

“Vapoconductivity”. Sorption of Organic Vapors Causes Large Increases in the Conductivity of a Dendrimer

Larry L. Miller,^{*,†} Yoshihito Kunugi,[†]
Augusto Canavesi,[†] Stéphane Rigaut,[†]
Charles N. Moorefield,[‡] and George R. Newkome[‡]

Department of Chemistry, University of Minnesota,
Minneapolis, Minnesota 55455, and Department of
Chemistry, University of South Florida,
Tampa, Florida 33620

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We report on two new polyamido dendrimers (**1** and **2**, Scheme 1), peripherally modified with oligothiophene groups. These dendrimers have been oxidized to form cation radicals on the oligothiophene units. Enhanced interactions between peripheral groups on dendrimers are of current interest^{1,2} and we report on π -dimerization of the cation radicals. Films of oxidized dendrimers were produced and were electrically conducting, expanding the small number of conducting dendrimers^{3–5} that have been reported. We discovered that the conductivities of these new dendrimers are dramatically increased by the sorption of certain volatile organic compounds, and we report herein some initial studies of this phenomenon.

There is continuing interest in designing sensors for volatile organic compounds. “Vapoconductivity” effects have been noted for films of conducting polymers, especially oxidized polypyrrole,^{6–8} however, the changes in conductivity observed for chemically inert vapors are typically only a few percent increase or decrease. Arrays of conducting polymer electrodes are being studied and commercialized as “electronic noses”, which are able to distinguish volatile compounds based on the different responses of similar electrodes. Polypyrrole/insulating polymer blends,⁹ carbon particle/insulating polymer blends,¹⁰ and different polypyrroles¹¹ have been used. These materials do not give large increases in

conductivity in response to vapor sorption like those reported here.

It has been reported that the conductivity of a film consisting of a polyamidoamine (PAMAM) dendrimer peripherally decorated with naphthalene diimide anion radicals is sharply increased (500 \times) in response to increased humidity above the film,³ and it was anticipated that other modified dendrimer films might be sensitive to various vapors. Because cation radicals give p-type conductors, and these are known to be more stable in air, we chose to explore this idea using a new class of modified dendrimers for which the conducting entities are oligothiophene cation radicals. With considerable experience with the cation radical chemistry and conductivity of oligothiophenes,¹² it seemed that the new dendrimers would be intrinsically interesting and that a useful material for sensors might result.

A modified dimethoxybithiophene (**3a**) and dimethoxy-quaterthiophene (**4a**) (Scheme 2) were prepared which had one terminal position blocked with an electron-donating substituent and the other substituted with a (2-hydroxyethyl)thio group. The latter served as the linker to the dendrimer. The thio and methoxy substituents have been shown to stabilize cation radicals formed on oligothiophenes; however, only recently have unsymmetrically substituted examples been reported¹³ which would allow attachment to a polymer without linking polymer molecules together. The dendrimer **5**¹⁴ was chosen because, unlike PAMAM, it is not oxidized by oligothiophene cation radicals, and it has functionality suitable for the modification. Esterification of **5**, which has 36 peripheral carboxylic acid groups, with **3** or **4**¹⁵ using diisopropylcarbodiimide and 1-hydroxybenzotriazole as coupling agents, gave **1** and **2**. NMR, IR, and UV spectra were consistent with the desired, partially loaded structures. NMR analysis comparing peak areas of the modifier and interior structure indicated that the average loading was 60–70% for both **1** and **2**. Vis spectra, analyzed assuming the ϵ value of the attached moieties was equal to that of model oligomers indicated 60–75% loading. MALDI TOF MS analysis of **1** and **2** gave most abundant ions at 11 966 and 7791 respectively, with polydispersities of 1.08 for each sample.

Cyclic voltammetry on **1** and **2** in CH₂Cl₂ (0.1 M Et₄NPF₆) at a glassy carbon electrode showed a distorted anodic peak and a very sharp cathodic peak on the return half cycle. The anodic peak potential (vs SCE) was 0.49 V for **1** and 0.38V for **2**. The peak shapes

[†] University of Minnesota.

