Enriched with Iron

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A Nanoscopic 3D Polyferrocenyl Assembly: The Triacontakaihexa(ferrocenylmethylthiolate) $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$**

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Strategies for the incorporation of multiple di(η^5-cyclopentadienyl)iron (ferrocene) fragments onto molecular architectures have advanced on many fronts. Examples of these successes include the functionalization of dendrimers,[1] polymers,[2] and the surfaces of metal nanoparticles[3] and supramolecular assemblies[4] with these redox active moieties. The motivation for these research efforts is driven in part by their potential for applications in fields of conducting polymers,[5] specialty electrodes,[6] and anion recognition.[7] Recently, the effects on the photophysical properties of incorporating surface ferrocenylalkylthiolates on the surfaces of semiconductor quantum dots (CdSe/ZnS) have been deomonstrated,[8] and exploited for the sensing of fluoride ions.[9] Monolayer protected gold nanoparticles with ferrocenylalkylthiolates have also been prepared in order to modulate the electron-inductive properties of the stabilizing ligand shell with "fully ferrocenated" monolayer protected nanoparticles having been recently reported.[3,6] On a complementary front, recent reports on the preparation of structurally characterized Ag_2S nanoclusters have illustrated that these too can be stabilized with surface thiolate ligands exclusively. These preparations have offered an entry into large molecular frameworks with an insulating (aryl) ligand shell.[10] With a suitably designed ferrocenyl reagent, it should be possible to use a monodisperse Ag_2S architecture for the formation of ferrocenyl-passivated semiconductor nanoclusters. Herein we report the facile preparation of polynuclear ferrocenylmethylthiolate complexes including the high yield synthesis of the redox active nanocluster $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$ (**1**).

The high solubility of trimethylsilylchalcogenide reagents $RESiMe_3$ (E = S, Se, Te) allows for the homogeneous reaction conditions required to prepare and crystallize nanoscopic metal–chalcogen complexes. They react with metal carboxylates to afford Me_3SiO_2CR, which does not interfere with product crystallizations.[11] We have previously employed $[CpFeC_5H_4SeSiMe_3]$ to tailor cluster surfaces with $FcSe^-$, however cyclic voltammetry together with constant potential electrolysis illustrated that oxidation of the Fe^{II} centers in $[Cd_4(SeFc)_6Cl_4]^{2-}$ clusters resulted in the formation of FcSe-SeFc with concomitant degradation of the metal–chalcogen frameworks.[12] The incorporation of one methylene spacer unit between the cyclopentadienyl ring and the chalcogen center was chosen to avoid potential oxidative degradation of the cluster, and where the short $-CH_2-$ spacer would likely not interfere with the formation of crystallographically ordered structures. $[CpFeC_5H_4CH_2SSiMe_3]$ ($[FcCH_2SSiMe_3]$) can be prepared from $[CpFeC_5H_4CH_2Cl]$[13] with $[Li\{SSiMe_3\}]$.[14]

The reaction of $[FcCH_2SSiMe_3]$ with Ph_3P-solubilized AgOAc yields small amounts of $[Ag_{10}(\mu_2\text{-}SCH_2Fc)_{10}(PPh_3)_4]$ (see Supporting Information) as yellow crystals and $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$ (**1**), isolated as orange, single crystals in about 40% yield [Eq. (1)]. The cluster **1** was analyzed by single-crystal diffraction in order to elucidate its structural features.

$$\begin{array}{l}(Ph_3P)_2\cdot AgOAc + FcCH_2SSiMe_3 \rightarrow \\ [Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]\ (\mathbf{1})\ + OAcSiMe_3 + (FcCH_2)_2S\end{array} \qquad (1)$$

Single crystals of **1** are highly solvated, fragile, and weakly diffracting, however a satisfactory data set was obtained after screening diffraction data on several samples. The molecular structure of **1** in the crystal is illustrated in Figure 1. The structure of **1** consists of 48 silver(I) centers, which display either a distorted linear or trigonal planar coordination geometry; there are six interstitial S^{2-} ligands, each tetrahedrally coordinated to four Ag^I and there are 36 μ_2/μ_3-$FcCH_2S^-$ ligands on the nanocluster surface. The cluster is characterized by crystallographic site disorder of some silver centers and surface ferrocenymethylthiolate groups, but the $Ag^I\cdots Ag^I$ contacts are all greater than 2.8 Å consistent with their assigned oxidation state.[10b] Notably, the surface is devoid of phosphine ligands used to solubilize the silver carboxylate. This feature minimizes the random agglomeration/condensation reactions that can occur when redissolving phosphine ligated metal–chalcogen nanoclusters due to facile dissociation of these ligands.[11] The origin of S^{2-} in **1** is likely through the formation and elimination of small amounts of $(FcCH_2)_2S$. Thirty-six $FcCH_2$ moieties form a closely packed shell on the surface of a $Ag_{48}S_{42}$ core (Figure 2). The dimensions of the

