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.

Acknowledgment. The authors wish to thank the Office of Naval Research for the support of this work under contract N00014-90-J-4106, and C.D'S.[10] thanks the SERC and Fellowship of Engineering for support.

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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, $Z = 1$, $D_{\text{calcd}} = 1.377$ 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, $Z = 4$, $D_{\text{calcd}} = 1.395$ 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, $Z = 4$, $D_{\text{calcd}} = 1.363$ 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, $Z = 2$, $D_{\text{calcd}} = 1.298$ mg mm^{-3}, $R = 0.041$ for 2016 observed reflections.

(5) Dunitz, J. D.; Seiler, P. *Acta Crystallogr.* **1974**, *B30*, 2739.

(6) (a) Tuladhar, S. M.; Williams, G.; D'Silva, C. *Anal. Chem.* **1991**, *63*, 2282. (b) Williams, G.; Tuladhar, S. M.; D'Silva, C. *J. Phys. Org. Chem.* **1992**, *5*, 437.

(7) (a) Kimura, K.; Yano, H.; Kitazawa, S.; Shono, T. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1945. (b) Kimura, K.; Matsuo, M.; Shono, T. *Chem. Lett.* **1988**, 615.

(8) The higher homolog tricubyl-1,4-dibridged diester crown-6 (30-membered ring) has been synthesized. Moriarty, R. M.; Rao, M. S. C. Unpublished results, 1992, U.I.C.

(9) Valinomycin is an excellent specific ionophore for K^+. (a) Pioda, L. A. R.; Stankova, V.; Simon, W. *Anal. Lett.* **1969**, *2*, 665. (b) Jenny, H.-B.; Riess, C.; Ammann, D.; Magyar, B.; Asper, R.; Simon, W. *Mikrochem. Acta* **1980**, *II*, 309. Valinomycin is a 32-membered crown ether just as **1** is a 32-membered cyclic system.

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

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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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(1) Chidsey, C. E.; Murray, R. W. *Science* **1986**, *231*, 25–31.

(2) Wrighton, M. S. *Science* **1986**, *231*, 32–37.

(3) Burroughs, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.

(4) Sailor, M. J.; Klavetter, F. L.; Grubbs, R. H.; Lewis, N. S. *Nature* **1990**, *346*, 155–157.

(5) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109* (22), 6627–6631.

(6) Garnier, F.; Horowitz, G.; Peng, X. E.; Fickov, N. *Adv. Mater.* **1990**, *2*, 592–594.

(7) Zhao, J.; Jurbergs, D.; Yamazi, B.; McDevitt, J. T. *J. Am. Chem. Soc.* **1992**, *114*, 2737–2738.

(8) Pinkowski, A.; Jüttner, K.; Lorenz, W. J. *J. Electroanal. Chem.* **1990**, *287*, 203–213.

(9) Peck, S. R.; Curtin, L. S.; McDevitt, J. T.; Murray, R. W. *J. Am. Chem. Soc.* **1992**, *114*. 6771–6775.

(10) Kaneto, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1987**, *26* (11), L1842–L1844.

(11) Dijkkamp, D.; Venkatesan, T.; Wu, X. D.; Shaheen, S. A.; Jisrawi, N.; Min-Lee, Y. H.; McLean, W. L.; Croft, M. *Appl. Phys. Lett.* **1987**, *51* (8), 619–621.

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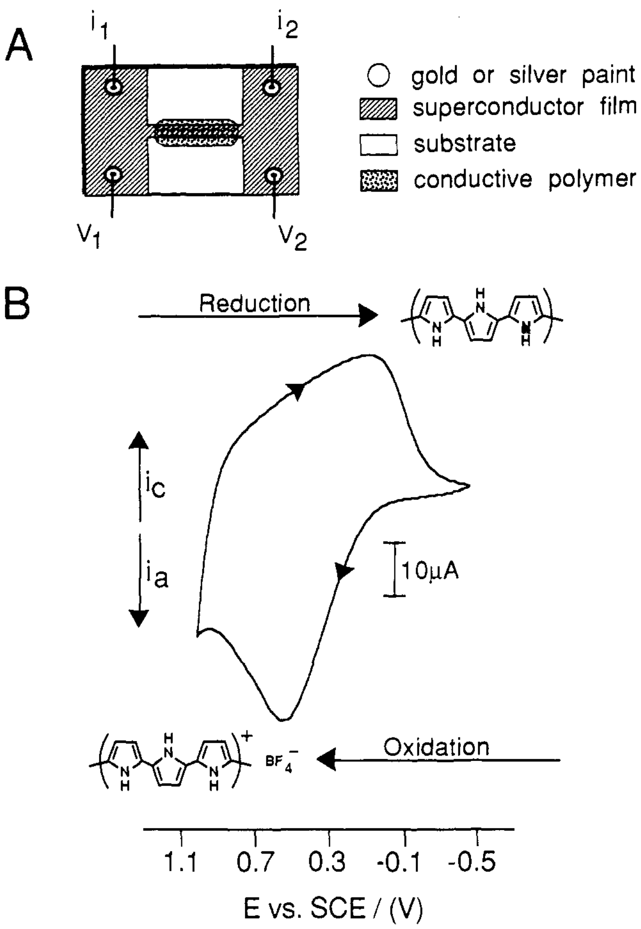