[‡] University of South Florida.

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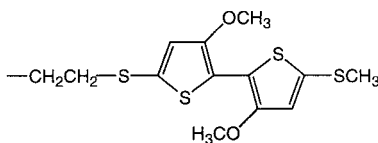
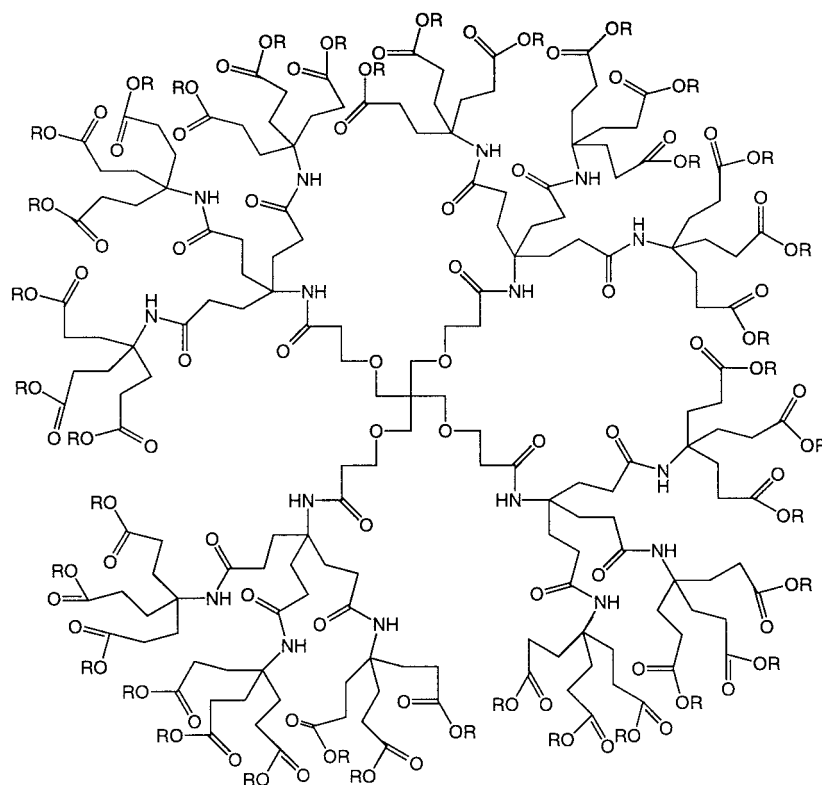
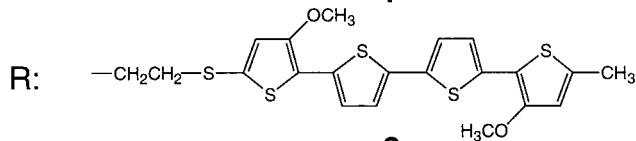
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(15) Esterification was accomplished at 50 °C using an excess of oligothiophene compared to the number of carboxylic acid groups on the dendrimer. Diisopropylcarbodiimide and 1-hydroxybenzotriazole were used as coupling agents (1.1 equiv per carboxylic acid unit). Details of the preparation are in the Supporting Information.

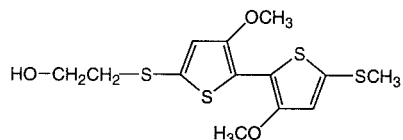
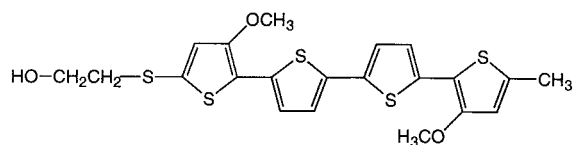
Scheme 1

**1**

R:

