

## Surveying the Surface Coordination Chemistry of a Superconductor: Spontaneous Adsorption of Monolayer Films of Redox-Active "Ligands" on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Important recent studies by Murray and co-workers have demonstrated that cuprate superconductors coated with Ag and Au can be modified with thiol adsorbate molecules.<sup>1a</sup> However, direct covalent attachment of molecules onto the surface of high- $T_c$  phases has yet to be demonstrated. The development of such chemistry is particularly important for the fabrication of new-molecule-based superconductor devices, a long-standing goal of the McDevitt group,<sup>2</sup> since it would yield chemical control over the surface properties of the superconductor through choice of adsorbate molecule. The Mirkin group has had a sustained interest in synthesizing adsorbate molecules that allow one to probe structural, chemical, and electrochemical issues regarding monolayer films on semiconducting and metallic substrates.<sup>3</sup> Drawing on inorganic coordination chemistry concepts and taking advantage of the room temperature conducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , we have conducted the first preliminary survey of the surface coordination chemistry of a high- $T_c$  superconductor. With redox-active ligands 1–6, Table 1, we have studied the chemical adsorption properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and utilized cyclic voltammetry to determine the efficiency of the chemical adsorption process. Herein, we report the spontaneous adsorption of monolayer films of amine- and thiol-containing 1, 2, and 6 onto the surfaces of epoxy-encapsulated polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  electrodes<sup>4</sup> and thin film electrodes of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (1200–1800 Å) that were prepared by the laser ablation method.<sup>5</sup>

A series of epoxy-encapsulated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  disk electrodes were treated in 1 mM acetonitrile (ACN) solutions of the adsorbate molecules with varying functional groups, including an alkylamine 1,<sup>6a</sup> an arylamine 2,<sup>7a</sup> an amide 3,<sup>6b</sup> a phosphine

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(6) (a) Compound 1 was synthesized by reacting  $\text{FcC}(\text{O})\text{Cl}$  with excess  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  in  $\text{CH}_2\text{Cl}_2$ . MS (EI):  $M^+ = 272$  m/z.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.05 (1H, C(O)NH), 4.63, 4.05, 3.98 (9H, Cp), 3.21 (2H), 2.37 (2H). (b) Compound 3 was synthesized by reacting  $\text{FcC}(\text{O})\text{Cl}$  with 0.5 equiv of  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  in  $\text{CH}_2\text{Cl}_2$ . MS (EI):  $M^+ = 484$  m/z.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.75 (2H, C(O)NH), 4.71, 4.33, 4.15 (18H, Cp), 3.58 (4H,  $\text{CH}_2$ ).

Table 1. Surface Coverages for Redox-Active Ligands 1–6

"ligands" <sup>a</sup>	surface coverage (mol/cm <sup>2</sup> )	
	ceramic	thin film
$\text{FcC}(\text{O})\text{NHCH}_2\text{CH}_2\text{NH}_2$ , <b>1</b>	$4 \times 10^{-9}$	$2 \times 10^{-9}$
$p\text{-FcC}_6\text{H}_4\text{NH}_2$ , <b>2</b>	$4 \times 10^{-10}$	$2 \times 10^{-11}$
$\text{FcC}(\text{O})\text{NHCH}_2\text{CH}_2\text{NHC}(\text{O})\text{Fc}$ , <b>3</b>	no <sup>b</sup>	no
$\text{FcOCH}_2\text{CH}_2\text{PPh}_2$ , <b>4</b>	no	no
$\text{FcCH}_2\text{OH}$ , <b>5</b>	no	no
$\text{FcC}(\text{O})(\text{CH}_2)_{10}\text{SH}$ , <b>6</b>	$2 \times 10^{-9}$	$9 \times 10^{-10}$

<sup>a</sup> Fc: ferrocenyl. <sup>b</sup> No significant surface coverage measured.

