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Toward Volatile and Nonvolatile Molecular Memories: Fluorescence Switching Based on Fluoride-Triggered Interconversion of Simple Porphyrin Derivatives

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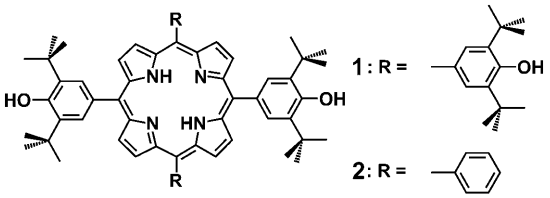
Molecular species are promising candidates for incorporation into electronic or optical devices because of their synthetic flexibility, processability and small size.[1] During prototyping of suitable molecules, it is likely that new methods for information storage and processing will be discovered. Previously, molecular solid-state and solution-based analogues of traditional solid-state electronic processes have been presented,[2,3] some involving tetrapyrrolic molecules,[4] and those works have illustrated the scope of using discrete molecular species in a variety of states. Solution-based switching presents a novel concept for information processing, and it could be combined with other solution-state technologies, such as nanofluidics or ink-jet fabrication. Solution-based technologies should also facilitate interface with biochemical systems.

The initial challenge in preparing an information processing system is to develop molecular memory and logic functions.[2] Data might be stored in binary form, based on changes in optical or electronic properties, and toggled using an external stimulus, such as light, temperature, chemical concentration, voltage or a magnetic field. Changes in optical absorbance and/or fluorescence can be detected as photonic output(s) and these may contain more information than simple electronic outputs. Thus, the switching of photonic output from dye molecules is an ideal prototype for solution-based memory. In this work, we have developed both volatile- and nonvolatile-type memory elements due to fluorescence switching and based on subtle structural modifications of dye molecules. These memory elements are operated primarily by using fluoride anions as specific writing components. The use of fluoride anions is notable because complementary anion-related molecular devices, including logic gates,[5] shuttles[6] and allosteric switches,[7] are already available, so that combination with these systems might be possible in the pursuit of increasing complexity.

Our study uses the simple porphyrin derivatives **1** and **2** shown in Scheme 1. Derivatives **1** and **2** possess four and two redox-active 3,5-di-*tert*-butyl-4-hydroxyphenyl groups,



Scheme 1. Structures of porphyrin derivatives **1** and **2** for volatile and nonvolatile memory systems.

respectively, substituted at their *meso* positions and each compound is stable in neutral solution. They exhibit optical properties typical of porphyrin derivatives, including intense fluorescence of their solutions.[8] Structural variation at the *meso* substituents of these porphyrin derivatives permits access to quite different memory cycles for **1** and **2**, which could be repeated as shown in Figure 1. Addition of a large excess of tetra-*n*-butylammonium fluoride (F^-), which is required for fast reaction (see below), to a solution of **2** in CH_2Cl_2 (10^{-5} M; Figure 1B, a) results in a nonfluorescent solution (Figure 1B, b). Subsequent removal of F^- by washing with water reinstates its fluorescence (Figure 1B, c). This volatile behaviour is typical of anion-responsive molecular switches,[9] since toggling from OFF to ON states is usually due to hydrogen bonding of anions, thus requiring their constant presence at ON. In the case of **1**, emission quenching by the addition of F^- is also observed under similar conditions (Figure 1A, a and b), but the non-emissive state is re-

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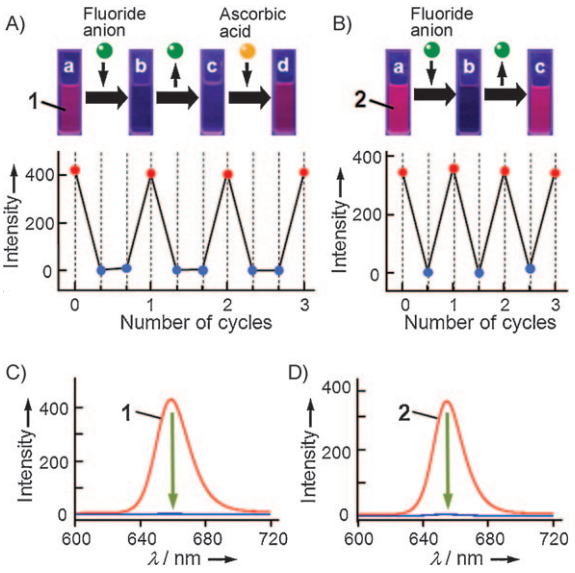


Figure 1. Repeated memory cycles using **1** (A) and **2** (B), in which each state was detected by its emission intensity (659 nm for **1**; 655 nm for **2**) obtained from 10^{-6} M solutions of **1** and **2** in CH_2Cl_2 excited at the wavelength of the Soret band (426 nm for **1**; 423 nm for **2**). Photographs showed each 10^{-5} M solution of **1** and **2** under a UV lamp at 365 nm. Fluorescence emission spectral changes upon addition of F^- into 10^{-6} M solutions of **1** (C) and **2** (D) in CH_2Cl_2.

