SAM Photochemistry

Photoconversion of a Redox-Active Self-Assembled Monolayer: In Situ Probing of Photoinduced CO Dissociation from a Triruthenium Cluster Center on Gold**

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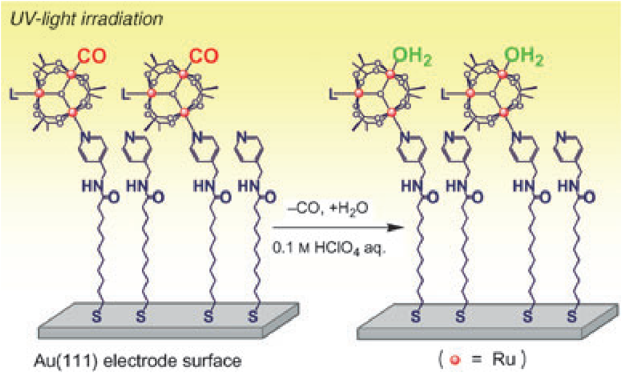
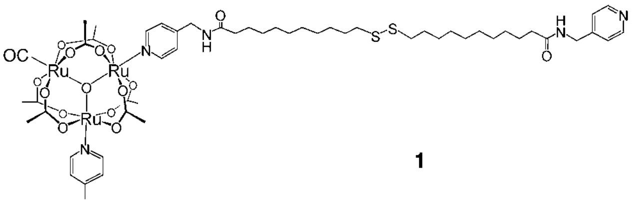
Investigations on the photoreactivity of molecular compounds assembled on solid surfaces or at solid/solution interfaces are a prerequisite for the photochemical design of functional molecular thin films.[1] Extensive studies have been made on the fabrication of photoresponsive molecular layers on electrode surfaces by using organic, inorganic, and biological building blocks, in which, for example, isomerization,[2] chemical bond formation and cleavage,[3] and directional electron transfer are observed.[4]

Photoinduced ligand substitution is an additional potential candidate for controlling surface properties of thin films that are constructed from transition-metal coordination compounds. Although significant progress has been made in solution-phase photoinduced substitution reactions,[5] their application to precise tuning of thin-film properties at solid surfaces have rarely been exploited to date.[6] Here we describe the in situ observation and analysis of photoinduced CO dissociation from a self-assembled monolayer (SAM) of a triruthenium cluster on Au(111), which is, to our knowledge, the first well-defined example of clean photoconversion of a redox-active SAM that leads to a significant shift of the redox potential. We also report on photocurrent generation by the present SAM, which is an unprecedented finding for this class of cluster molecules. This study thus provides a new route to photochemical design of redox-active molecular films on electrode surfaces, which should be of considerable use in molecular electronics and devices.

Scheme 1 illustrates the proposed photochemical reaction in the SAM. We employed disulfide-functionalized, CO-ligated triruthenium cluster **1** as photoresponsive molecule.[7] This compound was chosen because of its well-defined photoinduced CO dissociation in solution[8] and the availability of a methodology for preparing densely packed SAMs on the surface of a gold electrode.[7] Trinuclear clusters of this type[9] have been used to construct ligand-bridged extended molecular architectures by chemical synthesis[10–14] and layer-by-layer deposition on gold surfaces,[15] as well as to fabricate a ligand switching device.[16] Complex **1** is a mixed-valent $Ru_3^{II,III,III}$ complex in which the +II oxidation state is localized at the ruthenium site bound to CO[17,18] (here we designate the triruthenium redox moiety as $\{Ru^{II}\text{-}CO\}Ru^{III}Ru^{III}$). The CO ligand of **1** remains coordinated to the ruthenium center in the SAM as long as the $\{Ru^{II}\text{-}CO\}Ru^{III}Ru^{III}$ oxidation state is maintained, but it dissociates when the one-electron-oxidized $\{Ru^{III}\text{-}CO\}Ru^{III}Ru^{III}$ state is prepared electrochemically by holding the applied potential at +0.8 V (vs Ag/AgCl in 0.1 M $HClO_4$) to form an H_2O-terminated SAM as the result of interfacial ligand substitution.[7]



Scheme 1. Proposed photoinduced CO dissociation from a monolayer of **1** self-assembled on Au(111). L = 4-methylpyridine.



