

Covalently Linked Scaffold of Cobalt Corrins on Graphite for Electrochemical Catalysis in Microemulsions

De-Ling Zhou,[†] Christopher K. Njue, and James F. Rusling*

Contribution from the Department of Chemistry, Box U-60, University of Connecticut, Storrs, Connecticut 06269-3060

Received December 3, 1998

Abstract: Catalytic films were constructed by covalently binding poly-L-lysine (PLL) onto oxidized carbon electrodes and then forming covalent amide linkages from PLL to the cobalt corrin vitamin B₁₂ hexacarboxylic acid [B₁₂(COOH)₆]. Covalent bonds from electrode to PLL and PLL to B₁₂(COOH)₆ provided good stability in microemulsions. PLL–B₁₂(COOH)₆ films gave reversible electron transfer for the Co(II)/Co(I) redox couple and exhibited characteristic voltammetric features of surface-confined electrochemistry. Formal potentials of the Co(II)/Co(I) couple in the films were controlled by the concentration of electrolyte in the fluid and by Coulombic interactions with surfactant. PLL–B₁₂(COOH)₆ films demonstrated excellent catalytic activity in microemulsions for the reduction of vicinal dihalides to olefins, for dechlorination of trichloroacetic acid, and for alkylation of an activated olefin. Turnover numbers for conversion of dibromocyclohexane to cyclohexene in microemulsions were 3-fold larger for PLL–B₁₂(COOH)₆ on carbon cloth cathodes than those for the same cobalt catalyst chemisorbed onto nanocrystalline TiO₂ cathodes.

Introduction

Public health issues are driving a search for environmentally benign methods of organic synthesis. Mediated electrochemical synthesis in low-toxicity fluids provides an attractive approach. Transition metal complexes can mediate (catalyze) many electrode-driven organic transformations without large quantities of chemical reductants.^{1–3} The use of microemulsions of oil, water, and surfactant avoids toxic, expensive organic solvents.⁴

Much effort has been directed toward catalytic modification of electrodes,^{5–7} but few systems have been successfully applied to electrochemical synthesis. This is often due to poor stability of the electrode coatings under synthetic conditions.⁸ In our work, we place stringent requirements on electrode stability, since we wish to employ catalytic electrodes in microemulsions, which are excellent solvents for polar and nonpolar compounds and polymers.

Microemulsions are macroscopically homogeneous, microscopically heterogeneous mixtures of oil, water, and surfactant. They are usually less toxic and less expensive⁹ than alternative organic solvents. Oil-in-water (o/w) and bicontinuous micro-

emulsions can be made in conductive forms suitable for electrochemical synthesis.^{10,11} O/w microemulsions feature surfactant-coated oil droplets in a continuous water phase. Bicontinuous microemulsions are dynamic, intertwined microscopic networks of oil and water with surfactant at the interfaces. We reported unique pathway control and selectivity for a variety of mediated electrochemical reactions using these fluids.^{4,12–15}

Catalytic films which are stable in water or organic solvents are often unstable in microemulsions. For example, films of myoglobin and a cationic surfactant were used to reduce organochlorides¹⁶ but suffered mechanical damage in microemulsions upon extended synthetic use. Also, nanocrystalline TiO₂ cathodes coated with vitamin B₁₂ hexacarboxylic acid mediated olefin and 1-decalone formation from the appropriate organohalides, but the mediator was partly leached from electrodes during the reaction.¹⁷

Inexpensive carbon materials make excellent electrodes for synthesis.^{8,18–21} Elegant strategies have been developed to

[†] Present address: Indium Corp. of America, Clinton, NY 13323.

(1) Pletcher, D.; Walsh, F. C. *Industrial Electrochemistry*, 2nd ed.; Blackie Academic: London, 1993.

(2) Torii, S. *Synthesis* **1986**, 873–886.

(3) Scheffold, R. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Wiley: New York, NY, 1983; Vol. 3, pp 355–439.

(4) Rusling, J. F.; Zhou, D.-L. *J. Electroanal. Chem.* **1997**, *439*, 89–96.

(5) (a) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135–141. (b) Rocklin, R. D.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 2104–2112. (c) Lennox, J. C.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 3710–3714. (d) Lennox, J. C.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *78*, 395–401.

(6) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, NY, 1984; Vol. 13, pp 191–368.

(7) Murray, R. W. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Techniques of Chemistry Series 22; Wiley-Interscience: New York, NY, 1992.

(8) Besenhard, J. O.; Fritz, H. P. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 950–975.

(9) Friberg, S. *Adv. Colloid Interface Sci.* **1990**, *32*, 167–182.

(10) Rusling, J. F. In *Modern Aspects of Electrochemistry*; Conway, B. E., Bockris, J. O'M., Eds.; Plenum Press: New York, NY, 1994; No. 26, pp 49–104.

(11) Bourrel, M.; Schechter, R. S. *Microemulsions and Related Systems*; Marcel Dekker: New York, NY, 1988.

(12) Zhou, D.-L.; Carrero, H.; Rusling, J. F. *Langmuir* **1996**, *12*, 3067–3074.

(13) Gao, J.; Rusling, J. F.; Zhou, D.-L. *J. Org. Chem.* **1996**, *61*, 5972–5977.

