Fig. 4A, propagation through 5 mm of fully ionized helium gas with an electron density n_e of 9.7×10^{19} cm^{-3} would lead to pulse compression down to 75 as; that is, about 3 atomic units, using H_{25} to H_{55}, without loss in transmission (Fig. 4C). Alternatively, thin filters with linear negative group velocity dispersion could be used to compensate more accurately for the temporal drift. Our analysis holds for single attosecond bursts produced by few-femtosecond laser pulses or by temporal confinement of harmonic emission (*28*, *29*). We look forward to eventually reducing pulse duration below one atomic unit of time and thus tracking the fastest electron processes in matter with few-cycle soft x-ray pulses.

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Fig. S1
References

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Molecular Memories That Survive Silicon Device Processing and Real-World Operation

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If molecular components are to be used as functional elements in place of the semiconductor-based devices present in conventional microcircuitry, they must compete with semiconductors under the extreme conditions required for processing and operating a practical device. Herein, we demonstrate that porphyrin-based molecules bound to Si(100), which exhibit redox behavior useful for information storage, can meet this challenge. These molecular media in an inert atmosphere are stable under extremes of temperature (400°C) for extended periods (approaching 1 hour) and do not degrade under large numbers of read-write cycles (10^{12}).

Since Aviram and Ratner's pioneering paper suggesting that molecules could perform the functions of semiconductor electronics (*1*), there has been ample demonstration that molecules can function as diodes, switches, and capacitors and that these basic molecular-based electronic components can be assembled into prototypical memory and logic architectures (*2*, *3*). To date, however, the fundamental and critical question of whether organic materials can meet the minimum functionality standards that are expected of electronic devices has yet to be answered. These standards require that molecular components 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 (~10^{12}) (*4*–*6*).

There is considerable skepticism about whether molecular materials possess adequate stability to meet the extreme performance conditions required for any type of practical device. Indeed, studies of prototype molecular devices are typically carried out over a limited number of cycles, often at cryogenic temperatures. The self-assembly processes used to construct the molecular devices are generally performed at ambient

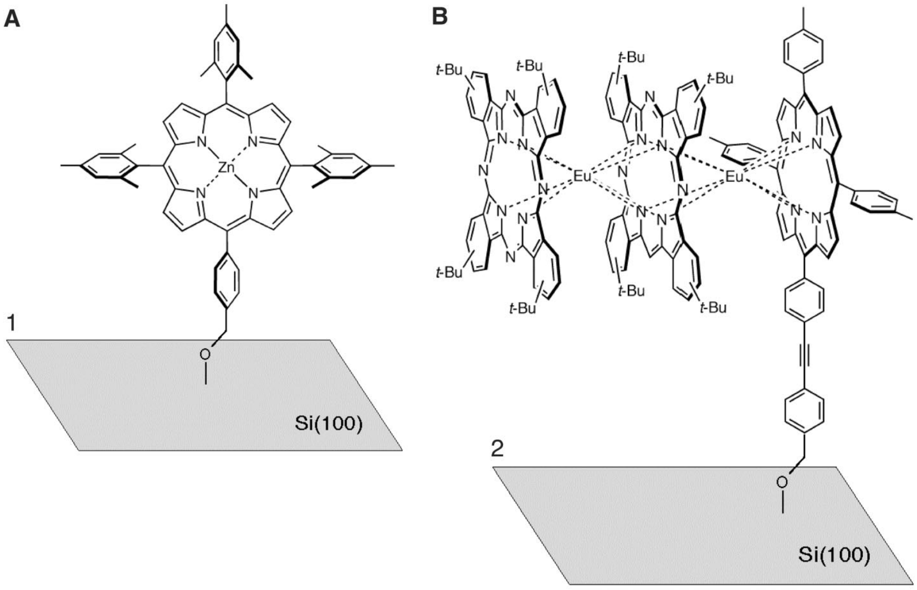

Fig. 1. Structure of the Si-tethered porphyrins. The monomeric porphyrin **1** (**A**) has two accessible cationic states below 1.6 V (*7*), whereas the triple decker **2** (**B**) has four states below 1.6 V (*8*). The availability of multiple redox states affords the possibility of multibit information storage.