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Cyclic voltammetry was used to probe photoinduced CO dissociation from the redox-active SAM on Au(111). A SAM-modified Au(111) disk ($A = 0.44\ cm^2$), together with a platinum-coil counterelectrode and an Ag/AgCl reference electrode, was placed in a photoelectrochemical cell filled with an Ar-purged aqueous solution of 0.1 M $HClO_4$. An Hg lamp (250 W; Ushio, USH-250D) was employed for irradiation through the 2 mm-thick quartz-plate window of the cell. To probe the photolytic reaction of the SAM, cyclic voltam-

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[**] This work was supported, in part, by Grant-in-Aids for Scientific Research on Priority Area of "Reaction Control of Dynamic Complexes" and "Electrochemistry of Ordered Interfaces" (Nos. 16033201 and 09237106, respectively) from the Ministry of Education, Science, Sports, and Culture of Japan, and Sasakawa Scientific Research Grant from the Japan Science Society. Experimental assistance by Dr. H. Noda (Hokkaido University) is acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the authors.

DOI: 10.1002/ange.200460651

mograms (CVs) were recorded at constant time intervals of irradiation. During irradiation, the electrode potential was held at +0.3 V, a value that is more negative than $E_{1/2}$ of the SAM, to avoid electrochemical dissociation of CO from the cluster center.[7]

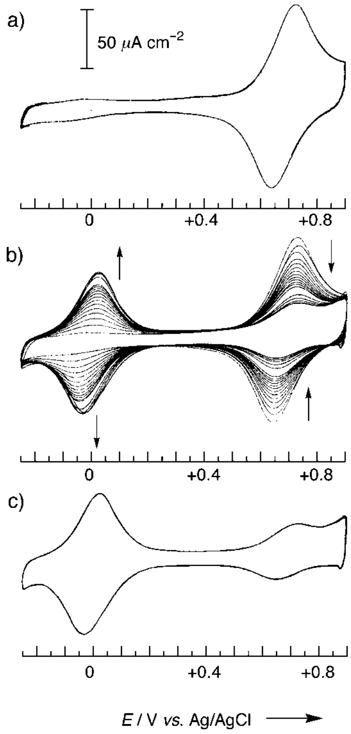

Figure 1. CVs of the SAM-modified Au(111) electrode. a) Prior to irradiation. b) Sequential variation in CV during UV irradiation ($0 < t < 520$ s). Upward and downward arrows represent the increase and decrease, respectively, in current of the redox waves. c) After 520 s irradiation. Electrolyte: 0.1 M aqueous $HClO_4$. Applied potential during irradiation: +0.3 V versus Ag/AgCl. Scan rate for CV: 500 mV s^{-1}.

Figure 1 shows changes in CV on photolysis of an SAM of **1** on Au(111) in contact with 0.1 M $HClO_4$ aqueous solution at RT. Prior to irradiation (Figure 1 a), the CV shows a redox wave which corresponds to the {Ru^{II}-CO}Ru^{III}Ru^{III}/{Ru^{III}-CO}Ru^{III}Ru^{III} process[7] at +0.68 V versus Ag/AgCl with a surface coverage of $\Gamma = 2.5\times10^{-10}$ mol cm^{-2}. When the SAM-modified Au(111) electrode was exposed to UV light from the Hg lamp (Figure 1 b), the redox wave at $E_{1/2} = +0.68$ V decreased in intensity, while a new redox wave appeared and increased in intensity at $E_{1/2} = 0.00$ V, a value that is very close to that of the H_2O-terminated SAM generated electrochemically.[7] This value is also close to that of CO-free solvento complex [Ru$_3$(μ_3-O)(μ-CH$_3$COO)$_6$(4-methylpyridine)$_2$(H$_2$O)]$^+$ dissolved in acetonitrile containing 0.1 M nBu$_4$NPF$_6$ ($E_{1/2} = +0.04$ V vs Ag/AgCl).[19] After 520 s of UV exposure (Figure 1 c), nearly complete transformation of the monolayer is observed. More direct evidence for photolytic dissociation of CO was obtained by IR spectroscopy.[20] The SAM of **1** assembled on Au(111) displays an intense absorption peak due to ν(CO) at $\tilde{\nu} = 1944$ cm^{-1}, which exhibits, as expected, a significant decrease in intensity after photolysis.

