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Molecules for Charge-Based Information Storage

JONATHAN S. LINDSEY*, † AND DAVID F. BOCIAN*, ‡
†Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States, and ‡Department of Chemistry, University of California, Riverside, California 92521-0403, United States

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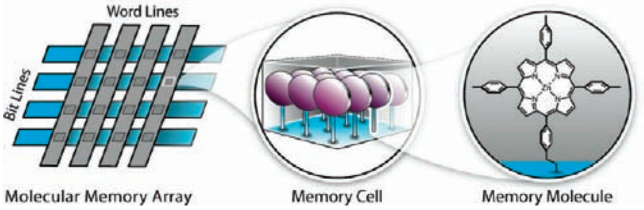

The inexorable drive to miniaturize information storage and processing devices has fueled the dreams of scientists pursuing molecular electronics: researchers in the field envisage exquisitely tailored molecular materials fulfilling the functions now carried out by semiconductors. A bottom-up assembly of such all-molecular devices would complement, if not supplant, the present top-down lithographic procedures of modern semiconductor fabrication. Short of these grand aspirations, a more near-term objective is to construct hybrid architectures wherein molecules are incorporated in semiconductor-based devices. Such a combined approach exploits the advantages of molecules for selected device functions while retaining the well-developed lithographic approaches for fabrication of the overall chip.

In this Account, we survey more than a decade of results from our research programs to employ porphyrin molecules as charge-storage elements in hybrid semiconductor–molecular dynamic random access memory. Porphyrins are attractive for a variety of reasons: they meet the stability criteria for use in real-world applications, they are readily prepared and tailored synthetically, they undergo read–write processes at low potential, and they store charge for extended periods (up to minutes) in the absence of applied potential. Porphyrins typically exhibit two cationic redox states. Molecular architectures with greater than two cationic redox states are achieved by combinations of porphyrins in a variety of structures (for example, dyads, wherein the porphyrins have distinct potentials, triple deckers, and dyads of triple deckers). The incorporation of porphyrins in hybrid architectures has also required diverse tethers (alkyl, alkenyl, alkynyl, aryl, and combinations thereof) and attachment groups (alcohol, thiol, selenol, phosphonate, and hydrocarbon) for linkage to a variety of surfaces (Au, Si, SiO_2, TiN, Ge, and so forth).

The porphyrins as monolayers exhibit high charge density and are robust to high-temperature excursions (400 °C for 30 min) under inert atmosphere conditions. Even higher charge densities, which are invaluable for device applications, were achieved by in situ formation of porphyrin polymers or by stepwise growth of porphyrin–imide oligomers. The various molecular architectures have been investigated by diverse surface characterization methods, including ellipsometry, atomic force microscopy, FTIR spectroscopy, and X-ray photoelectron spectroscopy, as well as a variety of electrochemical methods. These studies have further revealed that the porphyrin layers are robust under conditions of deposition of a top metal contact.

The results to date indicate the superior features of selected molecular architectures for molecular electronics applications. The near-term utilization of such materials depends on further work for appropriate integration in semiconductor-based devices, whereas ultimate adoption may depend on advances that remain far afield, such as the development of fully bottom-up assembly processes.

Introduction

The development of molecular-based materials for electronics applications has been stimulated by the prospect that devices relying on the bulk properties of semiconductors will fail to retain their characteristic properties as sizes decrease to nanoscale dimensions. The use of molecules in electronic devices is attractive owing to the intrinsic scalability of molecular properties and the ability to tune

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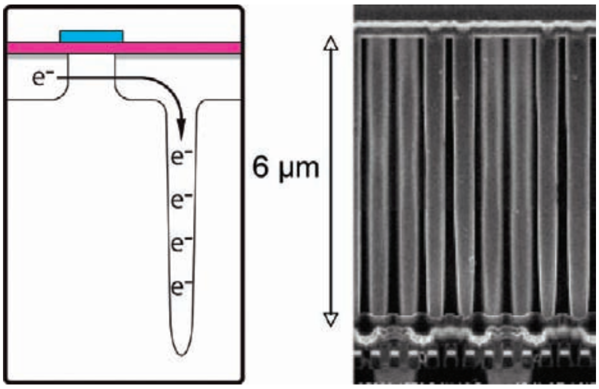


FIGURE 1. Trench capacitor. Conceptual illustration showing crossbars (red, blue), transistor, and trench capacitor (left). Image of a 78-nm trench DRAM cell (with 70:1 aspect ratio) showing numerous trenches (right).

electronic properties over a broad range through molecular design and chemical synthesis.[1] However, the molecular components employed must remain robust under daunting conditions including high-temperature processing steps during manufacture (~400 °C), relatively high-temperature operating conditions (up to 140 °C), and very large numbers of operational cycles over a lifetime ($\geq 10^{12}$).[2]

One of the long-term objectives of molecular electronics is to learn to construct circuitry using molecular components in a bottom-up approach. A more near-term strategy entails the development of hybrid semiconductor/molecular devices wherein molecules are used to augment the features of traditional, semiconductor-based, photolithographically constructed circuitry, thereby taking advantage of the vast infrastructure of the semiconductor industry. Toward this latter goal, our laboratories have been engaged over the past decade in the development of a molecular-based information-storage medium that can be readily incorporated into existing semiconductor processing technologies.[3−52] Our general approach uses a collection of redox-active porphyrin molecules covalently attached to an electroactive surface wherein information is stored in the discrete redox states of the molecules.[3]

Our porphyrin-based charge-storage medium forms the basis for constructing a hybrid semiconductor/molecular dynamic random access memory (DRAM).[2] DRAM serves as the central memory element in numerous devices, most notably in the standard desktop and laptop computers. A key advantage of DRAM over other types of memory technologies, such as static random access memory (SRAM), is its small feature size, hence the capability of achieving high-memory density. The small feature size of DRAM arises because the basic cell consists of one transistor and one capacitor (Figure 1). Charge stored on the capacitor indicates the bit level (either 0 or 1). To store sufficient charge (~200 000 electrons) for accurate readout, a trench (or stack) type capacitor is utilized.[2] These designs lead to extremely high aspect ratios, which are not easily scalable to the smallest feature sizes now achievable via lithography (~20 nm).

Another disadvantage arising from the small dimensions of the transistor gate in the DRAM cell is that the charge on the capacitor decays rapidly (tens of milliseconds in current constructs) via a leakage current through the transistor. Thus, the data stored in each memory location must be periodically refreshed by reading it out and then writing it back again. The frequency at which this refresh must be repeated is determined by the magnitude of the capacitance and the leakage current; thus, a key design feature in the miniaturization of DRAM cells is the available capacitance as the feature size shrinks. If DRAM cells could reach the same feature size now possible via lithography, a memory density in excess of 1 terabit/cm^2 in a planar format could be achieved (or 10 000 terabit/cm^3 in a three-dimensional format). A DRAM based on molecular properties would be compatible with this memory density.[2]

The use of molecules as the charge-storage element in a DRAM device has the general 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 because a number of discrete molecules constitute a single memory storage element. Our program to develop porphyrin-based charge-storage molecules for DRAM focused both on designing the requisite features for facile information storage and on developing strategies for the incorporation of the molecules into hybrid semiconductor/molecular memory chips. A cycle of molecular design, chemical synthesis, and physical characterization was iterated over the course of which >350 compounds were prepared and tested during the past decade. The program grew out of our longstanding research in molecular photonics[53] and necessitated substantial advances in porphyrin synthetic chemistry.[10,40,52,54] The chief results of this program are the focus of this Account.

Porphyrin-Based Charge-Storage Memory Elements

The basic concept of the porphyrin-based charge-storage memory element is illustrated in Figure 2. Porphyrins were chosen owing to certain specific characteristics of their redox

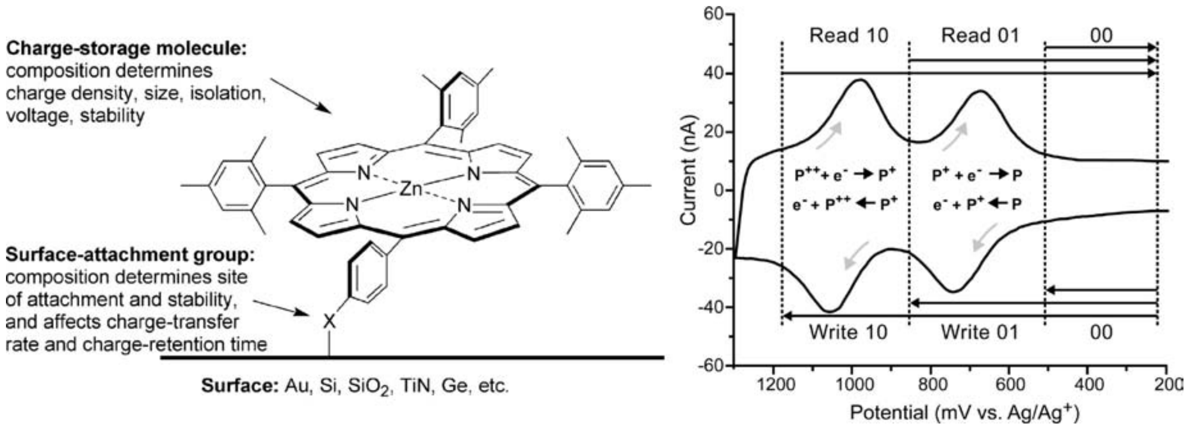


FIGURE 2. Porphyrin-based memory element (left panel). Redox-based read/write process; P = porphyrin (right panel).

properties, which provide the basis for writing/reading the memory cell.[3] Accordingly, some type of an electrolyte material is an integral part of the memory cell. The important redox characteristics of porphyrins include the following: (1) They form π-cation radicals that are relatively stable under ambient conditions, facilitating real-world applications. (2) They exhibit multiple cationic states that are accessible at relatively low potentials, affording multibit information storage with low power consumption. (3) They are capable of storing charge for extended periods (up to minutes) in the absence of applied potential, further diminishing power consumption and significantly attenuating the refresh rates required in a memory device.

