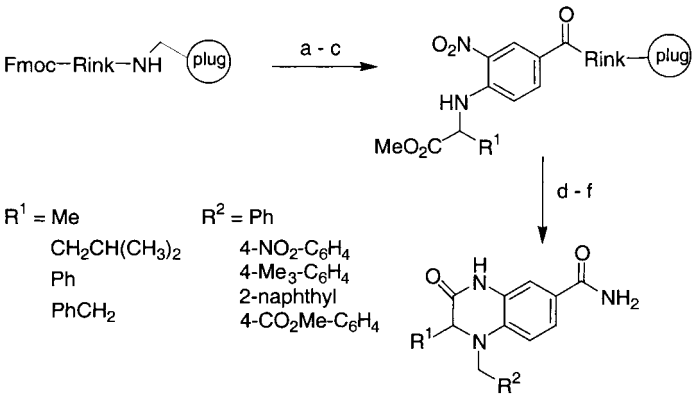
average purity of 90–95% (HPLC) was observed for the sulfonamides, amides, and ureas, falling to 80–90% for the tertiary amines. The weight recovery per plug for each purified compound was good and ranged between 5–12 mg. Based on the starting plug loading, the overall yields of cleaved purified materials were 36–86%.

A third small library of 3,4-disubstituted 7-carbamoyl-1,2,3,4-tetrahydroquinoxalin-2-ones was prepared on the resin plugs. The synthesis (Scheme 4) was adapted from the literature.[11] A representative compound (Table 3, entry 9) was isolated with an overall yield of 40% (literature, 48%). The average crude product purity by HPLC was 52%.



Scheme 4. Library of 3,4-disubstituted 7-carbamoyl-1,2,3,4-tetrahydroquinoxalin-2-ones. a) 20% piperidine/DMF, 20 min; b) (4-F,3-NO_2)PhCOCl (5 equiv), DIPEA (5 equiv); c) $H_2NCH(R^1)CO_2Me$ (10 equiv), DIPEA (10 equiv), DMF, 3 days; d) $SnCl_2 \cdot H_2O$ (20 equiv), DMF, 3 days; e) R^2CH_2Br (25 equiv), K_2CO_3 (25 equiv), $(CH_3)_2CO$, reflux, 48 h; f) 95% TFA.

Table 3. Library of 3,4-disubstituted 7-carbamoyl-1,2,3,4-tetrahydroquinoxalin-2-ones.

Entry	R^1	R^2	HPLC purity [%]
1	Me	Ph	69
2	Me	4-Me-C_6H_4	43
3	Me	2-naphthyl	39
4	$CH_2CH(CH_3)_2$	Ph	42
5	$CH_2CH(CH_3)_2$	2-naphthyl	52
6	$CH_2CH(CH_3)_2$	4-CO_2Me-C_6H_4	59
7	Ph	Ph	44
8	Ph	4-Me-C_6H_4	75
9	CH_2Ph	4-Me-C_6H_4	40
10	CH_2Ph	2-naphthyl	57

In summary, we have developed a new method of resin handling. Considering the huge effort in the area of solid-phase synthesis and solution chemistry using resin scavengers/reagents, the approach of resin sintering offers a cheap and readily available method of preparing discrete, easy to handle, encoded materials for multiple parallel synthesis, defined mix and split synthesis and scavenging/immobilized reagents, in whatever formats are deemed appropriate, and with any resin desired. We are currently investigating the use of resin plugs in further reactions and their use as scavengers, supported reagents and catalysts and will communicate our results in due course.

