

Chapter 5

Charge–Retention Characteristics of Self-Assembled Monolayers of *Molecular–Wire*-Linked Porphyrins on Gold

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A molecular approach to information storage employs redox-active molecules attached to an electroactive surface as the memory storage element. Information is stored in the distinct oxidation states of the molecules. Three “molecular-wire” linked porphyrins have been examined each of which forms a self-assembled monolayer (SAM) on a Au microelectrode. The charge-retention time of each “molecular-wire” linked porphyrin mono and dication is considerably shorter than that for phenyl-alkyl chain linked porphyrins.

It is uncertain whether devices that rely on the bulk properties of semiconductor materials will retain the required functionality as feature sizes shrink below 0.1 μm .¹ To overcome the physical limitations of materials used in semiconductor devices, several chemical systems have been investigated with the goal of using discrete molecular properties to replicate the bulk properties of conventional electronic components. Towards this end, molecular switches,^{2–4}

diodes,^{5,6} and wires^{7,8} have recently been realized. The integration of molecular components is particularly critical in an information storage system that employs a dynamic random access memory (DRAM).

The basic DRAM cell consists of a capacitor and transistor, where charge is stored to indicate the bit level (0 or 1). This charge decays rapidly in the absence of applied voltage (due to numerous factors), thereby necessitating a periodic refresh. This is the root of the volatile nature of information storage in a DRAM chip. The frequency of the refresh is determined by the magnitude of the capacitor, the voltage at which it was written, and the leakage current. As the feature size of DRAM cells shrink, so does the available capacitance. Recently a DRAM capacitor with a feature size of 0.14 μm has been fabricated with a cell capacitance of ~ 25 fF.⁹ A smaller feature size ($< 0.1 \mu\text{m}$) will further reduce the effective capacitance to what appears to be a limit based on the bulk properties of doped semiconductors. Only a DRAM based on molecular properties is compatible with a feature size below this limit.

We recently embarked on a program aimed at the design of a molecular-based DRAM.¹⁰ In our approach, a collection of redox-active molecules in a self-assembled monolayer (SAM) attached to an electroactive surface serve as the memory storage element. Information is stored in the distinct oxidation states of the molecules. This approach has the attributes of (1) electrical writing/reading, (2) operation under ambient conditions, (3) low power consumption, (4) no moving parts, (5) reliable operation under multiple cycles, (6) scalability to small dimensions, and (7) fault tolerance through the use of a number of molecules in a given memory storage location.

We have prepared over 100 molecules for studies of molecular-based information storage.¹¹⁻¹⁷ In each case, the generic architecture consists of the following units: surface attachment group, linker, and redox-active molecules. We have examined a variety of redox-active molecules, including monomeric porphyrins,^{11,12} ferrocene-porphyrins,¹⁴ weakly coupled multimeric porphyrins,¹⁵ tightly coupled multimeric porphyrins,¹⁶ and lanthanide triple deckers of porphyrins and phthalocyanines.¹⁷ The emphasis on the multimeric systems and triple deckers was to achieve an increased number of oxidation states, thereby increasing the information storage density. In each case, a thiol group was employed for attachment of the molecules to the surface of Au electrodes. A number of the information-storage molecules were prepared with linkers of different length and composition. The motivation for exploring different linkers was to investigate the effect of linker structure on the duration of charge storage (i.e., charge-retention time) in the SAM after disconnection of the potential applied in the writing process. The ability to retain charge in the absence of applied potential is a key property of this molecular-based approach. A long charge-retention time simultaneously increases the time between refresh cycles (allowing the memory cell to be available for reading and writing a larger percent of the time) and also reduces the total power consumption of the information storage system.

This report focuses on information storage in the multiple oxidation states of porphyrin SAMs on Au surfaces. We have previously shown that SAMs of monomeric porphyrins retain charge for hundreds of seconds after disconnection of the applied potential, almost five orders of magnitude longer than state-of-the-art DRAM elements.¹⁸ Our previous studies of porphyrin monomers bearing phenyl or alkylphenyl linkers revealed that charge-retention times can be altered by ~10-fold via structural modification of the linker. Herein, we conduct similar studies that address the effects of conjugated linkers on charge-retention. The structures of these porphyrins are shown in Figure 1.

