with C_{60} to form monolayer films of the fullerene, Scheme I.

In a typical experiment, a base-treated indium-tin-oxide (ITO) electrode is soaked in a 0.25 M benzene solution of $(MeO)_3Si(CH_2)_3NH_2$ under reflux conditions for 8-12 h. The electrode is then rinsed with benzene, dichloromethane, and acetonitrile; and the decreased hydrophilicity of the resulting surface is verified with contact angle measurements ($\Theta = 46°$), Table I.[8] The $(MeO)_3Si(CH_2)_3NH_2$-treated electrode is then soaked in a 1 mM benzene solution of C_{60} for 1-2 days under reflux conditions. The electrode is rinsed and sonicated in benzene for 2 min to remove residual physisorbed C_{60}. The relative hydrophobicity of the resulting C_{60}-modified surface is confirmed via contact angle measurements ($\Theta = 72°$), Table I. Quartz and glass may be modified with C_{60} in a similar manner.

The transmission UV-vis spectrum of quartz first treated with $(MeO)_3Si(CH_2)_3NH_2$ and then with C_{60} is similar to the spectrum of C_{60} cast on quartz and shows three bands with λ_{max}'s at 226, 256, and 286 nm. The cyclic voltammetry of a $(MeO)_3Si(CH_2)_3NH_2$-treated ITO electrode modified with C_{60} yields the electrochemical response shown in Figure 1A.[9] The $E_{1/2}$ values for the reductive waves (−1.14 and −1.51 vs Fc/Fc^+) observed in Figure 1A are substantially more negative than the $E_{1/2}$ value for the first two reductions for unmodified C_{60} (−0.98 and −1.38 V).[10] These shifts of −0.16 and −0.13 V, respectively, are consistent with a bond-forming reaction between the self-assembled C_{60} molecules and the underneath amine layer. Similar shifts in potential, although substantially larger in magnitude (−0.50 and −0.54 V, respectively), have been reported for a hexasubstituted amine (morpholine) adduct in solution.[6] Although the number of surface amine units which react with each C_{60} molecule cannot be unequivocally determined, on the basis of comparison between the electrochemical data for SAMs of C_{60} and the hexaamine adduct,[6] we suspect that no more than two surface amine units react per C_{60} molecule. The resolution of the waves in Figure 1A reflects the homogeneity of the surface fullerene species and suggests that each of the fullerenes in the SAM has a similar chemical identity, mono- and/or disubstituted adducts. Assuming that each wave in Figure 1A corresponds to a one-electron transfer, integration of the current associated with these waves is consistent with monolayer coverage ($\sim 1.7 \times 10^{-10}$ mol/cm^2). Models based on crystallographic data for C_{60}[11] predict a surface coverage of $\sim 1.9 \times 10^{-10}$ mol/cm^2 for a closed packed monolayer of C_{60}.

Significantly, SAMs of C_{60} can be further modified with a series of amine reagents; the water contact angles of the resulting films were measured and are displayed in Table I. There is excellent correlation with the type of amine reacted with SAMs of C_{60} and the expected wettability of the surface obtained from such a reaction. For example, ethylmethylamine yields a surface with a contact angle of 63° while 2-(methylamino)ethanol yields a relatively hydrophilic surface ($\Theta = 42°$) because of its pendant alcohol functionality. *p*-Ferrocenylaniline yields a hydrophobic surface ($\Theta = 67°$) with redox activity associated with the pendant ferrocene, Figure 1B. The cyclic voltammetry of a SAM of C_{60} on amine-treated ITO after reaction with *p*-ferrocenylaniline shows reductive waves ($E_{1/2} = -1.16$ and −1.56 V vs Fc/Fc^+) expected for materials containing C_{60} as well as an additional wave which we assign to ferrocene oxidation ($E_{1/2} = 0.04$ V vs Fc/Fc^+). The surface coverage of the *p*-ferrocenylaniline layer is 1.2×10^{-10} mol/cm^2 as determined by integration of the current associated with the wave assigned to ferrocene oxidation, Figure 1B. The $E_{1/2}$ for the adsorbed *p*-ferrocenylaniline is 0.10 V more positive than the $E_{1/2}$ for *p*-ferrocenylaniline in solution (−0.06 V vs Fc/Fc^+). This indicates that the NH_2 of *p*-ferrocenylaniline has reacted with C_{60}, and the shift in $E_{1/2}$ to more positive values reflects the electron-withdrawing nature of C_{60}.[12] The broadness of the waves associated with reduction of C_{60} may be attributed to the variety of possible ferrocenylaniline–C_{60} adducts formed from such a reaction. The regiochemistry of the amine addition to the surface C_{60} molecules may not be determined experimentally. The *p*-ferrocenylaniline–C_{60} bilayer films are indefinitely stable to cycling through ferrocene oxidation, but electrodes modified with these bilayer films lose electrochemical activity when held at negative potentials (−1.8 V) for extended periods of time. XPS studies before and after electrochemical cycling confirm the removal of the ferrocenylaniline and C_{60} layers from the surface.[13]

