

A New Class of Self-Assembled Monolayers: *closo*-B₁₂H₁₁S³⁻ on Gold

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We report the fabrication of a new class of inorganic self-assembled monolayers (SAMs) prepared by the spontaneous adsorption of the polyhedral borane derivative, *closo*-B₁₂H₁₁S³⁻, onto gold. Although conventional SAMs composed of organothiolates have been widely heralded for their potential application in sensors and nanoelectronics, they have many undesirable characteristics; they oxidize easily upon exposure to air,^{1–4} decompose at moderately elevated temperatures,⁵ and desorb when immersed in organic solvents.^{6,7} Consequently, we have prepared and characterized *closo*-B₁₂H₁₁S³⁻ SAMs as potentially more robust alternatives capable of bringing structure–function relationships not available by other means to surface chemistry and nanoarchitectures.⁸ In this communication, we show that *closo*-B₁₂H₁₁S³⁻ monolayers form spontaneously when gold substrates are exposed to solutions of Cs₂[*closo*-B₁₂H₁₁SH]. We also demonstrate that the adsorption process is remarkably similar to that of organothiol self-assembly on gold; adsorption occurs through the sulfur atom and is accompanied by cleavage of the S–H bond and the formation of a strong polar covalent sulfur–gold bond. *closo*-B₁₂H₁₁S³⁻ monolayers represent a new class of SAMs that extend self-assembly and thin film architectures into previously unexplored areas of structure and bonding.

The *closo*-B₁₂H₁₁S³⁻ monolayers were prepared by immersing electrochemically roughened polycrystalline gold electrodes in a 5 mM aqueous solution of Cs₂[*closo*-B₁₂H₁₁SH] for ca. 17 h.^{9,10} The electrodes were then removed and thoroughly rinsed with water to ensure complete removal of any physisorbed Cs₂[*closo*-B₁₂H₁₁SH]. The monolayers were characterized by surface-enhanced Raman spectroscopy (SERS) using 735-nm excitation.

Figure 1 presents the Raman spectrum of solid Cs₂[*closo*-B₁₂H₁₁SH] (a) and the SER spectrum of the monolayer-coated electrode (b). All of the bands in the SER spectrum are assignable to vibrational modes of adsorbed *closo*-B₁₂H₁₁S³⁻. Although the infrared and Raman spectra of both Cs₂[*closo*-B₁₂H₁₂] and Cs₂[*closo*-B₁₂H₁₁SH] have been published, complete vibrational assignments have not been reported for the latter.^{11–15} Table 1

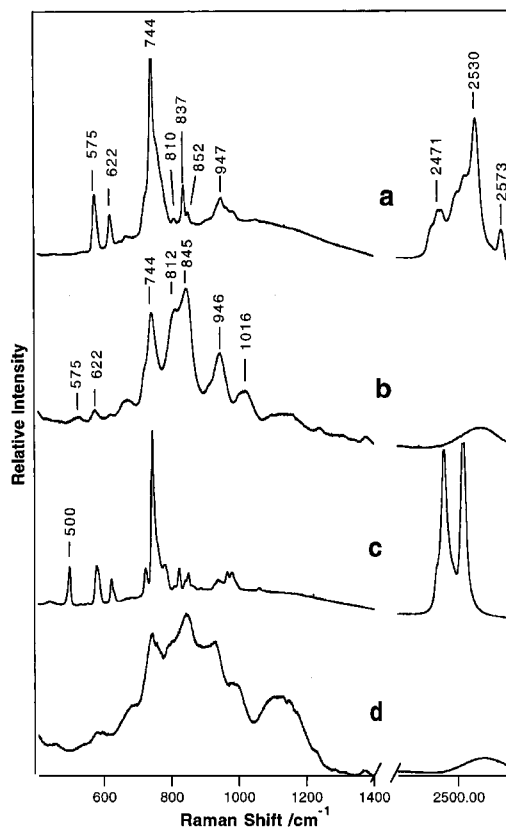


Figure 1. (a) Raman spectrum of solid Cs₂[*closo*-B₁₂H₁₁SH]. (b) SER spectrum of a monolayer prepared by immersing a roughened gold electrode in 5 mM aqueous Cs₂[*closo*-B₁₂H₁₁SH]. (c) Raman spectrum of solid Cs₄[*closo*-B₁₂H₁₁S]₂. (d) SER spectrum of a monolayer prepared by immersing a roughened gold electrode in 5 mM aqueous Cs₄[*closo*-B₁₂H₁₁S]₂.

