p*-terphenyl radical anions as a reductant to activate the $\text{Fe}(4+)$ to $\text{Fe}(1+)$, and showed the formation of CO and H_2 as reduction products. In this system, the activation process of the Fe-centered corroles relies on the random collision processes between the photochemically produced *p*-terphenyl radical anions and the Fe corrole. Although the direct coupling of the MET complex and the CT chromophore is an important requirement for effective utilization of MET catalysts in artificial photosynthetic assemblies, most MET complexes reported in the literature have been activated either by adding strong reducing (or oxidizing) reagents in solution or by electrochemical redox reactions. Since

the materials and methods reported here can be applied to other organometallic complexes, these are of importance to identify efficient heterogeneous molecular assemblies that can undergo the MET processes under light irradiation.

The main drawback of this approach lies on low durability of the system owing to the self-oxidation reaction under light irradiation. This is a fundamental problem in photosystems if organometallic complexes are used as a building block for catalytic sites or chromophores. Certainly, the development of organic-ligand-free MET photosystems is a challenge for the successful utilization of the MET process in artificial photosynthetic materials.¹ In this regard, it is worth noting the atomically defined polynuclear metal-oxide clusters, polyoxometalates, which are reported to have a variety of MET-based catalytic properties in the presence of soluble reducing and oxidizing reagents. For example, ruthenium substituted tungsten polyoxometalates were identified to act as efficient homogeneous water oxidation catalysts upon adding Ce^{4+} or photochemically synthesized $[\text{Ru}(\text{bpy})_3]^{3+}$ as an oxidizing reagent.^{22,23} Accordingly, anchoring of such inorganic MET clusters with an single- or a bimetallic charge-transfer chromophore using oxo-bridged bimetallic linkages, presented in this work, would enable us to construct an organic-ligand-free heterogeneous MET photosystem. Those redox properties and absorption wavelength can be rationally designed and controlled by changing a metal combination of oxo-bridged bimetallic CT linkages.

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