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Influence of Metals and Reduced Oxygen Species on the Photooxidation of 2-Propanol with a Cesium Peroxidotitanate Complex

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Keywords: Photooxidation / Reaction mechanism / Peroxides / Molecular approach

The mechanism of the photocatalytic degradation of 2-propanol under anaerobic condition was investigated in the presence of the novel cesium peroxoidotitanate complex $Cs_2(NH_4)_6[Ti_4(O_2)_4(Hcit)_2(cit)_2]Cl_2{\cdot}8H_2O$ (**1**) (cit = citrate). This complex contains two different kinds of peroxido units. Two peroxido groups bind to the titanium atom in a side-on η^2-fashion, the other peroxido units are directly bonded to the titanium and cesium atoms. These bridging peroxido groups are responsible for the inhibited activity in the photooxidation in contrast to what was found in previous studies about unbridged peroxidotitanate complexes. The decelerated oxidation of the alcohol is useful for the determination of the mechanism during the photocatalytic oxidation process. Therefore, ESI mass spectrometry and ^{13}C NMR spectroscopy were applied to obtain a deeper insight into the mechanism in the alcohol oxidation. Furthermore, an influence of the metal salt (Cs vs. Li) with respect of the photocatalysis was detected. The cesium peroxido complex **1** shows significant results in the photochemical oxidation of 2-propanol to acetone. More than 50 % acetone was obtained without detection of any side products. The conversion yield from 2-propanol to acetone was monitored by ^{1}H and ^{13}C NMR spectroscopy and by Raman spectroscopy. The catalytic activity is not limited to 2-propanol; 1-phenylethanol could also be oxidized by **1**. An intermediate of the photooxidation could be isolated and was characterized.

Introduction

In recent decades, much attention has been focused on developing measures to convert organic pollutants into nontoxic compounds.[1] Among these detoxification techniques, semiconductor photocatalytic oxidation (PCO) has been developed.[2,3] A complete understanding of the photocatalytic mechanism on the surface of the photocatalyst is still in the early stages. In the case of the photocatalytic oxidation of 2-propanol under UV irradiation, products like acetone, mesityl oxide, CO_2 and propene are reported in different yields, depending on the modified titania and the reaction conditions.[4,5] In many cases, these TiO_2 catalysts are modified with metal salts during the synthesis in order to reduce the bandgap energy of the resulting photocatalyst.[6,7] For the excitation of such a photocatalyst like TiO_2, energy in the UV-light region is necessary.[8] No reaction occurs without UV irradiation because the frequency of the light has to be higher than the bandgap energy of the semiconductor. The bandgap for pure anatase TiO_2 is 3.2 eV, such that its absorption edge occurs below 400 nm.[9] Different metal-doped titania systems were used in the PCO, such as alkali and noble metals. They show high activity in different oxidation processes.[10] The reduction of molecular oxygen during the photocatalytic process taking place on the surface of TiO_2 particles, is important for the PCO of organic pollutants.[11] To investigate the role of reduced oxygen in the photooxidation of alcohols, we transfer the situation from the catalyst surface to a molecular level. By applying a model approach, we have synthesized a well-defined oxidotitanate complex modified by different kinds of peroxido units and cesium ions. We have previously reported that different metal-containing peroxidotitanate complexes show high activity in the photooxidation of 2-propanol, whereas similar complexes without any peroxido units did not show any activity in the PCO.[12] The influence of alkali metals as promoting species in the catalysis is well known.[13] Cs-doped titania systems play an important role in different oxidation processes. Catalytic measurements demonstrated that cesium is a strong promoter of the activity and selectivity in the oxidation of *o*-xylene to phthalic anhydride by V/Ti/O catalysts.[14] We decided therefore to incorporate cesium instead of lithium in the structure of supramolecular peroxidotitanate complexes. The complex contains two different peroxido units. Two peroxido groups bind to the titanium atom in a side-on η^2-fashion, the other peroxido units form bridges between titanium and cesium atoms. In contrast to our previous studies, this coordination seems to be essential for an inhibited oxidation activity and therefore more adequate to study the mechanism and the role of reduced oxygen species in the alcohol oxidation under photochemical conditions.