(Supporting Information) contains our preliminary vibrational assignments based on published spectra and assignments for M₂-[*closo*-B₁₂H₁₁X] derivatives (X = F, Cl, Br, and I).^{16,17} The bands near 575, 744, and 947 cm⁻¹ are assigned to B–B bending and stretching modes, and the group of bands near 2500 cm⁻¹ to the signature B–H stretching modes.¹⁸ The sharp band at 622 cm⁻¹ is assigned to δ(B–B–S). The group of bands between 810 and 852 cm⁻¹ contains contributions from ν(B–S);¹⁹ although the exact assignments are not certain, they are known to be substituent-related because they are absent from the spectrum of Cs₂-[*closo*-B₁₂H₁₂], appear only upon monosubstitution, and shift with changing mass of the substituent.¹⁶ The ν(B–S)-related bands at 813 and 845 cm⁻¹ are significantly enhanced relative to other bands in the SER spectrum, indicating proximity to the metal.²⁰ In the spectrum of solid Cs₂[*closo*-B₁₂H₁₁SH], there is a very intense band at 2573 cm⁻¹ arising from the ν(S–H) mode. This band is absent from the monolayer SER spectrum, showing that

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- (1) Tarlov, M. J.; Newman, J. G. *Langmuir* **1992**, *8*, 1398–1405.
- (2) Li, Y.; Huang, J.; McIver, R. T.; Hemminger, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2428–2432.
- (3) Chadwick, J. E.; Myles, D. C.; Garrell, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10364–10365.
- (4) Garrell, R. L.; Chadwick, J. E.; Severence, D. L.; McDonald, N. A.; Myles, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 11563–11571.
- (5) Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117–1127.
- (6) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.
- (7) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528–12536.
- (8) Muetterties, E. L.; Knoth, W. H. In *Polyhedral Boranes*; Marcel Dekker: New York, 1968.
- (9) The oxidative–reductive cycles used to prepare the gold electrodes for SER spectroscopy, along with the Raman instrumentation, have been described elsewhere.⁴ Typical incident power for obtaining SER spectra was 75 mW at the sample, with spectral integration times of 2–15 s. The data presented here have been corrected for the instrumental response function.
- (10) Cs₂B₁₂H₁₁SH was a gift from Callery Chemical Co. (Evans City, PA) and was used as received. It is readily prepared by the method described in Tolpin, E. I.; Wellum, G. R.; Berley, S. A. *Inorg. Chem.* **1978**, *17*, 2867–2873. Cs₄[(B₁₂H₁₁S)₂] was prepared by the method of Wellum et al.¹⁴
- (11) Muetterties, E. L.; Merrifield, R. E.; Miller, H. C.; Knoth, W. H., Jr.; Drowning, J. R. *J. Am. Chem. Soc.* **1962**, *84*, 2506–2508.

- (12) Muetterties, E. L.; Balthis, J. H.; Chia, Y. T.; Knoth, W. H., Jr.; Miller, H. C. *Inorg. Chem.* **1964**, *3*, 444–451.
- (13) Abdul-Fattah, M.; Butler, I. S. *Can. J. Spectrosc.* **1977**, *22*, 110–112.
- (14) Wellum, G. R.; Tolpin, E. I.; Soloway, A. H.; Kaczmarczyk, A. *Inorg. Chem.* **1977**, *16*, 2120–2122.
- (15) Green, T. A.; Switendick, A. C.; Emin, D. *J. Chem. Phys.* **1988**, *89*, 6815–6822.
- (16) Srebný, H.; Preetz, W.; Marsmann, H. C. *Z. Naturforsch., A: Phys. Sci.* **1984**, *396*, 189–195.
- (17) Thomsen, H.; Haecckel, O.; Krause, U.; Preetz, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 2061–2064.
- (18) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. In *Introduction to Infrared and Raman Spectroscopy*; 3rd ed.; Academic Press: Boston, 1990.

