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High-Temperature Superconductors

Tuning the Critical Temperature of Cuprate Superconductor Films with Self-Assembled Organic Layers**

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Many of the electronic properties of high-temperature cuprate superconductors (HTSC) are strongly dependent on the number of charge carriers put into the CuO_2 planes (doping). Superconductivity appears over a dome-shaped region of the doping-temperature phase diagram. The highest critical temperature (T_c) is obtained for the so-called "optimum doping". The doping mechanism is usually chemical; it can be done by cationic substitution. This is the case, for example, in $La_{2-x}Sr_xCuO_4$, in which La^{3+} is replaced by Sr^{2+}, thus adding a hole to the CuO_2 planes. A similar effect is achieved by adding oxygen as in the case of $YBa_2Cu_3O_{6+\delta}$ (YBCO), where δ represents the excess oxygen in the sample. Herein, we report on a different mechanism, one that enables the addition or removal of carriers from the surface of the HTSC. This method utilizes a self-assembled monolayer (SAM) of polar molecules adsorbed on the cuprate surface. In the case of optically active molecules, the polarity of the SAM can be modulated by shining light on the coated surface. This results in light-induced modulation of the superconducting phase transition of the sample. The ability to control the superconducting transition temperature with the use of SAMs makes these surfaces practical for various devices such as switches and detectors based on high-T_c superconductors.

In cuprate superconductors, the value of T_c has an approximately quadratic dependence on carrier concentration.[1] The carrier concentration is an order of magnitude lower than that of metals and the screening is weaker. This raises the possibility of modifying the carrier concentration by applying an electric field to the surface. One approach was to use field-effect devices.[2,3] Herein, we report on an alternative approach to doping the surface of the HTSC, namely with the use of a molecular self-assembly method.

A self-assembled monolayer (SAM) is an organized layer of molecules in which one end of the molecule, the binding group, is designed to interact favorably with the solid surface of interest to form a well-organized monolayer on it.[4] The SAM is terminated with a functional group—in our case these are surface-dipole-forming molecules or optically active moieties. The expected change in the work function owing to a dipole moment of 1 Debye per molecule in a "typical" SAM with molecular density of 5×10^{14} cm^{-2} is approximately 0.5 eV. The resulting electric field is compensated by charge transfer between the substrate and the SAM. The amount of charge transfer per molecule is $q=\mu/r$, where r is the length of the molecule, and μ is the dipole moment. When adsorbed on a cuprate surface, this charge transfer can be designed to induce holes and thus change the surface carrier density and the resulting critical temperature. In the case of photoactive molecules, this change in T_c can be induced by shining light on the SAM via electron-hole–pair excitation. In earlier work, several groups studied SAM adsorption on YBCO but found no change in the critical temperature after adsorption of various SAMs on the superconducting surface.[5]

In this study, several types of molecular monolayers and heterostructures were designed. These compounds exhibit strong charge-transfer characteristics and photoresponse when adsorbed on cuprate surfaces. To investigate the effect of SAMs on cuprates, three types of representative films were chosen, each targeted to a specific response upon adsorption or light excitation.

The first monolayer consists of carboxyfullerene (CF) coupled to CdS quantum dot (CF/QD; Scheme 1 a). In general, CF can be reduced by one electron per molecule. This reduction can occur upon application of a gate voltage.[6] In our case, the gate voltage is replaced by a CdS overlayer, which reduces the charge in the CF monolayer, thus forming an interfacial dipole between the two layers. This structure is used to study the effect of an interfacial dipole on T_c.

An optically active, azobenzene derivative (1-butanethiol,4[4-(phenylazo)phenoxy] (AZ); Scheme 1 b), was used to modulate the value of T_c with light. This molecule exhibits a reversible light-induced conformational change, which results in two distinct dipole states (−0.15 D and +1.53 D for *trans* and *cis* conformations, respectively). The AZ monolayer has been shown to modulate the magnetism of thin gold surfaces[7] and change the transport and superconducting properties of thin niobium films.[8] Herein, we demonstrate the ability of an AZ monolayer to modulate the transition temperature of high-T_c superconductors.

