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The First Surface-Attached Catenane: Self-Assembly of a Two-Component Monolayer

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We report here the two-point anchoring of a charge-transfer complex to a gold surface that results in the formation of an interfacial structure containing two mechanically interlocked components. This structure can be viewed as a catenane in which one of the intertwined macrocycles is closed by the attachment to the electrode surface.

The self-assembly of organosulfur compounds on gold surfaces has become a mature field of chemical research.[1] A large number of self-assembled monolayer structures on gold[2] and other surfaces[3] have been reported during the last five years. A few examples of selective ion or molecular recognition by self-assembled monolayers containing appropriately designed binding sites have been recently described.[4] Our approach, inspired by Stoddart's work,[5] is based on the templating and directing effects exerted by noncovalent, charge-transfer interactions between π-donor aromatic subunits and a cyclophane (compound $\mathbf{1}^{4+}$) which has a strong π-acceptor character.[6] We reasoned that these interactions could also be utilized in the construction of surface-attached molecular assemblies. For instance, the bis(thiol) hydroquinol derivative[7] **2** is complexed by $\mathbf{1}^{4+}$ due to the π-donor character of the aromatic nucleus of **2**. The charge-transfer complex was easily detected in acetonitrile (MeCN) using visible spectroscopy (λ_{max} = 460 nm). The equilibrium binding constant was determined to be 253 ± 12 M^{-1} at 25 °C in this solvent.[8] ^{1}H-NMR spectra clearly indicate that the complex is of the inclusion type. When it is bound, the aromatic nucleus of compound **2** threads the cavity of the tetracationic receptor so that the thiol-terminated side chains project out at different sides of the cavity. Related structures have been reported with analogs of **2** possessing terminal alcohol groups instead of thiol groups.[5b] In the case of **2**, the well-known affinity of the thiol groups for gold makes anchoring of the inclusion charge-transfer complex to a gold surface possible. The two-point surface attachment closes the hydroquinol molecular "cycle", generating a structure that can be viewed as a catenane in which the gold surface is an integral component of one of the two in-

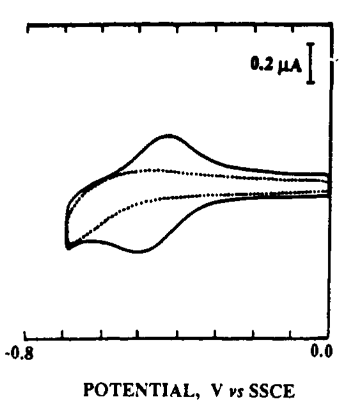
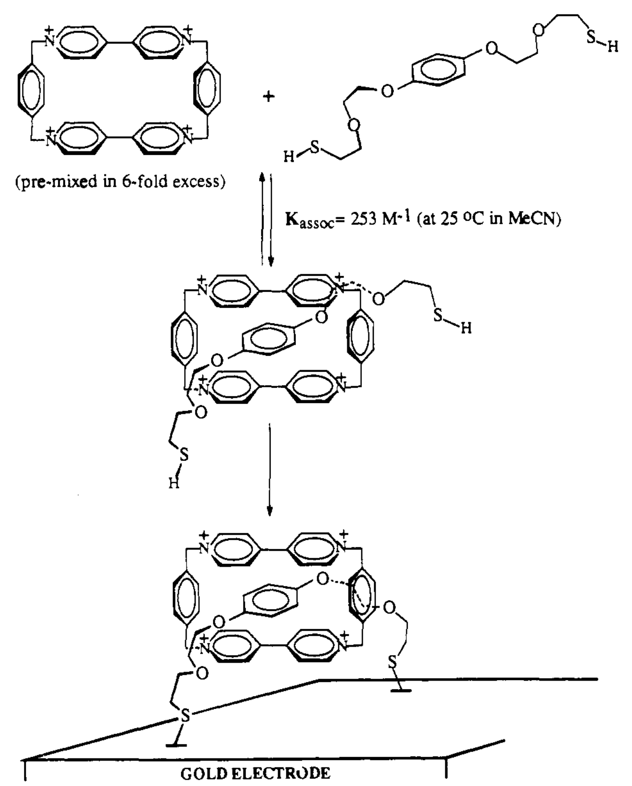


Figure 1. Cyclic voltammetric response (at 200 mV/s) of monolayer-covered gold electrodes in 0.1 M Na_2SO_4. The continuous line voltammogram was obtained as follows: A clean gold bead electrode was immersed for 24 h in a deoxygenated acetonitrile–methanol solution (3:2 v/v) containing 4.8 mM $\mathbf{1}^{4+}$ and 0.8 mM **2**. Then the electrode was rinsed with acetonitrile and purified water and finally immersed in 0.1 M Na_2SO_4 for voltammetric analysis. The dotted line voltammogram was obtained following the same treatment but replacing bis(thiol) **2** by monothiol **3**.

