α-Diazo ketone self-assembled monolayer modified electrode: a proposed photoreactive template for electrode derivatisation

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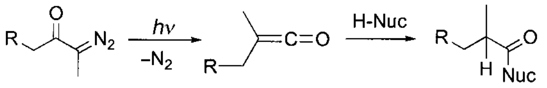
A gold electrode modified with an α-diazo ketone has been prepared and its photo-Wolff chemistry investigated in the presence of MeOH as a ketene trap; results suggest that these modified electrodes are a potential photoreactive template for surface modifications.

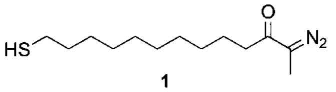
Modification of electrode surfaces with monolayers of organic substrates *via* self-assembly continues to be an area of active investigation. In particular, there are a great number of studies whose goals are to prepare electrode surfaces modified with the appropriate organic functionality at the interface to provide the site for molecular recognition or modulation of electronic factors for a sensing action.[1,2] Despite the power of photochemistry to provide careful control of surface modifications of organic functionality through photo-patterning techniques, this approach remains relatively unexplored considering the enormous amount of work in the area of self-assembly of organic substrates on metals. Examples of the types of photoreactions of substrates on gold surfaces that have been reported include photoextrusion of nitrogen from aryl azide,[3] *E–Z* photoisomerisation of stilbenes[4] and azo compounds[5] and other photochromic materials,[5] and photodimerization reactions.[6]

Our approach is to employ the photochemistry of α-diazocarbonyl compounds to serve as a photoreactive template for further surface modifications. Compounds containing an α-diazo ketone functionality are known to produce a ketene intermediate, *via* the photo-Wolff rearrangement, upon photoexcitation and loss of nitrogen [eqn. (1)]. The resulting ketenes are known to react with a wide range of nucleophiles to form a variety of functional groups. Simple examples include water, alcohol and amine nucleophiles to form carboxylic acids, esters and amides, respectively. Owing to their wide-ranging reactivity, α-diazocarbonyl compounds[7] and ketenes[8] have been extensively used in solution phase synthetic strategies. Of particular interest to us is extending this chemistry to provide a template for ways to derivatize selectively the monolayer surface with a variety of nucleophile substrates. Here we report the first example of an α-diazo ketone functionality incorporated into the interface of a self-assembled monolayer on a gold electrode. As proof of concept that this modified surface has potential as a template for photo-Wolff chemistry, we have photolysed this novel surface in the presence of MeOH as the nucleophile to form an ester derivatized surface.



(1)

The α-diazo ketone monolayer precursor, 2-diazo-13-mercaptotridecan-3-one **1**, was synthesized in four steps from 11-bromoundecanoic acid. First, the acid was converted into its acid chloride by refluxing in $SOCl_2$. This was followed by diazotisation of the acid chloride using $MeCHN_2$ to form 13-bromo-2-diazotridecan-3-one. The latter was thioesterified with AcSK to form $AcS(CH_2)_{10}C(O)C(N_2)Me$. Finally, the thioester was hydrolysed to the thiol with methanolic K_2CO_3 and then purified by repeated column chromatography to yield analytically pure **1**, in 10% overall yield. The structure of **1** was confirmed by ^1H and ^{13}C NMR, infrared and mass spectroscopy.[9] For latter comparison the transmission IR of **1** taken as a thin film on a NaCl plate is shown in Fig. 1(*c*).