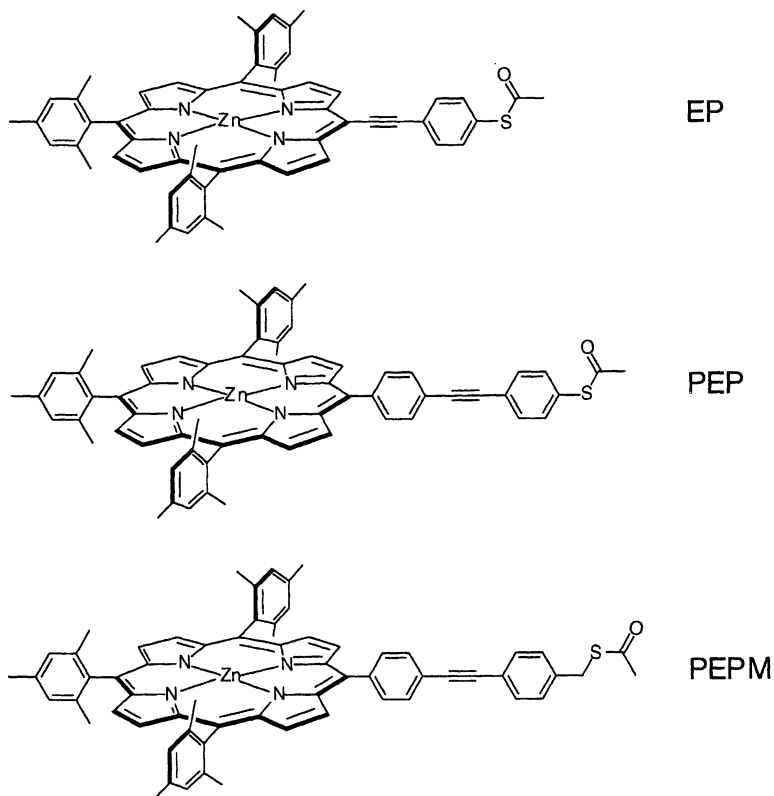


Figure 1. Porphyrins for preparing SAMs with the designations EP (ethynylphenyl linker), PEP (phenylethynylphenyl linker) and PEPM (phenylethynylphenylmethyl linker).

These molecules, designated EP, PEP, and PEPM, differ only with respect to the linker that connects the porphyrin ring and the sulfur atom (ethynylphenyl, phenylethynylphenyl, and phenylethynylphenylmethyl, respectively).

Experimental

The EP, PEP, and PEPM compounds were synthesized as *S*-acetylthio derivatives as previously described.¹¹ The *S*-acetyl protecting group has been shown to undergo facile cleavage upon exposure to the Au surface.^{12,19}

Au ball working electrodes were prepared from 5- μm diameter Au wire (Alpha Aesar) sealed in soft glass. Initially a $\sim 500\text{-}\mu\text{m}$ segment of the wire was protruding from the end of 1-mm i.d. soft glass tubing. When exposed to a flame, the glass forms a tight seal around the Au. The wire exposed to the flame melts into a ball that terminates at the surface of the glass. The electrode was then cooled in a stream of nitrogen and used immediately, resulting in electrodes with an average electrochemical area of $1.5 \times 10^{-4} \text{ cm}^2$.²⁰

SAMs were formed by placing the electrode in a 1 mg/mL solution of porphyrin for 5 min. The electrode was then removed from the sample solution and rinsed with distilled CH_2Cl_2 (Aldrich). All electrochemical potentials, open circuit potential (OCP) measurements, and open circuit potential amperometry (OCPA) measurements were in reference to a bare silver wire (Ag/Ag^+) immersed in dried, distilled CH_2Cl_2 containing 0.1 M Bu_4NPF_6 (Aldrich, recrystallized three times from methanol and dried under vacuum at 110°C). All cyclic voltammograms were recorded at 100 V/s with an in-house constructed potentiostat using a routine written in LabVIEW (National Instrument, Austin, TX).

