A Red-Shifted Chlorophyll
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using a resistive heater, with the devices packaged in ceramic dips. Field applications would make use of a vacuum package, which also prevents surface oxidation and additionally eliminates viscous drag forces during switch operation.

Inverter operation has been demonstrated at 500°C (Fig. 4) with V_{DD} = 6 V and V_{SS} = –6 V, at an operating speed of 500 kHz. The logic level is clearly higher than the existing Si logic devices, which operate at 3 V or lower. However, the threshold voltage of the fabricated switches is compatible to other competing high-temperature electronics (*3*, *4*). The logic level can be further reduced by narrowing the actuation gap (*21*) as the nanofabrication technology advances. NEMS switches based on carbon nanotubes exhibiting a threshold voltage smaller than 4 V have been demonstrated with gaps smaller than 100 nm (*22*, *23*). In theory, the actuation voltage of the NEMS switches can be scaled beyond the threshold voltage of CMOS, whose scaling is limited by the thermal voltage k_BT/q (here, k_B is the Boltzmann constant, T is temperature, and q is the charge of an electron). The active area of the demonstrated inverter consisting of two complementary NEMS switches is ~8 μm^2, excluding connecting traces and contact pads. Compared to modern (90-nm gate length) nanoscale Si CMOS logic devices, which have a standard-cell inverter gate with a minimum active area of ~0.1 μm^2 (*24*), the presented device is much larger. However, this demonstrated inverter is already about three orders of magnitude smaller than most reported high–temperature, JFET-based logic gates, which have gate lengths ranging from tens to few hundreds of microns (*3*, *4*). With improvement in nanolithography, it appears very plausible to scale the dimensions of the NEMS switches to achieve higher integration density, along with lower operating voltage and higher switching speed.

Typical switches have operated ≥21 billion cycles at 25°C and ≥2 billion cycles at 500°C; the measured leakage current at the OFF state is less than 10 fA (below the noise floor of the measuring tool). Failure at 25°C is breakage of the switching cantilever beam at the location of highest stress, characterized by a clean fracture. However, at 500°C, the broken cantilever beam has a ball of SiC at one side of the fracture gap that is likely to be local melting—an unexpected event because SiC sublimates at 1800°C. Thus, the mechanism for the high-temperature failure is not yet understood. Overall, this achievement of a SiC NEMS-based inverter operating at 500°C creates a pathway toward energy-efficient high-temperature computation.

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Supporting Online Material

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A Red-Shifted Chlorophyll

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Chlorophylls are essential for light-harvesting and energy transduction in photosynthesis. Four chemically distinct varieties have been known for the past 60 years. Here we report isolation of a fifth, which we designate chlorophyll f. Its in vitro absorption (706 nanometers) and fluorescence (722 nanometers) maxima are red-shifted compared to all other chlorophylls from oxygenic phototrophs. On the basis of the optical, mass, and nuclear magnetic resonance spectra, we propose that chlorophyll f is [2-formyl]-chlorophyll a ($C_{55}H_{70}O_6N_4Mg$). This finding suggests that oxygenic photosynthesis can be extended further into the infrared region and may open associated bioenergy applications.

Chlorophylls (Chls) are the essential pigments of photosynthesis, for which they both harvest light and transduce it into chemical energy. There are four chemically distinct chlorophylls known to date in oxygenic photosynthetic organisms, termed Chls a, b, c, and d in the order of their discovery (*1*, *2*). All four pigments are present in light-harvesting complexes, though until recently only Chl a was thought to be indispensable for energy transduction in the photosystem reaction centers (*3*). This paradigm was challenged when Chl d, long considered an artifact since its discovery in 1943 (*4*), was shown to constitute up to 99% of all Chl in the cyanobacterium *Acaryochloris marina* (*5*). In this and related organisms, Chl d can replace Chl a in the photosystems of oxygenic photosynthesis, thereby extending to the red the spectrum of light that can be harvested for carbon fixation (*6*). Here we report yet another chlorophyll, which we designate Chl f (*2*), that absorbs even further to the red.