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Monolayers of **1** on gold (Au-**1**) were prepared by immersion of clean Au[10] in a 50 mM deareated EtOH solution of **1** for 1–96 h. The homogeneity of the monolayer was examined qualitatively using cyclic voltammetry, by monitoring the reversible $Fe^{2+/3+}$ redox chemistry of $Fe(CN)_6^{3-}$ in aqueous solution above the Au-**1** derivatized electrodes. On average soaking times of 16 h resulted in a overall current decrease of greater than 10^3 [*i.e.* no detectable $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox activity] compared to the bare gold electrode (no further current reduction was observed on samples soaked for up to 4 days). This overall current decrease and the observed cyclic voltammograms of the blocked gold electrodes are similar to those published for other organic thiol self-assembled monolayer systems on Au using the same redox probe.[6,10] A grazing angle infrared spectrum of an Au-**1** substrate prepared in a similar manner is shown in Fig. 1(*a*). Note that the spectral features compare well to the transmission IR spectrum of the same compound measured as a thin film on NaCl [Fig. 1(*c*)]. Diagnostic absorptions are listed in Table 1; also listed for comparison are the absorptions for a thin film of **1**. In particular we note that the characteristic methylene symmetric and asymmetric stretching frequencies and intensities are similar to other densely packed, well-ordered Au-alkyl monolayers of similar length.[11] Also diagnostic are the C=N=N asymmetric and C=O stretching absorptions at 2086 and 1698/1646 cm^{-1}, respectively.[12] The C=O absorption appears to be split into two in Au-**1**. This may be due to (i) a solid state correlation effect,[13]

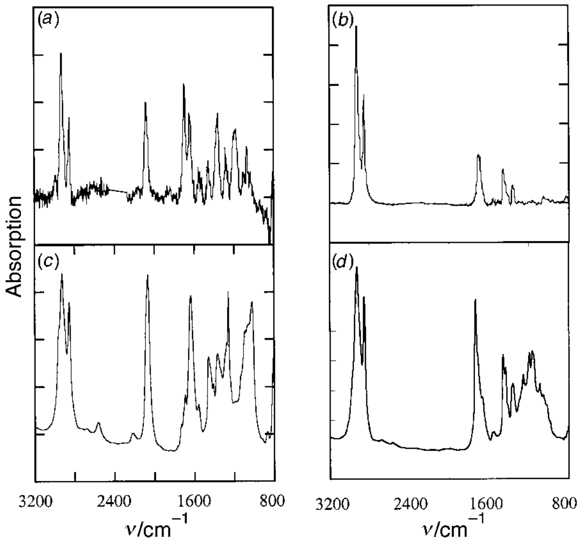
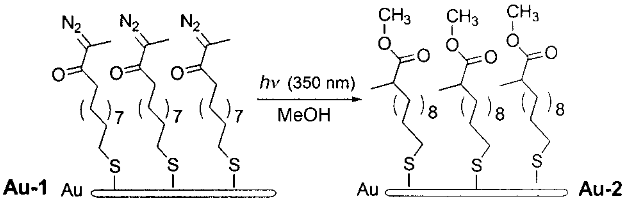


Fig. 1 Grazing angle fourier transform infrared spectra of (*a*) Au-**1** and (*b*) Au-**2** on gold and absorption FTIR of (*c*) **1** and (*d*) **2** as neat thin film samples on NaCl plates. Note: in the spectrum of Au-**1** the absorptions due to CO_2 have been deleted for clarity.

Table 1 Diagnostic infrared assignments for Au-**1** and **1** prior to and after irradiation in MeOH (Au-**2** and **2**)

	ν/cm^{-1}			ν/cm^{-1}	
Assignment, mode[a]	Au-**1**	**1**	Assignment, mode	Au-**2**	**2**
CH_2, asymmetric (d−)	**2926**	**2926**	**CH_2, asymmetric (d−)**	**2924**	**2926**
CH_2, symmetric (d+)	**2854**	**2854**	**CH_2, symmetric (d+)**	**2856**	**2854**
S–H, stretch (weak)		2565			2567
C=N=N, asymmetric, o.o.p.	**2086**	**2068**			
C=O stretch, conjugated	**1646** **(1698)**[c]	**1639**	**C=O stretch (ester)**	**1710**	**1739**
CH bend (CH_2, scissor)[b]	1457	1459	CH bend (CH_2, scissor)	1458	1463
			O–CH_3 deformation[b]		1435
CH bend (CH_2, i.p.)	1362	1371	CH bend (CH_2, i.p.)	1363	1363
	1288	1261	C(CO)–O asymmetric[b]		1262
C–O carbonyl and/or CH_2 twist[b]	1179		C–O carbonyl and/or CH_2 twist[b]		1198
			C(CO)–O symmetric[b]		1168

[a] Assignments are based on similar systems and from ref. 12. [b] Tentative assignment, since multiple modes are possible in this region. [c] See text.