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In this work, we present a well-defined peroxido-rich molecular complex, $Cs_2(NH_4)_6[Ti_4(O_2)_4(Hcit)_2(cit)_2]Cl_2\cdot8H_2O$ (**1**) (cit = citrate) and show its activity in the oxidation of 2-propanol and 1-phenylethanol under anaerobic conditions and UV irradiation. Complex **1** shows an absorption maximum at 360 nm (see Supporting Information), and therefore UV-A light has the appropriate energy to activate the complex. No reaction occurs without UV irradiation.

Results and Discussion

The hydrolysis of $TiCl_4$ and addition of H_2O_2, citric acid and cesium carbonate led to the novel cesium peroxidotitanate complex $Cs_2(NH_4)_6[Ti_4(O_2)_4(Hcit)_2(cit)_2]Cl_2\cdot8H_2O$ (**1**). X-ray diffraction analysis revealed that **1** consists of ammonium and cesium cations, (citrato)peroxidotitanate anions, lattice water molecules, and chloride anions. Figure 1 shows the structure and labeling scheme of the unit cell of the complex. The complex forms 3-dimensional polymer chains. The anions are interlinked through the bridging carboxyl group of one citrato ligand.

The coordination number around each Ti^{IV} ion is seven, reflecting a distorted pentagonal-bipyramidal coordination environment. The O–O bond lengths in **1** [1.47 Å for $Ti–O_2$] are similar to those found in related peroxidotitanate complexes.[12] Moreover, the citrato ligands also coordinate to the cesium ions. The cesium ions in **1** are octacoordinated, surrounded by two water molecules, one peroxido group which also binds to a Ti^{IV} centre. The O–O and Ti–O bond lengths are comparable with those in metal-free peroxidotitanate complexes.[15] In order to confirm the moleculare structure of **1**, ^1H and ^{13}C NMR and Raman spectra were recorded. The determined structure of this compound is in agreement with the corresponding Raman spectra. Sharp bands at 894 cm^{-1} (νO–O) and 636 cm^{-1} ($\nu Ti–O_2$) are assigned to η^2-peroxido groups.[16] Brigding and nonbridging peroxido groups are not distinguishable in the Raman spectra. The photocatalytic degradation of 2-propanol in D_2O solution under anaerobic conditions and UV light was investigated. In the first experiment, the conversion yield of acetone was studied by ^1H and ^{13}C NMR spectroscopy. Figure 2 shows the variation of the yield of acetone in the presence of **1** during the PCO of 2-propanol as a function of the elapsed time. After 65 h of UV irradiation, the yield of acetone shows saturation, and 55% of acetone is formed.

Figure 2 presents also the yield of acetone produced with the use of lithium-containing peroxido complex $Li_2(NH_4)_4[Ti_2(O_2)_2(cit)(Hcit)]_2\cdot5H_2O$.[12] In contrast to this complex, **1** shows a nearly linear trend in the production of acetone. Furthermore, the complex needs a longer time to produce the same amount of acetone than the lithium complex. This is justified by the different structural motives of the peroxido units. In the lithium complex all peroxido units are easily accessible. In contrast, **1** consists of two kinds of peroxido units. The accessibility of the alcohol to the bridging peroxido groups in complex **1** is lower (Figure 1). The activity of **1** in the PCO is therefore inhibited with elapsed time. Under these conditions, the reaction is a stoichiomet-