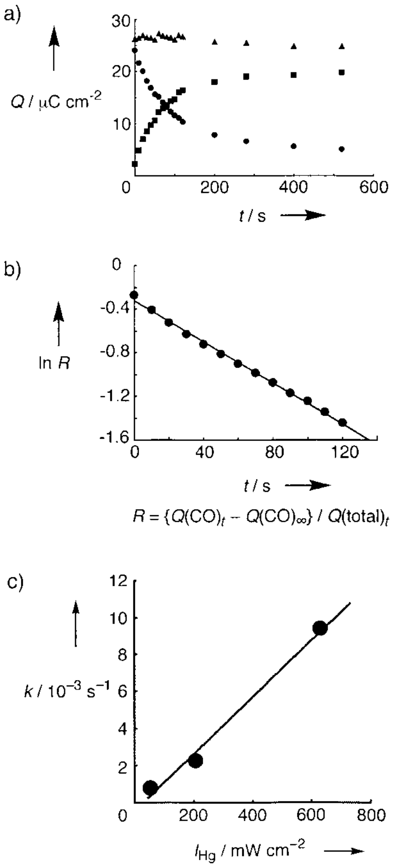

Figure 2. Analysis of photoinduced CO dissociation. a) Variation of charge Q of surface species obtained from CVs presented in Figure 1. ●: CO-terminated SAM; ■: H_2O-terminated SAM; ▲: sum of the two components. b) First-order plot of the decay of CO-terminated SAM as a function of irradiation time t. c) Linear dependence of the rate constant k for CO dissociation on light intensity I_{Hg}.

The photoinduced transformation was quantitatively analyzed by integrating charge density under the two redox waves presented in Figure 1. Figure 2 a shows charge density profiles of surface-assembled **1**, H_2O-terminated photoproduct, and the sum of the two against irradiation time. As is visible from Figure 2 b, the photoinduced dissociation of CO is well described by first-order kinetics with a rate constant of $(2.3\pm0.1)\times10^{-3}$ s^{-1} at a light intensity of 210 mW cm^{-2}. The rate constant increases linearly with increasing light intensity (Figure 2 c). Changing the electrolyte solution from 0.1 M $HClO_4$ to 0.05 M H_2SO_4 does not affect the rate constant of photodissociation; this suggests that the electrolyte anions do not participate in the photoexcited state of the cluster.

We emphasize that the photochemical transformation of the monolayer is clean: the two redox-active moieties remain undesorbed from the surface during irradiation (Figure 2 a). The preservation of the monolayer on the electrode surface was also supported by a reductive desorption experiment (0.5 M aqueous KOH solution), which showed a well-defined Au–S desorption peak at −0.92 V for the photolytically generated H_2O-terminated SAM.[21] We speculate that the closely packed character of the photoactive cluster moieties, as well as the deaerated conditions employed for the measurement, minimize possible photodegradation of the SAM.[22]

We recently established photoinduced dissociation of CO from $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(\text{pyridine})_2(CO)]$ in CH_3CN.[8] Photoexcitation at the cluster-to-CO ligand charge-transfer band at about 300 nm results in dissociation of CO to afford the corresponding CH_3CN complex $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(\text{pyridine})_2(CH_3CN)]$ with a quantum yield of 0.012 at 298 K, while an intense absorption band at $\lambda_{max} = 585$ nm is not totally responsible for CO dissociation. In the present study, the importance of photoexcitation wavelength for triggering ligand substitution at the monolayer/solution interface was demonstrated by two experiments. First, when irradiation was performed with an Hg lamp through long-pass cutoff filters, the rate constant for CO dissociation ($k = 5.3 \times 10^{-4}\,s^{-1}$ for $\lambda > 340$ nm and $1.4 \times 10^{-4}\,s^{-1}$ for $\lambda > 380$ nm) became approximately one order of magnitude smaller than that obtained on unfiltered irradiation, that is, the photoactive band(s) lies in the UV region. Irradiation at 400 nm or longer wavelength does not cause any CO dissociation. Second, irradiation with visible light from an Xe lamp (630 $mW\,cm^{-2}$) also retarded the photoinduced substitution ($k = (8.1 \pm 0.1) \times 10^{-4}\,s^{-1}$).[23]