Scheme 1

suggesting that even the groups at the interface are well ordered, (ii) different rotational isomers of the O=C–C(N2) (*i.e.* s-*cis* and s-*trans*) that become more prevalent in the densely packed monolayer compared to **1**, or (iii) the rotational restrictions may lead to some decrease in the conjugation due to steric interactions in the densely packed monolayer.

Au-**1** samples above were irradiated in a nitrogen saturated MeOH solution at 350 nm using a medium pressure Hg-lamp with appropriate filters. A grazing angle IR spectrum of the Au-substrate after complete photolysis is shown in Fig. 1(*b*) and characteristic absorptions are listed in Table 1. Note the complete absence of the C=N=N asymmetric stretch; the appearance of the IR spectrum measured at intermediate times shows gradual loss of the characteristic C=N=N absorption concomitant with a change in the spectral region of the carbonyl absorption. The new C=O absorption is shifted to slightly higher energy consistent with that for a CH_2–C(O)–OMe ester.[13] The intensity of the C=O absorption of the ester is somewhat reduced compared to the thin film; we assign this tentatively to an orientation effect, where the C=O mode is aligned roughly parallel to the metal surface. The relative intensities of the absorptions due to the methylene groups of the long chain tether in the irradiated sample compared to those of Au-**1** before irradiation do not vary, indicating that under the photolysis conditions the monolayer remains intact and relatively ordered. After irradiation the same extent of electrochemical blocking of the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ redox probe also remained.

Fig. 1(*d*) shows an infrared spectrum of the corresponding thiol ester, methyl 12-mercapto-2-methyldodecanoate **2** synthesized from solution phase photochemical trapping of the ketene derived from photolysis of **1** in MeOH. Its spectrum compares favorably with the spectrum of photolysed Au-**1** [Fig. 1(*b*)]. In the solution phase photochemistry of **1** in MeOH using 350 nm irradiation, over 98% of the product isolated after complete photolysis was **2**, formed from MeOH trapping of the ketene intermediate. Based on this, we propose the photochemical modification of Au-**1** to Au-**2** as shown in Scheme 1. Under the conditions outlined no evidence was found for ‘intra’-monolayer reactivity between a ketene and a neighbouring C=O or between two ketene moieties.[14]

These results suggest that Au-**1** is a potential photoreactive template for derivatisation of the self-assembled monolayer. Because of the absorption characteristics of the C(=N_2)C=O moiety, the photoinitiated Wolff rearrangement and ketene chemistry can be activated with comparatively long wavelengths of light in the presence of a large number of organic trapping agents that absorb at much higher energy and are transparent in the region where we irradiate. We believe that this particular feature makes the use of the photo-Wolff a powerful technology for synthetic modifications. The generality of this photochemistry for surface modifications, and photopatterning, and the limitations of this important technology are currently being investigated by extending the studies to other ketene trapping nucleophilic reagents.

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Notes and references

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9 *Selected data* for **1**: δ_H($CDCl_3$, 300 MHz) 2.49 (2H, q), 2.43 (2H, t), 1.92 (3H, s), 1.52–1.64 (4H, m), 1.20–1.36 (12H, m); δ_C($CDCl_3$, 75 MHz) 195.0, 62.0, 37.8, 34.0, 29.4, 29.3, 29.2, 29.0, 28.3, 24.9, 24.6, 8.1.

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