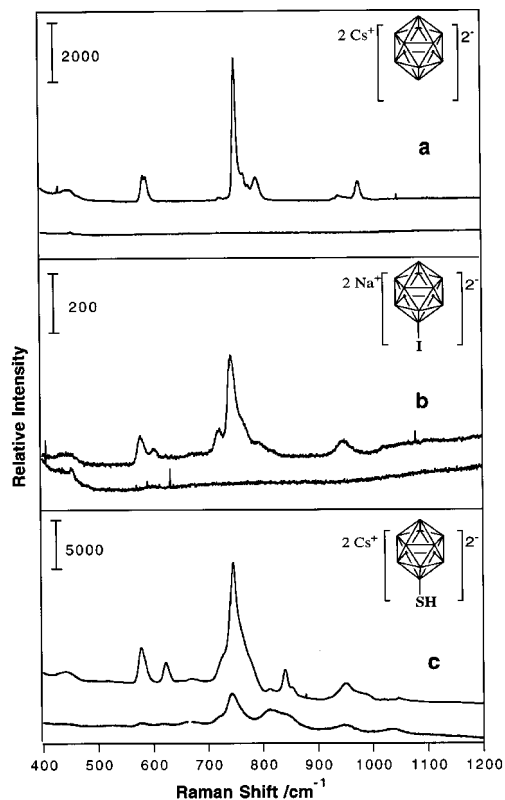


Figure 2. (a) Top, surface Raman spectrum of a multilayer of $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]$ on a roughened gold electrode; bottom, spectrum obtained after rinsing with water. (b) Top, surface Raman spectrum of a multilayer of $\text{Na}_2[\text{closo-B}_{12}\text{H}_{11}\text{I}]$ on a roughened gold electrode; bottom, spectrum obtained after rinsing the same electrode with water. (c) Top, surface Raman spectrum of a multilayer of $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ on a roughened gold electrode; bottom, spectrum obtained after rinsing the same electrode with water.

the S–H band has cleaved upon adsorption, just as when organothiols adsorb on gold.²¹ Repeated rinsing of the monolayer with water causes no change in the SER spectrum (data not shown). This is evidence that a reasonably strong sulfur–gold bond has formed. The lack of both an S–H stretching vibration and any changes upon rinsing shows that there is only a monolayer on the surface, not multilayers.

To confirm that adsorption of $\text{closo-B}_{12}\text{H}_{11}\text{S}^{3-}$ occurs through the sulfur atom and not the borate cage, we deposited thin films of $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]$, $\text{Na}_2[\text{closo-B}_{12}\text{H}_{11}\text{I}]$, and $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ by evaporating solutions onto roughened gold electrodes and acquired SER spectra both before and after rinsing with water. If adsorption occurred through the cage, one would expect similar adhesion in all three cases. As shown in parts a and b of Figure 2, $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{12}]$ and $\text{Na}_2[\text{closo-B}_{12}\text{H}_{11}\text{I}]$ are completely removed by rinsing. Neither the underivatized dodecaborate nor the monosubstituted cage adheres to gold. Figure 2c shows the results of the same experiment conducted with $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$. In this case, rinsing removes physisorbed thiol, leaving the chemisorbed thiolate monolayer intact. Thus, only when the dodecaborate cage is modified with a thiol group do these molecules adhere to gold.

Last, we investigated the adsorption of the disulfide derivative of $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ onto gold. It is well-known that orga-

nothiolate SAMs can be formed from dialkyl disulfides, although longer formation times are required to achieve densely packed, well-ordered monolayers.²² Parts c and d of Figure 1 show the Raman spectra of solid $\text{Cs}_4[\text{closo-(B}_{12}\text{H}_{11}\text{S)}_2]$ and the SER spectrum obtained after immersing a roughened gold electrode in 5 mM aqueous $\text{Cs}_4[\text{closo-(B}_{12}\text{H}_{11}\text{S)}_2]$. Spectrum 1d shows that we form a monolayer whose structure is noteworthy. The $\nu(\text{S}-\text{S})$ vibration at 500 cm^{-1} is conspicuous in the Raman spectrum (Figure 1c) but is completely absent from the SER spectrum of the monolayer (Figure 1d). We have shown previously that with SERS we can detect as little as 5% monolayer coverage of disulfide.⁴ The absence of this band from the monolayer spectrum provides direct evidence that the S–S bond cleaves upon adsorption, just as when dialkyl disulfides adsorb on gold.^{22,23} Comparison of the SER spectrum of the monolayer formed from $\text{Cs}_4[\text{closo-(B}_{12}\text{H}_{11}\text{S)}_2]$ (Figure 1d) with that of the monolayer prepared from $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ (Figure 1b) shows the two spectra to be nearly identical. The slight differences in relative intensities and bandwidth are within normal experimental variability from monolayer to monolayer; the origins of these differences will be described elsewhere.²⁴ The key observation is that monolayers prepared from either $\text{Cs}_4[\text{closo-(B}_{12}\text{H}_{11}\text{S)}_2]$ or $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ produce the same SER spectra and that both species adsorb as the thiolate.²⁵