The read/write strategy for the porphyrin-based memory cell is also illustrated in Figure 2. The oxidation of the neutral porphyrin to the mono-π-cation radical constitutes writing of a bit of information. Subsequent reduction of the mono-π-cation radical to the neutral molecule constitutes reading out that bit of information. Accordingly, the read protocol is by its nature destructive. Monomeric Zn porphyrins exhibit two distinct cationic states. This is illustrated in Figure 2 by the oxidation/reduction (write/read) to/from the di-π-cationic state of the porphyrin.

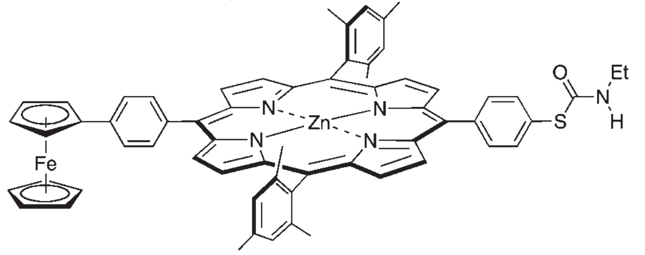
Tuning Electronic Properties of Molecules Using Synthetic Design

One objective of our studies was to create molecular architectures for multibit information storage. For useful multibit storage at least three distinct cationic states are needed. Such multiple states, each at a distinct potential, are not individually addressable. The states resemble a Coulomb ladder and thereby constitute what is more appropriately called a molecular counter. One approach is to employ mixtures of redox-active molecules.[26] A second approach is to incorporate multiple redox states into a single molecule. Examples of the latter are provided in Figure 3.

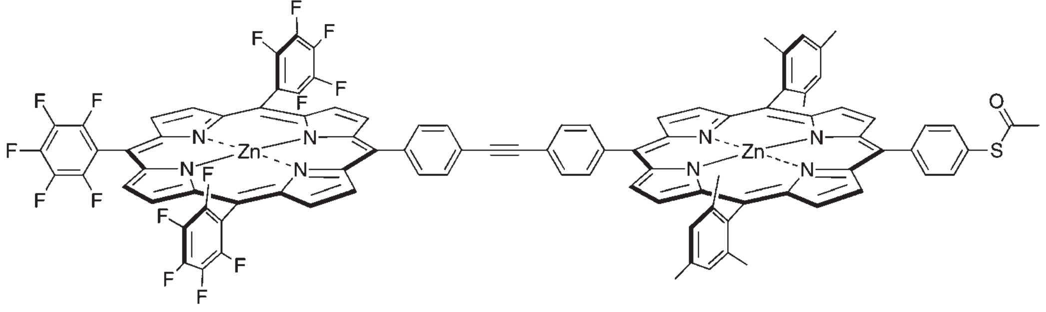
The ferrocene–porphyrin dyad A provides three distinct cationic states.[5] The porphyrin dyad B is designed so that the two cationic states of the porphyrin proximal to the surface attachment group are at lower potential than those of the distal porphyrin; accordingly, the dyad affords four distinct cationic states.[6] The potentials of the porphyrins are tuned by the electronic properties of the nonlinking meso substituents (electron-releasing mesityl versus electron-withdrawing pentafluorophenyl). Finally, the dyad C employs two porphyrins with essentially identical meso substituents, but only one carbon–carbon single bond joining the two porphyrins.[7] In contrast with dyad B, where the electronic interactions between the constituent porphyrins are weak, such interactions in dyad C are relatively strong. Consequently, dyad C affords four distinct cationic states.

Other redox-active constituents examined for molecular information storage include the triple-decker lanthanide sandwich compounds.[8–10,15,20,23,25,43] A triple decker typically exhibits four distinct cationic states, which can be tuned by choice of (1) metals, (2) ligand composition (porphyrins, phthalocyanines), and (3) substituents about the perimeter of a given ligand. One representative triple decker is shown in Figure 4. We designed several dyads of triple deckers in an effort to construct an octal counter (i.e., 8 states = 3 bits).[12,19,36] The dyad shown in Figure 4 is composed of a Pc-Eu-Pc-Eu-Por triple decker and a Por-Eu-Pc-Ce-Por triple decker where Pc and Por represent the ligands of the phthalocyanine and porphyrin, respectively. While eight states could be achieved, the triple decker occupied a very large footprint, which decreased the charge density per state relative to that of a porphyrin monomer. The large footprint stems from the size of the triple deckers, the placement of

(A) Ferrocene-porphyrin



(B) Porphyrin dyad



(C) Porphyrin dyad

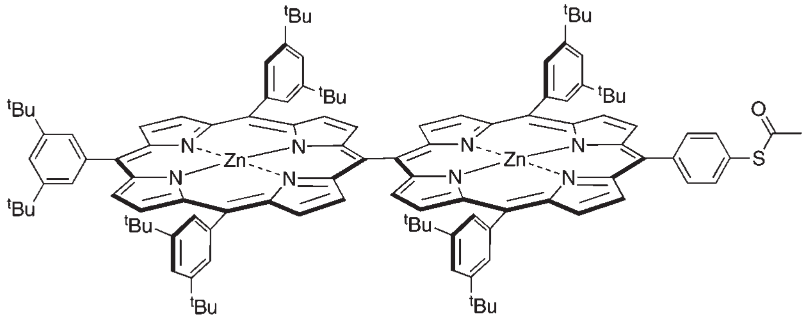


FIGURE 3. Multistate molecular architectures.

the linker on an outer ligand, and the overall orientation of the dyad in a nonvertical fashion.[12,19]

The tether portion of the molecular architecture serves multiple functions: (1) attach the redox-active molecule to the surface, (2) orient the molecule with respect to the surface, and (3) perhaps provide a conduit for electrical communication. The tether includes a linker and a surface attachment group. Initially, we employed thiols as the surface attachment group so as to attach the molecules to a Au surface.[3−8,11−13,15,18−20,23,30,36,37,45] The resulting self-assembled monolayers on Au are readily characterized in laboratory studies; however, Au cannot be used inside chips owing to the facile diffusion of Au atoms in Si-based semiconductors under the conditions employed for fabrication. The need for attachment to industry-compatible surfaces such as oxides (e.g., SiO_2, WO_2) was met with phosphonates,[17,21,22,28,31] whereas attachment to Si itself was accommodated first by alcohols,[14,16,20,24−27,32,41,46,47] thiols,[20,27,32,45] and selenols[20,27,32,40] and later by all-carbon tethers.[29,33−35,38,41−46,48,49] A selection of tethers is shown in Figure 5. A surprising variety of all-carbon tethers were successfully attached to Si.