The OCPA measurements were performed as described previously.¹⁰ Initially, the SAM is oxidized with a 20 ms (\gg than the RC time constant of the cell) pulse that is $\sim 100 \text{ mV}$ above the formal potential of the desired state. The applied potential is disconnected from the counter electrode for a period of time. This disconnection time was varied to evaluate the charge-retention properties. During this time, two events take place: (1) the applied potential is changed to match the empirically determined open circuit potential (OCP) which is $\sim 160 \text{ mV}$ vs. Ag/Ag^+ and (2) the electrochemical cell relaxes to the OCP. After the disconnect time, the SAM is reduced upon reconnection of the counter electrode and the resulting current is monitored. The magnitude of the observed current is directly proportional to the number of molecules that remain oxidized on the surface while the counter electrode is disconnected. A dramatic reduction in charging current results from the fact that the electrochemical cell is already poised at the OCP before reconnection of the counter electrode. Charge retention is measured by successively changing the disconnect time up to a point where essentially all of the molecules that were initially oxidized have decayed back to the neutral state.

Results and Discussion

Voltammetric Characteristics

The EP, PEP, and PEPM SAMs were characterized by cyclic voltammetry. The electrochemical data for the SAMs are summarized in Table I. The

voltammetric data indicate that the nature of the linker has very little effect on the $E_{1/2}$ values. A representative cyclic voltammogram of PEPM is shown in Figure 2. The voltammogram of the porphyrin SAM exhibits the rapid and reversible oxidative characteristics that are typical of other porphyrin SAMs we have studied,¹⁰ where each porphyrin SAM exhibits two reversible oxidative waves below 1 V. Repeated voltammetric experiments reveal that these characteristic features do not degrade with successive scans and are stable for hours in solution. The availability of multiple, low-potential oxidation, stable states provides a potential means of storing more than one bit of information in a single storage location, with consumption of relatively little power.

The charge densities of the oxidized SAMs were calculated from the integrated current from the cyclic voltammogram of each molecule, using the electrochemically determined electrode area.²⁰ The values for PEPM and PEP were comparable, 7.54 and 8.25 $\mu\text{C}/\text{cm}^2$, respectively, while that for EP was considerably less, 3.22 $\mu\text{C}/\text{cm}^2$. The lower value for EP is not a result of a larger molecular area, but more likely due to a lower packing density on the surface of the electrode. This is manifested in the voltammogram of EP, which exhibits reduced peak current (which also results in a smaller signal to background charging current ratio). Regardless, the lower surface coverage exhibited by EP does not alter the voltammetric characteristics of this SAM relative to those of PEP or PEPM.

Charge-Retention Characteristics.

Coulometry is the most straightforward technique available for the quantitation of redox species. Faraday's Law $\{Q = nFN$, where Q is charge (Coulombs), n is the number of electrons in each reactions, F is Faraday's constant and N is the number of redox molecules (moles) $\}$ describes the fundamental relationship between the measured charge (corresponding to the

Table I. Half-wave potentials for thiol-derivatized molecular-wire linked Zn porphyrins^a

<i>Porphyrin</i>	<i>Half-wave potential (V)</i>		<i>Charge density ($\mu\text{C}/\text{cm}^2$)</i>
	$E_{0 \rightarrow 1}$	$E_{+1 \rightarrow 2}$	σ^b
PEPM	0.58	0.93	7.54
PEP	0.60	0.97	8.25
EP	0.59	0.98	3.31

^aObtained in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 vs. Ag/Ag^+ ; scanrate = 100 V/s.

^bCharge density ($\mu\text{C}/\text{cm}^2$) determined from cyclic voltammetry.