(14) (a) Gao, J.; Rusling, J. F. *J. Org. Chem.* **1998**, *63*, 218–219. (b) Carrero, H.; Gao, J.; Rusling, J. F.; Lee, C. W.; Fry, A. J. *J. Org. Chem.*, submitted.

(15) Zhou, D.-L.; Gao, J.; Rusling, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 1127–1134.

(16) Nassar, A.-E. F.; Bobbitt, J. M.; Stuart, J. D.; Rusling, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 10986–10993.

(17) Mbindyo, J. K. N.; Rusling, J. F. *Langmuir* **1998**, *14*, 7027–7033.

(18) Osa, T.; Kashiwagi, Y.; Bobbitt, J. M.; Ma, Z. In *Electroorganic Synthesis [Manuel M. Baizer Memorial Symposium]*; Little, R. D., Weinberg, N. L., Eds.; Dekker: New York, NY, 1991; pp 343–54.

(19) Boehm, H.-P. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 533–544.

(20) Bobbitt, J. M.; Yagi, H.; Shibuya, S.; Stock, J. T. *J. Org. Chem.* **1971**, *36*, 3006–3010.

deposit electroactive films onto carbon.^{5–7,18} Since the amount of mediator may limit reaction kinetics,²² polymer-coated electrodes containing more than a monolayer of catalytic sites have also been explored.^{6,7,18}

To achieve stability in microemulsions with their high dissolving power, a viable approach might feature a porous catalytic scaffold held onto the carbon surface by covalent bonds. Multiple functional groups on a polymer can be used to make bonds to the carbon surface and also to link to catalyst molecules. By grafting different mediators onto these films, electrodes might be designed for a variety of catalytic syntheses. This paper reports our first exploration of this approach for the fabrication of films suitable for catalytic electrochemical synthesis in microemulsions.

Vitamin B₁₂ and other cobalt complexes catalyze many organic reactions,^{2,3,12–15,23–26} including carbon–carbon bond formation essential for the synthesis of complex organic molecules. The key step is reduction of the cobalt complex to Co^IL (L = ligand), which acts as a highly efficient reductant or nucleophile, as the synthesis requires. Scheffold et al. deposited polymerized *m*-phenylenediamine-vitamin B₁₂ onto carbon electrodes²⁷ and used them for synthesis in organic solvents. These films had no covalent links to the electrode surface.

Films of polylysine (PLL) and its derivatives on electrodes have been investigated,²⁸ but to our knowledge no reports of covalent binding to electrodes have appeared. Grimshaw et al. studied electroactive derivatives of PLL, some of which gave unstable films on electrodes in organic solvents.^{28a–c} Protonated PLL layers were used as models to study charge transport^{28d} and to electrostatically bind negatively charged redox proteins for reversible voltammetry.^{28e–g}

In this paper, we describe covalent attachment of vitamin B₁₂ hexacarboxylate 8-aminocobyrinic acid *c*-lactam [B₁₂(COOH)₆] (see below) onto poly-L-lysine which had been covalently bound to graphite electrodes, yielding a fully covalently linked ionic polymer coating which is relatively stable in microemulsions. Pyrolytic graphite (PG) electrodes coated with PLL–B₁₂(COOH)₆ gave reversible electrochemical production of the catalytically active Co^IL form. Reductive dehalogenations and carbon–carbon bond formation were efficiently catalyzed by these films in water and microemulsions.

Experimental Section

Chemicals and Solutions. Poly-L-lysine hydrobromide (average MW 150 000–300 000) was from Aldrich. 1-[3-(Dimethylamino)propyl]-

(21) McCreery, R. L. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, NY, 1991; Vol. 17, pp 221–374.

(22) Andrieux, C. P.; Savéant, J.-M. In *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Techniques of Chemistry Series 22; Wiley-Interscience: New York, NY, 1992; pp 207–270.

(23) Scheffold, R.; Rytz, G.; Walder, L.; Orlinski, R.; Chilmoneczyk, Z. *Pure Appl. Chem.* **1983**, *55*, 1791–1797.

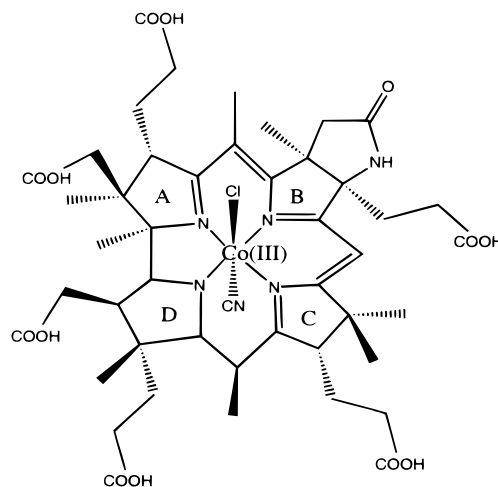
(24) Scheffold, R.; Abrecht, S.; Orlinski, R.; Ruf, H.-R.; Stamouli, P.; Tinembert, O.; Walder, L.; Weymuth, C. *Pure Appl. Chem.* **1987**, *59*, 363–372.

(25) Scheffold, R. *Chimia* **1985**, *39*, 203–211.