Characterization and Optimization of Properties of Molecules on Surfaces

Understanding the properties of the porphyrin monolayers on surfaces is essential for utilizing these molecular architectures in viable electronic components. Accordingly, the properties of the various monolayers on surfaces were investigated in detail. These studies addressed issues including monolayer stability/robustness,[25] surface binding/adsorption geometry,[30,32,33,35,37,45] electron-transfer rates,[15,16,32,33,35,50,51] and charge-retention times.[3,11,13,14,32,33,35] Each of these characteristics in turn reflects a key feature of

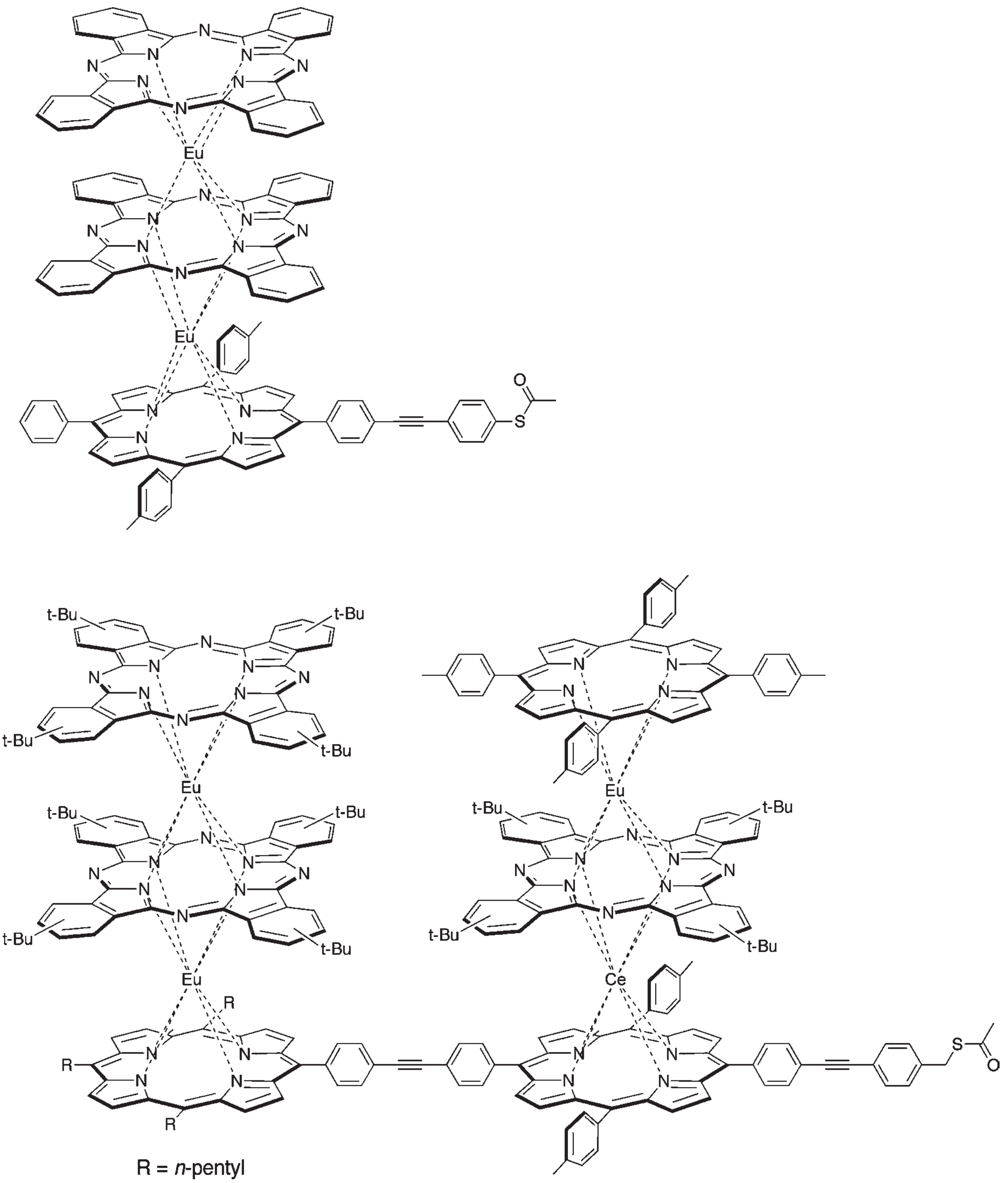


FIGURE 4. Triple deckers (monomer and dyad).

device performance. (1) The monolayer stability/robustness ultimately determines the device viability under conditions of manufacture and operation. (2) The surface binding/adsorption geometry influences the charge densities that are achievable. (3) The electron-transfer rates dictate the read/write speed of the memory cell. (4) The charge-retention times dictate the refresh rates of the memory cell and, hence, affect power consumption.

Semiconductor fabrication processes often entail excursions at temperatures reaching as high as 400 °C. We subjected a porphyrin monolayer formed (covalent Si–O–C linkage) on a Si(100) platform to a temperature of 400 °C for 30 min under inert atmosphere conditions.[25] The voltammetric response of the porphyrin monolayer is identical to that of porphyrin monolayers that have not been subjected to elevated temperatures and demonstrates that molecular

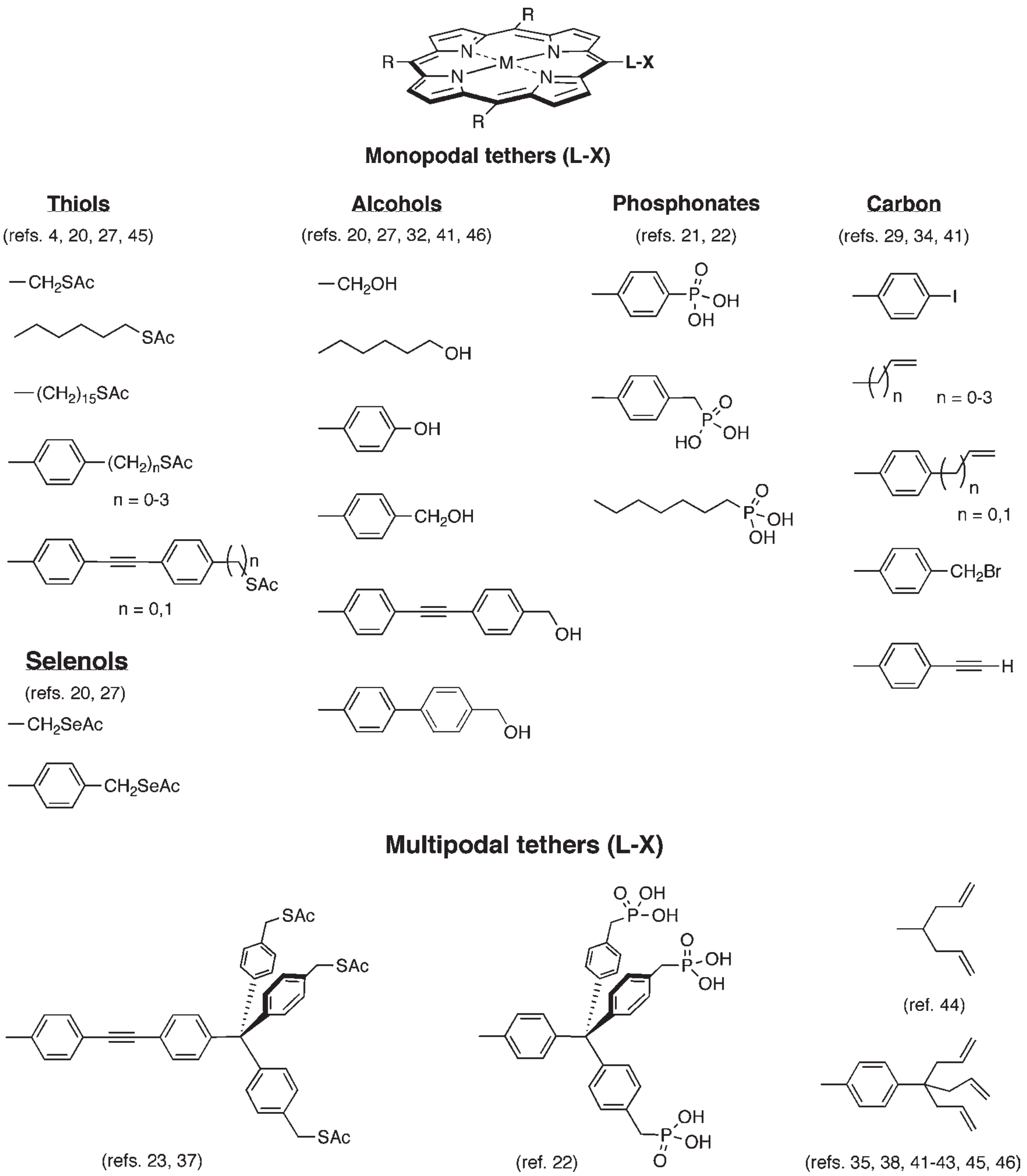


FIGURE 5. Tethers (linkers and surface attachment groups).

integrity is maintained at temperatures where most organic molecules (e.g., ferrocene) decompose. Similar high-temperature stability has been observed for a variety of porphyrin architectures tethered to silicon, including a triple-decker complex.