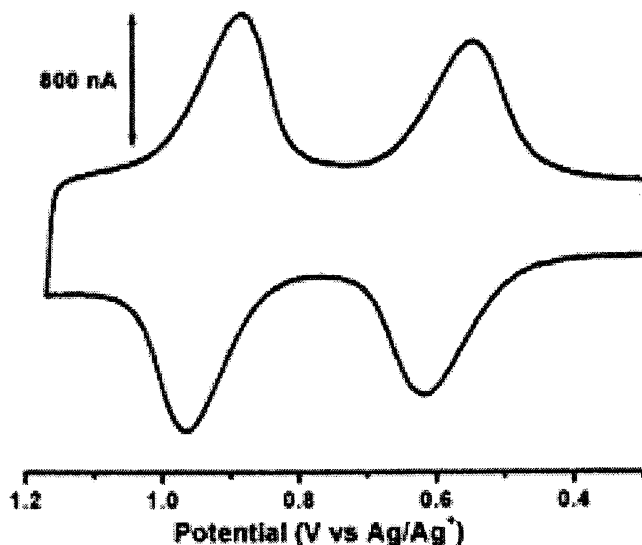


Figure 2. Cyclic staircase voltammetry (100 V s^{-1}) of PEPM SAM on a Au ball electrode immersed in a solution of $0.10 \text{ M Bu}_4\text{NPF}_6$ in dried, distilled CH_2Cl_2 using Ag wire as a counter electrode.

oxidation or reduction of the redox species) and the number of molecules consumed in the redox process. The only assumption in this relationship is that all the measured charge results from faradaic processes and not due to charging of the electrochemical double layer. Thus, it is necessary to minimize the background charging current to accurately determine the number of molecules participating in the redox process. One way to accomplish this is to discharge the charging current prior to the measurement of the charge associated with a redox process.

Measurement of stored charge in a SAM has been accomplished using the OCPA technique.¹⁰ This technique requires that (1) the OCP of the electrochemical cell can be readily determined, and is at an analytically useful potential; (2) the molecules in the SAM remain oxidized under open circuit conditions; and (3) the molecules that remain oxidized are readily reduced upon reconnection of the counter electrode at the OCP. As previously shown,^{10,13,18} SAMs of various porphyrins satisfy these conditions.

Representative data for the OCPA of PEPM are shown in Figure 3A. The traces are the reductive current required to neutralize the mono-oxidized SAM ($E_{\text{applied}} = 0.8 \text{ V}$). The different traces were measured at various times following the reconnection of the counter electrode. The current transients are integrated to yield the number of molecules that remain oxidized after the disconnect time (Figure 3B). The integrated charge measured after $80 \mu\text{s}$ represents essentially

the total retained charge of the SAM. For all three molecules, the decay in the total charge as a function of disconnect time fits a first-order rate law with a high fidelity ($r^2 = 0.98$) for both oxidation states ($E_{+2} \rightarrow E_0$ and $E_{+1} \rightarrow E_0$). Simple exponential decay is not expected for the decay of the second state owing to the fact that it presumably decays via a sequential process ($E_{+2} \rightarrow E_{+1} \rightarrow E_0$). Nevertheless, we have also observed pseudo-first order decay for the higher oxidation states of other porphyrin SAMs.¹³

The (pseudo) first-order charge-retention kinetics exhibited by the porphyrin SAMs allows the determination of a half-life ($t_{1/2}$) for charge retention. The $t_{1/2}$ values for the EP, PEP, and PEPM SAMs are listed in Table II. The charge at time zero (σ_0) is extrapolated from the fits of the decay curves and corresponds to the total charge in the SAM at a disconnect time of zero seconds. This value represents the amount of stored charge (oxidized molecules) in the SAM prior to any decay process and correlates very well with the integrated voltammograms (as can be seen in Tables I and II). The values are given as charge densities to facilitate comparison of different electrode sizes. The good agreement between the values indicates that the charge observed in OCPA is well correlated to the faradaic current measured with cyclic voltammetry.