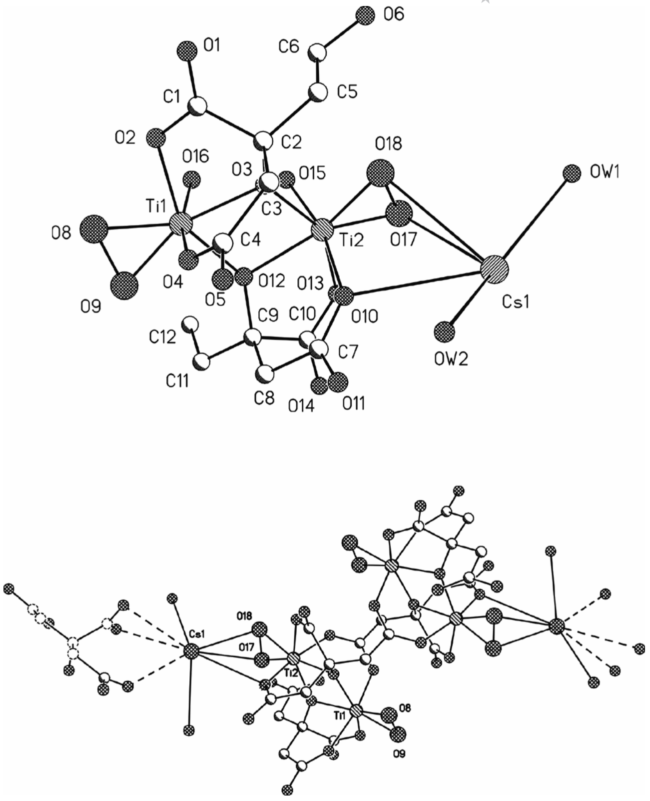


Figure 1. Molecular structure of $Cs_2(NH_4)_6[Ti_4(O_2)_4(Hcit)_2(cit)_2]$-$Cl_2\cdot8H_2O$ (**1**); hydrogen atoms, ammonium cations and chloride anions are omitted for clarity; selected distances [Å] and angles [°]: Ti(1)–O(8) 1.876(5), Ti(1)–O(9) 1.893(5), Ti(1)–O(12) 2.008(4), Ti(1)–O(15) 2.049(4), Ti(1)–O(2) 2.047(5), Ti(2)–O(18) 1.874(5), Ti(2)–O(17) 1.868(5), Cs(1)–O(17) 2.959(5), Cs(1)–O(18) 3.295(5), O(8)–O(9) 1.471(6), O(17)–O(18) 1.467(7); O(8)–Ti(1)–O(9) 45.9(2), O(8)–Ti(1)–O(12) 131.7(2), O(8)–Ti(1)–O(2) 78.06(19), O(17)–Ti(2)–O(18) 46.2(2), O(17)–Cs(1)–O(18) 26.45(12), Ti(2)–O(17)–Cs(1) 111.01(19).

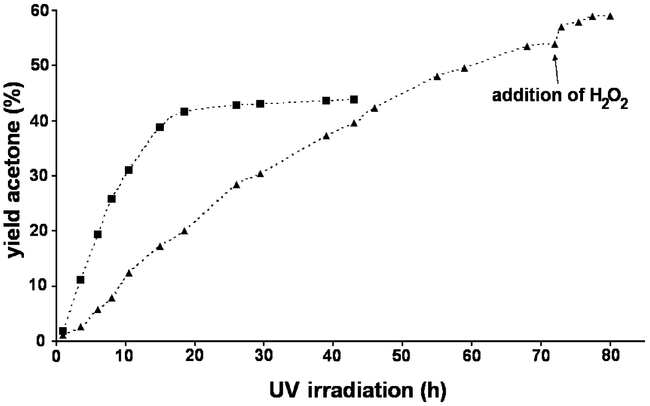


Figure 2. Acetone formation during the photochemical oxidation of 2-propanol in the presence of the cesium peroxidotitanate complex **1** (triangles) and $Li_2(NH_4)_4[Ti_2(O_2)_2(cit)(Hcit)]_2\cdot5H_2O$ (squares). After 73 h of UV irradiation, H_2O_2 (30%) was added to the sample under UV light.

