

Figure 1. Molecular structure of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{Tempo})_2$ (**1**) with thermal ellipsoids shown at the 50% probability level. Primed atoms are related to unprimed ones by a center of inversion located at the midpoint of the Rh-Rh bond.

ground-state configuration is extraordinarily sensitive to the identity of the adduct atoms,²⁴ but for oxygen donors like H_2O or Tempo the configuration is $\pi^4\sigma^2\delta^2\pi^*4\delta^*2$.¹⁹ The long axial Rh-O bond distances (2.22–2.29 Å) found here and in other $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4\text{L}_2$ structures⁸ reflect a weak σ donor interaction that is not expected to contribute significantly to the superexchange pathways for the Tempo radicals in **1**–**3**. However, the greater electronegativity of Rh compared to Mo¹⁹ combined with the filled antibonding orbitals for Rh in $\text{M}_2(\text{O}_2\text{CR})_4\text{L}_2$ compounds affords an effective π -back-bonding interaction with axial donors, and it is the energetic proximity and correct orbital symmetry that allows the filled Rh-Rh π^* orbitals to interact with the Tempo nitroxyl π^* orbitals containing the unpaired electrons. From the structures of **1** and **2** above, the C_2NO planes make dihedral angles of 47–52° with the equatorial carboxylate oxygen O_4 planes at distances of 2.22–3.29 Å. Complete spin pairing is known to occur in solid-state nitroxyl dimers²⁵ separated by up to 3.2 Å, an interaction that occurs through overlap of the $\pi^*-\pi^*$ orbitals.

For $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{Tempo})_2$ the nitroxyl oxygen lone pair is expected to interact very weakly with the Mo atoms in line with the insensitivity of the Mo_2^{4+} unit to axial donors.^{8,26} More importantly, all of the low-lying orbitals are filled in the $\sigma^2\pi^4\delta^2$ ground-state configuration involved in $\text{Mo}^4\text{-Mo}$ and Mo-O -(carboxylate) bonding. No orbitals drop into the proper range^{19,20} to interact with the nitroxyl π^* orbitals containing the unpaired electrons, and as such the quadruple bond allows no spin pairing of the axial nitroxyl groups.

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Registry No. **1**, 91443-89-9; **2**, 91443-90-2; **3**, 91443-91-3; **4**, 91443-92-4; $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4(\text{Tempo})_2$, 91443-93-5.

Supplementary Material Available: Listings of atomic positional parameters for **1** and **2**, and structure factor tables for **1** and **2** (33 pages). Ordering information is given on any current masthead page.

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Chemical Derivatization of an Array of Three Gold Microelectrodes with Polypyrrole: Fabrication of a Molecule-Based Transistor

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We wish to report the fabrication of a chemically derivatized microelectrode array that can function as a transistor when immersed in an electrolyte solution. The key finding is that we have been able to show that a small signal (charge) needed to turn on the device can be amplified. The device to be described mimics the fundamental characteristics of a solid-state transistor,¹ since the resistance between two contacts can be varied by a signal to be amplified. Figure 1 illustrates the device fabricated and the external circuit elements needed to characterize it. The chemical transistor is the set of three (drain, gate, and source) Au microelectrodes covered with polypyrrole. Three features are essential: (1) the three independent Au microelectrodes are closely spaced, 1.4- μm apart, allowing an easily measurable current to pass between the source and drain when V_D is significant and V_G is above the threshold, V_T ; (2) the polypyrrole exhibits a sharp change in conductivity upon oxidation;² the potential at which this occurs is V_T ; (3) each of the microelectrodes can be individually contacted. The input signal to the gate to be amplified is that needed to oxidize the polypyrrole.³ Importantly, V_T and the magnitude of signal needed to achieve V_T can be manipulated by variation of the molecule-based material. Conceptually, the device described here stems from the molecule-based "diode" and "triode" fabricated by derivatizing a macroscopic electrode with a redox polymer and a porous metal outer contact.⁴ Additionally, the device represented in Figure 1 is a type of "chemiresistor"⁵ where an electrical signal can change the resistance of the chemical layer.