An additional interesting feature of the present SAM is the observation of photocurrent generation. Figure 3 shows the photocurrent action spectrum of the monolayer assembled on Au(111) and the UV/Vis absorption spectrum of **1** in acetonitrile. The anodic photocurrent response of the monolayer is shown in the inset. The photocurrent action spectrum shows a remarkable dependence on the irradiation wavelength. The maximum photocurrent was observed for excitation at 320 nm, while the photocurrent intensity was markedly decreased at shorter and longer wavelengths. Irradiation at 350 nm or longer wavelength did not lead to photocurrent generation, which clearly shows the inactivity of the absorption band in the visible region ($\lambda_{max} = 584$ nm) in the photocurrent response. The maximum peak of the action spectrum definitely corresponds to the location of the absorption shoulder in **1**, which has been tentatively assigned to cluster-to-ligand or cluster-to-CO charge-transfer transitions.[8] Since the intensity of the monochromated light employed here is fairly low (280 $\mu W\,cm^{-2}$), the action spectrum obtained indeed reflects the photocurrent response of the CO-terminated SAM. We note that the monolayer shows reproducible photocurrent data as long as the $\{Ru^{II}\text{-}CO\}$ bond in **1** remains intact. Work to accurately determine the nature of the photocurrent and to fully address its mechanism is currently in progress. Our preliminary observation indicates that the aqua-terminated monolayer formed on intense irradiation of its CO-terminated counterpart also exhibits an anodic photocurrent but with much lower intensity. These observations indicate that photochemical ligand replacement can be used to tune not only the redox potential but also the photocurrent characteristics of our SAM on Au.

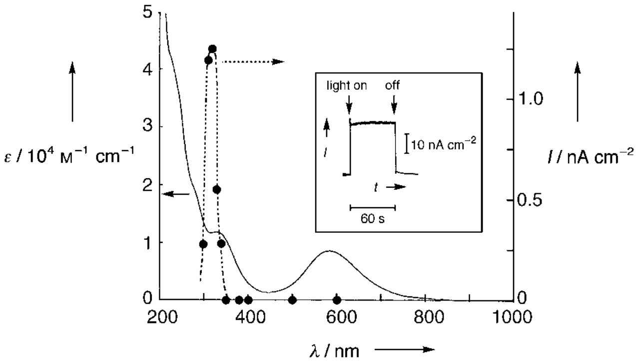

Figure 3. Absorption spectrum of **1** in acetonitrile (solid line) and photocurrent action spectrum (filled circles) of the monolayer of **1** on Au(111) in contact with 0.1 M $HClO_4$. Monochromated light intensity: 280 $\mu W\,cm^{-2}$. Applied potential: +0.3 V versus Ag/AgCl. Inset: anodic photocurrent response with irradiation from an Hg lamp (210 $mW\,cm^{-2}$).

In conclusion, we have described photochemical ligand substitution reaction of a redox-active SAM for the first time. We expect that suitable selection of photoresponsive coordination compounds, a CO-ligated triruthenium complex in our case, may offer a route to significant development in the fabrication of redoxactive and photoactive layers that can show device characteristics at an electrochemical interface.

Experimental Section

The Au(111) disk for SAM preparation was electrochemically etched and annealed as described in ref. [24]. The surface area was estimated from a cyclic voltammogram recorded in 0.1 M aqueous H_2SO_4, based on the charge under the cathodic wave due to gold oxide reduction.[25] The roughness factor of the Au(111) surface was 1.15. Prior to SAM formation, the Au(111) disk surface was flame-annealed with a hydrogen burner and slowly cooled in air. For SAM formation, the disk was immersed in an ethanol solution of **1** (50 μM) for 2 d at RT. The SAM-modified Au(111) was rinsed with ethanol and Milli-Q water, dried by blowing nitrogen gas over the surface, and it was subjected to photoelectrochemical measurements. The electrode potential was controlled by a Hokuto Denko HA-151 potentiostat, while the external potential was provided by a Hokuto Denko HB-111 function generator. The light intensity was determined by an optical power meter. For recording of the photocurrent action spectrum, monochromated light from the Hg lamp was used. The light intensity was adjusted to 280 $\mu W\,cm^{-2}$ for each measurement.