ric one. Therefore, after 70 h of UV irradiation, no further acetone could be detected, because at this point all peroxido units had been consumed for the oxidation of 2-propanol. In this case, complex **1** reacts as an oxidant and not as a catalyst. To obtain a deeper insight into the role of the peroxido groups, we studied in a second experiment with nearly half the amount of complex **1** (in comparison to experiment 1) the influence of the peroxido units during the photooxidation by Raman spectroscopy. Upon increase of UV-irradiation time, the intensity of the peroxido bands decreased. After an irradiation time of 39 h, an absorption band of peroxido groups with small intensity could be detected (Figure 3). This indicates that the peroxido units are required for the oxidation process under anaerobic conditions. In contrast to the described first experiment (Figure 2), the complex in the second experiment is no longer active after 39 h because of the different ratio of substrate/complex. Additional treatment of the solution after the degradation (70 h) of the peroxido groups with hydrogen peroxide seems to have an influence on the further formation of acetone. The Raman spectra of the solid after treatment with H_2O_2 show the formation of peroxido units (see Supporting Information). The intensity of the absorption bands corresponding to the generated peroxido units are much lower in comparison to the Raman absorption bands of the starting material. Based on this observation, we have investigated the treatment of pure titania with different concentrations of H_2O_2 and found that only an absorption band with low intensity could be assigned to peroxido units at the surface of TiO_2 by Raman spectroscopy. For this reason, in the generated solid we also detected only a minor amount of peroxido groups as compared to the starting material because of the low sensitivity of the Raman absorption for peroxido-modified materials. Figure 3 shows the Raman spectra before and after 39 h of UV irradiation.

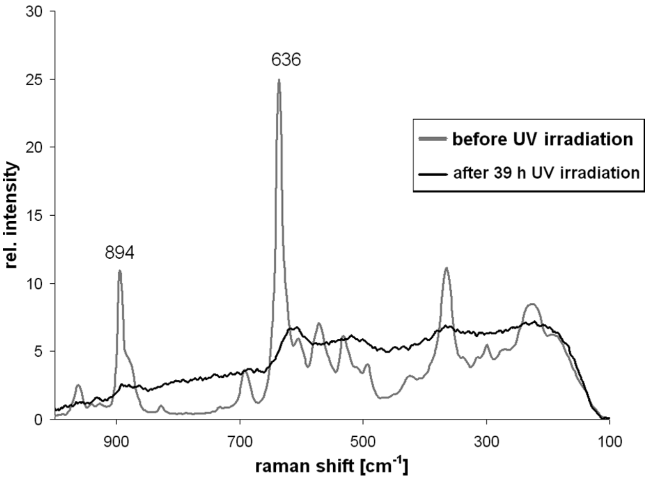
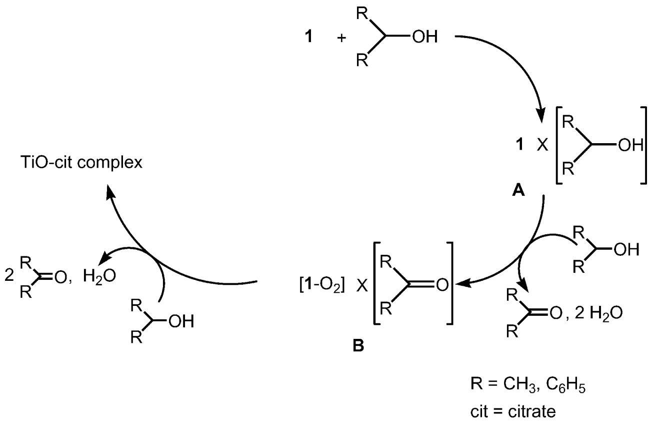


Figure 3. Raman spectra of **1** before the photochemical oxidation of 2-propanol and after 39 h of UV irradiation. The assigned bands at 894 cm^{-1} for ν(O–O) and 636 cm^{-1} for ν(Ti–O_2) decrease during the UV irradiation.