The self-assembly of C_{60} onto oxide surfaces is the first example of covalent attachment of a fullerene to a surface and represents the first step toward rationally designed, supramolecular multilayered structures consisting of alternating layers of fullerenes and other chemical reagents. Indeed, the demonstration that such films may be modified with a variety of amine reagents illustrates the potential of the self-assembly process for growing layered three-dimensional fullerene structures. We are currently probing the chemical and physical properties of these novel films and exploring the possibilities of using other fullerene building blocks to grow layered structures with desirable properties.

Acknowledgment. We thank Northwestern University for support of this work and acknowledge Professor John Ketterson for supplying us with fullerene-rich soot.

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[7] $(MeO)_3Si(CH_2)_3NH_2$ was first immobilized on oxide surfaces by the following: (a) Moses, P. R.; Wier, L.; Murray, R. W. *Anal. Chem.* **1975**, *47*, 1882. (b) Haller, I. *J. Am. Chem. Soc.* **1978**, *100*, 8050.

[8] A Ramé-hart Model A-100 goniometer was used for all contact angle measurements. Contact angle measurements are commonly used to assess surface composition. See: Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321 and references therein.

[9] All electrochemistry was performed in CH_2Cl_2/0.1 M Bu_4NPF_6.

[10] Our electrochemical data for C_{60} was taken at an ITO working electrode and compares well to literature values: (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (c) Allemand, P.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. (d) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

[11] The model assumes a molecular diameter of 7 Å and a mean distance between molecular centers of 3 Å. See: Liu, S.; Lu, Y.; Kappes, M. M.; Ibers, J. A. *Science* **1991**, *254*, 408.

[12] Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134 and references therein.

[13] The strong Fe(2p) peaks observed prior to potential excursions to −1.8 V diminished in intensity. The relative intensity of C(1s) to N(1s) also decreased in a similar fashion.

Crown Ether Ionophores. Construction of Neutral Carrier Ion-Selective Electrodes

Robert M. Moriarty,[*,†] M. Suresh Chander Rao,[†]
Sudersan M. Tuladhar,[†] Claudius D'Silva,[‡] Gwyn Williams,[‡]
and Richard Gilardi[§]

Department of Chemistry (M/C 111)
University of Illinois at Chicago
Box 4348, Chicago, Illinois 60680
Institute of Molecular and Biomolecular Electronics
University of Wales, Dean Street, Bangor
Gwynedd LL 57 IUT, United Kingdom
Naval Research Laboratory, Laboratory for the
Structure of Matter, Code 6030
4555 Overlook Avenue SW, Washington, D.C. 20375-5000

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We report the synthesis of novel crown ether ionophores which contain a 1,4-bridged cubyl system as a rigid lipophilic component.[1]

[†] University of Illinois at Chicago.

[‡] University of Wales.

[§] Laboratory for the Structure of Matter.