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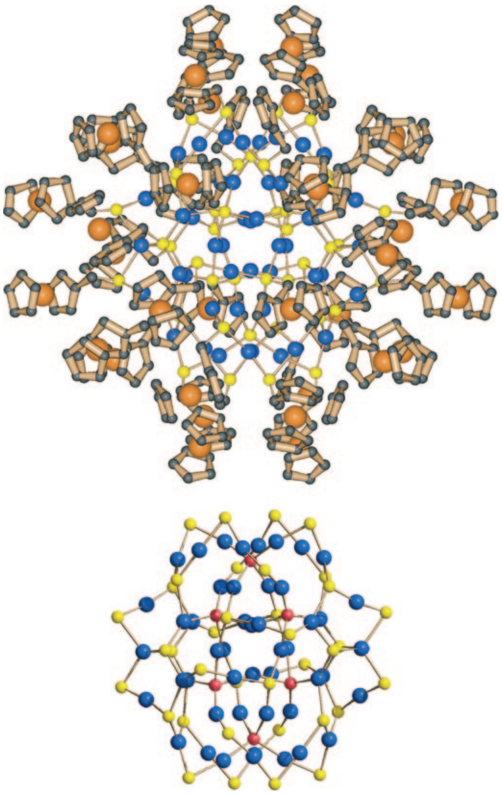

Figure 1. Top: ball and stick representation of the molecular structure of $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$ (**1**) emphasizing the coverage of the ferrocenylmethylthiolates (hydrogen atoms omitted for clarity; Fe orange, C gray, Ag blue, S yellow). Bottom: the $Ag_{48}S_{42}$ core framework in **1** with the six tetrahedral S^{2-} ligands highlighted in red.

disc like $Ag_{48}S_{32}$ frame are ca. $1.7\times1.7\times1.3\ nm^3$ with overall molecular dimensions of ca. $3.0\times3.0\times2.2\ nm^3$. A similar discus motif was reported for the anionic nanocluster $[Ag_{50}S_7(SC_6H_4tBu\text{-}4)_{40}]^{4-}$.[10a]

Crystals of **1** can be dissolved in polar organic solvents, and dynamic light scattering experiments of solutions of **1** in THF suggest retention of the cluster when dissolved, a single species observed with a hydrodynamic diameter of 3.0 nm. ^{1}H NMR spectra of **1** in solution in $[D_8]$THF reflect the magnetic inequivalence of the Cp moieties, with nine resolved resonances (Supporting Information). However, cyclic voltammetry of THF solutions of **1** (0.04 mM, Supporting Information) display only a single reversible redox wave ($i_{pc}/i_{pa}\approx1$) with the standard potential, E^0, of 0.46 V (vs. SCE; scan rate 50 mV s^{-1}) assigned to the one-electron oxidation/reduction of the Fe^{II} centers, suggesting all ferrocenyl moieties oxidize at the same (or very similar) potentials. The shapes of the redox wave and its response to scan rate do not suggest accumulation of the oxidized species on the surface of the electrode, as has been observed for gold ferrocenylalkylthiolate nanoparticles.[6] The shape of the voltammogram shows that ferrocenyl moieties are chemically reversible at these scan rates and suggests that the cluster framework remains intact upon oxidation of the Fe^{II} centers. Unlike for some dendrimer based polyferrocenyl arrangements with closely spaced ferrocenyl moieties,[15] only one redox peak is observed at a single potential. The presence of a single reversible oxidation wave implies that the ferrocenyl units are oxidized independently, with little interaction, and that each ferrocenyl moiety has the same or similar closely spaced E^0 (within 30 mV). Furthermore, the reversibility indicates that alkyl spacer ultimately prevents any oxidation of the thiolate centers at these potentials. The formation and characterization of **1** illustrate the possibility of designing chalcogenolate ligands for tailored surfaces onto monodisperse nanocluster Ag_2S frameworks. We are currently developing the reaction chemistry of $[Fc(CH_2)_nESiMe_3]$ (E = S, Se) and related metallocene based ligands.

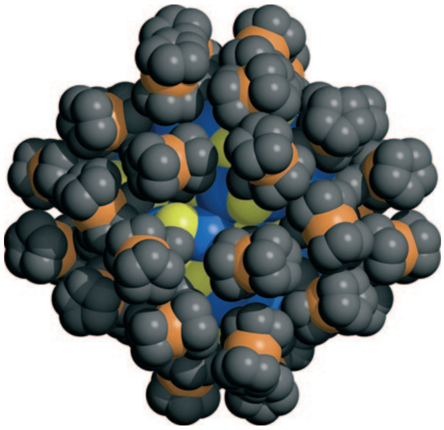

Figure 2. A space filling representation of the molecular structure of $[Ag_{48}(\mu_4\text{-}S)_6(\mu_{2/3}\text{-}SCH_2Fc)_{36}]$ (**1**) illustrating the surface coverage of the ferrocenylmethylthiolates (hydrogen atoms omitted; Fe orange, C gray, Ag blue, S yellow).