It is known that acetone is finally oxidized to CO_2 in the photooxidation on titania catalysts under aerobic conditions.[17] In contrast to these studies the anaerobic photooxidation of 2-propanol in the presence of **1** shows acetone to be the main product after a long period of time. No other side product is detectable by NMR spectroscopy or gas chromatography. Additionally, we had monitored a small amount of CO_2 during the UV irradiation by a CO_2 detector. This result is in accordance with our previous observations in the PCO of 2-propanol with other metal-containing peroxidotitanate complexes.[12] We showed that a small amount of CO_2 was produced by the degradation of citrate from the complex by UV irradiation and from the residue by the complete oxidation of acetone. This reaction runs almost parallel to the formation of acetone but is much slower.

Although the mechanism is still unknown, it is reasonable to assume that the initial step of the reaction of complex **1** with a secondary alcohol occurs via several multinuclear titanium species as outlined in Scheme 1.



Scheme 1. Proposed mechanism and role of peroxido units in the photochemical oxidation of secondary alcohols with complex **1**.

Our attempts to detect intermediates in the reaction mixture of **1** with secondary alcohols were of partial success. We applied ^{13}C NMR spectroscopy and ESI mass spectrometry for the detection of intermediates in the reaction mixtures. During the photocatalytic oxidation of 1-phenylethanol, the intermediate **1**·[R_2CHOH], which is coordinated to 1-phenylethanol, (**A**) could be identified by ^{13}C MAS NMR spectroscopy. The signal of the carbon atom which is directly bonded to the OH group of the alcohol is shifted to low field in comparison to free 1-phenylethanol (from δ = 73 ppm to δ = 80.7 ppm). The shift of this carbon signal is larger than for the other carbon atoms in 1-phenylethanol because of direct bonding between the OH group and complex **1**. The methyl group ^{13}C NMR signal at δ = 27 and 25 ppm and the aromatic carbon signals from the phenyl ring (δ = 128 and 144 ppm) did not show such a significant shift in comparison to free 1-phenylethanol. The molar excess of free 1-phenylethanol is not observable in solid-state ^{13}C NMR spectra. For comparison, a ^{13}C NMR spectrum of pure 1-phenylethanol in solution is given in the Supporting Information. The methylene CH_2 (δ = 45 ppm), C–OH (δ =86 ppm) and carboxylic (C=O) carbon atoms of the citrato ligand in the complex did not show any shift in comparison to the starting material **1** without 1-phenylethanol. A possible coordination of the alcohol to a titanium atom in the complex leads to a long distance over several bonds to the next carbon atom in the complex. Due to this reason no significant shift should be observed. IR spectroscopic studies did also not show any satisfactory evidence of the coordination side of the complex. Complex **1** shows absorption bands at 1619 cm^{-1} for the carbonyl groups of the organic ligand and a ν(O–O) absorption at 882 cm^{-1} for the peroxido units. The IR spectra after the reaction of **1** with 1-phenylethanol shows a lower intensity for the absorption of the peroxido units. The ^{13}C MAS NMR spectrum is shown in Figure 4.

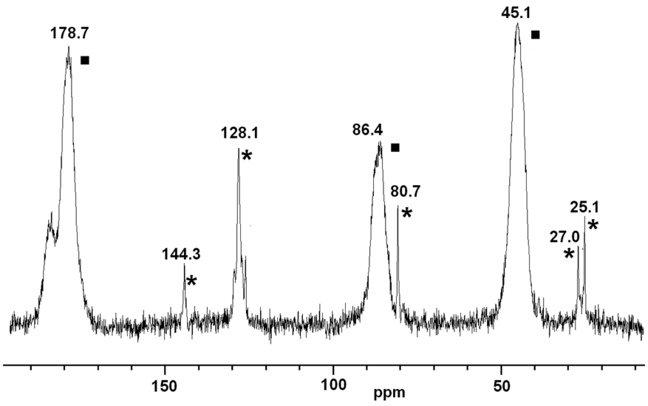


Figure 4. ^{13}C MAS-NMR of the residue after UV irradiation (5 h) of **1** with 1-phenylethanol (astersiks 1-phenylethanol; squares citrate from **1**).