We have demonstrated that inorganic monolayers can be formed by self-assembly of thiol-supported borane clusters such as $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ and $\text{Cs}_4[\text{closo-(B}_{12}\text{H}_{11}\text{S)}_2]$ onto gold, thereby opening a new realm of SAM structure and function. Qualitative vibrational assignments for the free thiol and adsorbed thiolate have been presented. The self-assembly process is analogous to that of organothiols and disulfides on gold; cleavage of S–H or S–S bond occurs, and a new covalent link is formed between the sulfur atom and gold surface. These new monolayer components are unique in their size, aspect ratio, and electronic structure and thus represent novel model systems for probing the steric and electronic requirements of the self-assembly process and the chemical interactions that lead to adhesion. The hydrophilicity, delocalized negative charge, and presence of cations in the adlayer²⁴ make the $[\text{closo-B}_{12}\text{H}_{11}\text{S}]^{3-}$ monolayers fundamentally distinct from hydrocarbon thiolate SAMs. The size of the borate cages can be varied, and they are easily functionalized, providing routes toward completely new types of monolayers and thin film architectures. Such monolayers may offer improved stability since the aromatic borate cages are unusually robust.¹² We are currently evaluating the thermal and oxidative stability of $[\text{closo-B}_{12}\text{H}_{11}\text{S}]^{3-}$ monolayers and determining their packing arrangement and degree of order.

Supporting Information Available: Table of Raman and SER spectra (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9809253

(22) Nuzzo, R. G.; Zargarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733–740.

(23) Ishida, T.; Yamamoto, S.; Mizutano, W.; Motomatsu, M.; Tokumoto, H.; Hokari, H.; Azebara, H.; Fujihira, M. *Langmuir* **1997**, *13*, 3261–3265.

(24) Yeager, L. J.; Saeki, F.; Shelly, K.; Hawthorne, M. F.; Garell, R. L., manuscript in preparation.

(25) The possibility that the aqueous $\text{closo-B}_{12}\text{H}_{11}\text{SH}^{2-}$ or $\text{closo-B}_{12}\text{H}_{11}\text{S}^{3-}$ spontaneously oxidized, forming the disulfide, was considered. ¹¹B NMR was used to analyze the composition of (a) fresh 50 mM aqueous $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$, (b) the rinse solution collected after the gold electrode was immersed in 50 mM aqueous $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ for 5 min, and (c) 50 mM aqueous $\text{Cs}_2[\text{closo-B}_{12}\text{H}_{11}\text{SH}]$ that was exposed to air at room temperature for 2 days. The spectra of all three solutions were identical, with chemical shifts (δ) at -10.1 (1B), -14.7 (5B), -16.8 (5B), and -20.6 (1B) ppm relative to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$. The chemical shifts of $\text{B}_{12}\text{H}_{11}\text{SH}^{2-}$ published by Tolpin et al.¹⁰ are -10.4 (1B), -14.8 (5B), -17.0 (5B), and -20.5 (1B) ppm relative to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$, essentially identical to our spectrum. By contrast, the chemical shifts of the disulfide, $\text{B}_{12}\text{H}_{11}\text{SSB}_{12}\text{H}_{11}^{4-}$, are -6.7 (2B), -15.6 (10B), -17.2 (10B), and -20.3 ppm (2B), quite distinct from those of the thiol.¹⁰ Thus, we find no evidence for oxidation of the thiol to the disulfide under our conditions.

(19) There is a conspicuous absence of a band assignable to $\nu(\text{B}-\text{S})$. For the solid, this mode gives rise to a very intense doublet at 1055 and 1080 cm^{-1} in the infrared, but unfortunately, it has a very low Raman cross section. We are attempting to obtain reflectance IR spectra to determine whether the band at 1016 cm^{-1} can be attributed to a highly downshifted $\nu(\text{B}-\text{S})$ mode.

(20) Garell, R. L. *Anal. Chem.* **1989**, *61*, 401A–408A.

(21) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 8284–8293.