Figure 1. (A) Schematic illustration showing the conductive polymer/high temperature superconductor sandwich device. To prepare such a system, a $YBa_2Cu_3O_{7-\delta}$ thin film is deposited onto a MgO(100) substrate, then a microbridge is patterned into the central portion of the film, and finally a conductive polymer layer is deposited electrochemically onto the microbridge area. (B) Cyclic voltammetry (5 mV/s) recorded at room temperature in 0.1 M Et_4NBF_4/acetonitrile for a $YBa_2Cu_3O_{7-\delta}$ thin film electrode assembly coated with polypyrrole.

onto the microbridge. A schematic diagram of the completed polymer/superconductor sandwich is presented in Figure 1A.

The electrochemical procedure provides a convenient and versatile method to cycle the polymer between its neutral and oxidized forms.[15] The fact that the superconductor-localized polypyrrole films display voltammetry (see Figure 1B) similar to that acquired at Pt electrodes[16] demonstrates that electrical charge flows readily between polypyrrole and $YBa_2Cu_3O_{7-\delta}$. While conductive polymers have been grown on bulk high-T_c samples,[9,13,17] to our knowledge, these studies represent the first time that a high-T_c thin film has been used as an electrode template for the study of conductive polymer electrochemistry.

The most fundamentally important, novel and unusual aspect of the study of polymer/superconductor structures is that the oxidation state of the polymer can be used to modulate values of T_c and J_c (critical current) of the underlying superconductor.

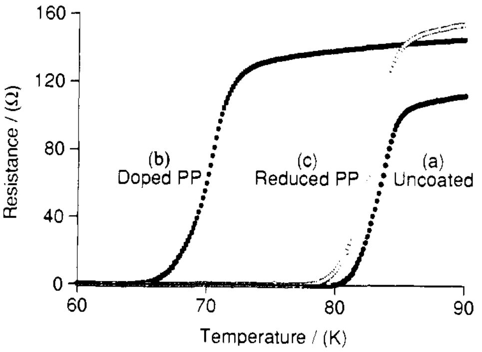

Figure 2. Resistance vs temperature curves for a 100 μm wide × 3 mm long microbridge created from a film of $YBa_2Cu_3O_{7-\delta}$ (polycrystalline superconductor specimen with thickness varying between ~500 and ~3000 Å and displaying a J_c value of ~1×10^5 A/cm² at 25 K). Three curves are shown for the following conditions: (a) uncoated microbridge; (b) microbridge coated with ~2-μm film of doped polypyrrole (deposited from 0.25 M Et_4NBF_4/pyrrole by cycling at room temperature 15 times between 0.21 and 1.21 V vs SCE at 100 mV/s); and (c) polypyrrole-coated microbridge following its room temperature electrochemical reduction (completed in 0.25 M Et_4NBF_4/acetonitrile by holding the potential at −0.5 V vs SCE for 3 min).

Figure 2 illustrates the effect for a microbridge formed from a film of $YBa_2Cu_3O_{7-\delta}$ coated with ~2 μm of polypyrrole. Before polymer deposition onto the microbridge, the bare junction displays a value of $T_{c(mid)}$ of 83 K. Upon deposition of the doped polymer, $T_{c(mid)}$ shifts down by nearly 15 K. However, subsequent electrochemical reduction of the polymer increases $T_{c(mid)}$ back up close to its original value. Cycling of the polymer between its oxidized (conductive) and neutral (insulating) forms can be accomplished several times yielding similar behavior (provided that the electrochemical potentials are not taken to extreme values and corrosive reagents such as water are not present in the electrolytic fluid). When precautions are taken to avoid chemical damage to the superconductor, this modulation of T_c is quite reproducible.