In fact, no matter which is the mechanism of oxidation, either a hydride abstraction from the carbon–hydrogen bond or an electron transfer from the substrate to the peroxidometal complex followed by the loss of a proton, the next step will be the formation of the TiO complex [**1**-O_2]·[R_2C=O] (**B**) which involves only one peroxido group. The second peroxido unit is needed for the oxidation of 1-phenylethanol. Complex **1** contains two kinds of peroxido groups (Figure 1); the free peroxido unit is better accessible, and therefore this group reacts primarily with the alcohol. Brigding peroxido units in the complex are less accessible for the oxidation process. This observation is in harmony with the conversion of 2-propanol as a function of the elapsed UV-irradiation time (Figure 2) because of the inhibited activity of **1** compared to the lithium-containing complex $Li_2(NH_4)_4[Ti_2(O_2)_2(cit)(Hcit)]_2\cdot 5H_2O$ which contains only free peroxido units.[12] The NMR spectrum of the remaining residue shows signals of the citrate ligand which indicates the formation of a highly aggregated TiO-citrate complex which could not be characterized in detail. The presence of **B** in the reaction mixture is confirmed by its ESI mass spectrum which shows a peak at *m/z* = 816.8 with the typical pattern of titanium isotopes. A simulation of the mass peak shows that its pattern at *m/z* = 817.0 is in good agreement to the fragment $[Ti_2(O_2)cit(Hcit)_2]\cdot C_8H_8OH$ (Figure 5).

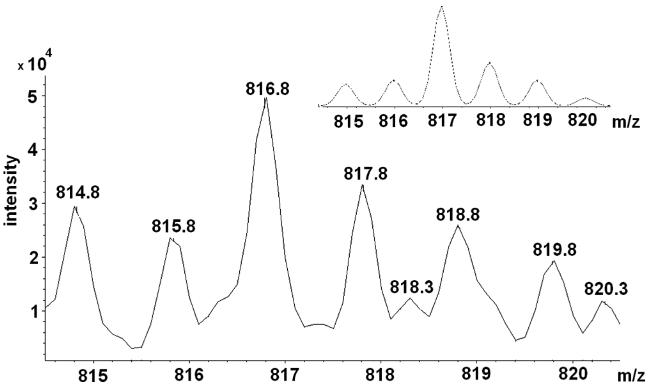


Figure 5. ESI MS spectra of the intermediate (line) and the simulated pattern for $[Ti_2(O_2)cit(Hcit)_2]\cdot C_8H_8OH$ (dots).

The formation of such species is comparable with investigations of oxidation of secondary alcohols by anionic peroxidomolybdenum complexes $[MoO(O_2)_2(RNOCOO)]$.[18] The authors proposed a mechanism which involves the cleavage of one Mo–O peroxidic oxygen bond and the association of the substrate to a free coordination site of the remaining $Mo(O_2)$ complexes as initial products.

Conclusions

The sensitivity of the photochemical oxidation reaction of alcohol by metal peroxidotitanate complexes is a suitable tool for a deeper insight into the mechanism of the PCO of alcohols on the TiO_2 surface. The presence of peroxido groups in the titanium complex are necessary for the oxidation under anaerobic conditions and are comparable with reduced oxygen species which are produced during the aerobic PCO in the presence of TiO_2.

The controlled anaerobic photochemical oxidation of 2-propanol by the novel cesium peroxidotitanate complex $Cs_2(NH_4)_6[Ti_4(O_2)_4(Hcit)_2(cit)_2]Cl_2\cdot 8H_2O$ (**1**) leads to the formation of acetone as the main product. Only a small amount of CO_2 is formed as side product. The photocatalytic activity depends on the coordination sphere of the peroxido units. Brigding peroxido units are less accessible than free peroxido units, and, therefore, **1** shows inhibited activity in the alcohol oxidation in comparison with complexes with free peroxido groups. From these observations, intermediates during the PCO could be detected by ^{13}C NMR spectroscopy and ESI mass spectrometry. **1**·[R_2CHOH] and [**1**-O_2]·[R_2C=O] are formed during the photooxidation of 1-phenylethanol in the presence of **1**. On the basis of these results, further investigations on primary instead of secondary alcohols are important to gain a deeper insight into the mechanism of the oxidation. Particularly, it will be interesting to investigate the different photochemical oxidation pathways and products of primary alcohols.