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[1] a) K. S. Lam, M. Lebl, V. Krchnak, *Chem. Rev.* **1997**, *97*, 411; b) E. M. Gordon, M. A. Gallop, D. V. Patel, *Acc. Chem. Res.* **1996**, *29*, 144; c) A. W. Czarnik, *Chemtracts: Org. Chem.* **1995**, *8*, 13; d) D. J. Ecker, S. T. Crooke, *Biotechnology* **1995**, *13*, 351; e) M. A. Gallop, R. W. Barret, W. J. Dower, S. P. A. Fodor, E. M. Gordon, *J. Med. Chem.* **1994**, *37*, 1233; f) N. K. Terret, M. Gardner, D. W. Gordon, R. J. Kobylecki, J. Steele, *Tetrahedron* **1994**, *51*, 8135; g) E. J. Martin, J. M. Blaney, M. A. Siani, D. C. Spellmeyer, A. K. Wong, W. H. Moos, *J. Med. Chem.* **1995**, *38*, 1431; h) H. M. Geysen, R. H. Meloen, S. J. Barteling, *Proc. Natl. Acad. Sci. USA* **1984**, *81*, 3998.
[2] R. A. Houghten, *Proc. Natl. Acad. Sci.* **1985**, *82*, 5131.
[3] a) R. M. Valerio, A. M. Bray, N. J. Maegi, *Int. J. Pept. Protein Res.* **1994**, *44*, 158; b) A. M. Bray, D. S. Chiefari, R. M. Valerio, N. J. Maeji, *Tetrahedron Lett.* **1995**, *36*, 5081; c) R. M. Valerio, A. M. Bray, H. Patsiouras, *Tetrahedron Lett.* **1996**, *37*, 3019; d) A. A. Virgilio, J. A. Ellman, *J. Am Chem. Soc.* **1994**, *116*, 11580; e) B. A. Bunin, M. J. Plunkett, J. A. Ellman, *New J. Chem.* **1997**, *21*, 125; f) A. A. Virgilio, A. A. Bray, W. Zhang, L. Trinh, M. Snyder, M. M. Morrissey, J. A. Ellman, *Tetrahedron* **1997**, *53*, 6635; g) B. A. Bunin, M. J. Blunkett, *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 4708; h) B. A. Bunin, J. A. Ellman, *J. Am. Chem. Soc.* **1992**, *114*, 10997.
[4] a) K. C. Nicolaou, N. Winssinger, D. Vourloumis, T. Ohshima, S. Kim, J. Pfefferkorn, J.-Y. Xu, T. Li, *J. Am. Chem. Soc.* **1998**, *120*, 10814; b) S. Shi, X.-Y. Xiao, A. W. Czarnik, *Biotechnol. Bioeng.* **1998**, *61*, 7; c) C. J. Anres, R. T. Swann, K. Grant-Young, S. V. D'Andrea, M. S. Deshpande, *Comb. Chem. High Throughput Screening* **1999**, *2*, 29; d) K. C. Nicolaou, X.-Y. Xiao, Z. Parandoosh, A. Senyei, M. P. Nova, *Angew. Chem.* **1995**, *107*, 2476; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2289.
[5] N. Hird, I. Hughes, D. Hunter, M. G. J. T. Morrison, D. C. Sherrington, L. Stevenson, *Tetrahedron* **1999**, *55*, 9575.
[6] a) J. A. Tripp, J. A. Stein, F. Svec, J. M. J. Fréchet, *Org. Lett.* **2000**, *2*, 195; b) A. R. Vaino, K. D. Janda, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 7692.
[7] This technology was developed in conjunction with Porvair Sciences Ltd and is the subject of Patent Application GB99/03406.
[8] V. Sarin, S. Kent, J. Tam, R. Merrifield, *Anal. Biochem.* **1981**, *117*, 147.
[9] M. S. Bernatowicz, S. Daniels, H. Koster, *Tetrahedron Lett.* **1989**, *30*, 4645.
[10] Transponders were supplied by Avid PLC, UK.
[11] L. Jung, W. V. Murray, R. A. Rivero, *J. Org. Chem.* **1997**, *62*, 3874.

Adsorption-Mediated Electrochemical Sensing of Halides**

Richard Michalitsch and Paul E. Laibinis*

Measurements of halide concentrations are crucial in many clinical and environmental analyses and in many areas of industrial chemistry.[1] Ion-selective electrodes (ISEs) have been increasingly used for monitoring the concentrations of many ions such as halides.[2, 3] These electrodes incorporate a solid membrane that allows the selective diffusion of one ion to its surface to produce an electrochemical potential that is proportional to the concentration of the ion in solution.

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Commercial halide-ISEs often exhibit an interference by ions such as CN^-, S^{2-}, SCN^-, and other halides, and show a selectivity for the target ion that is far from specific. Despite efforts to optimize the properties of these electrodes, ISEs continue to face two principal limitations,[2, 3] namely 1) erroneous signals from ions that either compete with the target ion in the detection process or that form a precipitate on the membrane surface and block access to the electrode by the ion of interest, and 2) a modest level of sensitivity that requires concentrations of 0.5 to 10 μM for detection. The use of luminescent dyes and a combination of absorption and fluorescence measurements has been recently reported as an alternative method for monitoring chloride concentrations;[4] however, such approaches are sensitive to changes in pH and are susceptible to photobleaching.