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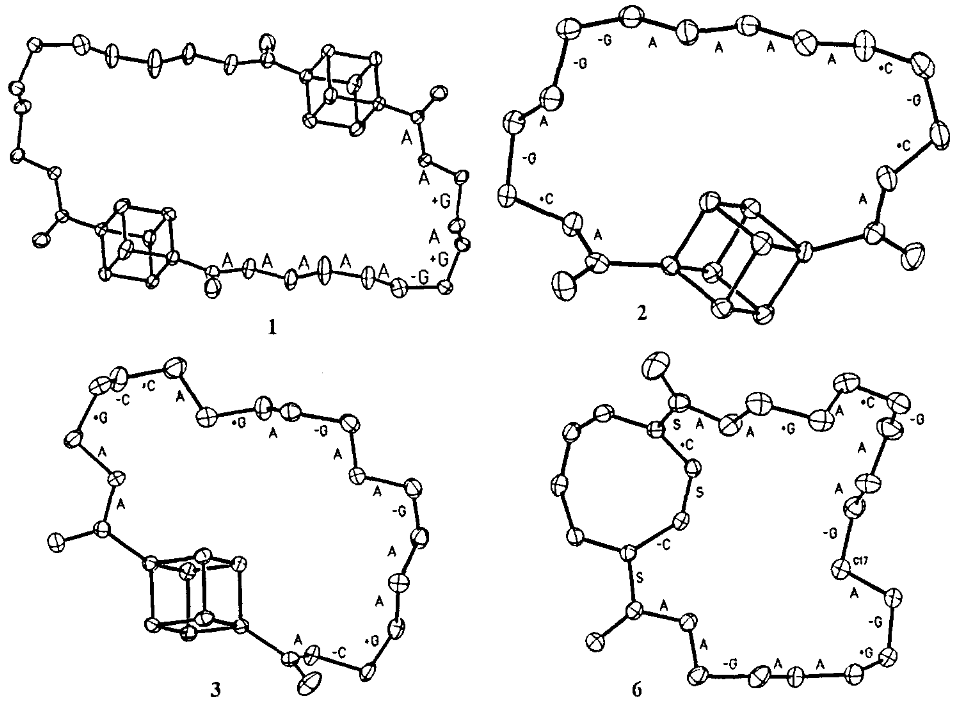
Chart I



1

2

3

6

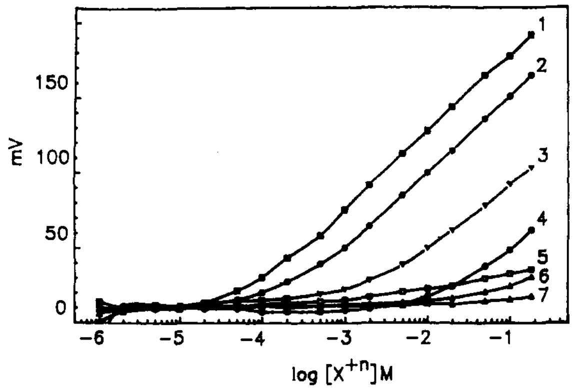


Figure 1. Calibration curve of an electrode based upon ionophore **1** in 0.1 M Tris-HCl (pH 7.5). Electrode exposed to salts of (1) Cs^+, (2) K^+, (3) NH_4^+, (4) Na^+, (5) Ca^{2+}, (6) Li^+, and (7) Mg^{2+}.

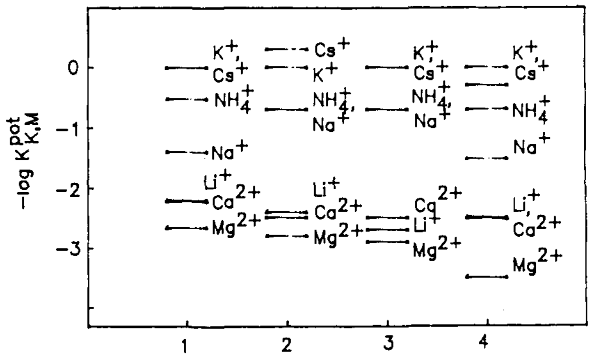


Figure 2. Selectivity coefficients obtained using the fixed interference method for K^+ electrodes with ionophores **1**, **2**, **3**, and **4**.

