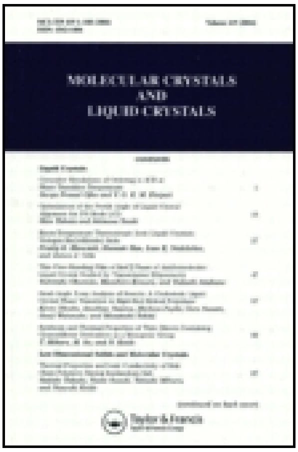

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MOLECULE/HIGH-T_C SUPERCONDUCTOR STRUCTURES AS OPTICAL SENSORS

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Abstract By combining patterned high-temperature superconductor thin films with overlayers of molecular materials, a new generation of hybrid optical sensors is obtained. Here, the ability of molecular dye layers to influence the light sensing properties of a high-T_C superconducting bolometer is described. These dye-coated devices are shown to display selective optical responses which are dependent on the properties of the molecular layer. Two different types of molecular absorbing layers prepared from molecular dyes and conductive polymers are examined in this paper Furthermore, the prospects for producing wavelength tunable detectors from hybrid conducting polymer/superconductor structures are addressed.

INTRODUCTION

In the past few years, molecular materials have increasingly been studied for use as active and passive elements in electronic devices. In this regard, molecular dyes and conducting polymers have both been examined. Molecular dyes have been utilized in combination with metal or semiconductor templates in order to fabricate chemical sensors, wavelength-selective optical detectors, and photovoltaic cells.[1] Moreover, conducting polymers have been incorporated into electronic devices such as electrochromic windows, diodes, triodes, transistors, optical switches, and optical memory devices.[2-7] Furthermore, the ability to produce light-emitting diodes (LED) from conducting polymers has been demonstrated recently.[8] These newly discovered LED's have been reported to display efficiencies which rival those of conventional solid-state LED's, and have tunable optical emission characteristics that are not achievable with conventional devices.[9] Even though the switching speeds of molecule-based electronics generally do not exceed those that can be obtained with conventional solid-state devices,[3] molecular materials offer prospects for enhanced sensitivity and selectivity that are not possible with conventional devices. Furthermore, the ability to alter the electronic and optical properties of molecular materials through chemical derivatization provides opportunities to create a vast array of useful devices from these materials.[9, 10]

With the discovery of high temperature superconductivity in the cuprate materials by Bednorz and Müller,[11] new opportunities exist to examine electronic interactions between molecular and superconducting materials. Accordingly, earlier we reported the first two classes of molecule/superconductor devices. For the first device a hybrid optical sensor was fabricated from a $YBa_2Cu_3O_{7-\delta}$ element coated with a molecular dye layer.[12] Using a $YBa_2Cu_3O_{7-\delta}$ microbridge junction coated with a thin film of polypyrrole, we later demonstrated that conducting polymers can be used to modulate the superconducting transition temperature (T_c) and critical current (J_c) of a high-T_c superconductor thin film structure.[13]

In this paper, we describe the preparation and characterization of molecule/superconductor hybrid optical sensors which utilize thin films of molecular dyes as a light absorbing layer. Furthermore, we examine the prospects for combining conducting polymers and superconductor elements in order to prepare a new generation of hybrid optical sensors.

EXPERIMENTAL

Thin films of $YBa_2Cu_3O_{7-\delta}$ were deposited onto MgO and $LaAlO_3$ single crystal substrates using the laser ablation technique. Microbridge junctions were patterned into the central region of the $YBa_2Cu_3O_{7-\delta}$ thin films by diamond scribe etching. The organic dyes H_2-octaethylporphyrin (H_2-OEP)[Aldrich] and H_2-phthalocyanine (H_2-Pc)[Strem] were purified by sublimation. Similarly, vacuum sublimation was used to deposit dye layers onto substrates which were maintained at liquid nitrogen temperatures. The conducting polymer poly(3-hexylthiophene) [P3HT] was synthesized and deposited as previously described.[14, 15] Thin films of P3HT were deposited onto $YBa_2Cu_3O_{7-\delta}$ thin films using spray-coating deposition method which was completed at room temperature. Optical measurements of the dye/superconductor composite structures were taken using conditions described earlier.[12, 16, 17]

RESULTS

As described previously, hybrid molecule/superconductor sensors can be prepared from patterned $YBa_2Cu_3O_{7-\delta}$ thin films coated with a thin film of an organic dye such as H_2-octaethylporphyrin.[12] In Figure 1A, the optical response of a bare $YBa_2Cu_3O_{7-\delta}$ microbridge and the same microbridge coated with H_2-octaethylporphyrin is provided. The variation in magnitude of the optical response noted as a function of wavelength for the uncoated $YBa_2Cu_3O_{7-\delta}$ microbridge can be attributed to the throughput for the monochromator/quartz-tungsten-halogen light source. This response is similar to that which is obtained for a thermal detector such as a pyroelectric sensor.