(26) Torii, S.; Inokuchi, T.; Yukawa, T. *J. Org. Chem.* **1985**, *50*, 5875–5877.

(27) Ruhe, A.; Walder, L.; Scheffold, R. *Helv. Chim. Acta* **1985**, *68*, 1301–1311.

(28) (a) Abeysekera, A. M.; Grimshaw, J.; Perera, S. D.; Vipond, D. J. *Chem. Soc., Perkin Trans. 2* **1989**, 43–51. (b) Grimshaw, J.; Perera, S. D. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1711–1718. (c) Abeysekera, A. M.; Grimshaw, J.; Perera, S. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1797–1800. (d) Anson, F. C.; Saveant, J.-M.; Shigehara, K. *J. Am. Chem. Soc.* **1983**, *105*, 1096–1106. (e) Bianco, P.; Haladjian, J.; Giannandrea-Derocles, S. *Electroanalysis* **1994**, *6*, 67–74. (f) Taniguchi, I. *Electrochem. Soc. Interface* **1997**, *6*, 34–37. (g) Glenn, J. D. H.; Bowden, E. F. *Chem. Lett.* **1996**, 399–400.



Structure of B₁₂(COOH)₆

3-ethylcarbodiimide hydrochloride (EDC·HCl) was from Fluka (Bio-Chemika) or Aldrich (98+%). B₁₂(COOH)₆ was synthesized as described previously.²⁹ Trichloroacetic acid (TCA), ethylene dibromide (1,2-dibromoethane, EDB, >99%), and *trans*-1,2-dibromocyclohexane (DBCH, 99%) were from Aldrich. Ordinary pyrolytic graphite (HPG-99) was from Union Carbide. Water was purified by an Hydro Nanopure system to specific resistance >15 MΩ·cm. α-Al₂O₃ (0.05 μm) was from Buehler. Cetyltrimethylammonium bromide (CTAB, 99%) and sodium dodecyl sulfate (SDS, 99%) were from Acros. All other chemicals were reagent grade.

Microemulsions were prepared by mixing components by weight: (1) 5% CTAB/5.4% *n*-pentanol/1% hexadecane/88.6% H₂O, oil-in-water;³⁰ and (2) 13.3% SDS/26.7% *n*-pentanol/8.0% tetradecane/52.0% 0.1 M NaCl(aq), bicontinuous.³¹

Coating of Electrodes. PG disk electrodes (*A* = 0.16 cm²) were constructed as previously described¹⁵ and polished with 0.05-μm α-Al₂O₃ slurry on a nylon polishing cloth (Mark V Lab, No. NC2A), followed by washing and sonication in water. Electrodes were oxidized in aqueous 2.5% K₂Cr₂O₇/10% HNO₃ by scanning once from 1.5 to 1.7 V vs saturated calomel electrode (SCE) at 5 mV s⁻¹. After the electrodes were rinsed in water, the following solutions were deposited uniformly onto the surface with a microsyringe: 5 μL of 24 mM aqueous EDC,³² and then after 20 min, 5 μL of PLL solution (4 mM in lysine residues). After the electrodes were left to stand at room temperature for 4–18 h, 5 μL each of 1 mM B₁₂(COOH)₆ and 24 mM EDC were deposited onto the electrode. Each electrode was covered with a small vial during drying, which improved film uniformity. After 8–24 h at room temperature, the electrodes were washed with water. No significant differences in voltammetry were found for electrodes prepared within the above reaction time ranges.

Large-scale electrolyses were done on 2.5- × 7-cm carbon cloth (National Electrical Carbon Corp.) cathodes in a divided cell with SCE reference and carbon rod counter electrodes. The cathode was oxidized in aqueous 2.5% K₂Cr₂O₇/10% HNO₃ by scanning four times from 1.5 to 1.7 V vs SCE at 5 mV s⁻¹. After being rinsed in water, the electrode was immersed for 30 min in 24 mM EDC, transferred to PLL solution (4 mM of lysine residues), and left to stand overnight. This electrode was then immersed for 30 min in 24 mM EDC, transferred to 2 mM B₁₂(COOH)₆, and left to stand overnight. This coated electrode was rinsed with water and then with the microemulsion to be used. Analysis of reaction mixtures by gas chromatography was described previously.¹⁷

(29) Miauw, C.-L.; Hu, N.; Bobbitt, J. M.; Ma, Z.; Ahmadi, M. F.; Rusling, J. F. *Langmuir* **1993**, *9*, 315–322.

(30) See Supporting Information.

(31) Georges, J.; Chen, J. W. *Colloid Polym. Sci.* **1986**, *264*, 896–902.

(32) (a) When water is used as the solvent, preparation of fresh EDC solution just prior to use is necessary, since carbodiimide reacts slowly with water to form the corresponding urea. (b) Protonated PLL will not form stable adsorbed layers on oxidized PG surfaces; EDC was necessary for binding.

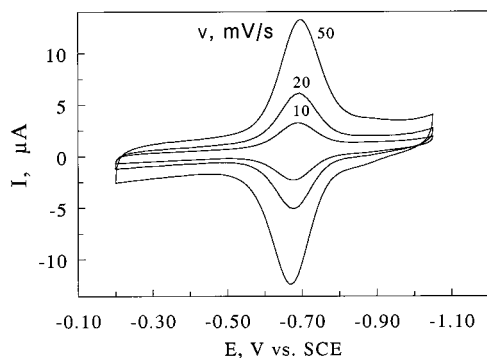


Figure 1. Cyclic voltammograms of PLL-B₁₂(COOH)₆ on a PG electrode at varying scan rates in pH 7.1 Tris buffer (5 mM) + 45 mM NaCl.