Herein we report that underpotentially deposited (upd) Ag adlayers on Au surfaces can provide a means to measure Cl^-, Br^-, and I^- concentrations in a manner that offers several advantages over present electrochemical methods of detection. These Ag adlayers are easily prepared by an electroplating process[5] and provide the ability *by a single electrode* to identify each of these halides and to quantify their concentrations in aqueous solutions. These electrodes show a higher sensitivity for measuring halide concentrations than provided by most conventional detection systems.

The basis for halide detection is an effected electrochemical change to the Ag upd layer on Au(111) by halide adsorption.[6, 7] Figure 1 schematically illustrates various stages during the adsorption process for chloride ions onto a Ag upd adlayer on Au(111) and its effected electrochemical changes to the modified electrode. Herein we focus on the detection of chloride for simplicity; however, related results were obtained from experiments performed by using bromide and iodide. In this process, the chloride ions adsorb spontaneously onto the Au/Ag(upd) electrode surface, and cause replacement of the native Ag stripping peak at 535 mV versus Ag^+/Ag^0 by a stripping peak at 615 mV that can be assigned to the formation of Au/Ag(upd)–Cl. Notably, the adsorption of chloride onto the Ag adlayer shifts the stripping potential for the affected Ag adatoms by about 80 mV. The adsorption of the halide onto the Au(111)/Ag(upd) electrode surface produces temporal variations in the relative integrated charge densities for the peaks at 535 and 615 mV that correlate with the amount of adsorbed chloride, and their ratio can be related to the concentration of chloride in the test solution (see below).

Figure 2 shows kinetic data for the conversion of a fresh Au(111)/Ag(upd) sample to Au(111)/Ag(upd)–Cl for various

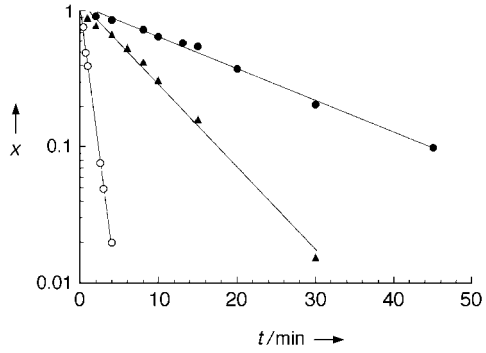

Figure 2. Kinetic data for the conversion of the native Ag upd layer to its halide-derivatized state for various contact times with 0.5 (●), 1.0 (▲), and 10 (○) μM KCl(aq) test solutions. The three data sets exhibit a first-order decay in the fractional intensity of the unconverted Ag(upd)/Au(111) signal (x), and the rates of conversion across these data sets vary linearly with their halide concentration.