The robustness of the porphyrin information-storage medium was further examined by repeatedly performing the cycle of (1) oxidizing the electrically neutral monolayer and (2) reducing the resulting positively charged monolayer to its electrically neutral state.[25] The five voltammograms in Figure 6a show the response of the system after 0, 2.5×10^4, 1.8×10^6, 1.1×10^9, and 1.0×10^{10} oxidation/reduction cycles. During the experiment, the nature of the electrical cycling was varied. On some days, the system was continuously cycled for 24 h. On others, cycling was stopped intentionally for periods ranging from a few minutes up to 12 h. The data indicate that after an initial "burn-in" period of $\sim 10^7$ cycles, the voltammetric response stabilizes. This robustness of the system is further illustrated in Figure 6b wherein the integrated voltammetric signal (corresponding to the charge in the monolayer) is plotted as a function of the number of cycles. These data indicate that the charge-storage

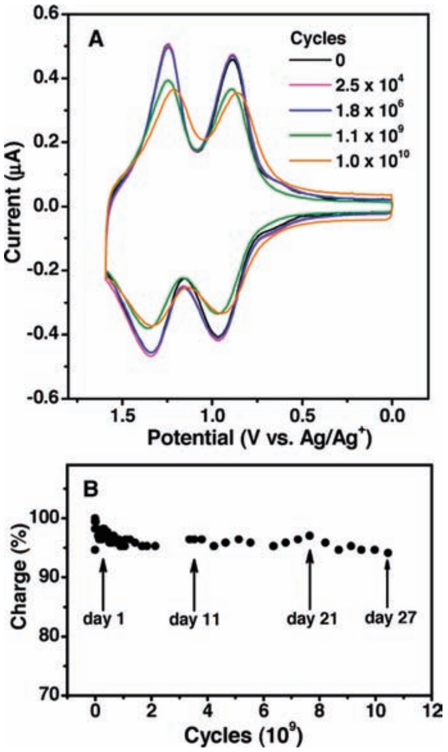
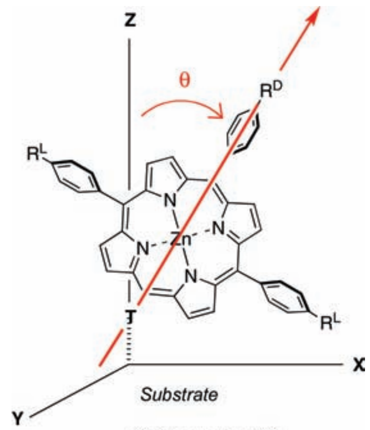


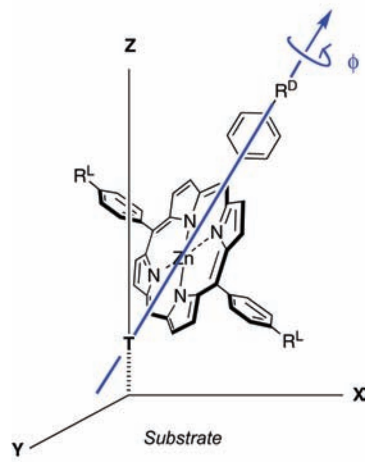
FIGURE 6. (A) Voltammetric response upon repeated cycling of a monolayer of Zn trimesitylporphyrin–benzyl alcohol attached to Si-(100). (B) Integrity of charge storage over 10^{10} cycles.

characteristics of the monolayer exhibit minimal variation (few percent) over the course of the entire experiment. At the time that cycling was arbitrarily stopped ($>10^{10}$ cycles; ~27 days), the system showed no signs of degradation. Similar results were obtained in a second series of experiments where the system was cycled ~10^{12} times over the course of 61 days. The robustness of the porphyrins to redox cycling is attributed to the fact that the positive charge on the molecules is delocalized over a number of carbon and nitrogen atoms in the macrocycle, thereby minimizing the number of "hot spots" and diminishing susceptibility to attack from adventitious chemical agents.

Our studies of porphyrin monolayers on both metal and semiconductor surfaces showed that important physical characteristics such as electron-transfer rates depend on factors such as surface coverage (packing density).[15,16] The surface coverage is in turn influenced by factors such as the relative orientation of the porphyrins with respect to one another and with respect to the plane of the surface. Consequently, determining the surface orientation of porphyrin molecules became a focal point of our studies of monolayers on both metals and semiconductors. Our early studies showed that porphyrins tethered to either Au(111) or Si(100) assume neither an upright nor a prone orientation on the surface but instead are on average tilted with respect to the surface normal by angles ranging from 35° to 55°.[30,32,33,35]



tilt from normal (θ)



rotation about molecular axis (φ)

FIGURE 7. Orientations of molecules on a surface.

A series of porphyrins bearing vibrational spectroscopic labels enabled distinction of the two in-plane axes of the porphyrin ring.[45] The spectroscopically labeled molecules allow evaluation of both the tilt angle (θ) with respect to the surface normal and the rotation angle (ϕ) about the molecular axis (Figure 7). Surface IR studies suggest that all of the porphyrins on both Au(111) and Si(100) exhibit a distribution of tilt and rotation angles. The distribution of ϕ angles is (nearly) random about the molecular axis; the distribution of tilt angles is less broad owing to steric interactions between the porphyrin substituents and the surface. The surface coverage affects the distribution of both the tilt and rotation angles. At lower surface coverage, the molecules exhibit larger tilt angles and rotation angles, that is, the porphyrin is more coplanar with the surface. The fact that all of the porphyrins on both Au(111) and Si(100) exhibit qualitatively similar surface orientation characteristics suggests that the adsorption geometry is primarily controlled by properties intrinsic to the porphyrin macrocycle rather than by properties of the tether or the surface.

The read/write speed of a memory cell and the rate at which charge dissipates in the absence of applied potential are important characteristics that affect overall device performance. Consequently, we examined the redox kinetics of a large number of porphyrin-containing monolayers on various metal and semiconductor surfaces.[3,15,16,30,32,35] The measurements probed both the rate of electron-transfer (k^0) for oxidation (in the presence of applied potential) and the rate of charge dissipation after the applied potential is disconnected (characterized by a charge-retention half-life ($t_{1/2}$)). The studies revealed that the k^0 values for all the porphyrin monolayers are in the range of 10^4-10^5 s^{-1}. The exact rate depends on the length of the tether and the extent of electronic communication between the porphyrin and the tether—the shorter the tether and greater the electronic communication, the faster the rate. The trends observed in the k^0 values are paralleled in the $t_{1/2}$ values, that is, monolayers that exhibit relatively faster electron-transfer rates also exhibit faster charge-dissipation rates (shorter $t_{1/2}$ values). However, the charge-dissipation rates (no applied potential) are approximately 6 orders of magnitude slower than the electron-transfer rates (applied potential). Both the k^0 and $t_{1/2}$ values for the porphyrin monolayers are sensitive to the surface coverage of the molecules. The rates for both processes decrease as the monolayers become more densely packed. This behavior was shown to be due to exclusion of solvent/counterions or space–charge effects.[47] The effect of surface coverage on rates overshadows differences that result from differences in linker length and type.

A key aspect of the electron-transfer characteristics of the porphyrin monolayers is that the rates are in the 10–100 kHz regime. These rates are far slower than those of modern DRAM chips, which lie in the gigahertz regime, thus signaling a potentially serious limitation in the implementation of porphyrin charge-storage elements in memory devices.[2] However, other considerations suggest that the observed rates may not be as large a constraint as might be implied. In particular, the k^0 values are determined at the standard redox potential of the monolayer; thus, minimal driving force is being applied to induce the redox event. Application of an overpotential is expected to increase the rates exponentially; a 500 mV overpotential could theoretically increase the rates to the gigahertz regime.

The most important aspect of the charge-retention characteristics of the porphyrin monolayers is that the $t_{1/2}$ values are in the range of tens of seconds to minutes. These times are much longer than the tens of milliseconds charge-retention times exhibited by typical DRAM memory cells.[2] Accordingly, memory cells based on porphyrin charge storage could be refreshed much less frequently than those in a typical DRAM device.

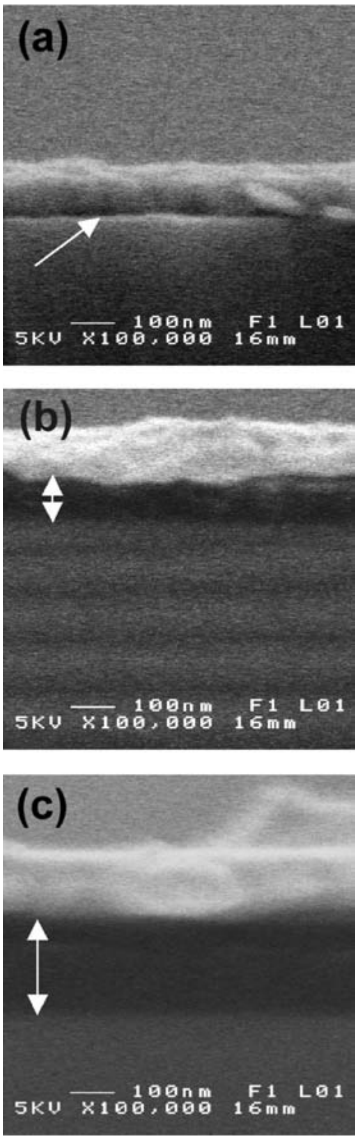


FIGURE 8. SEM images following polymerization of porphyrin–ethynes.