2**H****5**

Scheme 2

**3****4**

indicate that the cation radicals aggregate and precipitate. Photolytic oxidation of **1** and **2** in a trifluoroacetic

acid/methylene chloride solution gave stable cation radicals. The vis near-IR spectrum for oxidized **2** ($\lambda_{\text{max}} = 590, 904, 1200 \text{ nm}$) was quite similar to the spectrum of model quaterthiophene cation radical **4** in acetonitrile solution ($\lambda_{\text{max}} = 570, 889, 1200 \text{ nm}$). It has been demonstrated that this spectrum is due to cation radical π -dimers.¹² Since **4** cation radicals do not π -dimerize in the less polar methylene chloride, the data demonstrate that the dendrimer structure enhances π -dimerization. The vis NIR spectrum for oxidized **1** showed $\lambda_{\text{max}} = 467, 512, 677, \text{ and } 737 \text{ nm}$, which is consistent with a mixture of π -dimerized and undimerized cation radicals. The smaller propensity for dimerization is not surprising since it is known that bithiophene cation radicals dimerize less than their quaterthiophene analogues.¹²

When the oxidized forms of **1** and **2** were used for casting, the resulting films were of poor quality, but

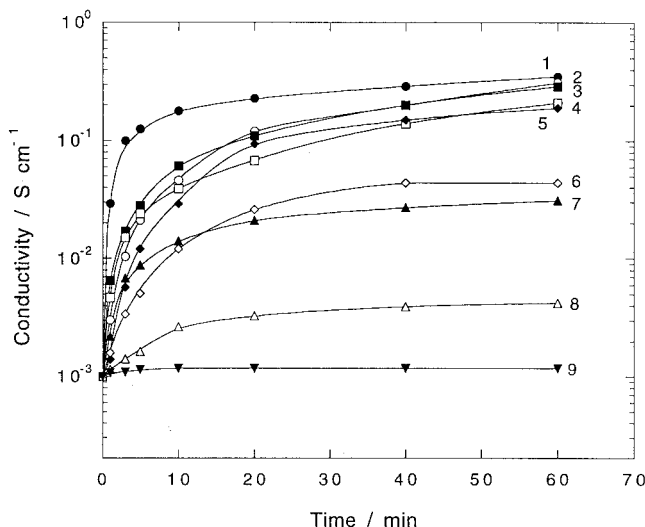


Figure 1. Time dependence of the conductivity of the I₂-doped **2** film by exposure to (1) ether, (2) acetonitrile, (3) ethanol, (4) ethyl acetate, (5) acetone, (6) methanol, (7) dichloromethane, (8) toluene, and (9) hexane.

films cast of the neutral polymers from CH₂Cl₂ were visually homogeneous and continuous. Oxidation with iodine vapor over a period of 1 day gave films with $\sigma = 10^{-3}$ S/cm for both **1** and **2**. Rapid switching of the applied current or long-term current passage suggested that the conductivity was electronic, not ionic. The conductivities were stable for several weeks in ambient laboratory conditions. This conductivity is similar to that of the anion radical modified PAMAM in dry air,³ but significantly lower than that of an oxidized polythiophene grafted onto a dendritic polyphenylene.⁵

Vapoconductivity experiments were conducted using these iodine oxidized films on glass with four probes in a controlled atmosphere bell jar. The film (ca. 10 μ m thick) was exposed to argon which had been bubbled through the liquid of interest and the response of the conductivity to the vapor was measured over a period of time. The conductivity increased in every case, reaching an equilibrium value in a few minutes (Figure 1). Sweeping the vapor out from the bell jar with pure argon rapidly returned the conductivity to its initial value. The change in conductivity was fully reversible for several cycles and the results were reproducible to within a few percent for a single sample. Using different samples of the conducting dendrimer gave values reproducible to within about 10%. In general, experiments performed in air gave the same results. The changes (Table 1) were quite large for polar organic compounds, up to 800 times the original conductivity in the case of acetone vapor over oxidized **1**. Interestingly, water had little effect on the conductivity of either polymer, but all vapors increased the conductivity.