Inspection of the $t_{1/2}$ values shown in Table II reveals that EP exhibits the shortest charge-retention characteristics; the $t_{1/2}$ for the first oxidation state of this SAM is ~ 31 s. The $t_{1/2}$ values become successively longer for PEP and PEPM and are 43 and 58 s, respectively. The $t_{1/2}$ values for the second oxidation states of the SAMs follow the same trend but are systematically longer than those of the first oxidation state. The longer $t_{1/2}$ for the higher oxidation states are consistent with our studies on other multiply oxidized porphyrin SAMs.¹³

The monotonically increasing $t_{1/2}$ values, EP < PEP < PEPM, are qualitatively consistent with the increasing length of the linker in the three molecules. However, the correlation between the $t_{1/2}$ values and actual linker length is poor. In particular, the $t_{1/2}$ value(s) for PEP are only about 30% longer than those for EP, despite the fact that the additional phenyl ring in the linker of PEP results in a tether length that is approximately double that of EP. An equivalent (or larger) increase in $t_{1/2}$ value is observed for PEPM versus PEP, where a much shorter methylene group has been added to the linker. These observations suggest that factors other than tether length may affect the $t_{1/2}$ values. In this connection, it is interesting that the σ_0 value for EP is significantly less (approximately half) than that for PEP or PEPM (Tables I and II). As noted above, the lower charge density for EP indicates lower surface coverage. The lower surface coverage could reflect either a different tilt angle of the molecules with respect to the surface or different packing arrangement (or both). The distance of the electroactive molecule from the surface and/or the molecular packing could also influence the $t_{1/2}$ value.

Results from an earlier study by our group shed additional light on the effects of tether length on charge retention. In this study, we investigated the effects of methylene spacers on the $t_{1/2}$ values of a series of analogous porphyrin SAMs containing phenyl-(CH₂)_n linkers, where $n = 0 - 3$ (termed PMn), shown in Figure 4. The molecular area occupied by each of these molecules is similar suggesting similar tilt angles and molecular packing arrangements. The $t_{1/2}$

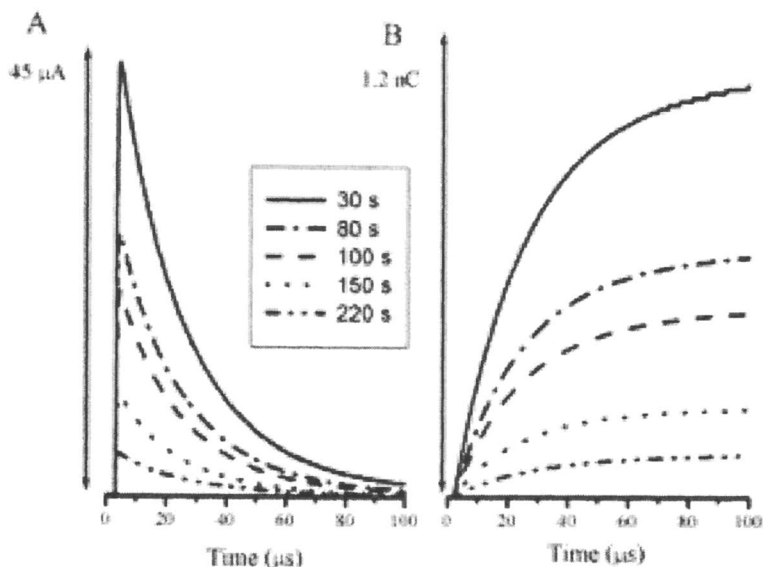


Figure 3. (A) Au electrode with a PEPM SAM was oxidized (poised at 0.8 V vs. Ag/Ag⁺ for 20 ms) then disconnected from the applied potential; (A) each transient results from the reconnection of the counter electrode at the empirically determined OCP (for a PEPM SAM on Au the OCP is −165 mV vs. Ag/Ag⁺) at 5 unique disconnect times ranging from 30 – 220 s; (B) the integration of the transients in (A).

Table II. Charge densities and charge-retention half-lives for thiol-derivatized molecular-wire linked Zn-porphyrins in SAMs^a

Porphyrin	State 1		State 2	
	$t_{1/2}$	σ_0	$t_{1/2}$	σ_0
PEPM	58	7.40	94	13.9
PEP	43	8.39	66	16.6
EP	31	4.30	59	8.73

^aCharge density at $t = 0$ s ($\mu\text{C}/\text{cm}^2$) and charge-retention half-life ($t_{1/2}$ /s) obtained by fitting the decay in the observed charge vs. disconnect time to a first-order rate law.

values for PMn SAMs were found to increase monotonically with the successive addition of each methylene group. In the case of the first oxidation state, these values are 116, 167, 656, and 885 s, respectively.¹⁰ Accordingly, when the molecular packing of the SAMs is similar, the $t_{1/2}$ values appear to be well-correlated with the tether length. Another noteworthy observation is that the $t_{1/2}$ values for the PMn SAMs are longer than those of EP, PEP or PEPM, despite the fact that linkers for the former SAMs are shorter than those of the latter (except perhaps in the case of EP versus PM3).