4,<sup>8</sup> an alcohol 5,<sup>9</sup> and a thiol 6.<sup>7b</sup> After soaking for 48 h in solutions of the redox-active species, the electrodes were thoroughly rinsed with ACN and  $\text{CH}_2\text{Cl}_2$ , solvents in which the molecular species are highly soluble. Cyclic voltammetry was used to assess the degree of surface modification, and only in the cases of the alkylamine 1, the arylamine 2, and the alkylthiol 6 were significant surface coverages measured, Table 1. For example, the cyclic voltammogram for a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  electrode modified with 1 exhibited a wave associated with ferrocenyl oxidation/reduction at  $E_{1/2} = 0.66$  V vs Ag wire, Figure 1A. This response, which is quite comparable to that observed for surface-confined monolayers of ferrocenyl alkanethiols adsorbed on noble metal substrates,<sup>10</sup> was persistent over repeated cycling in the potential window between  $-0.2$  and  $1.2$  V. The surface coverage for 1 on the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ceramic electrode, which was determined by integrating the current associated with ferrocenyl oxidation/reduction, was  $4 \times 10^{-9}$  mol/cm<sup>2</sup> and is approximately 10 times that expected for a monolayer of 1 on an ideally flat substrate ( $4.5 \times 10^{-10}$  mol/cm<sup>2</sup>, *vide infra*). The large values of the surface coverages for the ceramic electrodes are consistent with the rough surface morphology and porosity that are characteristic of such materials.<sup>4</sup>

If one is to use surface modification chemistry for the preparation of superconducting devices, it is important to demonstrate such chemistry on thin films of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  materials and assess the effect of chemical modification on their superconducting properties. Accordingly, compounds 1, 2, and 6 (but not 3–5) were found to adsorb spontaneously onto laser ablated *c*-axis-oriented films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  to form redox-active monolayers; surface coverage data is given in Table 1. For example, the cyclic voltammetry for a *c*-axis film of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  modified with 1 exhibits a surface-confined wave associated with ferrocenyl oxidation at  $0.73$  V vs Ag wire ( $\Delta E_p$  approaching 0 at low scan rates and  $i_p \propto \text{scan rate}$ ), Figure 1B. The surface coverage for 1 on the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film is closer to ideality than that measured for ceramic electrodes modified with 1 but is still larger than that expected for a perfectly flat surface. Indeed, atomic force microscopy (AFM) images of these superconductor films show that they are substantially rough on the nanometer scale. The morphology consists of individual spheroidal particles with diameters in the 20–100 nm range and large clusters of such particles ( $\sim 200$  nm in length). AFM images of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  thin films after modification with 1 and 2 show that the general surface morphology on the nanometer length scale does not change substantially.

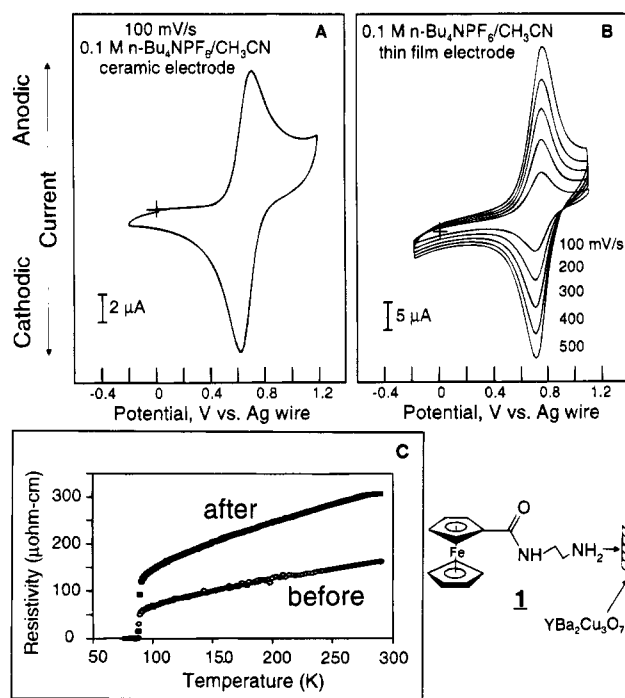
Of the six compounds studied, compound 1 consistently yielded the largest surface coverages and the most persistent electrochemical response; after 30 cycles at 200 mV/s, there was no detectable loss in electroactivity.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  modi-

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**Figure 1.** (A) Cyclic voltammetry for a YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> polycrystalline ceramic electrode (0.049 cm<sup>2</sup>) modified with **1**. (B) Sweep rate dependent cyclic voltammograms for a *c*-axis-oriented (1500 Å thick) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>/MgO(100) film electrode (0.35 cm<sup>2</sup>) modified with **1**. Electrode areas refer to geometric surface areas. (C) Resistivity vs temperature plot for a 1500 Å thick, *c*-axis-oriented film of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> on MgO(100) before (○) and after (■) soaking in a 1 mM solution of **1** for 3 h.

fied with compound **2** exhibited similar behavior, but with significantly lower surface coverages, Table 1. In contrast, monolayer films of **6** on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> thin films exhibited a slow but steady loss in electroactivity as a result of repeated cycling.