Integration of Molecules with Advanced Semiconductor Technology

The integration of molecular charge-storage molecules with advanced semiconductor technology required meeting multiple objectives, including achieving higher charge density and developing approaches for depositing a (metal) counter-electrode on top of the molecules. The first objective was

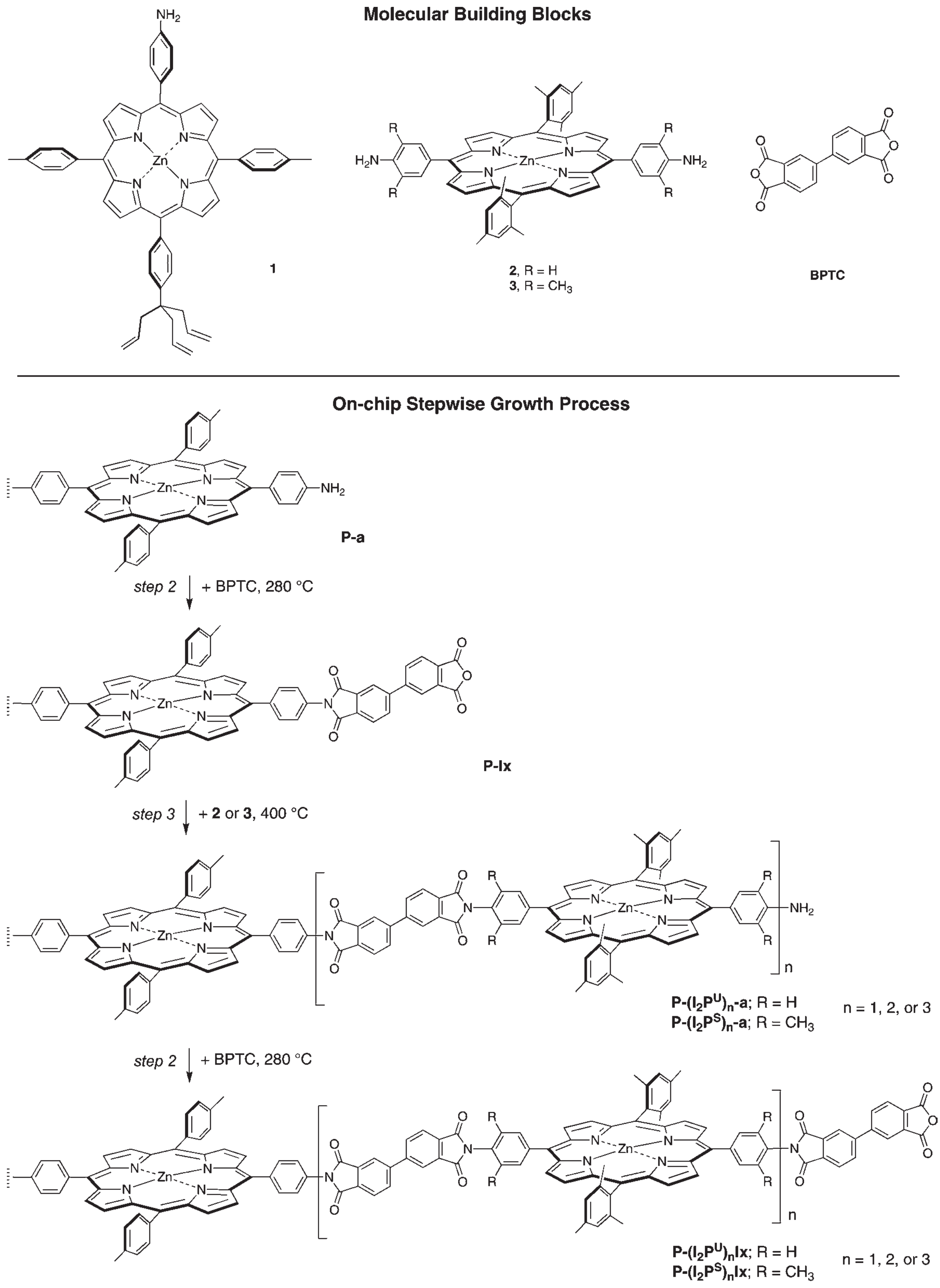


FIGURE 9. Stepwise synthesis of oligomeric charge-storage molecules on an electroactive surface from molecular building blocks.

met via three approaches: (1) incorporation of dyads and triads,[6,7,38,39] (2) in situ polymerization,[34] and (3) in situ stepwise synthesis.[41,42] Of these approaches, the polymerization and stepwise synthesis hold much greater promise for successful device integration than does utilizing dyads and triads. This is so because both polymerization and stepwise

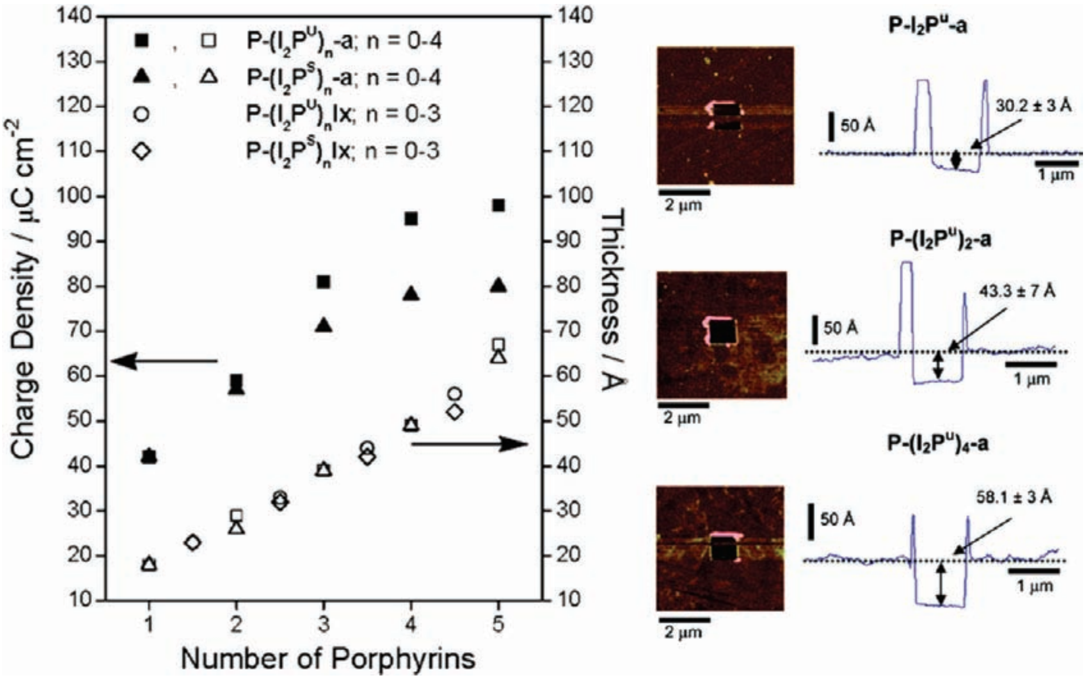


FIGURE 10. Increase in charge density accompanying stepwise synthesis (left panel). AFM examination of surface to assess stepwise synthesis of charge-storage molecules (right panel).

synthesis afford multiple molecular layers that build vertically off the surface, whereas dyads and triads are incorporated as monolayers. The use of the vertical dimension affords higher charge density than a monolayer and provides a more robust surface for deposition of a top contact.

Upon examination of diverse porphyrins for attachment via carbon-terminated groups to Si, porphyrins bearing two or more ethynes were found to afford polymers.[34] Films have been prepared on Si(100), SiO_2, Au(111), and glass. The thickness of the resulting polymer could be controlled by the amount of porphyrin and the duration of polymerization. SEM analysis indicates the porphyrin polymer films range in thickness from tens to hundreds of nanometers (Figure 8a−c). The polymers contain intact porphyrin macrocycles and are redox-active albeit with quite slow electron-transfer rates. Regardless, this serendipitous finding provided one solution to the challenge of creating redox-active materials with high charge density.

To exercise molecular-level control over size and composition, methods for stepwise syntheses[41,42] or patterning (i.e., selective derivatization)[27,41,46] of charge-storage molecules on an electroactive surface were developed. One strategy developed, while inspired by solid-phase synthesis of biomolecules, employs no protecting groups (Figure 9).[41,42] The first porphyrin (**1**) bears a tether for attachment to Si (in this case, an all-carbon tripod) and a distal amine. After attachment (step 1), a dianhydride (**BPTC**) reacts with the amine to give a monoimide, leaving one anhydride free (step 2). In step 3, a diamino-porphyrin (**2**) is attached to the anhydride, forming the imide and leaving the distal amine free. Repetition of steps 2 and 3 allows successive layers of porphyrins to be added to the growing chain. This on-chip assembly is compatible with semiconductor fabrication requirements.