To begin exploration of the origin of these large conductivity changes, we measured the amount of vapor absorbed using films coated on quartz crystal microbalance electrodes.^{3,6} Exposure to the analyte vapor in argon as above showed uptake and equilibration on the same time scale (Figure 2) as that for the conductivity change. The amounts of vapor taken up (calculated using the Sauerbrey equation) were relatively large (Table 1). In the case of acetone with **2**, for example, one can estimate that there are about 20 molecules of

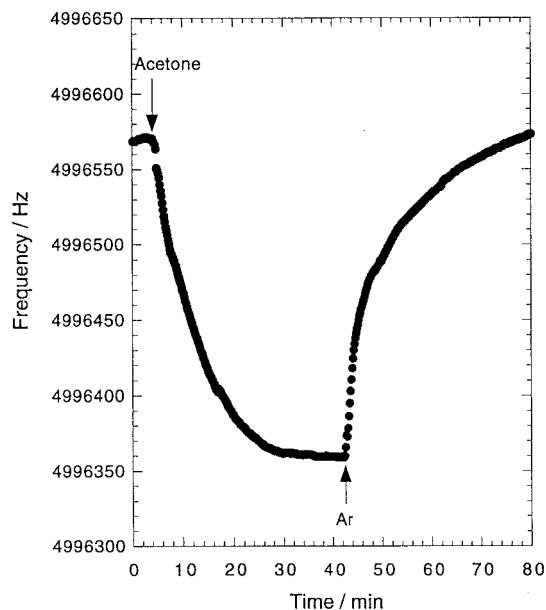


Figure 2. QCM frequency change for oxidized **2** exposed to acetone in Ar.

Table 1. Conductivity and Mass Changes of I₂-Oxidized Films Exposed to Various Vapors

vapor	σ/σ_0 ($\Delta M/M_0 \times 100$)	
	1	2
acetone	800 (11.4)	190 (9.6)
ethanol	380 (10.1)	290 (7.8)
ethyl acetate	280 (4.0)	210 (3.6)
ethyl ether	240 (6.4)	350 (7.3)
acetonitrile	140 (6.2)	310 (6.0)
dichloromethane	47 (9.2)	31 (9.1)
methanol	35 (18.4)	44 (15.3)
toluene	1.5 (4.0)	4.2 (3.9)
water	1.3 (16.9)	2.1 (20.1)
hexane	1.5 (4.3)	1.2 (3.7)

acetone per dendrimer molecule. Not surprisingly, these amounts are not directly related to the changes in conductivity. In the case of water and hexane, large amounts were sorbed, but there was only a small change in conductivity.

Since previous studies of conducting polymers have shown small and even decreases in conductivity with vapor sorption, these effects are of some interest. In the case of anion radical modified PAMAM, quartz crystal microbalance results suggested that the films were being plasticized.³ The QCM measurements on **1** and **2** gave no evidence that there was a viscoelastic phase change, but it was qualitatively observed that the films which took up water did not become more plastic, while films which had taken up acetone were more flexible and sticky. Accepting the possibility of plasticization still leaves the molecular mechanism unaddressed, and since the conductivity is electronic, not ionic, it is surprising that substantial dilution of the samples with organic solvents increases the conductivity. One hypothesis is that plasticization allows faster electron transport between the small stacks formed on individual dendrimers. This factor could be especially important for these dendrimers in comparison with long conjugated chain polymers such as oxidized polypyrrole, where rigidity and organization, not mobility, should be more important.

Regardless of the mechanism, the hypersensitivity of these films to chemically inert vapors provides a promising avenue for sensor design. Large changes in conductivity and large differences between the effects from similar molecules could provide improved sensitivity and selectivity compared to other conducting polymer sensors. In addition, these materials could be used with other conducting polymers in array sensors to provide a usefully diverse response profile. Preliminary experiments with conducting oligomers and conducting main chain polymers^{12c} do not show these effects and it would appear that the dendritic structure is important. Cer-

tainly it is true that independent variation of the dendrimer and redox modifier gives great latitude for the design of interesting sensor materials.

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Supporting Information Available: Details of the synthesis of the dendrimers (4 pages). See any current masthead page for ordering information.

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