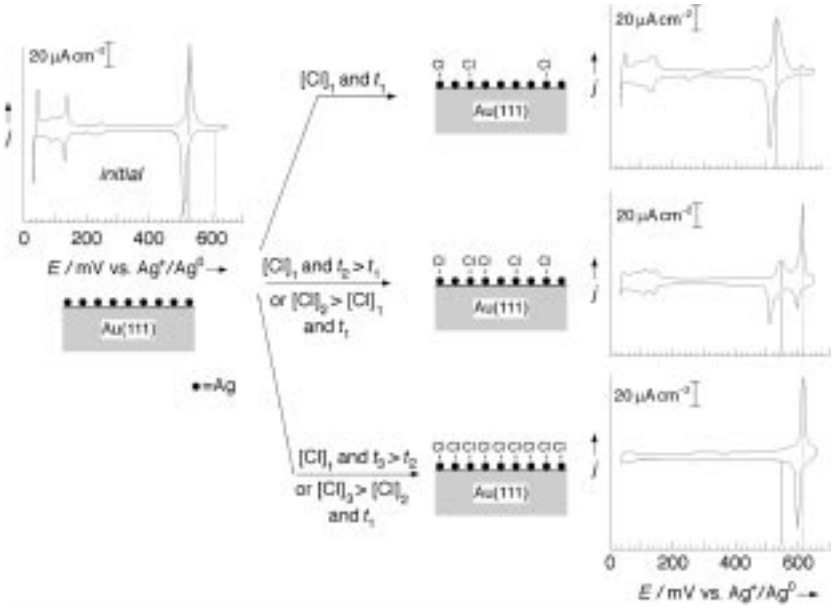

Figure 1. Schematic illustration of various stages during the adsorption of chloride onto a Ag upd layer on Au(111) and its effected electrochemical changes as monitored by cyclic voltammetry in 0.6 mM Ag_2SO_4/0.5 M H_2SO_4(aq). The stripping peak at 535 mV (initial Ag upd system, solid line) is stochastically replaced by a peak at 615 mV versus Ag^+/Ag^0 as a result of chloride adsorption (dashed line). $[Cl]_1 - [Cl]_3$ are different Cl concentrations in solution, $t_1 - t_3$ are different times of exposure of the electrode.

contact times with 0.5, 1.0, and 10 μM KCl(aq) solutions. A first-order process fits the data well, and the rate constants determined from the slopes of these fits scaled linearly with the halide concentration. These data provide the basis for quantifying Cl^- concentrations in an aqueous solution through Equation (1), where I

$$\ln\left(\frac{I_{\mathrm{Au/Ag(upd)}}}{I_{\mathrm{Au/Ag(upd)}} + I_{\mathrm{Au/Ag(upd)-halide}}}\right) = -k_{\mathrm{halide}} c_{\mathrm{halide}} t \qquad (1)$$

is the integrated intensity of a stripping peak, k_{halide} is a rate constant for halide adsorption, c_{halide} is the solution halide concentration, and t is the time the Au(111)/Ag(upd) electrode is exposed to the halide solution. Using Equation (1), we were able to determine the chloride concentrations across a variety of test solutions. For more concentrated solutions (such as a commercial sample of concentrated nitric acid with ca. 5 ppm of Cl^-), a 1000× dilution with water was required for analysis using a contact time of 1 min. In contrast, to measure the chloride content in a sample of deionized water (18.2 MΩ), a contact time of 1 h was required to

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produce a 20% conversion to the chloride-related stripping peak, corresponding to a measured chloride concentration of about 80 nM. By these methods, we were able to demonstrate the ability of the Ag upd adlayer to measure trace amounts of chloride (including those in the ppt range) across a variety of conditions. In addition, the method was suitable for detecting such low concentrations of Cl^- in solutions that also contained 0.5 M of NO_3^-, SO_4^{2-}, or PO_4^{3-} ions, and in those at acidic pH.

We also examined the effect of Br^- and I^- adsorption on the electrochemical stripping behavior of Au/Ag(upd) electrodes. Figure 3 contains cyclic voltammograms (CVs) for fully converted Au/Ag(upd)-Br and Au/Ag(upd)-I electrodes showing that the adsorption of these halides each produced distinct features in the CV that replaced the original deposition and stripping peaks of the native Ag upd adlayer. Specifically, the adsorption of Br^- onto the Ag adatoms increased the Ag upd stripping potential by about 40 mV to 575 mV versus Ag^+/Ag^0, while the adsorption of I^- decreased this potential by about 120 mV to ~415 mV. These differences in potential across Cl^-, Br^-, and I^- provide a direct means for identifying each of these solution-phase halides. Further, the adsorption kinetics for Br^- and I^- onto the Au/Ag(upd) surface showed a similar first-order behavior as for Cl^- adsorption (Figure 2),[8] and the amounts of adsorbed Br^- and I^- could be measured by simple integration of the stripping peaks for the native and reacted Ag adatoms and related to solution concentrations through use of Equation (1).

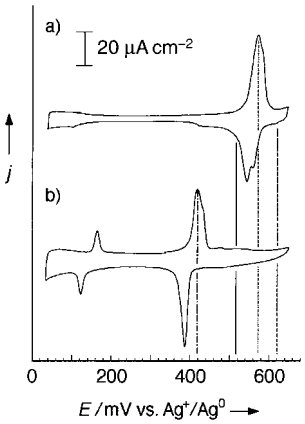

Figure 3. Cyclic voltammograms for the upd and stripping of Ag adlayers on Au(111) electrodes that were pretreated with a) Br^- and b) I^-. The adsorption of these halides each produces different changes to the cyclic voltammogram. The adsorption of Br^- onto the Ag adatoms increased the Ag upd stripping potential to 575 mV versus Ag^+/Ag^0 (dotted line), while the adsorption of I^- decreased the Ag upd stripping potential to ~415 mV (dotted-dashed line). The additional lines at 535 and 615 mV indicate the Ag upd stripping potentials for native (solid line) and Cl^--covered Ag adatoms (dashed line), respectively.