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temperatures. If molecular materials cannot compete with semiconductor materials under the much more rigorous conditions expected of real devices, the implementation of molecular components in electronic devices is fundamentally nonviable.

We have been engaged in a program aimed at developing molecular-based memory devices (*7–10*). Our approach for molecular-based information storage uses a collection of redox-active molecules attached to an electroactive surface wherein information is stored in the discrete redox states of the molecules (*7*). Porphyrins have been implemented as the active charge-storage elements for two main reasons. (i) Porphyrins form stable π-cation radicals whose redox potentials can be tuned through synthetic design. Monomeric porphyrins such as **1** (*10*) (Fig. 1A) exhibit two accessible cationic states (*7*), whereas triple-decker architectures such as that of lanthanide sandwich coordination compound **2** (*11*) (Fig. 1B) exhibit as many as four states (*8*). All of these redox states can be accessed at relatively low potentials (<1.6 V) (*7–10*). (ii) The porphyrin-based information-storage elements exhibit charge-retention times that are long (minutes) compared with those of the semiconductor elements in dynamic random access memory (tens of milliseconds) (*7–10*). Collectively, these properties of porphyrins afford the possibility of increased memory density (via multibit information storage) with decreased power consumption [low potentials and long charge-retention times (*12*)].

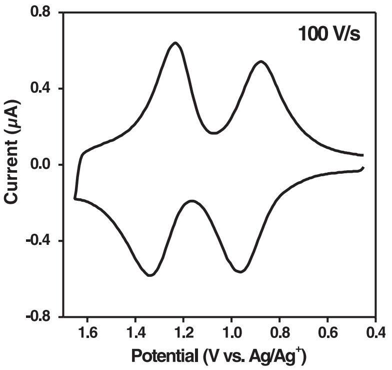

Fig. 2. Voltammetric response of a monolayer of porphyrin **1** after baking at 400°C for 30 min under inert atmosphere conditions [data acquired as previously described (*10*)]. The temperature of the Si platform was measured by attaching a thermocouple directly adjacent to the lithographically patterned area where the monolayer was attached.

Recently, we have shown that porphyrins can be covalently attached to device-grade silicon platforms to form the basis of first-generation hybrid molecular-semiconductor devices (*10*). Herein, we show that porphyrin-based information-storage media meet the processing and operating challenges required for use in electronic devices. In particular, we show that these molecules are stable under extremes of temperature (400°C) and large numbers of read-write cycles (10^{12}).

The cyclic voltammetric (CV) behavior of a porphyrin monolayer formed on a micrometer-scale photolithographically patterned, hydrogen-passivated Si(100) platform is shown in Fig. 2 [attachment is via a covalent Si-O-C linkage (*10*)]. The CV shown was obtained for a monolayer on a platform that was baked at 400°C for 30 min under inert atmosphere conditions. The voltammetric response of the porphyrin monolayer is identical to that of porphyrin monolayers that have not been subjected to elevated temperatures (*10*) and shows that molecular integrity is maintained at temperatures where most organic molecules thermally decompose. In this regard, we compared the thermal stability of the porphyrin monolayers to monolayers of electroactive ferrocene molecules [4-ferrocenylbenzyl alcohol (*10*)] that were attached to Si platforms via the same tether and covalent Si-O-C linkage as porphyrin **1**. At temperatures greater than 200°C for even relatively short times (5 min), the ferrocenes decomposed, as was evidenced by charring and the absence of the characteristic ferrocene voltammetric signature (*10*).