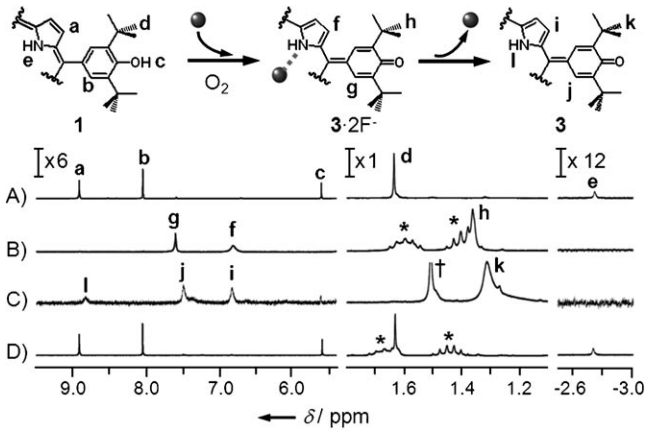
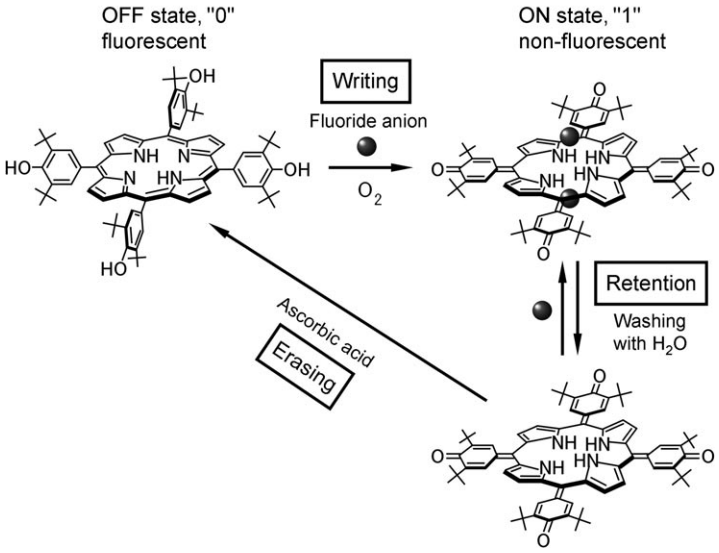


Figure 2. ^{1}H NMR spectra (in CD_2Cl_2) of A) **1** , B) **1** in the presence of F^- (9.2 equiv), C) **3** obtained by removal of F^- from the solution containing **1** and F^- and D) **1** in the presence of Cl^- (13.2 equiv). The peaks marked with * and † represent those due to H_2O and $-CH_2-$ in tetra-*n*-butylammonium salts, respectively.

tained even after removal of F^- (Figure 1 A, c). In our initial experiments, the subsequent dispersion of an excess of ascorbic acid in that solution followed by filtration caused return to the initial fluorescent state (Figure 1 A, d). This nonvolatile behaviour of **1** cannot be explained by a simple noncovalent interaction with F^-.

To investigate the origin of the nonvolatile behaviour of **1**, ^{1}H NMR, FTIR, UV/Vis spectroscopies were carried out at each step. Addition of 9.2 equiv of F^- to a CD_2Cl_2 solution of **1** (~1.4 mM) resulted in new resonances at 7.60, 6.82 and 1.36 ppm with disappearance of the resonances due to **1** in the ^{1}H NMR spectrum (Figure 2 B). Monitoring of this spectral change (23 °C) revealed a gradual increase in intensity of these new peaks with a concurrent decrease of those due to **1**. Upon removal of F^-, these peaks shifted upfield and a new peak appeared at $\delta = 8.83$ ppm (Figure 2 C). The resulting spectrum is identical to that of **3**,[10] obtained according to another method,[11] which indicates that porphyrin **1** has been oxidised to the oxoporphyrinogen **3**. The F^--induced aerobic oxidative conversion from **1** to **3** was confirmed by FTIR and UV/Vis spectroscopies (the C=O vibrational absorption is replaced by one OH in the FTIR spectrum, the UV/Vis spectrum is identical to that of **3**; see the Supporting Information). ^{1}H NMR spectral changes observed by removal of F^- are due to dissociation of the **3**·2F^- complex[12] because complementary spectral changes were observed by the addition of F^- to a solution of **3** in CD_2Cl_2 (see the Supporting Information). Subsequently, a reducing reagent, such as ascorbic acid or stannous chloride, reduced **3** to **1**. Addition of ascorbic acid (10 equiv) to a 10^{-5} M solution of **3** in CH_2Cl_2 restores the UV/Vis spectrum of **1**, indicating that no serious changes to the tetrapyrrole framework occur. During the reduction of **3** to **1** in CH_2Cl_2/methanol (c.a. 30:1 v/v)[13] at room temperature there is a gradual increase in the Soret band intensity (426 nm) with a concurrent decrease in intensity of the absorbance bands due to **3** (351 and 518 nm), showing isosbestic points (see the Supporting Information). Regression analysis of the plots of time dependency of the absorbance at 426 nm provide a correlation coefficient of $r > 0.999$, and the conversion rate and half-life were calculated to be 5.6×10^{-2} min^{-1} and 12.3 min, respectively. To summarise, the nonvolatile memory system based on **1** is achieved as follows (Scheme 2): 1) fluoride anions induce the oxidative conversion from **1** to **3** with subsequent complexation of **3** with F^- (writing), 2) then, removal of F^- does not cause any change in the structure of **3**, although a dissociation of the complex between **3** and F^-