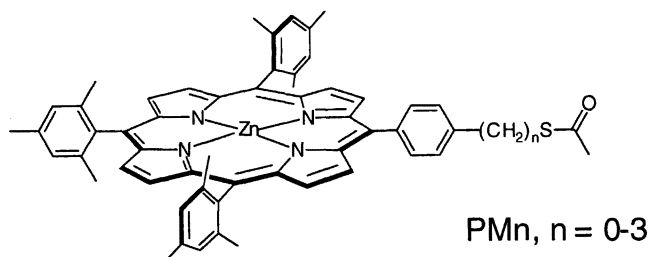


Figure 4. Phenylalkyl-linked porphyrins studied previously in SAMs.

The studies reported herein indicate that the nature of the linker plays a significant role in determining the charge-retention characteristics of the porphyrin SAMs. The length of the linker is clearly important, with longer linkers generally giving longer $t_{1/2}$ values. However, the relative $t_{1/2}$ values of the “wire-linked” porphyrins studied here versus those of the PMn SAMs studied previously show that the electronic properties of the linker have a strong influence on charge retention. The fact that the $t_{1/2}$ values for the “wire-linked” porphyrin SAMs are significantly shorter than those of the PMn SAMs is qualitatively consistent with greater electronic coupling between the Au surface and the porphyrin redox site through the more highly conjugated linkers of the wire-linked molecules. However, the detailed nature of the electronic coupling is clearly more complicated. In particular, there is no obvious rationale for why the $t_{1/2}$ value for the PM0 SAM, which contains a single phenyl linker, should be significantly longer than for the “wire-linked” porphyrin SAMs studied herein. The phenyl linker in PM0 should arguably facilitate electronic coupling comparable to (or stronger) than linkers such as diphenylethyne.

Finally, we close by noting that the charge-retention times for all of the porphyrin SAMs that we have studied reflect rates of charge recombination that are much longer than the rates of forward electron transfer that are characteristic of the oxidation process. This assessment is based on the observation that the current-transient response measured during oxidation is limited by the RC time

constant of the electrochemical cell, not the intrinsic rate of electron transfer.¹⁰ Accordingly, we do not know whether the rates of forward electron transfer in the porphyrin SAMs exhibit linker-dependent trends that parallel the rates of charge recombination. In this connection, however, the rates of forward electron transfer have been examined for SAMs of ferrocenes tethered by a variety of linkers. The forward electron-transfer rates for alkylferrocene SAMs monotonically decrease as the length of the alkyl chain increases.²¹⁻²³ In addition, the rates of electron transfer through conjugated linkers (such as oligophenylethyne) are much faster than through alkyl linkers.²⁴⁻²⁶ These trends are generally consistent with those we have reported herein and previously for charge retention (i.e., the rates of charge recombination decrease as methylene spacers are added to the linker and are generally faster for conjugated than for non-conjugated linkers).¹⁰ We also note that in a recent study, the rates of forward electron transfer in a series of oligophenylene-vinylene-tethered ferrocenes were shown to exhibit only a weak dependence on the number of conjugating elements in the linker (and therefore on the length of the linker).²⁷ This behavior is qualitatively similar to our observation that the rates of charge recombination in the "wire-linked" porphyrin SAMs are not appreciably different for phenylethyne and diphenylethyne linkers. Regardless, a more detailed analysis of the correlation between the rates of forward electron transfer and charge recombination as a function of linker must await further studies wherein the rates of forward electron transfer are explicitly measured for a series of porphyrin SAMs. Gaining a fundamental understanding of the relationship between linker structure and electron-transfer rates is essential for the rational design of molecules for specific information-storage applications.

Acknowledgments

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