Received: May 14, 2004
Revised: September 29, 2004

Keywords: electrochemistry · monolayers · photochemistry · surface chemistry

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[1] For example: a) R. L. Carroll, C. B. Gorman, *Angew. Chem.* **2002**, *114*, 4556; *Angew. Chem. Int. Ed.* **2002**, *41*, 4378; b) A. N. Shipway, I. Willner, *Acc. Chem. Res.* **2001**, *34*, 421.

[2] a) D. G. Water, D. J. Campbell, C. A. Mirkin, *J. Phys. Chem. B* **1999**, *103*, 402; b) A. Doron, E. Katz, M. Portnoy, I. Willner, *Angew. Chem.* **1996**, *108*, 1626; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1535; c) I. Willner, S. Rubin, *Angew. Chem.* **1996**, *108*, 419; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 367; d) M. Lion-Dagan, S. Marx-Tibbon, E. Katz, I. Willner, *Angew. Chem.* **1995**, *107*, 1730; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1604; e) I. Willner, V. Pardo-Yissar, E. Katz, K. T. Ranjit, *J. Electroanal. Chem.* **2001**, *497*, 172; f) K. T. Ranjit, S. Marx-Tibbon, I. Ben-

Dov, I. Willner, *Angew. Chem.* **1997**, *109*, 90; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 147; g) I. Willner, F. Patolsky, J. Wasserman, *Angew. Chem.* **2001**, *113*, 1913; *Angew. Chem. Int. Ed.* **2001**, *40*, 1861.

[3] a) S. Abbott, J. Ralston, G. Reynolds, R. Hayes, *Langmuir* **1999**, *15*, 8923; b) S. Sortino, S. Petralia, G. G. Condorelli, S. Conoci, G. Condorelli, *Langmuir* **2003**, *19*, 536.

[4] a) K. Uosaki, T. Kondo, X.-Q. Zhang, M. Yanagida, *J. Am. Chem. Soc.* **1997**, *119*, 8367; b) T. Kondo, T. Kanai, K. Uosaki, *Langmuir* **2001**, *17*, 6317; c) H. Yamada, H. Imahori, Y. Nishimura, I. Yamazaki, T. K. Ahn, S. K. Kim, D. Kim, S. Fukuzumi, *J. Am. Chem. Soc.* **2003**, *125*, 9129; d) D. Hirayama, K. Takimiya, Y. Aso, T. Otsubo, T. Hasobe, H. Yamada, H. Imahori, S. Fukuzumi, Y. Sakata, *J. Am. Chem. Soc.* **2002**, *124*, 532; e) Y. Kuwahara, T. Akiyama, S. Yamada, *Langmuir* **2001**, *17*, 5714.

[5] a) M. Wrighton, *Chem. Rev.* **1974**, *74*, 401; b) G. L. Geoffroy, M. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, **1987**, p. 242; c) P. C. Ford, D. Wink, J. Dibenedetto, *Prog. Inorg. Chem.* **1983**, *30*, 213; d) J. G. Bentsen, M. S. Wrighton, *J. Am. Chem. Soc.* **1987**, *109*, 4530; e) M. F. Desrosiers, D. A. Wink, R. Trautman, A. E. Friedman, P. C. Ford, *J. Am. Chem. Soc.* **1986**, *108*, 1917; f) N. E. Leadbeater, J. Lewis, P. R. Raithby, G. N. Ward, *J. Chem. Soc. Dalton Trans.* **1997**, 2511; g) E. Eskelinen, M. Haukka, T. Venäläinen, T. A. Pakkanen, M. Wasberg, S. Chardon-Noblat, A. Deronzier, *Organometallics* **2000**, *19*, 163; h) K. Koike, J. Tanabe, S. Toyama, H. Tsubaki, K. Sakamoto, J. R. Westwell, F. P. A. Johnson, H. Hori, H. Saitoh, O. Ishitani, *Inorg. Chem.* **2000**, *39*, 2777; i) F.-W. Grevels, K. Kerpen, W. E. Klotzbücher, K. Schaffner, R. Goddard, B. Weimann, C. Kayran, S. Özkar, *Organometallics* **2001**, *20*, 4775; j) A. S. DelNegro, S. M. Woessner, B. P. Sullivan, D. M. Dattelbaum, J. R. Schoonover, *Inorg. Chem.* **2001**, *40*, 5056.