Next, we studied porphyrin-based SAMs coupled to porphyrin nanotubes (Scheme 1 c). Light-induced charge

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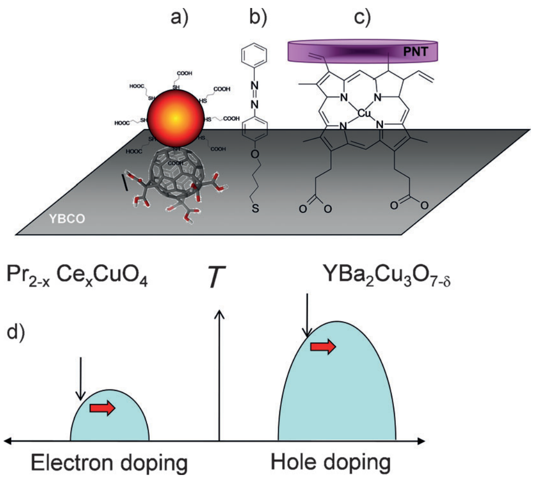

Scheme 1. Schematic illustration of the various molecular films deposited on the HTCS. a) CF monolayer coated with CdS. b) AZ monolayer. c) Heterostructure SAM composed of porphyrin nanotubes (PNT) condensed on porphyrin monolayer. For a CF monolayer, upon addition of CdS, an increase in T_c value was observed. Reversible T_c modulation was achieved by an AZ monolayer and the porphyrin-based heterostructure. d) Phase diagram of the two superconductors used. The horizontal axis is the carrier concentration (n) or doping. The origin represents the undoped insulating compound. Moving to the left (or right) represents increasing electron (or hole) doping. Superconductivity is observed in the dome-shaped regions of this doping-temperature phase diagram. The shift on the phase diagram resulting from the SAM for both electron- (overdoped) and hole-doped (underdoped) cuprates is indicated by the red arrow. The SAM extracts electrons from both types of surfaces and this results in an increase in T_c value.

transfer between porphyrins and carbon nanostructures[9] or metals[10] has been demonstrated. In the latter case, a photopotential of several tenths of a millivolt was measured. In our study, we exploited the special properties of porphyrin nanotubes, which, upon illumination, are expected to induce holes in the superconductor.

Scheme 1 d shows the phase diagram of the cuprate superconductors used: the hole-doped $YBa_2Cu_3O_{6+\delta}$ (YBCO) and the electron-doped $Pr_{2-x}Ce_xCuO_4$ (PCCO). Although the parent compounds are antiferromagnetic insulators, upon addition of charge carriers to the CuO_2 planes, the material becomes superconducting and has a critical temperature that depends on the carrier concentration, reaching its maximum at the so-called optimum doping; increasing the carrier concentration further results in a decrease in the value of T_c.

All our SAMs were tested on YBCO, which has a T_c over a temperature range accessible with liquid nitrogen. For a further demonstration of the physical effect that takes place at the surface, the CF/QD system was adsorbed on PCCO, which is an electron-doped cuprate superconductor,[11] as well as on YBCO. The black arrows in the Scheme 1 depict the carrier concentrations used in this experiment. YBCO underdoped and optimally doped samples were used, while for PCCO we used $x=0.17$, which is in the overdoped regime. For both underdoped YBCO and overdoped PCCO, the removal of electrons from the surface results in an increase in the value of T_c (shift indicated by the rightward-pointing red arrows in Scheme 1 d).

CF is known to form a dense monolayer when adsorbed on oxide surfaces.[12] We found that monolayers of similar quality are formed when CF is adsorbed on cuprates, as indicated by the large contact angle measured (see the Experimental Section). It is important to note that, upon addition of the QD layer, the dipolar field reverses its orientation, as inferred from the corresponding changes in T_c value. This reversal in the dipolar field is also evident from Kelvin force microscopy (KFM) measurements (see the Supporting Information).