Experiments have been carried out using "chips" consisting of a microelectrode array of eight individual Au electrodes deposited on a 0.45 μm thick SiO_2 insulator grown on (100) Si. Each of the eight microelectrodes can be addressed independently and is generally 3 μm wide \times 140 μm long \times 0.12 μm thick separated from each other by 1.4 μm .⁶ Microelectrodes can be functionalized with controlled amounts of polypyrrole by oxidizing 50 mM pyrrole in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}]\text{ClO}_4$ at +0.8 V vs. SCE, as described for macroscopic electrodes.² Microelectrodes derivatized in this manner can be characterized by cyclic voltammetry in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}]\text{ClO}_4$, revealing the typical response expected for surface-bound polypyrrole.²

When the microelectrode array is derivatized with a sufficiently large coverage of polypyrrole, the individual microelectrodes can

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(3) The particular arrangement shown in Figure 1 has been used for clarity. Any one of the three electrodes could be used as a "gate" with the other two being "source" and "drain". Use of the gate electrode allows a quantitative determination of the amount of charge necessary to turn the polypyrrole from insulating (off) to conducting (on). Thus, the "gate" allows a quantitative assessment of the behavior of a two-electrode device where the input "signal" could be a redox reagent that equilibrates with the polypyrrole to turn it on. The arrangement in Figure 1 explicitly differs from solid-state transistors where both the gate and drain potentials are fixed relative to the source.¹ The crucial fact is that polypyrrole undergoes a dramatic change in conductivity upon transfer of a small amount of charge.

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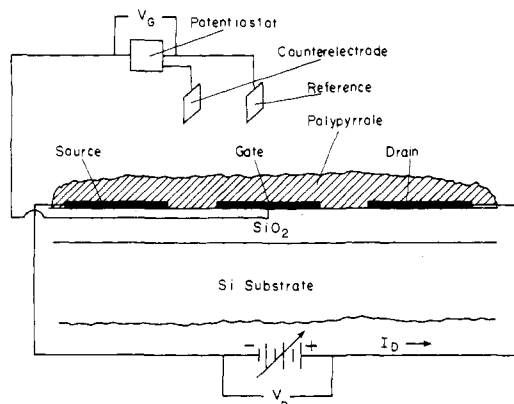


Figure 1. Cross-sectional view of the device fabricated and representation of the circuit elements used to characterize it. The SiO₂ layer is ~ 0.45 μm thick and is on a ~ 0.3 mm thick (100) Si substrate. The source, gate, and drain are Au, ~ 3 μm wide \times 140 μm long \times 0.12 μm thick coated with $\sim 10^{-7}$ mol/cm² of polypyrrole. When characterized, the derivatized microelectrode array, counter, and reference electrodes are immersed in electrolyte solution.

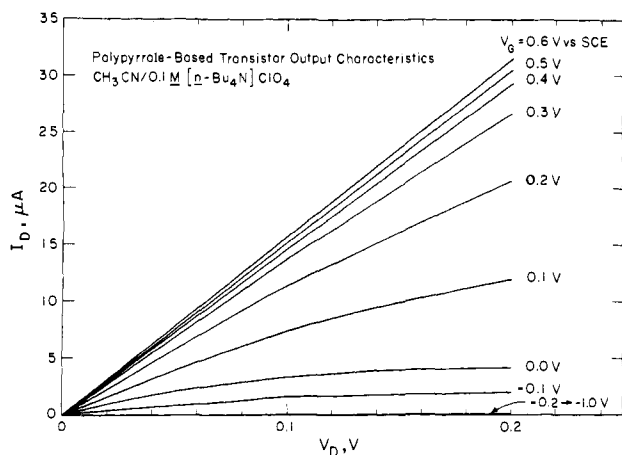


Figure 2. Output characteristics of the transistor shown in Figure 1 in CH₃CN/0.1 M [*n*-Bu₄N]ClO₄.

be electrically connected by the polymer.⁶ The experimental evidence for this is that all of the connected electrodes show the same cyclic voltammetry response (peak position, shape, and area), when measured individually and when they are externally connected together and driven as one electrode. When three microelectrodes are connected together with the polypyrrole as in Figure 1, the charge associated with the oxidation and reduction of the bound polymer is of the order of 10^{-2} C/cm² of exposed Au. Examination of derivatized microelectrode arrays by scanning electron microscopy confirms the presence of the polymer.