Voltammetry (25 ± 0.2 °C) and controlled potential electrolysis (20 ± 0.2 °C) were done with BAS-100B/W (Bioanalytical Systems) or PARC 273 electrochemical analyzers using three-electrode water-jacketed cells featuring an SCE reference, as described previously.¹⁵ Ohmic drop was fully compensated in voltammetry. For illumination of electrodes, a 100-W visible lamp was placed under the water-jacketed glass cell, with a metal cylinder directing the light to the underside of the cell.

Results

Pretreatment of PG. Electrode surfaces were relatively hydrophobic after polishing, as shown by beading of surface water droplets. After oxidation (see Experimental Section), water droplets spread and wet the surface, suggesting increased hydrophilicity from carboxyl and other oxygenated groups on the surface.^{8,21} Catalytic coatings prepared with oxidized graphite surfaces were significantly more stable and reproducible than those without surface oxidation.

Voltammetry. Cyclic voltammograms (CV) of PLL-B₁₂(COOH)₆ on PG electrodes were reproducible on second and subsequent scans.³³ All results are reported for this steady-state case. PLL-B₁₂(COOH)₆ electrodes in pH 7.1 buffer gave symmetric pairs of reduction-oxidation peaks near -0.7 V vs SCE with small peak separations at low scan rates (Figure 1). This potential is in the range^{17,29} of the formal potential of Co(II)/Co(I) B₁₂(COOH)₆ dissolved in aqueous solutions and microemulsions. Square wave voltammetry (SWV) and CV also revealed a broad, poorly reversible peak at about 0 V vs SCE (Figure 2), which is in a potential range similar to that of the Co(III)/Co(II) redox couple of B₁₂(COOH)₆ in solution.^{17,29} Thus, reversible peaks at more negative potentials in CV and SWV were assigned to the Co(II)/Co(I) redox couple, the key for mediating synthetic reactions and the main focus of this paper.

Voltammetric scans for PLL-B₁₂(COOH)₆ films in the CTAB and SDS microemulsions (Figure 3) were similar to those in aqueous buffers (Table 1). CV reduction and oxidation peak currents in pH 7.1 buffer and microemulsions were equal and proportional to scan rate from 5 to 50 mV s⁻¹. These data and the symmetric CV peaks are characteristic⁶ of surface-confined electrochemistry. As the scan rate increased above about 20 mV s⁻¹, peak separations became larger (see Supporting Information).

(33) During initial scans, films equilibrate with the fluid medium, as evidenced by a significant increase in cell RC (resistance-capacitance) time constant with a constant R, estimated by using the Auto *iR* Comp function of the BAS-100B/W. While R values varied significantly from film to film (75–140 Ω), a typical example had RC = 1150 ms, R = 108 Ω before scanning, and RC = 1550 ms, R = 108 Ω after one scan. Successive scanning after the first did not change RC or R significantly.

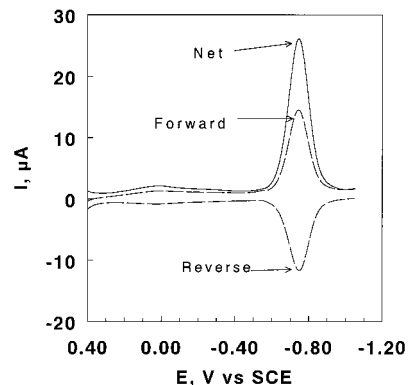


Figure 2. Square-wave voltammograms of PLL-B₁₂(COOH)₆ on a PG electrode in pH 7.1 Tris buffer (5 mM) + 45 mM NaCl. SWV at 5 Hz, 15 mV pulse height. Solid line is net current, and dashed lines are forward and reverse SWV currents.

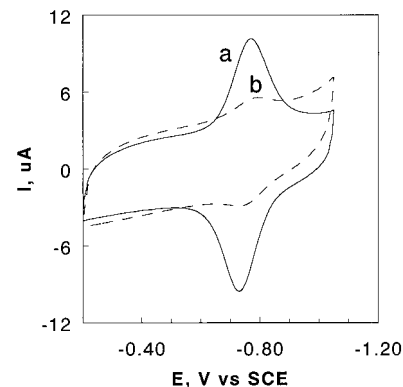


Figure 3. Steady-state cyclic voltammograms at 50 mV s⁻¹ in the 5% CTAB microemulsion for (a) PLL-B₁₂(COOH)₆ film prepared with the full covalent bonding procedure (see Experimental Section) and (b) PLL film prepared by procedure omitting EDC from the final B₁₂(COOH)₆ deposition step.