Experimental Section

UV Irradiation. Experiment 1 (Photochemical Oxidation of Alcohols): Photocatalytic experiments were carried out in an NMR quartz tube (5 mm) containing **1** (320 mg, 0.19 mmol), 2-propanol (45 µL, 0.59 mmol) or 1-phenylethanol (80 µL, 0.66 mmol) and deuterium oxide (800 µL). To dissolve the complex in D_2O before UV irradiation, it was necessary to heat the mixture to 90 °C. Before irradiation, the NMR tube was capped to exclude the presence of oxygen from air. The solution was then irradiated with a 150 W medium-pressure mercury lamp (Heraeus, TQ 150). The lamp generates light in the range of 300–500 nm, with a maximum wavelength intensity at 366 nm. The distance between the NMR tube and the Hg lamp was 5 cm in all cases. After no further production of acetone, the solution was treated with 84.8 µL of H_2O_2 (30%) and further irradiated. The formation of acetone was monitored by ^{1}H and ^{13}C NMR spectroscopy. **Experiment 2 (Raman Spectroscopic Studies):** In an NMR quartz tube (5 mm) a solution containing **1** (160 mg, 0.095 mmol), 2-propanol (45 µL, 0.59 mmol) and deuterium oxide (800 µL) was irradiated with a 150-W medium-pressure mercury lamp (Heraeus, TQ 150) under anaerobic condition for 39 h. After condensation of the solvent at room temperature, the resulting solid was analysed by Raman spectroscopy.

CO_2 Detection: The CO_2 developed during the UV irradiation was analysed by an IR detector from Leybold-Heraeus (Binos 1.2). Before the quantiative analysis, the detector was calibrated with argon and a mixture of 4% CO_2 in air.

Synthesis of $Cs_2(NH_4)_6[Ti_4(O_2)_4(Hcit)_2(cit)_2]Cl_2\cdot 8H_2O$ (1): As a typical experiment, titanium(IV) chloride (2.2 mL, 20 mmol) was added dropwise to distilled water (30 mL) and the mixture cooled in an ice bath. After hydrolysis, hydrogen peroxide (30%) (20 mL, 0.19 mol) and citric acid monohydrate (4.2 g, 20 mmol) were added. After being warmed to room temperature, the solution was treated with cesium carbonate (3.26 g, 10 mmol). The pH value was then adjusted to 2 by the addition of ammonia (33%). The desired product **1** crystallized as red-orange needles from a water/THF mixture at 4 °C after several days. Yield: 13.4 g (87.4%). M.p. > 200 °C (dec.). ^{1}H NMR (250 MHz, D_2O, 25 °C): δ = 2.3–3.6 (CH_2) ppm. ^{13}C MAS NMR (400 MHz, 25 °C): δ = 183.4, 181.1 (cit, COO); 177.9, 176.8 (Hcit, COO); 87.4 (cit, C-O); 85.8 (Hcit, C-O); 46.0 (cit, CH_2); 42.6 (Hcit, CH_2) ppm. Raman: $\tilde{\nu}$ = 2927 [ν(C–H)], 896 [ν(O–O)], 632 [ν(Ti–O_2)]. $C_{24}H_{58}Cl_2Cs_2N_6O_{44}Ti_4$ (1663.0): calcd. C 17.3, H 3.5, N 5.1; found C 17.5, H 3.2, N 5.0

CCDC-680943 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Raman spectra of the residue after 39 h of UV irradiation and treatment with H_2O_2, ^{13}C NMR spectrum of 1-phenylethanol, and UV/Vis spectrum of complex **1**.

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