Scheme I



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(1) See, for example: (a) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *101*, 522. (b) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87.

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(7) Compounds **2** and **3** were synthesized by thiolation of the corresponding terminal chloride derivatives with thiourea. ^{1}H NMR for **2** (400 MHz, $CDCl_3$): 1.60 (t, 2 H), 2.74 (q, 4 H), 3.68 (t, 4 H), 3.82 (t, 4 H), 6.83 (s, 4 H) ppm. Anal. Calcd for $C_{14}H_{22}O_4S_2$: C, 52.81; H, 6.96; S, 20.14. Found: C, 52.88; H, 7.00; S, 20.00. ^{1}H NMR for **3** (400 MHz, $CDCl_3$): 1.60 (t, 1 H), 2.73 (q, 2 H), 3.67 (t, 2 H), 3.76 (s, 3 H), 3.82 (t, 2 H), 4.08 (t, 2 H), 6.84 (q, 4 H) ppm. Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.87; H, 7.06; S, 14.04. Found: C, 57.63; H, 7.13; S, 14.07.

(8) All binding constants were determined using a previously reported method. See: (a) Goodnow, T. T.; Reddington, M. V.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 4335. (b) Bernardo, A. R.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* **1992**, *114*, 10624.

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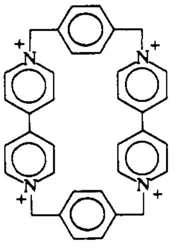
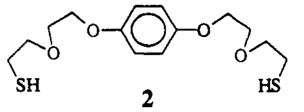
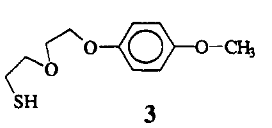
tertwined macrocycles (see Scheme I). The second macrocyclic component is provided by cyclophane **1**$^{4+}$, which is *indirectly, but irreversibly, attached to the electrode surface through its mechanical linkage to the hydroquinol ring.*



1^{4+}



2



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The confinement of **1**$^{4+}$ to the electrode surface was verified using electrochemical methods. Clean gold bead electrodes were first exposed overnight to a deoxygenated MeCN solution[9] containing both **2** and **1**$^{4+}$, rinsed extensively with MeCN and highly purified water, and immersed in deoxygenated aqueous 0.1 M Na_2SO_4 for voltammetric analysis. Figure 1 shows a typical cyclic voltammogram obtained with an electrode treated in this way. The voltammetric response confirmed the presence of surface-confined viologen groups. The set of waves centered around −0.46 V vs SSCE is consistent with the reversible monoelectronic reduction of the surface-confined viologen groups ($\Delta E_p \leq 40$ mV at scan rate ≤500 mV/s; linear i_{pc} vs scan rate plot). This voltammetric response was stable and did not exhibit significant changes after several hours of potential cycling. Furthermore, viologen reduction waves are observed only after the gold electrode is exposed to a solution containing both compounds (**2** and **1**$^{4+}$).[9] No faradaic response in the potential window of interest was observed if either one of these compounds was absent in the monolayer-forming solution. Similarly, exposing the gold electrode first to a solution of **2** and then to a solution of **1**$^{4+}$ does not result in the observation of reproducible surface-confined viologen waves. Experiments with monothiol hydroquinol **3** were particularly informative. This compound also forms an inclusion charge-transfer complex with **1**$^{4+}$ although the binding constant in MeCN at 25 °C was found to be lower (73 ± 5 M^{-1}) than the corresponding value for **2**. However, no viologen waves were detected in the voltammetric response of gold electrodes which were first exposed overnight to MeCN solutions containing **3** and **1**$^{4+}$, rinsed, and later transferred to the aqueous supporting electrolyte solution. The fact that one thiol group is not enough to afford surface-confined viologen groups clearly supports the formation of surface-attached catenanes in the case of the bis(thiol) **2**.

Assuming that the observed voltammetric waves correspond to a two-electron reduction per catenane species (monoelectronic reduction of each of the viologen groups),[10] the integration of the cathodic wave yields a value of (7.1 ± 1.6) × 10^{-12} mol/cm^2 (average of five independent determinations) for the surface coverage. This represents about 8% of the maximum coverage value (8.5 × 10^{-11} mol/cm^2) that is calculated using the catenane's molecular area (1.9 × 10^2 Å^2) estimated from molecular modeling methods.[11] That only a small fraction of the electrode surface is covered by the catenane structure is not unexpected, considering the complexity of the surface attachment process for this species.[12]

In conclusion, we have shown that *it is possible to utilize noncovalent intermolecular interactions, such as stacking forces between aromatic π-donor and π-acceptor subunits, to build catenane-like structures supported on gold surfaces.* This approach represents a significant contribution to the ongoing efforts to control molecular organization at the electrode solution interface.