The detection limit by the Au/Ag(upd) electrodes for chloride (and for bromide and iodide) is determined by the contact time between the electrode and the test solution. From a practical standpoint, a conversion of 2–3% of the Ag atoms on the Au electrode to Au/Ag(upd)–Cl (that is, ca. 50 pmoles of adsorbed Cl^- per cm^2) is necessary to produce a clearly distinguishable electrochemical signal for the Au/Ag(upd)–Cl peak that is needed for determining the chloride solution concentration [Eq. (1)]. Longer contact times increased the measured surface concentrations of adsorbed chloride on the electrode (as evidenced by an increase in the signal at 615 mV) effecting a decrease in the detection limit for the halide. For example, contact times of 1 and 10 min provided detection limits for Cl^- of 500 and 50 nM, respectively,[9] where the trade-off between contact time and concentration was inversely related as expected for a first-order reaction process. Detection limits for Br^- and I^- under these conditions were similarly in the submicromolar regime.

A notable feature of this strategy using the Au(111)/Ag(upd) surface for quantifying halide concentrations is its ability to produce distinguishable signals for Cl^-, Br^-, and I^- that provide their identification.[10] We note that a current challenge for this method (as it is for many other strategies) is that the presence of other halides, when present at a similar or higher concentration as the halide of interest, complicates measurements of concentration by the electrode. For example, Figure 4 shows a CV for a Au/Ag(upd) sample after contact for 1 min with a solution containing 2.5 μM KCl and 2.5 μM KI. The CV exhibits three distinct stripping peaks for the Ag upd layer at about 415, 535, and 615 mV versus Ag^+/Ag^0, that can be readily assigned to Au/Ag(upd)–I, Au/Ag(upd), and Au/Ag(upd)–Cl, respectively. The electrode clearly provides information that the solution contains both Cl^- and I^-,[11] but the presence of both species complicates their measurement by a simple analysis. For example, the concentration of both chloride and iodide in solution was equal; however, the intensity of the peak for Ag–Cl was significantly greater than that for Ag–I. The difference between the halide concentrations on the electrode surface and in solution results from a difference in their affinities for the electrode surface and a competition for adsorption sites by the two ions. A description of these processes is likely to result from an examination of the kinetic and thermodynamic factors underlying the adsorption processes for these halides,

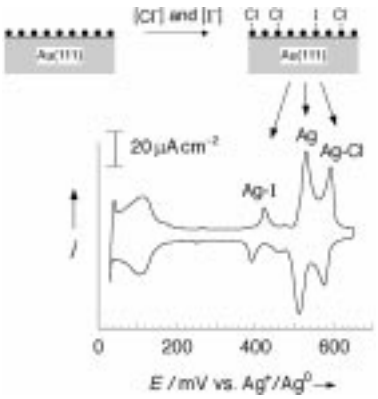

Figure 4. Cyclic voltammogram for a Au/Ag(upd) sample in 0.6 mM Ag_2SO_4/0.5 M H_2SO_4(aq) after contact with a solution containing 2.5 μM KCl/2.5 μM KI(aq) for 1 min. The CV exhibits three distinct stripping peaks for the Ag upd layer that identify the presence of Cl^- and I^- in the test solution. The temporal variations in these three stripping peaks are likely to provide an ability by these Au/Ag(upd) electrodes to detect and measure the concentrations of multiple halides.

and we are presently conducting such studies. With this information, we expect that the present strategy using Au/Ag(upd) electrodes for halide detection will provide the notable abilities to measure the concentrations of multiple halides simultaneously and to provide specific signals for confirming their identification.

Experimental Section

Materials: Au (99.99%) shot and Cr-coated tungsten filaments were obtained from Americana Precious Metals (East Rutherford, NJ) and R. D. Mathis (Long, Beach, CA), respectively. Sulfuric acid (double distilled, 98%) and silver sulfate ($c(Cl^-) \leq 0.02\%$) were obtained from Aldrich and used as received. KCl, KBr, and KI were obtained from Mallinckrodt and used as received. Au(111) samples were prepared by sequential evaporation of Cr (2–3 nm) and Au (150 nm) onto glass slides and a post-evaporation annealing in a hydrogen flame.[12]