Characterization of a derivatized three-electrode array shows that a transistor characteristic can be obtained (Figure 2).⁷ In this set of measurements the two outer electrodes are wired as source and drain and the middle electrode is the gate (Figure 1).³ Figure 2 shows the current between source and drain, I_D , as a function of the potential between source and drain, V_D , at various

fixed gate potentials, V_G . When V_G is held at a negative potential where the polypyrrole is expected to be insulating, the device is "off" and I_D is small at values of $V_D < 0.5$ V. When V_G is moved to potentials more positive than the oxidation potential of polypyrrole, ~ -0.2 V vs. SCE, the device "turns on" and a significant steady-state value of I_D can be observed for modest values of V_D . We take the redox potential of polypyrrole to approximate the value of V_T , the gate potential at which the device starts to turn on. For V_G more positive than V_T the value of I_D increases at a given value of V_D , in a manner consistent with increasing conductivity of polypyrrole with an increasing degree of oxidation. At sufficiently positive values of V_G , $\gtrsim +0.5$ V vs. SCE, I_D becomes insensitive to further positive movement of V_G at a given value of V_D , a result consistent with measurements⁶ of the resistance of the oxidized polypyrrole coated on a microelectrode array. We typically use only a small range of V_D values because we seek to minimize electrochemical reactions at the source/polymer and drain/polymer interfaces. All measurements are for deoxygenated solutions, owing to problems stemming from irreversible oxidation of the polymer. However, in the absence of O₂ good durability (several days of use) can be achieved. Shelf life in the dry state exceeds 1 week for derivatized arrays.

For the devices studied, some fraction of 10^{-8} C of charge is required to obtain the maximum steady-state value of I_D at $V_D = 0.2$ V; the value of I_D achievable with the device represented in Figure 1 is $\sim 4 \times 10^{-5}$ C/s. Thus, a small signal to the gate can be amplified in much the same way that a small electrical signal can be amplified with a solid-state transistor.¹ A major difference, of course, between the solid-state device and the molecule-based device is that the turn on/turn off time in the molecule-based system depends on the rate of a chemical reaction whereas no chemical reactions take place in the solid-state devices. For the devices fabricated the on-off time is of the order of 10 s; the curves in Figure 2 are steady-state curves. For the molecule-based system the properties such as V_T and minimum turn on signal can be adjusted with rational variation in the monomer used to prepare the polymer. Smaller dimensions can lead to faster switching times and different molecule-based gate materials may have superior rates of switching compared to polypyrrole.

The molecule-based transistor reported here has no immediate practical application. The fundamental accomplishment is the demonstration of the synthesis of an interfacial chemical system that has a specific function. There is presently considerable interest in interfacing microelectronic devices with chemical and biological systems for sensor applications⁵ and in "molecular electronics" in general.⁸ Our work establishes that principles learned from the study of polymer-modified macroscopic electrodes^{4,9-14} can

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be applied in a much smaller dimensional regime to achieve specific functions where the molecule-based material is the active element.

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Measurement of Deuterium Kinetic Isotope Effects in Organic Reactions by Natural-Abundance Deuterium NMR Spectroscopy

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Deuterium and tritium kinetic isotope effects have been widely used in the diagnosis of reaction mechanisms,² and the synthesis of isotopically labeled reactants has become a frequently necessary if often laborious task. However, deuterium is present in trace amounts (~0.015%)³ in all ordinary hydrogen-containing compounds, and the advent of high-field NMR instrumentation now permits the relatively easy assessment of the amount of deuterium at specific molecular sites. The studies of Martin et al.^{4a-c} and Grant et al.^{4d} have shown that there can be dramatic variations in the deuterium distributions within identical compounds from different sources, which must reflect the differing chemical histories of these molecules. The high sensitivity of modern NMR spectrometers should permit the measurement of deuterium kinetic isotope effects using only deuterium at natural abundance as the isotopic label.