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[9] The monolayer deposition solution contained a 6-fold molar excess of **1**$^{4+}$ to shift the equilibrium toward complex formation. Other experimental details are given in the figure caption.

[10] The reductive behavior of **1**$^{4+}$ in acetonitrile solution is essentially unchanged upon complexation of **2**. Voltammetric reduction takes place in two sequential two-electron steps for both the free tetracationic receptor and the complex.

[11] We used the software package PCMODEL, based on the MMX molecular mechanics field, as well as CPK models, to estimate the molecular area of the surface-attached catenane structure.

[12] We performed a variety of electrochemical experiments to assess the extent of blocking of the electrode surface. The results indicate that the gold surface is fully covered with organic material, suggesting that the portion of the surface not covered by catenane assemblies is derivatized by one- or two-point attachment of free **2**.

Novel Arene Complexes of Titanium(IV), Zirconium(IV), and Hafnium(IV)

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Although η^6-arene complexes of titanium, zirconium, and hafnium in lower oxidation states have been known for many years,[1] complexes of the d^0 tetravalent metals are extremely rare. To our knowledge, the only previously reported examples are cationic complexes of the type $[(\eta^6\text{-}C_6Me_6)MCl_3]^{+}$ [2a,b] and the zwitterionic compound $(\eta^6\text{-}C_6H_5BPh_3)Zr(CH_2Ph)_3$;[2c] a small number of analogous actinide complexes are also known.[2d-h] We now report the preparation of a novel homologous series of η^6-arene complexes of the type $[Cp^*MMe_2(\eta^6\text{-arene})][BMe(C_6F_5)_3]$ (M = Ti, Zr, Hf; Cp* = η^5-C_5Me_5; arene = benzene, toluene, mesitylene, and even styrene).

Treatment of solutions of Cp^*MMe_3[3a,b] (M = Zr, Hf) in toluene/hexanes (1:10) with equimolar amounts of $B(C_6F_5)_3$[4] results in the almost quantitative formation of yellow precipitates which, after being thoroughly washed and then dried in vacuo at 298 K, were identified on the basis of elemental analyses and spectroscopic properties as the cationic arene complexes $[Cp^*MMe_2(\eta^6\text{-PhMe})][BMe(C_6F_5)_3]$.[5] Apart from ^{1}H and

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[5] $[Cp^*ZrMe_2(\eta^6\text{-PhMe})][BMe(C_6F_5)_3]$: NMR ($CD_2Cl_2$ at 298 K) ^{1}H δ 7.78 (d, 2 H, *o*-H), 7.38 (t, 2 H, *m*-H), 7.04 (t, 1 H, *p*-H), 2.71 (s, 3 H, Ph*Me*), 1.96 (s, 15 H, Cp*), 0.48 (br s, 3 H, BMe), −0.11 (6 H, s, ZrMe); $^{13}C\{^1H\}$ δ 147.0 (toluene *ring C*), 134.8 (toluene *ring C*), 130.9 (toluene *ring C*), 129.2 (toluene *ring C*), 123.6 (Cp* *ring C*), 11.5 (Cp* *Me*), 45.5 (ZrMe), 22.4 (Ph*Me*), 10.2 (br s, BMe). Anal. Calcd for $C_{38}H_{32}BF_{15}Zr$: C, 52.12; H, 3.68. Found: C, 52.40; H, 3.75. $[Cp^*HfMe_2(\eta^6\text{-PhMe})][BMe(C_6F_5)_3]$: NMR ($CD_2Cl_2$ at 273 K) ^{1}H δ 7.55 (d, 2 H, *o*-H), 7.32 (t, 2 H, *m*-H), 7.28 (t, 1 H, *p*-H), 2.76 (s, 3 H, Ph*Me*), 2.10 (s, 15 H, Cp*), 0.56 (br s, 3 H, BMe), −0.28 (6 H, s, HfMe); $^{13}C\{^1H\}$ δ 146.8 (toluene *ring C*), 134.7 (toluene *ring C*), 130.5 (toluene *ring C*), 124.7 (toluene *ring C*), 121.7 (Cp* *ring C*), 46.5 (HfMe), 31.8 (Ph*Me*), 11.6 (Cp* *Me*), 10.2 (br s, BMe). Anal. Calcd for $C_{38}H_{32}BF_{15}Hf$: C, 47.38; H, 3.32. Found: C, 46.62; H, 3.41. Compare toluene: NMR (CD_2Cl_2 at 273 K) ^{1}H δ 7.23 (d, 2 H, *o*-H), 7.17 (t, 2 H, *m*-H), 7.13 (t, 1 H, *p*-H), 2.34 (s, 3 H, Me).

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