The stepwise growth process was readily observed by FTIR spectroscopy, XPS, AFM, and electrochemistry. FTIR spectroscopy enabled monitoring of the presence/disappearance of the anhydride. The increase in charge density with stepwise synthesis and assessment of the stepwise growth process by interrogation with AFM are shown in Figure 10.

The incorporation of molecules in electronic devices requires making hybrid junctions wherein molecules are sandwiched between two metal contacts or a metal and a semiconductor contact. However, the fate of molecules subsequent to deposition of a top metal contact has generally not been well characterized. Toward this goal, the interaction of evaporated Cu, Ag, and Au films deposited in varying thicknesses (3, 5, and 8 nm) on a series of monolayer-coverage porphyrins covalently attached to Si(100) substrates was investigated.[46,48,49] The methods of interrogation included ellipsometry, AFM, FTIR spectroscopy,

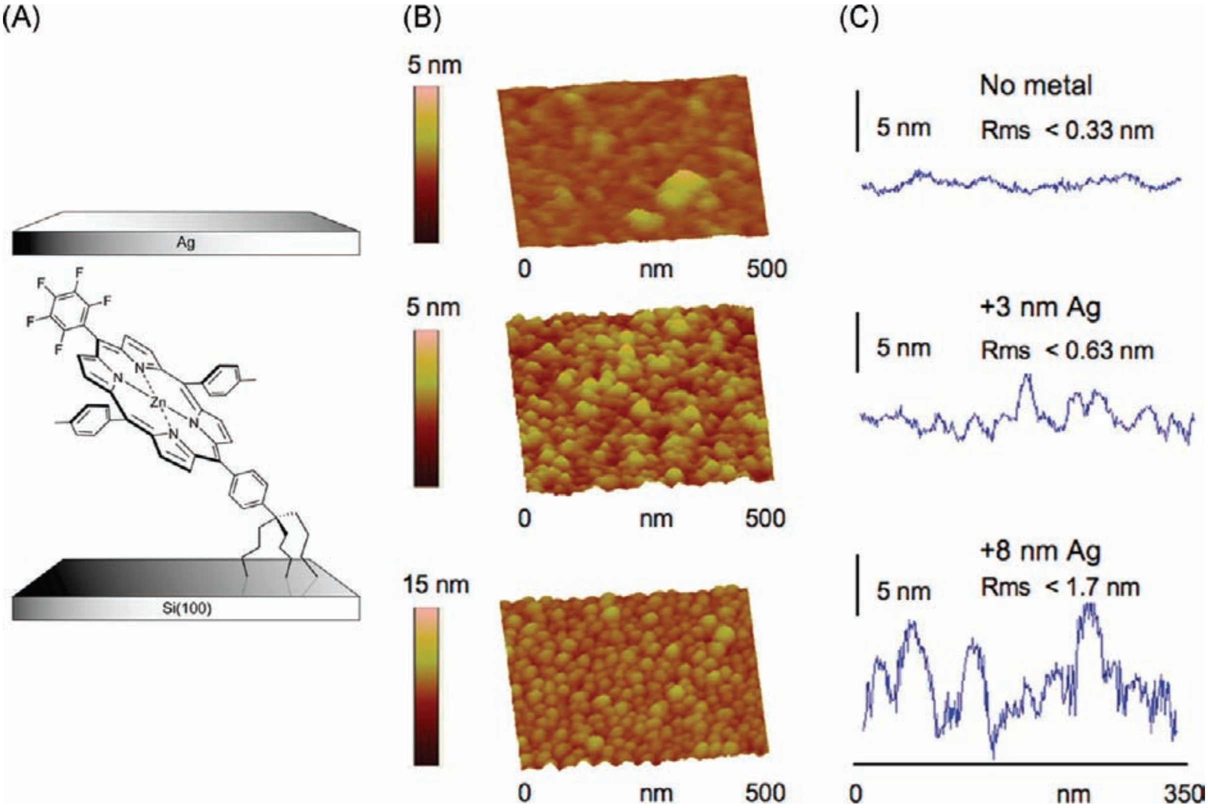


FIGURE 11. Metal deposition on redox-active molecules attached to a surface: (A) illustration of molecule with top contact; (B) AFM image of surface following Ag deposition; (C) profile of the surface following Ag deposition.

Raman spectroscopy, XPS, cyclic voltammetry, and current–voltage measurements (Figure 11). The studies indicate that all of the porphyrin monolayers are robust under the conditions of metal deposition. Neither Cu nor Ag penetrates through the monolayer to form electrically conductive filaments, whereas Au does penetrate through the porphyrin monolayer and contacts the Si substrate.

Demonstration of Low-Power, High Charge Density, Semiconductor/Molecular Memory Devices

The ultimate goal of our research program was to implement the charge-storage molecules in hybrid semiconductor/molecular memory devices. This goal was achieved in a prototypical 1-Mb DRAM test chip design (Figure 12).[2] The chip incorporates 4 × 256 kbit arrays of molecular–Si capacitors. The circuits on the chip were fabricated on a 0.35 μm flow process to avoid the high costs of masks prepared on smaller lithography nodes. A key feature of the chip architecture is that the capacitors are planar rather than utilizing the vertical dimension (trenches or stacks). Despite the planar area of the capacitor, the demonstrated charge-storage density in each molecular-based memory cell is equal to (or greater than) that achieved in trench/stack designs. This aspect of the hybrid semiconductor/molecular design was another key objective of our research program.

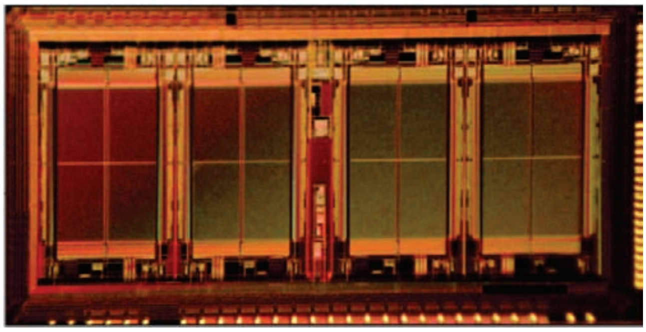


FIGURE 12. Photograph of 1 Mb test chip developed by ZettaCore, Inc.

Another important feature of the hybrid semiconductor/molecular DRAM is that all of the peripheral circuits were fabricated with conventional technology. Consequently, the only variation in the manufacturing process is where the hybrid molecular–Si structures are formed. Owing to the high charge density (and consequent planar design), the overall fabrication process requires less than 10% of the number of steps typically required in the fabrication of commercial DRAM chips. The process is also compatible with those available in modern foundries. Collectively, these features of the hybrid semiconductor/molecular DRAM suggest that manufacturing costs can be significantly lower than those of commercial DRAM chips.

While the demonstration of the prototypical semiconductor/molecular DRAM is an important advance toward the commercialization of such designs, much additional work is needed before this goal can be achieved. These studies require focus on basic scientific issues such as molecular design, on-chip fabrication strategies, and molecular factors that affect interfacial electron-transfer processes. Regardless, the demonstration of a fully functional hybrid semiconductor/molecular DRAM is a necessary step toward commercialization of such devices. Ultimately, molecular charge-based information storage may prove beneficial for low-power electronics,[55] the design of novel transistors,[56] and where circuitry must be deployed at low cost over large areas.[57]

BIOGRAPHICAL INFORMATION

Jonathan S. Lindsey (b. 1956) received a B.S. in Chemistry from Indiana University (1978) and a Ph.D. from Rockefeller University (1983), where he also did postdoctoral research. After 12 years at Carnegie Mellon University, he joined North Carolina State University (1996) as Glaxo Distinguished University Professor of Chemistry.

David F. Bocian (b. 1950) received a B.S. in Chemistry from North Carolina State University (1972) and a Ph.D. from the University of California, Berkeley (1976). He did postdoctoral research at Caltech and then joined the faculty at the University of California, Riverside, in 1979. He spent 6 years at Carnegie Mellon University (1985−1991) before returning to the University of California, Riverside, where he is now Distinguished Professor of Chemistry.

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FOOTNOTES

*E-mail addresses: jlindsey@ncsu.edu; David.Bocian@ucr.edu.

REFERENCES

1 Carroll, R. L.; Gorman, C. B. The Genesis of Molecular Electronics. *Angew. Chem., Int. Ed.* **2002**, *41*, 4378–4400.

2 Kuhr, W. G.; Gallo, A. R.; Manning, R. W.; Rhodine, C. W. Molecular Memories based on a CMOS Platform. *MRS Bull.* **2004**, *29*, 838–842.

3 Roth, K. M.; Dontha, N.; Dabke, R. B.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. Molecular Approach Toward Information Storage Based on the Redox Properties of Porphyrins in Self-Assembled Monolayers. *J. Vac. Sci. Technol. B.* **2000**, *18*, 2359–2364.