Table 1. Co(II)/Co(I) Formal Potentials and Surface Concentrations^a of PLL-B₁₂(COOH)₆ Films

fluid medium	no. of electrodes	no. of trials ^b	-E ^o , V vs SCE	Γ _o , nmol cm ⁻²	ΔE _p , mV ^c
water, pH 7.1	7	3–17	0.73 ± 0.06	1.88 ± 0.55	20 ± 10
5% CTAB μE	3	3	0.75 ± 0.02	0.99 ± 0.09	30 ± 9
13% SDS μE	3	3	0.66 ± 0.04	1.10 ± 0.09	28 ± 5

^a Data from CV at 10–20 mV s⁻¹. ^b Number of CVs averaged per electrode. ^c Reduction-oxidation peak separation.

The amount of electroactive catalyst in the films was estimated by integrating Co(II) reduction peaks and applying Faraday's law, yielding surface concentration Γ_o of B₁₂(COOH)₆ in nmol cm⁻². In the microemulsions, Γ_o was roughly two-thirds that in pH 7.1 buffer (Table 1). Reduction and oxidation peak separations were slightly smaller in the buffer than those in microemulsions.

Data in Table 1 illustrate film-to-film reproducibility of the preparation method. The amount of electroactive catalyst bound onto the electrode was reproducible within ±10% for films in microemulsions and within ±25% in buffer. Reproducibility of formal potentials, estimated as midpoint potentials between oxidation and reduction peaks, was ±60 mV in buffer, and slightly better in microemulsions.

To assess the effect of covalent bonding on catalyst loading and stability, we compared films made by the full PLL-B₁₂(COOH)₆ preparation method using EDC linkage to those made by a procedure in which EDC was omitted from the final

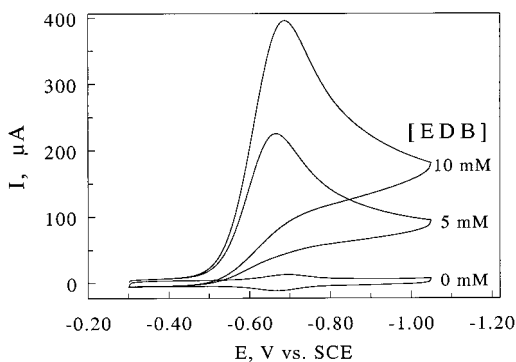


Figure 4. Cyclic voltammograms of PLL-B₁₂(COOH)₆ at 50 mV s⁻¹ in pH 7.1 Tris buffer (5 mM) + 45 mM NaCl, with dibromoethane [EDB] = 0, 5, and 10 mM. Direct reduction of EDB occurred at -1.76 V vs SCE on bare PG (see Supporting Information).

B₁₂(COOH)₆ linkage step. Without EDC, inclusion of B₁₂(COOH)₆ into the PLL film may still result from Coulombic interactions. However, as illustrated in the 5% CTAB microemulsion (Figure 3), the peak current of the steady-state CV in microemulsions was much larger when the full covalent bonding procedure was used compared to that when the final attachment of B₁₂(COOH)₆ was done without EDC. This result was similar in the SDS microemulsion, suggesting that covalent bonding of PLL amine groups to B₁₂(COOH)₆ provides efficient and stable catalyst loading onto the PLL layer.

PLL-B₁₂(COOH)₆ electrodes were stored in air, pH 7.1 buffer, or microemulsions. During continuous potential cycling in microemulsions, peak currents decreased 20% after 200 scans in the CTAB microemulsion, and 14% in the SDS microemulsion. Average decreases in reduction peak current upon storage in fluids were as follows: 6% after 5 days in pH 7.1 buffer, 37% after 5 days in CTAB microemulsion, and 37% after 4 days in SDS microemulsion. PLL-B₁₂(COOH)₆ electrodes stored in air degraded about twice as fast as electrodes stored in the pH 7.1 TRIS buffer.

Electrochemical Catalysis. Dehalogenation of trichloroacetic acid,³⁴ dibromoethane,³⁵ and 1,2-dibromocyclohexane^{15,35} and the alkylation of an activated olefin¹³ were used to evaluate the catalytic utility of PLL-B₁₂(COOH)₆ electrodes. Trichloroacetic acid and dibromoethane are sufficiently soluble for catalytic studies in water, but debromination of dibromocyclohexane and the alkylation reaction could be studied only in microemulsions because of low solubility in water. Almost no current for the Co(II)/Co(I) reaction was observed for the PLL-B₁₂(COOH)₆ films in common organic solvents, so catalytic reactions were not investigated in them.

When dibromoethane was added to solutions bathing PLL-B₁₂(COOH)₆ electrodes, a large increase of the Co(II) reduction current was observed (Figure 4). The Co(I) oxidation current disappeared, and the new reduction peak current was proportional to the concentration of dibromoethane.³⁶ The ratio of this new reduction peak's height to the reversible Co(II) reduction peak height decreased as scan rate increased. Dibromoethane was reduced directly on a bare PG electrode in pH 7.1 buffer at about -1.76 V. All these results are characteristic^{6,7} of