The morphological features of stromatolites provide a unique environment for specific but diverse cyanobacterial communities (*7*). We cultured a sample from Hamelin pool under near-infrared light (720 nm) (*8*). Analysis of a methanolic extract of stromatolites from Shark Bay, Western Australia, by high-performance liquid chromatography (HPLC) revealed a complex mixture of chlorophylls (Fig. 1A): In addition to a detectable amount of Chl a (peak 3) and bacteriochlorophyll a (peak B), there were trace amounts of Chl d and a new pigment, Chl f (peak 2 in Fig. 1A). The optical absorption spectrum of Chl f in neat methanol has a red-shifted Q_Y transition [wavelength of maximum absorption (λ_{max}) = 706 nm] compared to other chlorophylls and a blue-shifted Soret band (λ_{max} = 406 nm) (Fig. 1, B and D). The room-temperature fluorescence emission of isolated Chl f is maximal at 722 nm (with excitation wavelength of 407 nm) (Fig. 1D), which is also considerably red-shifted compared to other Chls (*9*). Chlorophyll f appears to be made by a filamentous cyanobacterium (fig. S3) based on the 16*S* ribosomal RNA (rRNA) sequence of our purest enrichment III culture (see supporting text), which contained only Chl a and Chl f by HPLC analysis.

We assigned the molecular formula of Chl f ($C_{55}H_{70}O_6N_4Mg$) by mass spectral analysis based on the molecular ion at 906 *m/z* (mass/charge ratio). Phytol ($C_{20}H_{38}$) was identified by the prominent fragment at 628 *m/z* (fig. S1B), and Mg as the central metal by the molecular ion of the pheophytin (Pheo) (884 *m/z*, $C_{55}H_{72}O_6N_4$). A

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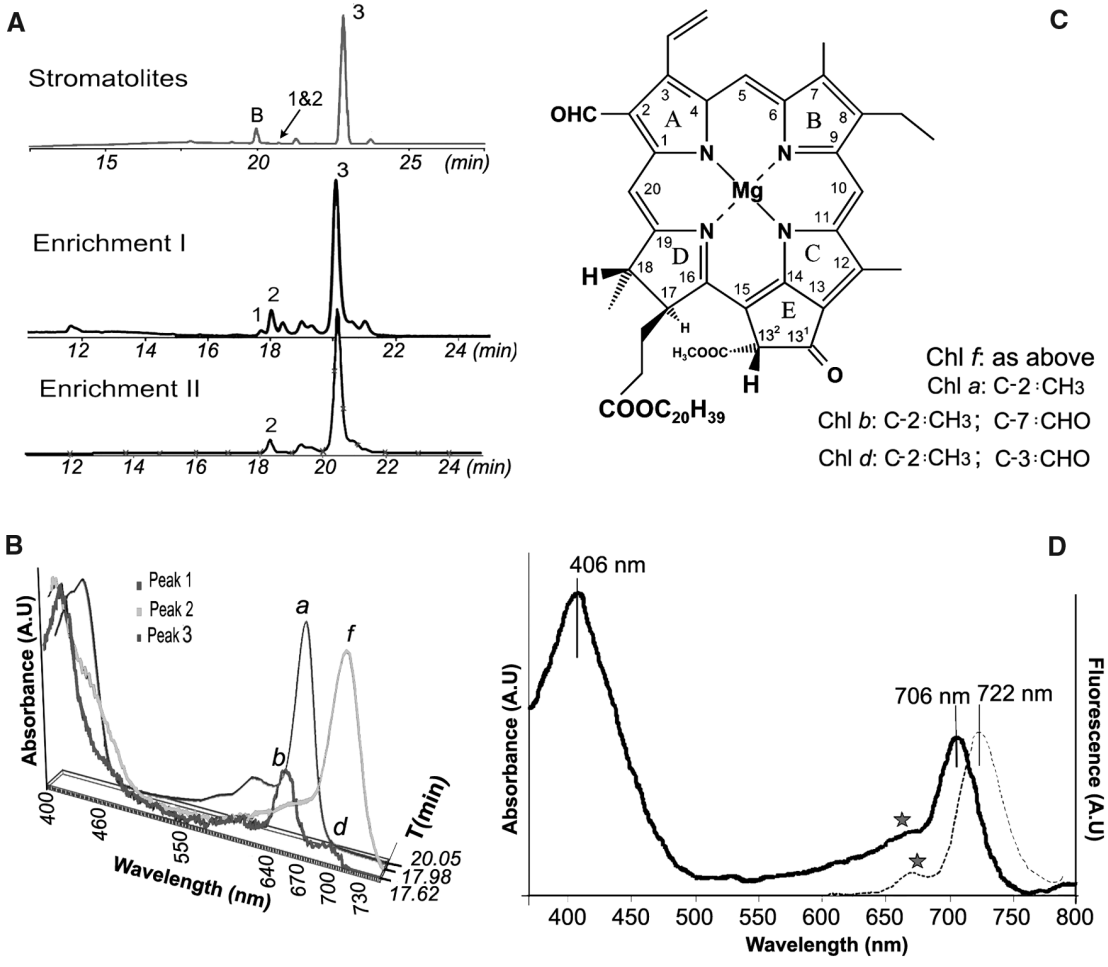