However, the optical response characteristics for the same microbridge coated with a thin layer of H_2-octaethylporphyrin shows dramatic changes in the spectral response features. The magnitude of the signal from the dye/$YBa_2Cu_3O_{7-\delta}$ microbridge device is increased substantially over the entire visible spectral region as compared to the uncoated device. This enhancement shows that the dye layer serves as an effective antenna for visible radiation and that it is able to effectively transfer the energy into the superconductor. Figure 1B displays the difference spectrum obtained when the response of the uncoated superconductor is subtracted from that of the dye-coated superconductor. Here the data is ratioed to the input power at each wavelength. Thus, the ratioed difference represents the enhancement caused by the dye.

Interestingly, the absorption spectrum obtained for a film of H_2-octaethylporphyrin deposited on glass obtained using a conventional UV/VIS spectrophotometer displays very similar spectral characteristics to those of the difference spectrum in Figure 1B. Thus, it is clear that the enhancements in the optical response of the dye-coated superconductor occur most prominently at those wavelengths which the dye most strongly absorbs light. These results demonstrate that efficient thermal coupling exists between the molecular dye and superconductor element.

More importantly, since the dye/superconductor device senses those wavelengths absorbed by the dye most strongly, the hybrid detector can be said to be wavelength selective. Unlike wavelength selective dye/semiconductor detectors in which the dye layer acts as a filter element to diminish the overall response of the detector[1], dye layers incorporated into dye/superconductor devices actually increase the overall responsivity of the detector. Furthermore, since the wavelength selectivity of the hybrid detector depends on the absorption properties of the dye, alterations of the dye layer can be accomplished through chemical modifications of the dye to provide a vast array of new optical sensors.

Through the use of dye layers, the ability of molecular materials to influence the properties of superconductors has been demonstrated. In order to further understand the physical properties of molecule/superconductor devices, it is important to utilize other molecular materials, such as conducting polymers, in hybrid

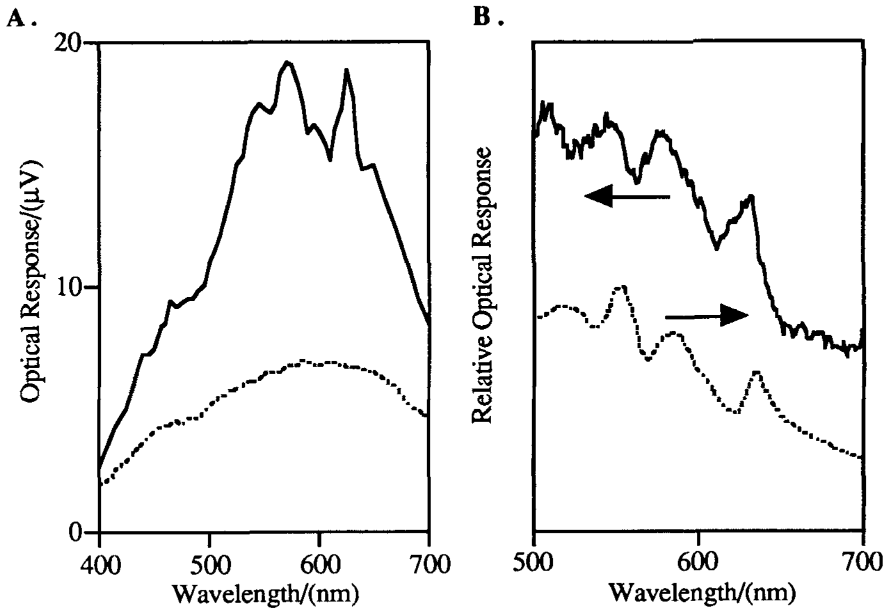

FIGURE 1 Optical response versus wavelength for a 3mm x 50µm $YBa_2Cu_3O_{7-\delta}$ microbridge device operating at a temperature just below T_c (mid): (A) unprocessed signals of bare junction (lower curve) and junction coated with 3300Å of H2-octaethylporphyrin (upper curve), (B) comparison between the absorbance spectrum of a H2-octaethylporphyrin film (1.1 µm thick) as measured by UV-visible spectrophotometry (lower curve) and the normalized optical signal of the dye-superconductor device with the uncoated junction response subtracted (upper curve).