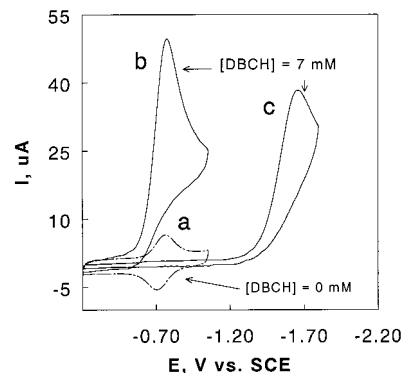


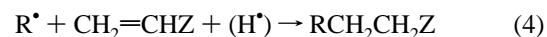
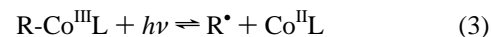
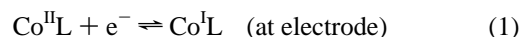
Figure 5. Cyclic voltammograms at 50 mV s⁻¹ in 5% CTAB microemulsion with (a) 0 mM DBCH and PLL-B₁₂(COOH)₆, (b) 7 mM DBCH and PLL-B₁₂(COOH)₆, and (c) 7 mM DBCH on bare PG.

electrochemical catalysis of the reduction of dibromoethane to ethylene¹⁶ via the active Co^IL reductant. The 1.08-V positive shift in the peak potential represents a large decrease in the activation energy due to catalysis of the reduction of dibromoethane. CV in the presence of trichloroacetic acid also showed clear evidence of catalytic reduction by the PLL-B₁₂(COOH)₆ films (see Supporting Information).

CV provided evidence of catalytic reduction of all organohalides studied in the two microemulsions. Figure 5 shows typical CV traces illustrating catalytic debromination on coated electrodes after DBCH was added to the CTAB microemulsion. Figure 6 shows similar data upon addition of TCA to the SDS microemulsion. In both cases, large catalytic reduction peaks are observed along with the disappearance of peaks for Co^IL oxidation. The shift of peak potential due to catalysis was 0.75 V for trichloroacetic acid and 0.90 V for 1,2-dibromocyclohexane.

Reactions of Co(I) vitamin B₁₂ derivatives with *n*-alkyl halides give alkylcobalt [R-Co^{III}L] intermediates. These organometallic complexes are stable in the dark when the electrode is held at the potential of formation of the Co(I) complex.³ Visible light cleaves R-Co^{III}L to give alkyl radical R[•], and Co^{II}L. R[•] can be trapped by activated olefin CH₂=CHZ (Scheme 1), where Z is an electron-withdrawing group.

Scheme 1. Pathway for Mediated C-C Bond Formation



We investigated the possibility of catalyzing such reactions with PLL-B₁₂(COOH)₆ films. On the first CV scan after addition of an alkyl iodide to a microemulsion, the oxidation peak decreased. Upon multiple scans, both reduction and oxidation peaks decreased (Figure 7). This suggests that most of the cobalt in the film has been converted to R-Co^{III}L, which is not electroactive at the Co(II)/Co(I) redox potential. Activated olefin 2-cyclohexen-1-one was then added to the microemulsion, and the electrode was illuminated with visible light in the thermostated cell to cleave R-Co^{III}L and trap R[•] by alkylation of 2-cyclohexen-1-one. Following this, the electrode was washed with microemulsion and placed in fresh microemulsion free of reactants. The next CV scan gave much larger peaks, approaching the heights of those of the original scan (Figure 7). This experiment suggests that R-Co^{III}L forms in the film, and that it

(34) Rusling, J. F.; Miaw, C. L.; Couture, E. C. *Inorg. Chem.* **1990**, *29*, 2025-2027.

(35) Owlia, A.; Wang, Z.; Rusling, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 5091-5098.

(36) Upon addition of EDB to the solution, the peak current increased as the contact time of the coating electrode with the solution increased until it reached a constant value. This may be related to slow permeation of EDB into the film. When the more hydrophilic trichloroacetic acid was used, no such growth of maximum catalytic current was observed.

Table 2. Data for Reductive Debromination of DBCH Using Different Catalytic Systems

electrode/catalyst	μE	initial DBCH, ^a μmol	time, h	catalyst, μmol	cyclohexene found, μmol	DBCH found, μmol	conversion, %	turnover no., ^b h^{-1}	ref.
C-cloth/PLL-B ₁₂ (COOH) ₆	SDS	120	0.5	0.5	86.4	15.6	83	340	this work
C-cloth/PLL-B ₁₂ (COOH) ₆	CTAB	120	2.0	0.12	75.6	39.6	94	320	this work
C-felt/Vit. B _{12a} dissolved in μE	CTAB	86.4	0.5	8	77	2.7	92	19	17
TiO ₂ /B ₁₂ (COOH) ₆ ^c	CTAB	98.4	13	0.06	80	7.3	89	100	17

^a DBCH = dibromocyclohexane. Microemulsions electrolyzed at -0.90 V vs SCE (10–12 mL) for the C-felt and TiO₂ electrodes, and -0.75 V vs SCE (12 mL) for the C-cloth/PLL-B₁₂(COOH)₆ electrodes; product analysis by gas chromatography, up to 15% of the products may be lost by evaporation.¹⁷ ^b Mole of products per mole of catalyst per hour. ^c B₁₂(COOH)₆ chemisorbed to nanocrystalline TiO₂ electrodes.