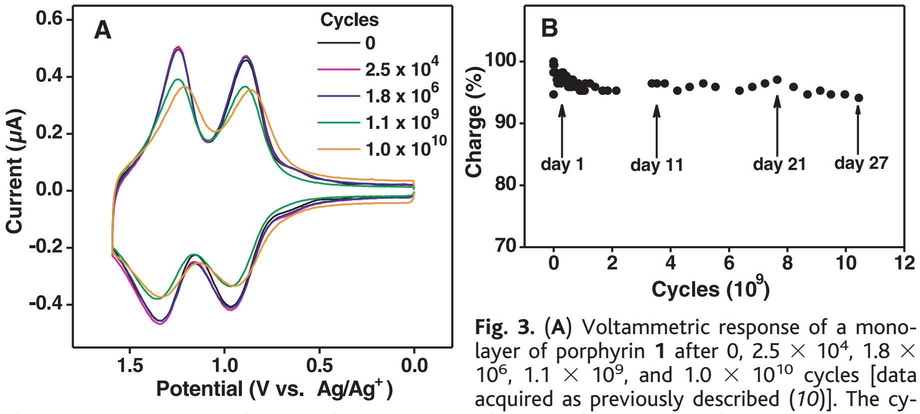

Fig. 3. (**A**) Voltammetric response of a monolayer of porphyrin **1** after 0, 2.5 × 10^4, 1.8 × 10^6, 1.1 × 10^9, and 1.0 × 10^{10} cycles [data acquired as previously described (*10*)]. The cycling process was carried out under inert atmosphere conditions via application of a 100-μs square-wave pulse of amplitude 1.2 V. (**B**) Plot of the integrated voltammetric signal (corresponding to the charge in the monolayer) as a function of the number of cycles.

The observation that the Si-O linkage of the porphyrin monolayers remains intact at high temperature is consistent with the very strong nature of this bond (~108 kcal mol^{-1}) (*13*). The high-temperature stability of the porphyrin molecules appears to be a generic feature of the porphyrin macrocycle. Indeed, similar high-temperature stability has been observed for a variety of porphyrinic architectures tethered to silicon, including the triple-decker **2**. Although the observation of high-temperature stability of porphyrins tethered to silicon is surprising, porphyrinic macrocycles function in a variety of extreme biological environments and also withstand prolonged extremes of temperature and pressure in sedimentary deposits (*14*).

The robustness of the porphyrin information-storage medium was further examined by repeatedly performing the cycle of (i) oxidizing the electrically neutral monolayer and (ii) reducing the resulting positively charged monolayer to its electrically neutral state. The oxidation event is equivalent to writing a bit of information; the reduction event is equivalent to erasing or destructively reading out the information. The five CVs in Fig. 3A 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. In this experiment, the pulse duration was 100 μs, which is much longer than necessary to fully write or erase the information (*10*). The long pulse duration further tests the endurance of the porphyrin information-storage medium.

During the experiment, the nature of the electrical cycling was varied. On some days, the system was continuously cycled for 24 hours. On others, cycling was stopped intentionally for periods ranging from a few minutes up to 12 hours. At one point, cycling was stopped unintentionally because of an electrical power failure. The data indicate that after an initial "burn-in" period of ~10^7 cycles the voltammetric response stabilizes. This robustness of the system is further illustrated in Fig. 3B, 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 characteristics of the monolayer exhibit minimal variation (a few percent) during the course of the entire experiment. At the time cycling was arbitrarily stopped (>10^{10} cycles; ~27 days), the system showed no signs of degradation. Essentially the same results were obtained in a second series of experiments in which the pulse duration was shortened to 2.5 μs and the system was cycled ~10^{12} times over the course of 60 days. The robustness of the porphyrins to oxidative cycling is attributed to the delocalization of the positive charge on the molecules over a number of carbon and nitrogen atoms in the macrocycle (*15*), which minimizes the number of "hot spots" and diminishes susceptibility to attack from adventitious chemical agents.

Collectively, the thermal stability and read-write cycling data indicate that the porphyrin-based information-storage medium is extremely robust. This stability indicates that these constructs can be readily adapted to current semiconductor fabrication technology and operated under the conditions required for a practical device. These characteristics augur well for the use of selected porphyrin molecules in hybrid molecular-semiconductor electronic devices.