Experimental Section

Synthesis of $[CpFe(\eta^5\text{-}C_5H_4CH_2SSiMe_3)]$: Ferrocenylmethylchloride (0.43 g, 1.83 mmol) and lithium trimethylsilythiolate (0.21 g, 1.83 mmol) were each dissolved in anhydrous tetrahydrofuran (50 mL and 10 mL, respectively) and cooled to 0 °C. The solutions were mixed and stirred for 1 h at room temperature. The solvent was removed in vacuo and 25 mL of ether was added to solubilize (ferrocenylmethyl)trimethylsilylsulfide giving a yellow/orange solution together with LiCl. The solid was removed by passing the mixture through a sintered glass frit packed with dried Celite. The solvent was again removed in vacuo yielding (ferrocenylmethyltrimethylsilyl)sulfide as an air sensitive, yellow solid. Yield : 0.47 g (85 %). ^{1}H NMR ($CDCl_3$): $\delta=4.18$ (vt, 2 H, $^3J_{HH}=2$ Hz), 4.13 (s, 5 H), 4.09 (vt, 2 H, $^3J_{HH}=2$ Hz), 3.50 (s, 2 H), 0.29 ppm (s, 9 H). ^{13}C NMR ($CDCl_3$): $\delta=$ 87.72 (C_5H_5), 68.70 (Cp substituted), 68.43 (Cp substituted), 67.79 (Cp substituted), 26.04 (CH_2), 0.92 ppm ($SiMe_3$). [M^+]: found at m/z 304.0.

Synthesis and characterization of $[Ag_{48}S_6(SCH_2Fc)_{36}]$ (**1**) and $[Ag_{10}(SCH_2Fc)_{10}(PPh_3)_4]$: Silver(I) acetate (0.12 g, 0.70 mmol) was solubilized with 2 equivalents of triphenylphosphine (0.37 g, 1.4 mmol) in chloroform (5 mL). $[CpFe(\eta^5\text{-}C_5H_4CH_2SSiMe_3)]$ (0.21 g, 0.70 mmol) was dissolved in chloroform (5 mL) and both solutions were cooled to −60 °C. The solutions were mixed at −60 °C and the yellow reaction mixture was warmed slowly to room temperature and was stirred for 2 h to yield an orange coloured solution. Diffusion of pentane (35 mL) over the reaction solution yielded two different types of crystals after 48 h. The major product **1** was isolated as orange crystals, and $[Ag_{10}(SCH_2Fc)_{10}(PPh_3)_4]$ was isolated as small yellow cubes. **1** (orange crystals, 0.098 g, 43 %) and

$[Ag_{10}(SCH_2Fc)_{10}(PPh_3)_4]$ (yellow crystals, trace amounts). Elemental analysis (%) calcd for **1**: C 34.74, H 2.92; found: C 34.83, H 2.63; calcd (%) for $[Ag_{10}(SCH_2Fc)_{10}(PPh_3)_4]$: C 49.29, H 3.86; found: C 49.19, H 4.00. Elemental analyses were performed by Columbia Analytical Services (Tucson, USA) and Guelph Chemical Laboratories (Guelph, Canada). Electrochemical measurements were obtained using a BAS 100W version 2.0 Electrochemical Analyzer potentiostat interfaced to a personal computer using BAS 100W version 2.0 software. A standard 3-electrode arrangement was used with a Pt working electrode, platinum flag counter electrode, and silver wire reference electrode in tetrahydrofuran with Bu_4NPF_6 (0.1 M) as the supporting electrolyte. All potentials are reported versus SCE and were referenced internally to ferrocene ($E^0 = 0.547$ V), added at the end of the experiment. Crystal data for **1**: $C_{403.50}H_{407}Ag_{48}Cl_{15}Fe_{36}S_{42}$, $M_r = 14322.9\ g\,mol^{-1}$, $0.25 \times 0.18 \times 0.12\ mm^3$, monoclinic, $C2/c$, $a = 27.646(6)$, $b = 44.274(9)$, $c = 43.101(9)$ Å; $\beta = 108.01(3)°$, $Z = 4$, $\rho_{calcd} = 1.896\ g\,cm^{-3}$, $\mu = 3.122\ mm^{-1}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 150 K, $2\theta_{max} = 50.0°$, 172079 reflections, 44118 unique ($R_{int} = 0.1095$), $R = 0.0981$, $wR = 0.2918$, largest diff. peak $-2.223\ e\,Å^3$. Data were collected on a Enraf–Nonius KappaCCD X-ray diffractometer using graphite-monochromated beams with ϕ and ω scans. CCDC 764611 (**1**) and 764610 ($[Ag_{10}(SCH_2Fc)_{10}(PPh_3)_4]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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