The extent to which the superconducting transition temperature can be modulated (i.e., ΔT) appears to be dependent on a number of factors, including the thickness and oxidation level of the polymer, critical current, weak link characteristics, thickness, and crystal orientation relative to the substrate of the superconductor. To achieve the impressive modulation of T_c shown in Figure 2, it was necessary to utilize a highly textured, polycrystalline $YBa_2Cu_3O_{7-\delta}$ specimen. Although the superconductor structure displayed an average thickness of ~3000 Å, there were many locations that were considerably thinner than this value (i.e., <500 Å). Modulation of superconductivity in these weak link regions is likely to be responsible for the sample's large value of ΔT. On the other hand, smooth $YBa_2Cu_3O_{7-\delta}$ films with uniform morphologies and with thicknesses of ~1000 Å typically yield ΔT values between 3 and 7 K. Moreover, high-quality $YBa_2Cu_3O_{7-\delta}$ films with thicknesses in excess of 3000 Å display little, if any, noticeable modulation of superconductivity.

At the present time, it is not possible to provide a definitive explanation for how superconductivity is altered by the conducting polymer layer. In this rather complex system, there are a number of important factors that must be considered. Since $YBa_2Cu_3O_{7-\delta}$ reacts readily with water, CO_2, CO, and acids,[18-20] chemical degradation processes could account for the initial decrease in T_c. However, the subsequent restoration of superconductivity to higher temperatures is not at all consistent with such behavior. Furthermore, uncoated superconductor films were cycled electrochemically in control studies, and no evidence was found for

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(12) Vase, P.; Yueqiang, S.; Freltoft, T. *Appl. Surf. Sci.* **1990**, *46*, 61–66.

(13) McDevitt, J. T.; McCarley, R. L.; Dalton, E. F.; Gollmar, R.; Murray, R. W.; Collman, J. P.; Yee, G. T.; Little, W. A. In *Chemistry of High-Temperature Superconductors II*, Nelson, D. L., George, T. F., Eds.; ACS Symposium Series 377; American Chemical Society: Washington, DC., 1988; Chapter 17.

(14) McCarley, R. L.; Morita, M.; Wilbourn, K. O.; Murray, R. W. *J. Electroanal. Chem.* **1988**, *245*, 321–330.

(15) Feldman, B. J.; Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1985**, *107*, 872–878.

(16) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, p 81.

(17) Osteryoung, J. G.; Magee, L. J., Jr.; Carlin, R. T. *J. Electrochem. Soc.* **1988**, *135* (10), 2653–2654.

(18) Riley, D. R.; McDevitt, J. T. *J. Electroanal. Chem.* **1990**, *295*, 373–384.

(19) Barns, R. L.; Laudise, R. A. *Appl. Phys. Lett.* **1987**, *51* (17), 1373–1375.

(20) Dou, S. X.; Liu, H. K.; Bourdillon, A. J.; Tan, N. X.; Zhou, J. P.; Sorrell, C. C.; Easterling, K. E. *Mod. Phys. Lett. B* **1988**, *1*, 363–368.

(21) Schwartz, M.; Cahen, D.; Rappaport, M.; Hodes, G. *Solid State Ionics* **1989**, *32–33*, 1137.

reversible modulation of T_c. Therefore, we can infer that electrochemically induced alterations in the superconductor lattice oxygen content[21] are not responsible for the effects observed here.

We speculate that modulation of superconductivity is the result of the occurrence of a superconducting proximity effect[22,23] within the composite assembly. If a proximity effect is indeed operative in our hybrid structures, there is an intriguing possibility that superconductivity may also be induced within conductive polymer structures that are in intimate contact with a superconductor. Studies are now in progress to search for such an unprecedented effect. Irrespective of the explanation, a new method for controlling the flow of electrical current in superconductor structures now has been demonstrated.

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(22) Meissner, H. *Phys. Rev.* **1960**, *117* (3), 672-680.

(23) Hilsch, P. *Z. Phys.* **1962**, *167*, 511-524.

Cholesterol-Induced Nearest-Neighbor Recognition in a Fluid Phospholipid Membrane[1]

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One of the most significant challenges presently facing chemists and biologists is to define the suprastructure of biological membranes.[2] In particular, the specific time-averaged lateral distribution of the lipids and proteins that make up these biological enclosures remains to be clarified. We have recently devised a chemical method for probing membrane suprastructure in simple model systems.[3,4] Unlike most other approaches that have previously been taken, ours is directly applicable to the physiologically-relevant fluid phase. The essence of our technique may be summarized as follows: a 1:1 molar mixture of two phospholipid homodimers (AA and BB) is equilibrated via a thiolate-disulfide interchange reaction.[5] In order to ensure that an equilibrium state has been reached, a similar equilibration reaction is carried out starting with the corresponding heterodimer AB (Figure 1). The extent to which the ratio of AA/AB/BB deviates from a molar ratio of 1/2/1 (a random distribution) reflects the thermodynamic preference for one phospholipid to become a covalently-attached nearest neighbor of another, i.e., it defines the ability of an equilibrating phospholipid monomer to "recognize" a nearest neighbor. When dimer distributions are found to be purely statistical, this fact, in and of itself, proves that the lipid components are randomly distributed throughout the membrane at the molecular level as well as at the supramolecular level. It establishes that there is no thermodynamic driving force for nearest-neighbor recognition and domain formation. For those cases in which nearest-neighbor recognition is observed, the existence of domains is inferred. This inference rests on the assumption that the packing forces that govern nearest-neighbor recognition are the same as (or very similar to) those that govern domain formation. Although such bilayers are not identical to those that are derived from single phospholipid molecules (the dominant component of natural biomembranes), they do provide us with a means for exploring membrane composition–suprastructure relationships in ways that have not, heretofore, been possible.