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6. The fastest dynamic random access memories (DRAMs) can be randomly cycled about once every 20 ns. This time is a "row cycle time" that senses a full row of DRAM cells. A full row can be anywhere from 2000 K to 64,000 K cells, depending on the device. In a computer with 10^9 memory cells, it would take $\sim$300 μs to read the entire memory (provided that 64 K cells could be read in each 20-ns cycle). Therefore, in the 10-year lifetime that is expected of modern memory (*4*), the entire memory could be subjected to as many as 10^{12} cycles. In contrast, if a memory cell could endure only 10^6 cycles, every one of the 10^9 memory cells would fail in the first 10 min of operation.
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12. Deep-trench capacitors in DRAM cells typically hold $\sim$40 fF at 1.5 V (*16*). The leakage rates of these capacitors requires that the cell be refreshed at least every 100 ms. As device sizes decrease further, the leakage rates will increase, thereby increasing the required refresh rate. Unless longer charge-retention times can be achieved in semiconductor-based devices, the refresh characteristics of the device will impose limits on the ultimate feature size. These limits may well be encountered before the device is limited by the failure of the bulk properties of semiconductors that are expected when feature sizes reach tens of nanometers (*2*, *3*). In contrast, the charge-retention characteristics of porphyrins are an intrinsic molecular property. Hence, the charge-retention time is independent of the size of the memory cell, even for cell dimensions of tens of nanometers, where each cell would contain an ensemble of many hundreds of electrically noninteracting porphyrins (*9*).
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Structure-Based Carbon Nanotube Sorting by Sequence-Dependent DNA Assembly

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Wrapping of carbon nanotubes (CNTs) by single-stranded DNA (ssDNA) was found to be sequence-dependent. A systematic search of the ssDNA library selected a sequence d(GT)n, n = 10 to 45 that self-assembles into a helical structure around individual nanotubes in such a way that the electrostatics of the DNA-CNT hybrid depends on tube diameter and electronic properties, enabling nanotube separation by anion exchange chromatography. Optical absorption and Raman spectroscopy show that early fractions are enriched in the smaller diameter and metallic tubes, whereas late fractions are enriched in the larger diameter and semiconducting tubes.

CNT separation is an enabling step for many potential applications and fundamental studies that require defined nanotube structures and properties (*1–5*). CNTs can be classified into two categories on the basis of their electronic structures: metallic and semiconducting tubes. The latter can be further classified by tube diameters, because the band gap of a semiconducting tube, a critical parameter that needs to be controlled for nanoelectronic applications, is inversely proportional to its diameter. Reports in the literature indicate that it is possible to separate metallic from semiconducting tubes by taking advantage of differences in their physical or chemical properties (*6–8*). Diameter-based separation is more difficult, because differences in the physical and/or chemical properties caused by diameter changes are smaller and because variations in tube length could be a dominant factor in physical-based separation methods (*9–11*). Here, we report our discovery of an oligonucleotide sequence that self-assembles into a highly ordered structure on CNTs, allowing not only markedly improved metal from semiconducting tube separation but also diameter-dependent separation.

We have previously reported that single-stranded DNA (ssDNA) interacts strongly with CNTs to form a stable DNA-CNT hybrid that effectively disperses CNTs in aqueous solution (*6*). One important issue not addressed previously is whether or not DNA wrapping on a CNT is dependent on the specific sequence of the DNA strand. Here, we found that anion exchange chromatography provides a macroscopic means to assay for electrostatic properties of nanoscale DNA-CNT hybrids. More specifically, we found that the outcome of anion exchange–based DNA-CNT separation, as measured by optical absorption spectral changes from fraction to fraction, is strongly dependent on the DNA sequence. To explore this dependence, we conducted a systematic but limited search of the huge ssDNA library under identical chromatographic conditions. The CNT dispersion procedure is a slight modification of that reported before (*6*). We found that sonication (i.e., disruption with sonic waves) effectively cuts CNTs in the presence of DNA and that short CNTs increase sample recovery from an anion exchange column. In a typical dispersion experiment, a DNA-CNT mixture was kept in an ice-water bath and sonicated (Sonics, VC130 PB, Newton, CT) for 120 min at a power level of 8 W. The average length of CNTs after this level of sonication is $\sim$140 nm, as measured by atomic force micoscopy (AFM). CNTs were "as produced HiPco (high pressure CO)" type from Carbon Nanotechnologies Inc. (Houston, TX), and DNAs were custom-made by Integrated DNA technologies, Inc. (Coralville, IA). We tested simple homopolymers of dA (deoxyadenylate), dC (deoxycytidylate), and dT (deoxythymidylate), as well as sub-libraries composed of totally random combinations of two of the four nucleotides [dG (deoxyguanylate), dA, dT, dC]: poly d(A/C), poly d(A/G), poly d(A/T), poly d(C/T), poly d(C/G), and poly d(G/T). Among these, poly d(G/T) and poly d(G/C) showed the largest variation in the optical absorption spectra from fraction to fraction. To narrow down the choice

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