Compound **1** is a dinuclear crown-8 example, while **2**, **3**, and **4** are mononuclear 1,4-bridged cubyl diester crown-5, crown-6, and crown-7 examples. Cubyl diester crown ethers **2**, **3**, and **4** undergo Rh(II)-catalyzed rearrangement to the corresponding 1,4-bridged 1,3,5,7-cyclooctatetraene (COT) crown-5, -6, and -7 ethers, **5**, **6**, and **7**, respectively.[2,3]

The structures of **1**, **2**, **3**, and **6** are rigorously established by X-ray crystallographic determination.[4] In the thermal ellipsoid

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(1) Compounds **1**, **2**, **3**, and **4** are formed via the reaction of the cubane-1,4-dicarbonyl dichloride with the appropriate ethylene glycol. **1** (15%): mp 128–129 °C; IR (KBr) 1723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.56 (8 H, s, OCH_2), 3.62–3.64 (8 H, m, OCH_2), 4.14 (12 H, s, CH), 4.16–4.19 (8 H, m, $COOCH_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 46.76, 55.5, 63.5, 68.98, 70.63, 171.01; CIMS (M^+ + 1) 613 (100). Anal. Calcd for $C_{32}H_{36}O_{12}$: C, 62.74; H, 5.92. Found: C, 62.45; H, 5.98. **2** (25%): mp 153–154 °C; IR (KBr) 1727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.57–3.6 (4 H, m, OCH_2), 3.62–3.64 (4 H, m, OCH_2), 3.68–3.70 (4 H, m, OCH_2), 4.29–4.31 (4 H, m, $COOCH_2$), 4.30 (6 H, s, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 47.06, 56.69, 64.18, 68.8, 70.34, 71.4, 171.27; CIMS (M^+ + 1) 351 (32); HR EIMS $C_{18}H_{22}O_7$ requires *m/z* 350.1366, found 350.1369. Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.84; H, 6.37. **3** (40%): mp 89–90 °C; IR (KBr) 1728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.57–3.59 (8 H, m, OCH_2), 3.62–3.64 (8 H, m, OCH_2), 4.22–4.24 (4 H, m, $COOCH_2$), 4.25 (6 H, s, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 46.81, 55.89, 63.54, 68.61, 70.25, 70.56, 70.92, 171.07; CIMS (M^+ + 1) 395 (28). Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64. Found: C, 61.00; H, 6.58. **4** (20%): mp 55–56 °C; IR (neat) 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.63–3.68 (20 H, m, OCH_2), 4.24–4.27 (4 H, m, $COOCH_2$), 4.25 (6 H, s, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 47.0, 55.85, 63.59, 68.80, 70.38, 70.71, 70.80, 71.15, 171.33; CIMS (M^+ + 1) 439 (36). Anal. Calcd for $C_{22}H_{30}O_9$: C, 60.26; H, 6.90. Found: C, 60.14; H, 6.87.

(2) Rh(II) rearrangement proceeds in high yield to give **5**, **6**, and **7**. Similar rearrangement of cubane to COT using Cu(I) and Pd(0) in refluxing triethylamine recently has been reported: Eaton, P. E.; Stössel, D. *J. Org. Chem.* **1991**, *56*, 5138. The Rh(I)-catalyzed rearrangement of cubanes to *syn*-tricyclooctadienes and their thermal opening to cyclooctatetraenes (Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 6366) can be used to prepare substituted cyclooctatetraenes): Eaton, P. E.; Chou, C.-T. Unpublished observations.