Although additional studies are required before the modes of surface coordination can be established unequivocally, the observation that amines such as **1** and **2** have large affinities for the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> materials strongly suggests that surface active sites are Cu-based. Amines are common ligands used in Cu(II) and Cu(III) coordination chemistry.<sup>11</sup> For the reaction involving **6**, the nature of the adsorbed species could be quite complicated, especially since YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> is a highly oxidizing material and thiols are susceptible to oxidation. If the Cu sites on the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> are assumed to be the ones used in the modification process involving **1** and **2**, the maximum surface coverages for **1** and **2** will be dictated by the steric constraints of their ferrocenyl head groups; the cross-sectional area of the ferrocenyl group, which has been estimated by others,<sup>12</sup> is large enough to encompass several Cu sites, which are spaced 3.8 Å apart in the CuO<sub>2</sub> sheets of the superconductor.

Significantly, the superconducting properties of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> thin films remain intact after chemical modification. For example, a temperature vs resistivity plot for a representative YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> film before and after surface modification with **1** shows little decrease in *T<sub>c</sub>* as a result of chemical modification, Figure 1C. No noticeable decrease in *T<sub>c</sub>* for the superconductor was noted after modification for short periods of time (~3 h), but longer treatments (48 h) led to small, but measurable, decreases in *T<sub>c</sub>* (~2 K). There is a small increase in room temperature resistivity for the superconductor after its derivatization

(Figure 1C), which may be due to the presence of a resistive surface layer; increasing the pressure of the contact electrodes led to decreases in the measured room temperature resistivity.

The stability of **1**-, **2**-, and **6**-modified YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> in air and solution is remarkable, especially since others have claimed that alkanethiols do not stably chemisorb onto high-temperature superconductors.<sup>1a,b</sup> The modified superconductor samples were prepared in air on the bench top under ambient conditions. The modified samples are stable in a variety of different organic solvents including ACN, THF, and CH<sub>2</sub>Cl<sub>2</sub>. Superconductors modified with **1** have been soaked in neat ACN for 3 days with no noticeable loss of electroactivity associated with the ferrocenyl monolayer. When unmodified YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> electrodes are soaked in ACN for 3 days under comparable conditions, they degrade, as evidenced by the formation of a passivating corrosion layer and the loss of electroactivity; this demonstrates the stabilizing effect of the monolayer with respect to chemical corrosion. It should be noted that, for these adsorbate molecules and relatively rough superconductor films, this stabilizing effect is limited to organic media since electroactivity associated with **1**-modified YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> is lost almost immediately when such samples are immersed in a H<sub>2</sub>O/0.1 M NaClO<sub>4</sub> electrolyte solution. This presumably is due to facile corrosion of the underlying YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> by water, which is a known process for this high-*T<sub>c</sub>* compound.<sup>13</sup>

This work is significant for several reasons. (1) It documents the first example of the direct chemical modification of the surface of a superconductor with a monolayer of a molecular reagent; such surface modification chemistry will provide unprecedented control over the interfacial properties of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> through choice of adsorbate molecule. (2) The preparation of redox-active monolayers on superconductors will provide new materials to study important energy and electron transfer processes between surface-confined molecular substances and the underlying superconductor. (3) We have shown that the corrosion properties of the superconductor can be impeded through its chemical modification, which suggests that through judicious choice of adsorbate molecule the corrosion resistance for such materials may be further improved. By combining the surface modification strategy reported herein with previously reported methods for stabilizing YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> superconductors through solid-state substitution reactions,<sup>14</sup> we anticipate the formation of superconducting structures and devices that are substantially more chemically robust than existing ones.

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**Supplementary Material Available:** Plot of anodic peak current as a function of sweep rate and AFM images for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>/MgO(100) thin film before and after modification with **1** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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