4 Gryko, D. T.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Synthesis of "Porphyrin-Linker-Thiol" Molecules with Diverse Linkers for Studies of Molecular-Based Information Storage. *J. Org. Chem.* **2000**, *65*, 7345–7355.

5 Gryko, D. T.; Zhao, F.; Yasseri, A. A.; Roth, K. M.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Synthesis of Thiol-Derivatized Ferrocene−Porphyrins for Studies of Multibit Information Storage. *J. Org. Chem.* **2000**, *65*, 7356–7362.

6 Clausen, C.; Gryko, D. T.; Dabke, R. B.; Dontha, N.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Synthesis of Thiol-Derivatized Porphyrin Dimers and Trimers for Studies of Architectural Effects on Multibit Information Storage. *J. Org. Chem.* **2000**, *65*, 7363–7370.

7 Clausen, C.; Gryko, D. T.; Yasseri, A. A.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Investigation of Tightly Coupled Porphyrin Arrays Comprised of Identical Monomers for Multibit Information Storage. *J. Org. Chem.* **2000**, *65*, 7371–7378.

8 Li, J.; Gryko, D.; Dabke, R. B.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Synthesis of Thiol-Derivatized Europium Porphyrinic Triple-Decker Sandwich Complexes for Multibit Molecular Information Storage. *J. Org. Chem.* **2000**, *65*, 7379–7390.

9 Gryko, D.; Li, J.; Diers, J. R.; Roth, K. M.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Studies Related to the Design and Synthesis of a Molecular Octal Counter. *J. Mater. Chem.* **2001**, *11*, 1162–1180.

10 Gross, T.; Chevalier, F.; Lindsey, J. S. Investigation of Rational Syntheses of Heteroleptic Porphyrinic Lanthanide (Europium, Cerium) Triple-Decker Sandwich Complexes. *Inorg. Chem.* **2001**, *40*, 4762–4774.

11 Roth, K. M.; Liu, Z.; Gryko, D. T.; Clausen, C.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. Charge-Retention Characteristics of Self-Assembled Monolayers of Molecular-Wire-Linked Porphyrins on Gold. In *Molecules as Components of Electronic Devices*; Lieberman, M., Ed.; ACS Symposium Series 844; American Chemical Society: Washington, DC, 2003, pp 51−61.

12 Schweikart, K.-H.; Malinovskii, V. L.; Diers, J. R.; Yasseri, A. A.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. Design, Synthesis, and Characterization of Prototypical Multistate Counters in Three Distinct Architectures. *J. Mater. Chem.* **2002**, *12*, 808–828.

13 Roth, K. M.; Lindsey, J. S.; Bocian, D. F.; Kuhr, W. G. Characterization of Charge Storage in Redox-Active Self-Assembled Monolayers. *Langmuir* **2002**, *18*, 4030–4040.

14 Li, Q.; Mathur, G.; Homsi, M.; Surthi, S.; Misra, V.; Malinovskii, V.; Schweikart, K.-H.; Yu, L.; Lindsey, J. S.; Liu, Z.; Dabke, R. B.; Yasseri, A.; Bocian, D. F.; Kuhr, W. G. Capacitance and Conductance Characterization of Self-Assembled Ferrocene Monolayers on Silicon Surfaces for Memory Applications. *Appl. Phys. Lett.* **2002**, *81*, 1494–1496.

15 Roth, K. M.; Gryko, D. T.; Clausen, C.; Li, J.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. Comparison of Electron-Transfer and Charge-Retention Characteristics of Porphyrin-Containing Self-Assembled Monolayers Designed for Molecular Information Storage. *J. Phys. Chem. B* **2002**, *106*, 8639–8648.

16 Roth, K. M.; Yasseri, A. A.; Liu, Z.; Dabke, R. B.; Malinovskii, V.; Schweikart, K.-H.; Yu, L.; Tiznado, H.; Zaera, F.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. Measurements of Electron-Transfer Rates of Charge-Storage Molecular Monolayers on Si(100). Toward Hybrid Molecular/Semiconductor Information Storage Devices. *J. Am. Chem. Soc.* **2003**, *125*, 505–517.

17 Li, Q.; Surthi, S.; Mathur, G.; Gowda, S.; Misra, V.; Sorenson, T. A.; Tenent, R. C.; Kuhr, W. G.; Tamaru, S.-I.; Lindsey, J. S.; Liu, Z.; Bocian, D. F. Electrical Characterization of Redox-Active Molecular Monolayers on SiO_2 for Memory Applications. *Appl. Phys. Lett.* **2003**, *83*, 198–200.

18 Tomizaki, K.-y.; Yu, L.; Wei, L.; Bocian, D. F.; Lindsey, J. S. Synthesis of Cyclic Hexameric Porphyrin Arrays. Anchors for Surface Immobilization and Columnar Self-Assembly. *J. Org. Chem.* **2003**, *68*, 8199–8207.

19 Schweikart, K.-H.; Malinovskii, V. L.; Yasseri, A. A.; Li, J.; Lysenko, A. B.; Bocian, D. F.; Lindsey, J. S. Synthesis and Characterization of Bis(S-acetylthio)-Derivatized Europium Triple-Decker Monomers and Oligomers. *Inorg. Chem.* **2003**, *42*, 7431–7446.

20 Balakumar, A.; Lysenko, A. B.; Carcel, C.; Malinovskii, V. L.; Gryko, D. T.; Schweikart, K.-H.; Loewe, R. S.; Yasseri, A. A.; Liu, Z.; Bocian, D. F.; Lindsey, J. S. Diverse Redox-Active Molecules Bearing O-, S-, or Se-Terminated Tethers for Attachment to Silicon in Studies of Molecular Information Storage. *J. Org. Chem.* **2004**, *69*, 1435–1443.

21 Muthukumaran, K.; Loewe, R. S.; Ambroise, A.; Tamaru, S.-I.; Li, Q.; Mathur, G.; Bocian, D. F.; Misra, V.; Lindsey, J. S. Porphyrins Bearing Arylphosphonic Acid Tethers for Attachment to Oxide Surfaces. *J. Org. Chem.* **2004**, *69*, 1444–1452.

22 Loewe, R. S.; Ambroise, A.; Muthukumaran, K.; Padmaja, K.; Lysenko, A. B.; Mathur, G.; Li, Q.; Bocian, D. F.; Misra, V.; Lindsey, J. S. Porphyrins Bearing Mono or Tripodal Benzylphosphonic Acid Tethers for Attachment to Oxide Surfaces. *J. Org. Chem.* **2004**, *69*, 1453–1460.

23 Wei, L.; Padmaja, K.; Youngblood, W. J.; Lysenko, A. B.; Lindsey, J. S.; Bocian, D. F. Diverse Redox-Active Molecules Bearing Identical Thiol-Terminated Tripodal Tethers for Studies of Molecular Information Storage. *J. Org. Chem.* **2004**, *69*, 1461–1469.

24 Gowda, S.; Mathur, G.; Li, Q.; Surthi, S.; Zhao, Q.; Lindsey, J. S.; Mobley, K.; Bocian, D. F.; Misra, V. Hybrid Silicon/Molecular Memories: Co-Engineering for Novel Functionality. *IEEE Int. Electron Devices Meet., Tech. Dig.* **2003**, 537–540.

25 Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. Molecular Memories That Survive Silicon Device Processing and Real-World Operation. *Science* **2003**, *302*, 1543–1545.

26 Li, Q.; Mathur, G.; Gowda, S.; Surthi, S.; Zhao, Q.; Yu, L.; Lindsey, J. S.; Bocian, D. F.; Misra, V. Multibit Memory Using Self-assembly of Mixed Ferrocene/Porphyrin Monolayers on Silicon. *Adv. Mater.* **2004**, *16*, 133–137.

27 Carcel, C. M.; Laha, J. K.; Loewe, R. S.; Thamyongkit, P.; Schweikart, K.-H.; Misra, V.; Bocian, D. F.; Lindsey, J. S. Porphyrin Architectures Tailored for Studies of Molecular Information Storage. *J. Org. Chem.* **2004**, *69*, 6739–6750.

28 Li, Q.; Surthi, S.; Mathur, G.; Gowda, S.; Zhao, Q.; Sorenson, T. A.; Tenent, R. C.; Muthukumaran, K.; Lindsey, J. S.; Misra, V. Multiple-Bit Storage Properties of Porphyrin Monolayers on SiO_2. *Appl. Phys. Lett.* **2004**, *85*, 1829–1831.

29 Liu, Z.; Yasseri, A. A.; Loewe, R. S.; Lysenko, A. B.; Malinovskii, V. L.; Zhao, Q.; Surthi, S.; Li, Q.; Misra, V.; Lindsey, J. S.; Bocian, D. F. Synthesis of Porphyrins Bearing Hydrocarbon Tethers and Facile Covalent Attachment to Si(100). *J. Org. Chem.* **2004**, *69*, 5568–5577.