Figure 1 shows the dependence of resistance on temperature for PCCO (left) and YBCO (right) adsorbed samples, as well as for the corresponding reference samples. The value of T_c decreased when a dense layer of CF was adsorbed on both surfaces. A remarkable increase in T_c value was observed for both the electron- and hole-doped cuprates when an additional layer of cadmium sulfide was added. The observed enhancement of T_c corresponds to a charge transfer of around 0.1 carriers per unit cell. This value is consistent with the change in surface potential found from KFM measurements (see the Supporting Information).

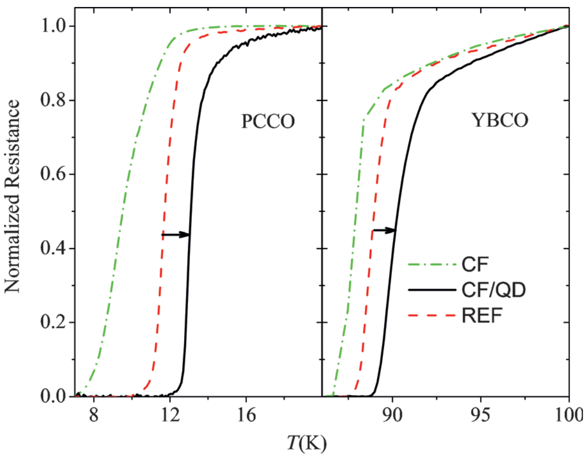

Figure 1. Normalized resistance measurement of CF coupled to CdS quantum dot on $Pr_{1.83}Ce_{0.17}CuO_4$ (left) and on $Y_1Ba_2Cu_3O_{7-\delta}$ (right) films. Bare film resistivities are about 80 μΩ·cm at 100 K for both samples. Adsorption of the CF SAM results in a decrease in T_c (dash-dot line) relative to the uncoated reference sample (dashed line) and CF/QD coated one (solid line), for which substantial T_c enhancement was observed for both types of cuprates.

Figure 2 (left) shows the light-dependence of the imaginary part of the induced alternating voltage (AC susceptibility) for a YBCO-coated AZ monolayer. In this measurement, the peak of the signal corresponds to the T_c value. A clear reversible light-induced switching of T_c was observed compared to the null effect found in the SAM-free reference sample (Figure 2, right). We attribute this effect to the conformational changes of the azobenzene ring accompanied by reversal of the molecule dipole induced by illumination (see Supporting Information and references therein). The long relaxation time of each molecular state may pave the

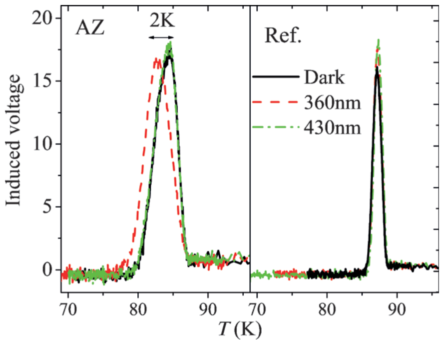

Figure 2. Reversible light-induced T_c switching of YBCO-coated AZ monolayer (left) compared to the null effect found in the SAM-free reference sample (right) measured by the imaginary component of the induced voltage in the AC susceptibility. Excitation by UV light (360 nm, dashed line) causes a 2 K decrease in T_c, whereas illumination with 430 nm (dashed-dot line) increases T_c to its original value (solid line). The value of T_c is defined by the peak in the signal. Light-induced T_c modulation of 2 K was observed.

way to zero-power switching devices and light-induced dissipationless memory storage.