molecule/superconductor devices. Conducting polymers, which were utilized in conducting polymer/superconductor structures, have already been shown to influence the electronic properties of high temperature superconductors.[13] Conducting polymers are also attractive candidates for use in hybrid optical devices due to their high absorptivity in the visible and near-infrared spectral regions. Moreover, the changes in the thermal diffusivity in these systems upon doping, which is associated with delocalized π-electrons, may be an important factor that can be utilized in order to prepare optical sensors with high sensitivities. Electroactive polymers, including both conjugated and redox polymers, provide further motivation for their utilization in preparing composite optical detectors due to their interesting electrochromic properties.[3, 18, 19]

In this regard, poly(3-hexylthiophene) is one of the best choices due to the dramatic color changes that occur when it is cycled from the neutral (red) form to the oxidized (blue) form. As can be seen in Figure 2, a thin film of poly(3-hexylthiophene) when coated onto a transparent electrode displays a modulatable visible absorption spectra which is easily controlled by the oxidation state of the conducting polymer. Furthermore, the potential range utilized to collect the spectra in Figure 2 falls within the potential window over which $YBa_2Cu_3O_{7-\delta}$ is stable. Therefore, substantial changes in spectral features are obtainable for P3HT coated onto $YBa_2Cu_3O_{7-\delta}$ electrodes/devices, and these features are tunable by using chemical or electrochemical doping. This ability, when utilized in a conducting polymer/superconductor detector, should provide the basis for wavelength tunable optical sensor.

Initial studies have shown that differences in the optical response characteristics of a P3HT/$YBa_2Cu_3O_{7-\delta}$ device are found when the conducting polymer is electrochemically cycled between its neutral and oxidized forms. To accomplished this objective, the underlying superconductor thin film was utilized as the working electrode, and tetraethylammonium tetrafluoroborate in acetonitrile was used as the

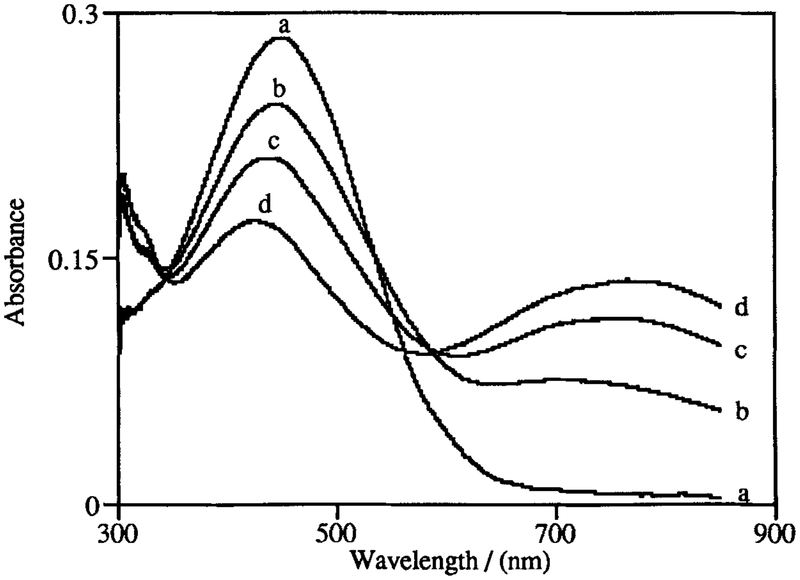

FIGURE 2 Spectroelectrochemistry data obtained for an indium tin oxide electrode coated with a 1000Å poly(3-hexylthiophene) film at different electrode potentials : (a) neutral form, (b) at 0.8 V, (c) at 0.9 V, (d) at 1.0 V vs SCE. The spectra were recorded in 0.1 M tetraethylammonium tetrafluoroborate/acetonitrile solution.

electrolytic fluid. The preliminary observations that we have found for the optical response of the conducting polymer/superconductor device are consistent with changes in the light absorbing properties of the conducting polymer as a function of doping level. Furthermore, there also appear to be differences in the efficiencies through which the energy is transferred to the superconductor element. It is evident that further optical studies of conducting polymer/superconductor systems need to be completed in order to obtain a better understand their properties.

CONCLUSIONS

Here we report strategies that can be exploited to prepare well-behaved molecule/superconductor structures. By combining molecular materials with patterned superconductor films, a new type of hybrid optical sensor has been demonstrated. Moreover, the initial results related to the utilization of conducting polymer thin films for the fabrication of wavelength tunable devices have been discussed.

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