(3) **5** (48%): mp 80 °C; IR (neat) 1721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.60–3.77 (12 H, m, OCH_2), 4.15--4.2 (2 H, m, $COOCH_2$), 4.39–4.44 (2 H, m, $COOCH_2$), 6.03 (2 H, s, $=CH$), 6.16 (2 H, s, $=CH$), 7.07 (2 H, s, $=CH$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 64.72, 68.82, 70.38, 70.91, 130.19, 132.26, 133.73, 142.23, 165.43; CIMS (M^+ + 1) 351 (100); HR EIMS $C_{18}H_{22}O_7$ requires *m/z* 350.1366, found 350.1374. **6** (52%): mp 79–80 °C; IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.62–3.72 (12 H, m, OCH_2), 3.75–3.81 (4 H, m, OCH_2), 4.25–4.38 (4 H, m, $COOCH_2$), 6.04 (2 H, s, $=CH$), 6.17 (2 H, s, $=CH$), 7.06 (2 H, s, $=CH$); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 64.83, 69.06, 70.95, 71.05, 71.27, 130.34, 132.24, 133.79, 142.0, 165.33; CIMS (M^+ + 1) 395 (100); HR EIMS $C_{20}H_{26}O_8$ requires *m/z* 394.1621, found 394.1628. **7** (40%): IR (neat) 1717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.6–3.7 (20 H, m, OCH_2), 4.2–4.4 (4 H, m, OCH_2), 5.9–6.2 (4 H, m, $=CH$), 7.0–7.15 (2 H, m, $=CH$); CIMS (M^+ + 1) 439 (100); HR EIMS $C_{22}H_{30}O_9$ requires *m/z* 438.1890, found 438.1891.

drawings in Chart I, single-letter torsion-angle codes are placed near the crown ether ring bonds: A = antiplanar (150–180°), C = anticlinal eclipsed (90–150°), G = gauche or synclinal (30–90°), and S = synplanar (0–30°).

The dinuclear example **1** possesses a center of symmetry, and this property likewise persists in fluid solution as revealed by the ^{1}H NMR.[1] The large-ring compound **1** displays a centric, approximately rectangular shape made up of antiplanar torsions along its sides, with one or two gauche torsions at each corner. This is very similar to the uncomplexed form of 18-crown-6 1,4,7,10,13,16-hexaoxacyclooctadecane.[5] The smaller ring compounds **2**, **3**, and **6** each contain atypical anticlinal torsion angles. These signal a certain amount of local strain (at least one CH bond eclipsed with a ring bond) probably caused by the introduction of a sterically rigid group into a closed ring. 1,4-COT-crown-6 (**6**) shows one of the double bonds of the COT directed toward the cavity of the polyether with the remaining triene essentially exocyclic to the cyclic polyether.

Crown ethers of such rigidly defined structures suggest applications in the construction of ion-selective electrodes, and this was pursued, with the results summarized and presented in Figures 1 and 2. Figure 1 shows sub-Nernstian responses of ionophore **1** to K^+ (52 mV), Cs^+ (48 mV), NH_4^+ (45 mV), and Na^+ (43 mV) in a poly(vinyl chloride)-2-nitrophenyl octyl ether (PVC-NPOE) KTClPB polymeric membrane to various cations.[6] These data indicate that there is no significant effect of ring size upon selectivity for the various ions, although subtle effects are observed for some ions, e.g., Cs^+ and Na^+. Importantly, the K^+/Na^+ potentiometric response difference of $\sim 10^{-1.5}$ (Figure 2) qualifies these series of compounds potentially to be good potassium-selective ionophores, in view of the range of further possible modifications to improve selectivity.

Efficacy of an ion-selective ionophore depends, inter alia, upon lipophilicity (solubility in membrane without loss to the aqueous ionic solution), conformational flexibility (ion selectivity and fast ion exchange), and relatively low molecular weight (high mobility). These factors are frequently mutually opposed. A long-chain hydrocarbon group increases membrane solubility with a commensurate increase in molecular weight and decrease in mobility.[7] The cubyl group may be viewed as a low molecular weight concentrated lipophilic center which fixes the ionophore in the membrane, and this is especially true in the case of macrocyclic polyethers containing two or more cubyl units such as **1**.[8] These C_8 centers anchor the polyether into the membranes.