Figure 3 shows T_c modulation with the use of a porphyrin-based heterostructure stimulated by a single light source. As expected, illuminating the sample results in an increase in T_c. The T_c value decreases to its original value when the light is switched off, indicating that the charge has been transferred back to the (hole-doped) cuprate layer. The change in carrier concentration inferred from the enhancement of T_c and the charge dynamics is in agreement with time-resolved surface-potential measurements taken by KFM (Figure 3, inset). This result indicates that light induces electron transfer to the porphyrin heterostructure. These electrons relax back to the cuprate surface once the light is switched off.

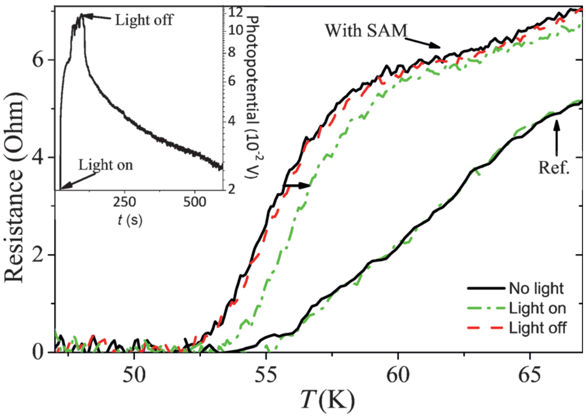

Figure 3. T_c modulation of YBCO sample with the use of a porphyrin-based heterostructure stimulated by a single light source. The T_c of the sample increased by 1 K when illuminated by 520 nm diode light (dashed-dot line). The T_c relaxes (dashed line) back almost to its original value (solid line) once the light is turned off. No effect was detected for the reference sample (the two right graphs). Inset: A photopotential of 120 mV was generated by light excitation of the porphyrin heterostructure. This photopotential relaxes to zero when the light is turned off. Both the surface potential and its dynamics are in qualitative agreement with the T_c modulation.

We shall now discuss the possible mechanisms of T_c modulation. The strong dipolar field created by the SAM is screened by charge transferred from the cuprate surface. In all cases described above, electrons are transferred from the superconductor, leaving a hole at the surface, which increases (decreases) the extent of hole (electron) doping. This process results in T_c enhancement for both underdoped YBCO and overdoped PCCO. A simple calculation of the charge transfer needed to compensate for the field, deduced from KFM surface-potential measurements, assuming a SAM thickness of a few nanometers, gives the right order of magnitude, namely 0.01 holes per unit cell.

However, our results suggest that the charge transfer occurs over a distance greater than the coherence or the screening lengths (a few nanometers for both cases). Otherwise, it is difficult to explain the decrease in T_c upon CF or AZ adsorption (see the Supporting Information). Charge transfer on relatively large length scales has been reported for electron-doped cuprates.[13] It is possible that this charge transfer, together with a proximity effect, results in T_c enhancement in a significant volume fraction of the film.

Of the various SAMs tested herein, it seems that the CF and the AZ SAMs are the most efficient. This conclusion is evident from the relatively large change in T_c obtained for PCCO when using the former and a significant change in YBCO in the vicinity of the dome maximum. During the preparation of this manuscript, we became aware that T_c enhancement of Nb thin films proximity-coupled to gold nanoparticles using organic linkers was recently reported.[14]

The novel approach for modulating T_c based on the design of functional SAMs presented herein may pave the way to new dissipationless memory storage and switches based on high-T_c superconductors.

Experimental Section

YBCO films 500 Å thick were deposited by RF sputtering at 770 °C and 400 mTorr oxygen pressure. For underdoped samples, the films were annealed at a low oxygen pressure of 0.1 Torr for 3 h. PCCO films were deposited by the pulsed-laser deposition technique at 780 °C and 230 mTorr N_2O. For all films used, one piece of the film was kept as a reference. It went through a process identical to that of the samples but without SAM adsorption.

Compounds A–C were synthesized by us and adsorbed as SAMs on the superconductor surfaces (see the Supporting Information).

Measurements: Resistance was measured with a modified Quantum Design PPMS platform that enabled us to shine light through an optical fiber during cool down. AC susceptibility was measured by a lock-in technique with the use of two coils.

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