Consider the insertion of a carbene into a C-H bond of cyclohexane. Approximately 0.18% of the cyclohexane molecules will contain exactly one deuterium, very few will contain two or more (0.0003%), and the vast majority will contain none. The reaction of interest is the insertion of the carbene into monodeuteriocyclohexane, which involves intramolecular competition between different isotopic species at several chemically equivalent positions. The concentration of multiply labeled molecules is

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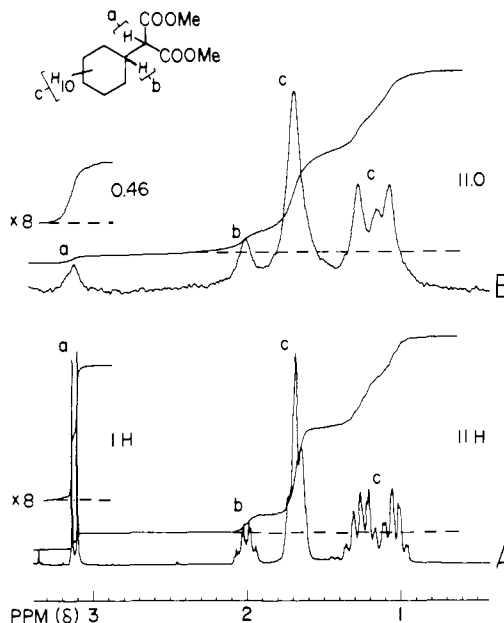


Figure 1. ¹H NMR (250 MHz) spectrum (A) and 38.4-MHz natural-abundance ²H NMR spectrum (B) of dimethyl 2-cyclohexylmalonate produced by photolysis of dimethyl diazomalonate in excess cyclohexane.

insignificant, and the undeuterated molecules will be invisible in the ²H NMR. It is clear from the analysis of Melander and Saunders⁵ that the ratio of the deuterium content of the product sites containing the hydrogens not transferred (*D*_{retained}) and that of the product sites containing the transferred hydrogen (*D*_{transferred}) will be constant throughout the course of the reaction and that the kinetic isotope effect for the C-H cleavage is given by

$$k_H/k_D = (D_{\text{retained}}/D_{\text{transferred}})[1/(n-1)] \quad (1)$$

where *n* is the number of chemically equivalent sites in the reactant.

The ¹H and ²H NMR spectra⁶ of dimethyl 2-cyclohexylmalonate prepared by photolysis of dimethyl diazomalonate⁷ in the presence of excess cyclohexane⁸ are illustrated in Figure 1. The deuterium resonances are readily assigned by comparison with the proton spectrum: the signals at δ 0.9-2.1 are due to the cyclohexyl group, while the peaks at δ 3.1 are those of transferred hydrogen. Comparison of the peak areas⁹ in both spectra indicates that the rate of deuterium transfer has been roughly half as great as that of protium. Setting the integral of the retained cyclohexyl deuterium is 11.0 in arbitrary units, the integral of the transferred deuterium is 0.46. Cyclohexane has 12 chemically equivalent sites, so, from eq 1, $k_H/k_D = (11.0/0.46)[1/(12-1)] = 2.2$. Data from three separate experiments gave an average value for k_H/k_D of 2.1 ± 0.1 . In a control experiment, dimethyl diazomalonate was photolyzed in the presence of 1:1 cyclohexane:cyclohexane-*d*₁₂;

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(6) The 38.4-MHz ²H NMR spectra were recorded on a Bruker WM250 Fourier transform spectrometer. Samples were prepared as 60-95% solutions in chloroform or carbon tetrachloride in 10-mm (o.d.) tubes. Spectra requiring 4000-16000 scans were obtained using a 90° pulse and a 4-s data acquisition of 4096 points with broad-band ¹H decoupling at 5 W of power. Free induction decays were weighted by using a 0.3-Hz line broadening and, in some cases, zero filled to 8192 points prior to Fourier transformation. The spectrometer was operated in the unlocked mode; to compensate for the slight drift in the magnetic field, FID's were acquired in blocks of 1000 scans. The blocks were individually transformed, and the resulting spectra were aligned and added.

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(9) Peak areas were measured by digital integration (shown in the figures) and by the cut-and-weigh method. There was no significant difference in the areas obtained by the two methods. Furthermore, neither exponential weighting nor zero-filling of the FID's had a significant effect on the relative peak areas.