In conclusion, the K^+/Na^+ selectivity achieved thus far is sufficient for analytical and biomedical applications. Obvious applications to valinomycin-like antibiotics involving transmembranal ion transport are subjects of active investigation.[9] The combination of the π-donor ligand system of 1,4-COT-crown-6 (**6**) and the Lewis base donors of the polyether makes this compound and reduced forms, such as COD, interesting ligands in organometallic chemistry.

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(4) Crystal data for **1**: space group $P\bar{1}$, $a = 7.805(2)$ Å, $b = 9.563(2)$ Å, $c = 10.664(3)$ Å, $\alpha = 105.21(2)°$, $\beta = 92.39(2)°$, $\gamma = 104.54(2)°$, $V = 738.6(3)$ Å^3, $Z = 1$, $D_{calcd} = 1.377$ mg mm^{-3}, $R = 0.043$ for 1685 observed reflections. **2**: space group $P2_1/c$, $a = 10.998(5)$ Å, $b = 19.272(9)$ Å, $c = 7.903(3)$ Å, $\beta = 95.08(3)°$, $V = 1668.4(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.395$ mg mm^{-3}, $R = 0.071$ for 1137 observed reflections. **3**: space group $Pca2_1$, $a = 8.652(2)$ Å, $b = 12.008(2)$ Å, $c = 18.501(3)$ Å, $V = 1922.2(6)$ Å^3, $Z = 4$, $D_{calcd} = 1.363$ mg mm^{-3}, $R = 0.039$ for 1381 observed reflections. **6**: space group $P\bar{1}$, $a = 8.283(2)$ Å, $b = 10.339(2)$ Å, $c = 12.033(3)$ Å, $\alpha = 93.32(2)°$, $\beta = 100.28(2)°$, $\gamma = 93.59(2)°$, $V = 1009.4(4)$ Å^3, $Z = 2$, $D_{calcd} = 1.298$ mg mm^{-3}, $R = 0.041$ for 2016 observed reflections.

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(10) Present address: School of Health Science, Pasteur Building, University of Sunderland, Sunderland, Tyne & Wear, SR1, 3SD, U.K.

Reversible Modulation of T_c in Conductive Polymer/High Temperature Superconductor Assemblies

Steven G. Haupt, David R. Riley, Christopher T. Jones,
Jianai Zhao, and John T. McDevitt*

Department of Chemistry and Biochemistry
University of Texas at Austin
Austin, Texas 78712

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The fabrication of electronic devices from conjugated polymers has attracted much attention recently. Molecular transistors, Schottky diodes, metal–insulator–semiconductor diodes, MIS field effect transistors, and light-emitting diodes have all been prepared utilizing these polymeric materials.[1-6] The active elements in these devices have been constructed by depositing the conductive polymer layer onto the surface of a metal, semiconductor, or insulating substrate. Here we report the preparation of a hybrid conducting polymer/high-temperature superconductor device consisting of a polypyrrole-coated $YBa_2Cu_3O_{7-\delta}$ microbridge. Electrochemical techniques are exploited to alter the oxidation state of the polymer, and in doing so, we observe for the first time that superconductivity can be modulated in a controllable and reproducible fashion by a polymer layer. Whereas the neutral (insulating) polypyrrole only slightly influences the electrical properties of the underlying $YBa_2Cu_3O_{7-\delta}$ film, the oxidized (conductive) polymer depresses T_c by up to 15 K. Thus, a new type of molecular switch for controlling superconductivity is demonstrated.

There are a number of important motivating factors for studying composite conductive polymer/high-T_c structures. The use of conductive polymers provides an alternative strategy for the construction of superconductor devices[7] and circuits. Moreover, the hybrid assemblies described in this paper may be utilized to study electron- and energy-transfer phenomena which occur at molecule/superconductor interfaces at temperatures above and below T_c.[8-10]

To prepare our polymer/superconductor sandwich devices, $\sim$1000 Å of $YBa_2Cu_3O_{7-\delta}$ is deposited onto a clean MgO(100) substrate using the pulsed laser ablation method.[11] A superconductor microbridge ($\sim$3 mm long and $\sim$100 μm wide) is created,[12] and pyrrole is electrochemically polymerized[13,14] directly

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