Electrochemical measurements: Cyclic voltammetry was conducted with a computer-controlled PAR Model 263A potentiostat. A solution of 0.6 mM Ag_2SO_4 and 0.1M H_2SO_4 in deionized water (Millipore, 18.2 MΩ) was used to deposit the Ag upd adlayer on gold. Modified electrodes were prepared by cycling once in this solution and being removed at a 300 mV versus Ag^+/Ag^0 under potentiostatic control.[13] The Au(111)/Ag(upd) electrodes were rinsed with deionized water and immersed into a halide test solution for varying amounts of time. The samples were rinsed with water and characterized electrochemically in a 0.6 mM Ag_2SO_4/0.1M H_2SO_4(aq) solution. A standard three-electrode configuration was used to obtain all CVs, and all potentials are quoted relative to silver wire (Ag^+/Ag^0).

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[1] *Handbook of Chemical and Biological Sensors* (Eds.: R. F. Taylor, J. S. Schultz), Institute of Physics, Bristol, **1996**, p. 553.
[2] a) J. Janata, *Principles of Chemical Sensors*, Plenum, New York, **1989**, p. 91; b) U. E. Spichiger-Keller, *Chemical Sensors and Biosensors for Medical and Biological Applications*, VCH, Weinheim, **1998**, p. 248.
[3] K. Cammann, *Working with Ion Selective Electrodes*, Springer, New York, **1979**, p. 76.
[4] a) C. D. Geddes, *Dyes Pigm.* **2000**, *45*, 243; b) C. D. Geddes, P. Douglas, C. P. Moore, T. J. Wear, P. L. Egerton, *Dyes Pigm.* **1999**, *43*, 59; c) C. Huber, T. Werner, C. Krause, O. S. Wolfbeis, M. J. P. Leiner, *Anal. Chim. Acta* **1999**, *398*, 137; d) C. Huber, T. Werner, C. Krause, I. Klimant, O. S. Wolfbeis, *Anal. Chim. Acta* **1998**, *364*, 143.
[5] D. M. Kolb, *Adv. Electrochem. Electrochem. Eng.* **1984**, *13*, 159.
[6] a) O. M. Magnusson, J. Hotlos, R. J. Nichols, D. M. Kolb, R. J. Behm, *Phys. Rev. Lett.* **1990**, *64*, 2929; b) S. Sugita, T. Abe, K. Itaya, *J. Phys. Chem.* **1993**, *97*, 8780; c) A. T. Hubbard, J. L. Stickney, S. D. Rosasco, M. P. Soriaga, D. Song, *J. Electroanal. Chem.* **1983**, *150*, 165.
[7] R. Michalitsch, B. J. Palmer, P. E. Laibinis, *Langmuir* **2000**, *16*, 6533.
[8] Measured rate constants were $k_{Cl} = 11.8$, $k_{Br} = 11.3$, and $k_I = 11.1\ mM^{-1}min^{-1}$.
[9] The detection limit of a chloride-ISE is 50 μM.[3]
[10] This ability is a notable advantage over other methods (such as ISEs) that provide a weighted aggregate view of ion concentration.
[11] Such a distinction is not possible with an ISE.
[12] D. Haiss, D. Lackey, J. K. Sass, K. H. Besocke, *J. Chem. Phys.* **1991**, *95*, 2193.
[13] G. K. Jennings, P. E. Laibinis, *J. Am. Chem. Soc.* **1997**, *119*, 5208.

Mid-Membrane Photolabeling of the Transmembrane Domain of Glycophorin A in Phospholipid Vesicles**

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The topography of membrane-bound proteins at atomic resolution is known only in rare cases.[1] Although the primary amino-acid sequence of glycophorin A (GPA), the major sialoglycoprotein of the human erythrocytes, has been known for more than twenty years and was the first membrane protein sequence elucidated,[2] a three-dimensional picture of the protein is still missing. We have previously developed the photoactivable membrane probe **1**. This is a phospholipid with two distal, polar heads (a bola-amphiphile) and carries a photosensitive group (benzophenone) in the middle of a transmembrane chain. It is easily incorporated into DMPC (1,2-dimyristoyl-*sn*-glycero-3-phosphocoline) vesicles, where it spans the bilayer at least in the presence of physiological concentrations of cholesterol. We demonstrated recently that the tandem use of the probe **1a** and cholesterol (for its ordering effect) in photolabeling experiments on DMPC vesicles led to a remarkable regioselective functionalization

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