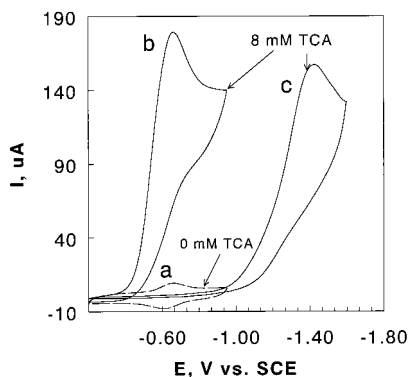


Figure 6. Cyclic voltammograms at 50 mV s^{-1} in 13.3% SDS microemulsion with (a) 0 mM TCA and PLL-B₁₂(COOH)₆, (b) 8 mM TCA and PLL-B₁₂(COOH)₆, and (c) 8 mM TCA on bare PG.

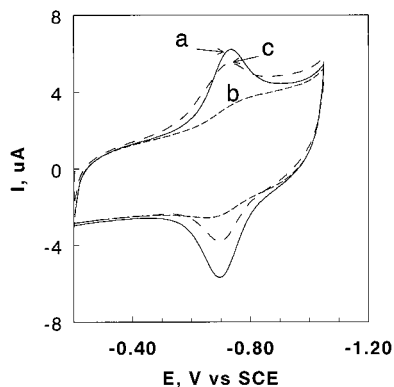


Figure 7. Cyclic voltammograms at 50 mV s^{-1} in 13.3% SDS microemulsion (a) PLL-B₁₂(COOH)₆ film with no butyl iodide present, (b) sixth repetitive scan in microemulsion containing 1 mM butyl iodide, and (c) after washing electrode with microemulsion, transferring to microemulsion containing 4.8 mM 2-cyclohexen-1-one, photolysis with visible light for 10 min, and then washing with microemulsion and transferring to fresh microemulsion which was free of all reactants.

can be cleaved with light and trapped via C–C bond formation. Similar results were obtained in CTAB and SDS microemulsions and when dodecyl iodide instead of butyl iodide was used as the alkylating agent.

Reduction of DBCH to Cyclohexene. Controlled potential electrolysis of DBCH was done on carbon cloth electrodes coated with PLL-B₁₂(COOH)₆. Table 2 compares analytical results of these electrolyses with results for those catalyzed by using vitamin B₁₂ dissolved in the CTAB microemulsion or with B₁₂(COOH)₆ chemisorbed onto a nanocrystalline TiO₂ cathode. Turnover numbers for PLL-B₁₂(COOH)₆ electrodes did not depend on the type of surfactant in the microemulsion (μE). Turnover numbers for PLL-B₁₂(COOH)₆ were 3-fold larger than those for TiO₂-B₁₂(COOH)₆ and 17-fold larger than those for vitamin B₁₂ dissolved in the CTAB microemulsion. Furthermore, the time required for roughly 90% reaction of starting

material was 0.5–2 h for PLL-B₁₂(COOH)₆, compared to 13 h for the TiO₂-B₁₂(COOH)₆ system.

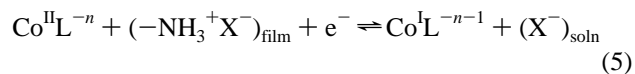
Discussion

Voltammetry of Co^{II}L/Co^IL. PLL-B₁₂(COOH)₆ films gave reversible voltammetry for the Co(II)/Co(I) redox couple in buffer (Figures 1 and 2) and in microemulsions (Figure 3, Table 1). SWV (Figure 2) supported the identity of the Co(II)/Co(I) peak by revealing broad, quasireversible peaks at 0 V attributed to the Co(III)/Co(II) couple.

Comparison of CVs of films prepared with and without covalent linkage of B₁₂(COOH)₆ (Figure 3) to PLL amine groups clearly shows the benefits of the chemical bonding in larger peak currents in the microemulsions. Results suggest much better catalyst loading or stability in microemulsions when using the full covalent bonding procedure compared to those using electrostatic binding.

While some losses of catalyst were observed under operating conditions, CV peak heights after 4–5 days of storage of films in microemulsions were >60% of the initial values. Only 6% of the peak height was lost in 5 days in pH 7.1 buffer, suggesting that the electrodes can be stored in buffer for several days without significant catalyst loss.

Differences in formal potentials of Co(II)/Co(I) in the films in microemulsions and buffer (Table 1) may stem from differences in electrolyte concentration and interactions between the redox site and the polymer matrix mediated by fluid components.⁷ Estimates of amounts of lysine residues and catalyst (from integration of CVs) suggest the presence of significant unreacted lysines in the catalytic films. Since the pK of lysine is 10.5, at pH 7 and in microemulsions, protonated amines will reside in the film and be partly neutralized by negative counterions. Following a model proposed for polymer-coated electrodes and verified for cationic metal complexes in films of Nafion,³⁷ we consider the oversimplified half-reaction:



where X[−] is an electroinactive counterion which exits the film upon reduction of Co^{II}L^{−n} to maintain charge neutrality, and $-n$ is the total charge on the cobalt complex site. Thus, the apparent formal potential (E_{app}°) of the redox couple in the film is

$$E_{\text{app}}^{\circ} = E_{\text{film}}^{\circ} + \frac{RT}{F} \ln \left(\frac{[\text{X}^-]_{\text{film}}}{[\text{X}^-]_{\text{soln}}} \right) \quad (6)$$

where E_{film}° is the formal potential of the redox sites in the film,

(37) Naegeli, R.; Redepenning, J.; Anson, F. C. *J. Phys. Chem.* **1986**, *90*, 6227–6232.