Fig. 1. (**A**) HPLC traces detected on the basis of Q_Y absorbance (600 to 750 nm) of methanolic extracts from the stromatolite sample and from aerobic enrichment cultures I and II (see supporting material). Differences in retention times between the top and the two lower traces are due to different chromatographic solvent systems (CH_3CN·CH_3OH to CH_3OH gradient above, CH_3OH·H_2O to CH_3OH gradient below). (**B**) Spectral comparison of HPLC peaks of interest from enrichment culture I: peak 1 (retention time t_r = 17.62 min) contains Chl b and Chl d, peak 2 (t_r = 17.98 min) mainly Chl f characterized by its red-shifted Qy absorption band (706 nm), and peak 3 (t_r = 20.05 min) Chl a. (**C**) Chemical structure of Chl f with comparison to other chlorophylls. (**D**) Absorbance and fluorescence emission spectra (λ_{exc} = 407 nm) of purified Chl f in methanol at room temperature. Contributions from a Chl a–like contaminant are indicated by stars.

formyl group was identified by ^{1}H nuclear magnetic resonance (NMR) spectroscopy of Chl f [δ = 11.35 ppm (parts per million)] (fig. S2); the red-shifted Q_Y optical transition (Fig. 1D) suggested substitution on rings A or C (Fig. 1C). The transformation of a methyl to a formyl moiety is a known modification of Chl a, producing Chl b (*10*). Because Chl d has a formyl group at C-3 (*3*), and differs in its properties, this leaves C-2 and C-12 as potential sites that comply with the mass spectrum. Substitution at C-2 is implicated by the methine pattern of the NMR spectrum (fig. S2): No methine resonates at δ > 10 ppm, which would be the expected chemical shift for the 10-H in the event of a neighboring 12-CHO group (*11*); moreover, the clustering of the C-5, C-10, and C-20 methine resonances at 9.86, 9.79, and 9.77 ppm is expected for C-2 substitution based on the known spectra of Chls a, b, and d and spectra simulated by density functional theory (DFT) (table S1). Substitution at C-2 is also supported by DFT calculations of the optical spectra, which predict a large red-shift of the Q_Y band relative to Chl a for a 2-CHO group (Δλ = 37.6 nm), and, surprisingly, a blue-shift for a 12-CHO group (Δλ = −6.5 nm) (table S2). Therefore, we propose that Chl f is [2-formyl]-Chl a (Fig. 1C). Isolation of cultivable pure strains bearing Chl f will be essential to define the function of this intriguing chromophore.

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