30 Yasseri, A. A.; Syomin, D.; Malinovskii, V. L.; Loewe, R. S.; Lindsey, J. S.; Zaera, F. Bocian, D. F. Characterization of Self-Assembled Monolayers of Porphyrins Bearing Multiple Thiol-Derivatized Rigid-Rod Tethers. *J. Am. Chem. Soc.* **2004**, *126*, 11944–11953.

31 Gowda, S.; Mathur, G.; Li, Q.; Surthi, S.; Zhao, Q.; Lindsey, J. S.; Bocian, D. F.; Misra, V. Modulation of Drain Current by Redox-Active Molecules Incorporated in Si MOSFETs. *IEEE Tech. Dig.* **2004**, 707–710.

32 Yasseri, A. A.; Syomin, D.; Loewe, R. S.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. Structural and Electron-Transfer Characteristics of O-, S-, and Se-Tethered Porphyrin Monolayers on Si(100). *J. Am. Chem. Soc.* **2004**, *126*, 15603–15612; *J. Am. Chem. Soc.* **2005**, *127*, 9308(Additions and Corrections).

33 Wei, L.; Syomin, D.; Loewe, R. S.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. Structural and Electron-Transfer Characteristics of Carbon-Tethered Porphyrin Monolayers on Si(100). *J. Phys. Chem. B* **2005**, *109*, 6323–6330.

34 Liu, Z.; Schmidt, I.; Thamyongkit, P.; Loewe, R. S.; Syomin, D.; Diers, J. R.; Zhao, Q.; Misra, V.; Lindsey, J. S.; Bocian, D. F. Synthesis and Film-Forming Properties of Ethynylporphyrins. *Chem. Mater.* **2005**, *17*, 3728–3742.

35 Padmaja, K.; Wei, L.; Lindsey, J. S.; Bocian, D. F. A Compact All-Carbon Tripodal Tether Affords High Coverage of Porphyrins on Silicon Surfaces. *J. Org. Chem.* **2005**, *70*, 7972–7978.

36 Lysenko, A. B.; Malinovskii, V. L.; Kisari, P.; Wei, L.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S. Multistate Molecular Information Storage using S-Acetylthio-derivatized Dyads of Triple-Decker Sandwich Coordination Compounds. *J. Porphyrins Phthalocyanines* **2005**, *9*, 491–508.

37 Wei, L.; Tiznado, H.; Liu, G.; Padmaja, K.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. Adsorption Characteristics of Tripodal Thiol-Functionalized Porphyrins on Gold. *J. Phys. Chem. B* **2005**, *109*, 23963–23971.

38 Thamyongkit, P.; Yu, L.; Padmaja, K.; Jiao, J.; Bocian, D. F.; Lindsey, J. S. Porphyrin Dyads Bearing Carbon Tethers for Studies of High-Density Molecular Charge Storage on Silicon Surfaces. *J. Org. Chem.* **2006**, *71*, 1156–1171.

39 Lysenko, A. B.; Thamyongkit, P.; Schmidt, I.; Diers, J. R.; Bocian, D. F.; Lindsey, J. S. Diverse Porphyrin Dimers as Candidates for High-Density Charge-Storage Molecules. *J. Porphyrins Phthalocyanines* **2006**, *10*, 22–32.

40 Zaidi, S. H. H.; Loewe, R. S.; Clark, B. A.; Jacob, M. J.; Lindsey, J. S. Nearly Chromatography-Free Synthesis of the A_3B-Porphyrin 5-(4-Hydroxymethylphenyl)-10,15,20-tri-p-tolylporphinatozinc(II). *Org. Process Res. Dev.* **2006**, *10*, 304–314.

41 Schmidt, I.; Jiao, J.; Thamyongkit, P.; Sharada, D. S.; Bocian, D. F.; Lindsey, J. S. Investigation of Stepwise Covalent Synthesis on a Surface Yielding Porphyrin-Based Multicomponent Architectures. *J. Org. Chem.* **2006**, *71*, 3033–3050.

42 Jiao, J.; Anariba, F.; Tiznado, H.; Schmidt, I.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. Stepwise Formation and Characterization of Covalently Linked Multiporphyrin-Imide Architectures on Si(100). *J. Am. Chem. Soc.* **2006**, *128*, 6965–6974.

43 Padmaja, K.; Youngblood, W. J.; Wei, L.; Bocian, D. F.; Lindsey, J. S. Triple-Decker Sandwich Compounds Bearing Compact Triallyl Tripods for Molecular Information Storage Applications. *Inorg. Chem.* **2006**, *45*, 5479–5492.

44 Schmidt, I.; Jiao, J.; Bocian, D. F.; Lindsey, J. S. A Bipodal-Tethered Porphyrin for Attachment to Silicon Surfaces in Studies of Molecular Information Storage. *J. Nanosci. Nanotechnol.* **2008**, *8*, 4813–4817.

45 Jiao, J.; Thamyongkit, P.; Schmidt, I.; Lindsey, J. S.; Bocian, D. F. Characterization of Porphyrin Surface Orientation in Monolayers on Au(111) and Si(100) Using Spectroscopically Labeled Molecules. *J. Phys. Chem. C* **2007**, *111*, 12693–12704.

46 Kulikov, O. V.; Schmidt, I.; Muresan, A. Z.; Lee, M. A.-P.; Bocian, D. F.; Lindsey, J. S. Synthesis of Porphyrins for Metal Deposition Studies in Molecular Information Storage Applications. *J. Porphyrins Phthalocyanines* **2007**, *11*, 699–712.

47 Jiao, J.; Nordlund, E.; Lindsey, J. S.; Bocian, D. F. Effects of Counterion Mobility, Surface Morphology, and Charge Screening on the Electron-Transfer Rates of Porphyrin Monolayers. *J. Phys. Chem. C* **2008**, *112*, 6173–6180.

48 Anariba, F.; Schmidt, I.; Muresan, A. Z.; Lindsey, J. S.; Bocian, D. F. Metal−Molecule Interactions Upon Deposition of Copper Overlayers on Reactively Functionalized Porphyrin Monolayers on Si(100). *Langmuir* **2008**, *24*, 6698–6704.

49 Anariba, F.; Tiznado, H.; Diers, J. R.; Schmidt, I.; Muresan, A. Z.; Lindsey, J. S.; Zaera, F.; Bocian, D. F. Comprehensive Characterization of Hybrid Junctions Comprised of a Porphyrin Monolayer Sandwiched Between a Coinage Metal Overlayer and a Si(100) Substrate. *J. Phys. Chem. C* **2008**, *112*, 9474–9485.

50 Jiao, J.; Schmidt, I.; Taniguchi, M.; Lindsey, J. S.; Bocian, D. F. Comparison of Electron-Transfer Rates for Metal- versus Ring-Centered Redox Processes of Porphyrins in Monolayers on Au(111). *Langmuir* **2008**, *24*, 12047–12053.

51 Jiao, J.; Taniguchi, M.; Lindsey, J. S.; Bocian, D. F. Activation Energies for Oxidation of Porphyrin Monolayers Anchored to Au(111). *Langmuir* **2010**, *26*, 15718–15721.

52 Lindsey, J. S.; Thamyongkit, P.; Taniguchi, M.; Bocian, D. F. Encoding Isotopic Watermarks in Molecular Electronic Materials as an Anti-Counterfeiting Strategy. Application to Porphyrins for Information Storage. *J. Porphyrins Phthalocyanines* **2011**,*15*, in press.

53 Holten, D.; Bocian, D. F.; Lindsey, J. S. Probing Electronic Communication in Covalently Linked Multiporphyrin Arrays. A Guide to the Rational Design of Molecular Photonic Devices. *Acc. Chem. Res.* **2002**, *35*, 57–69.

54 Lindsey, J. S. Synthetic Routes to Meso-Patterned Porphyrins. *Acc. Chem. Res.* **2010**, *43*, 300–311.

55 Venkatesan, R. K.; Al-Zawawi, A. S.; Sivasubramanian, K.; Rotenberg, E. ZettaRAM A Power-Scalable DRAM Alternative through Charge-Voltage Decoupling. *IEEE Trans. Computers* **2007**, *56*, 147–160.

56 Sarkar, S.; Suresh, A.; Myers, F. B.; Muth, J. F.; Misra, V. Modulating Indium Gallium Zinc Oxide Transistor Characteristics with Discrete Redox States of Molecules Embedded in the Gate Dielectric. *Appl. Phys. Lett.* **2008**, *92*, No. 223304.

57 Reuss, R. H.; Hopper, D. G.; Park, J.-G. Macroelectronics. *MRS Bull.* **2006**, *31*, 447–450.