R , T , and F have their usual electrochemical meanings, and the concentration ratio refers to X^- in film and solution, respectively.

Equation 6 can be used to rationalize experimental $E_{app}^{\circ'}$ values obtained in the three fluids (Table 1). Halide ion concentrations are 0.05 M in the buffer and about 0.14 M in the CTAB microemulsion. Assuming that $[X^-]_{film}$ is about the same for films in both fluids and neglecting CTA^+ interactions with the polymer network, eq 6 predicts that $E_{app}^{\circ'}$ should be -27 mV in the CTAB microemulsion with respect to the buffer. The experimental difference of -20 mV is in reasonable agreement.^{38a}

The SDS concentration in the SDS microemulsion is 0.45 M with chloride at 0.05 M, but the shift in $E_{app}^{\circ'}$ with respect to the buffer is $+70$ mV. In this case, we suggest that the known phenomenon of micellization within the polymer film network³⁹ occurs under the driving force of Coulombic interactions between protonated lysine residues and dodecyl sulfate ions. Film properties can be drastically changed by micellization in a polymer film.³⁹ Furthermore, the amount of counterions in the film in SDS microemulsions is likely to be much larger than that in the CTAB microemulsion or buffer solution. $[DS^-]_{film}/[DS^-]_{soln} > 1$ in eq 6 would tend to shift $E_{app}^{\circ'}$ relatively positive in the SDS microemulsion.^{38b}

The smaller Γ_o for the films in microemulsions (Table 1) may possibly be caused by restricted ion transport or polymer chain mobility. As mentioned, in aprotic solvents such as DMF and acetonitrile (containing electrolyte), *no CV peaks at all* were observed for PLL-B₁₂(COOH)₆ films that were electroactive in water, but full electroactivity was recovered after the electrode was returned to buffer. This drastic shutdown of electroactivity in organic solvents may result from severe inhibition of ion transport and/or redox center mobility.^{6,7} PLL is insoluble in these organic solvents, and we could envision a precipitation-like collapse of the film on the electrode surface in organic solvents. It is possible that the smaller Γ_o values observed for the films in microemulsions are the result of related phenomena.

Electrochemical Catalysis. Voltammetry in water and microemulsions (Figures 4–6) showed that PLL-B₁₂(COOH)₆ films are catalytically active for the reduction of trichloroacetic acid and vicinal dibromides. Large catalytic currents were observed, and positive shifts in the potential for catalytic

(38) (a) Negative shifts in $E_{app}^{\circ'}$ with increasing $[X^-]_{soln}$ were also observed in aqueous buffer and CTAB solutions. (b) Positive shifts in $E_{app}^{\circ'}$ with increasing $[DS^-]_{soln}$ were found in aqueous SDS solutions. Surfactant effects on $E_{app}^{\circ'}$ are under further study.

(39) Hansson, P.; Lindman, B. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 604–613.

organohalide reductions were 0.75 to 1.08 V, reflecting large decreases in activation free energy resulting from the catalysis. Microemulsions extend the range of possible reactants to water-insoluble compounds such as 1,2-dibromocyclohexane.

CV monitoring of the light-assisted reaction of alkyl-Co(III) complexes with 2-cyclohexen-1-one (Figure 7) suggested that the films mediate this alkylation. The decrease in Co(II)/Co(I) peaks upon repetitive cycling in the presence of alkylidides is consistent with storage of Co as R-Co^{III}L, via reactions in eqs 1 and 2 in Scheme 1. Photolysis with visible light with 2-cyclohexen-1-one present leads to significant recovery of the Co(II)/Co(I) peaks, suggesting cleavage of R-Co^{III}L to yield Co^{II}L (eq 3). Trapping of the radical (eq 4) must occur to inhibit the back reaction and produce Co^{II}L.

Electrochemical catalytic debromination of DBCH using PLL-B₁₂(COOH)₆ gave excellent yields of cyclohexene in short electrolysis times (Table 2). Based on turnover numbers, PLL-B₁₂(COOH)₆ was 3 times more active than B₁₂(COOH)₆ on nanocrystalline TiO₂, and 17 times more active than vitamin B₁₂ dissolved in a microemulsion. Little difference in catalytic activity was found in the two microemulsions. Results suggest the promise of PLL-B₁₂(COOH)₆ films for synthetic applications.

Conclusions

Films made by linking vitamin B₁₂ hexacarboxylic acid to polylysine covalently attached to graphite electrodes gave reversible Co(II)/Co(I) voltammetry and were reasonably stable for 4–5 days in microemulsions. The procedure should be suitable for covalently attaching a variety of coatings onto graphite surfaces. PLL-B₁₂(COOH)₆ films were active for dehalogenation of several organohalides in water and microemulsions and for alkylation of an activated olefin in microemulsions. Turnover numbers for conversion of DBCH to cyclohexene in microemulsions were 3-fold larger than those for another catalytic electrode, nanocrystalline TiO₂, utilizing the same cobalt catalyst.

Acknowledgment. This work was supported by Grant No. CTS-9632391 from NSF. The authors thank Dr. Chunnian Shi for helpful discussion.

Supporting Information Available: Data on characterization of CTAB microemulsion and 10 additional figures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>. JA984178L

JA984178L