[6] a) E. W. Wollman, D. Kang, C. D. Frisbie, I. M. Lorkovic, M. S. Wrighton, *J. Am. Chem. Soc.* **1994**, *116*, 4395; b) D. Kang, M. S. Wrighton, *Langmuir* **1991**, *7*, 2169.

[7] A. Sato, M. Abe, T. Inomata, T. Kondo, S. Ye, K. Uosaki, Y. Sasaki, *Phys. Chem. Chem. Phys.* **2001**, *3*, 3420.

[8] D. Akashi, H. Kido, M. Abe, Y. Sasaki, T. Ito, *Dalton Trans.* **2004**, 2883.

[9] R. D. Cannon, R. P. White, *Prog. Inorg. Chem.* **1988**, *36*, 195.

[10] H. E. Toma, K. Araki, A. D. P. Alexiou, S. Nikolaou, S. Dovidauskas, *Coord. Chem. Rev.* **2001**, *219–221*, 187.

[11] a) J. A. Baumann, S. T. Wilson, D. J. Salmon, P. L. Hood, T. J. Meyer, *J. Am. Chem. Soc.* **1979**, *101*, 2916; b) J.-L. Chen, L.-Y. Zhang, Z.-N. Chen, L.-B. Gao, M. Abe, Y. Sasaki, *Inorg. Chem.* **2004**, *43*, 1481.

[12] H. Kido, H. Nagino, T. Ito, *Chem. Lett.* **1996**, 745.

[13] T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, H. Kido, I. S. Zavarine, T. Richmond, J. Washington, C. P. Kubiak, *J. Am. Chem. Soc.* **1999**, *121*, 4625.

[14] T. Ito, N. Imai, T. Yamaguchi, T. Hamaguchi, C. H. Londergan, C. P. Kubiak, *Angew. Chem.* **2004**, *116*, 1400; *Angew. Chem. Int. Ed.* **2004**, *43*, 1376.

[15] M. Abe, T. Michi, A. Sato, T. Kondo, W. Zhou, S. Ye, K. Uosaki, Y. Sasaki, *Angew. Chem.* **2003**, *115*, 3018; *Angew. Chem. Int. Ed.* **2003**, *42*, 2912.

[16] S. Ye, W. Zhou, M. Abe, T. Nishida, L. Cui, K. Uosaki, M. Osawa, Y. Sasaki, *J. Am. Chem. Soc.* **2004**, *126*, 7434.

[17] S. Ye, H. Akutagawa, K. Uosaki, Y. Sasaki, *Inorg. Chem.* **1995**, *34*, 4527.

[18] a) J. A. Baumann, D. J. Salmon, S. T. Wilson, T. J. Meyer, W. E. Hatfield, *Inorg. Chem.* **1978**, *17*, 3342; b) M. Abe, Y. Sasaki, Y. Yamada, K. Tsukahara, S. Yano, T. Yamaguchi, M. Tominaga, I. Taniguchi, T. Ito, *Inorg. Chem.* **1996**, *35*, 6724.

[19] M. Abe, A. Sato, T. Inomata, T. Kondo, K. Uosaki, Y. Sasaki, *J. Chem. Soc. Dalton Trans.* **2000**, 2693.

[20] IR spectra were recorded prior to and after photolysis of the SAM on a JASCO FT-IR 660Plus spectrophotometer (see Supporting Information).

[21] See Supporting Information.

[22] Selected references describing monolayer photodegradation: a) N. J. Brewer, R. E. Rawsterne, S. Kothari, G. J. Leggett, *J. Am. Chem. Soc.* **2001**, *123*, 4089; b) J. Huang, J. C. Hemminger, *J. Am. Chem. Soc.* **1993**, *115*, 3342.

[23] See Supporting Information. Unlike irradiation from the Hg lamp, the use of the Xe lamp at a prolonged exposure time ($>10^4$ s) resulted in a significant loss of redox-active moieties from the gold surface (ca. 24%, based on CV charge).

[24] T. Kondo, J. Morita, M. Okamura, T. Saito, K. Uosaki, *J. Electroanal. Chem.* **2002**, *532*, 201.

[25] R. Woods in *Electroanalytical Chemistry, A Series of Advances, Vol. 9* (Ed.: A. J. Bard), Marcel Dekker, New York, **1988**, p. 1.