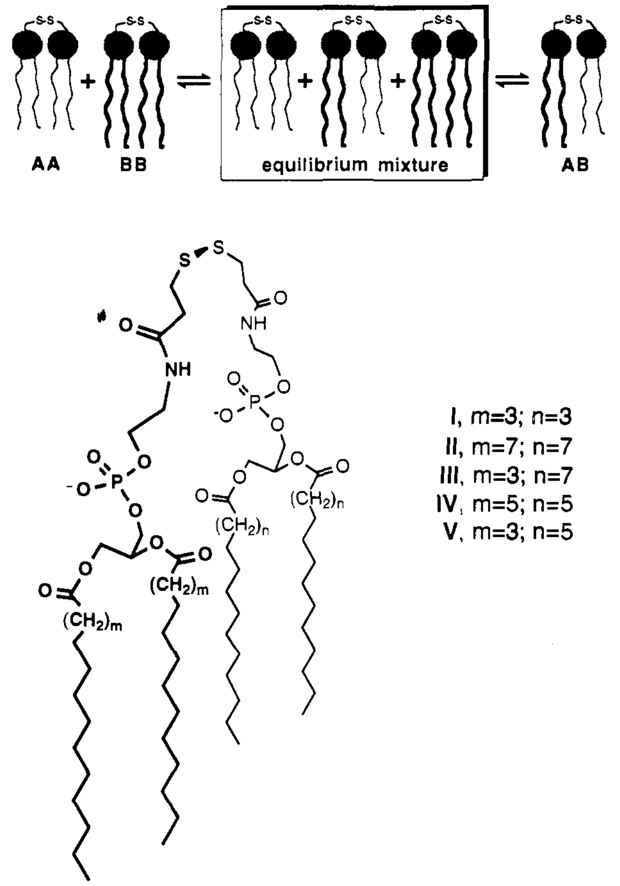

Figure 1. Stylized illustration of an equilibration reaction involving two phospholipid homodimers and one heterodimer. The specific dimers used in this study are I–V.

In the present study, we have examined the influence of cholesterol on nearest-neighbor recognition in fluid bilayers. The fact that mammalian cells are rich in cholesterol makes this particularly relevant from a biological standpoint. The specific phospholipid dimers that have been selected for this work are shown in Figure 1. On the basis of their fatty acid composition and their melting properties, lipids **I**, **II**, and **IV** may be viewed as dimeric analogs of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC), 1,2-distearoyl-*sn*-glycero-3-phosphocholine (DSPC), and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC), respectively; lipids **III** and **V** represent the corresponding heterodimers. The gel-to-liquid crystalline-phase transition temperatures for **I**, **II**, and **IV** are 22.7, 55.4, and 41.9 °C, respectively; for DMPC, DSPC, and DPPC, they are 23.9, 54.3, and 41.5 °C, respectively.[4,6]

In Figure 2 we show that equilibration of cholesterol-rich (40 mol %) membranes, which are comprised of phospholipid dimers **I**, **II**, and **III**, is essentially complete after 50 min at 60 °C.[7] Here, the equilibrium molar ratio of **I**/**III**/**II** is 1/(1.55 ± 0.04)/1; the error represents two standard deviations from the mean of eight

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(1) Supported by PHS Grant GM43787, awarded by the National Institute of General Medical Sciences. S.M.K. is grateful to Unilever for a graduate fellowship.

(2) Gennis, R. B. *Biomembranes: Molecular Structure and Function*; Springer-Verlag: New York, 1989; Chapter 4.

(3) Krisovitch, S. M.; Regen, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 8175.

(4) Krisovitch, S. M.; Regen, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 9828.

(5) Singh, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 6304.

(6) Mabrey-Gaud, S. *Liposomes: From Physical Structure To Therapeutic Applications*; Elsevier/North Holland: New York, 1981; Chapter 5.

(7) The experimental protocol that we have used to form large unilamellar vesicles (1000-Å diameter) and to promote thiolate–disulfide interchange has previously been described.[4]

0002-7863/93/1515-1198$04.00/0