Scheme 2. The writing–retention–erasing cycle of **1**.

occurs (retention) and 3) **3** is reduced to **1** by using ascorbic acid (erasing).

It should be noted that oxidation from **1** to **3** does not occur in the presence of less basic anions. Additions of Cl^-, Br^-, I^-, NO_3^-, BF_4^- or PF_6^- to solutions of **1** in CH_2Cl_2 result in no significant changes in optical absorbance or fluorescence (see the Supporting Information). ^{1}H NMR spectra of a solution containing **1** and excess Cl^- in CD_2Cl_2 also showed no variation in chemical shifts of peaks assigned to **1** (Figure 2D). These results indicate that Lewis basicity of anions is important for the oxidation of **1**. ^{1}H NMR spectroscopic monitoring of the oxidation of **1** by using different quantities of F^- clearly indicates that the rate of conversion from **1** to **3**·2F^- depends on F^- concentration and we observed that oxidation only reaches completion following addition of at least four equivalents of F^-, that is, only if phenolic groups of **1** are fully deprotonated. Importantly, the phenolic OH peak disappears rapidly during the initial stages of reaction (see the Supporting Information), suggesting that deprotonation of the phenolic groups of **1** by F^- triggers its oxidation. Thus, we routinely used quantities of fluoride anions in excess of four equivalents to ensure eventual oxidation of **1**. Also, oxidation of **1** in the presence of five equivalents of F^- was complete within 20 min under a dioxygen atmosphere, whereas complete oxidation took more than 3 h under a lower dioxygen concentration (see the Supporting Information). This strongly suggests that ambient dioxygen is responsible for oxidation of deprotonated **1**, and this aspect of **1** has been investigated previously.[14] In fact, oxidation of **1** in the presence of strong bases, such as hydroxide anions, has been observed. However, fluoride anions might be more useful in combination with complementary anion-related molecular devices.

When excess F^- was added to a solution of **2** in CH_2Cl_2, the solution colour changed from pale yellow to pale red (Figure 3B). This differs from the case for **1** in which pale yellow turns to deep blue[12] (Figure 3A). The UV/Vis spectrum for the solution of **2** in the presence of excess F^- contains a split Soret band (413 and 503 nm) of decreased intensity straddling the original Soret band position (419 nm), and a broad absorption band centred around 777 nm, which is characteristic of porphyrins with deprotonated phenolic groups as *meso* substituents. ^{1}H NMR spectroscopy also indicates deprotonation of phenolic groups in **2** by F^-: Addition of F^- (11 equiv) to a solution of **2** in CD_2Cl_2 resulted in upfield shifts of the β-pyrrolic and phenol group *meta*-proton peaks, and to the disappearance of the phenolic OH peak (see the Supporting Information). Cyclic voltammograms of **1** and **2** recorded in *o*-dichlorobenzene (with 0.1 M Bu_4NClO_4) contained two irreversible oxidation peaks.[15] Differential pulse voltammetry revealed that oxidation peaks of **2** are located at more positive potentials than those of **1** ($\Delta E_{1/2} = E_{1/2(\mathbf{2})} - E_{1/2(\mathbf{1})} = 0.04$ and 0.12 V for the first and second oxidations, respectively; see Supporting Information), indicating that **2** is relatively electron deficient and consequently more difficult to oxidise. Therefore, the differing memory behaviours of **1** and **2** can be explained as follows: the phenolic *meso* substituents of both **1** and **2** are deprotonated by fluoride anions, but only deprotonated **1** can be transformed to stable porphyrinogen **3** because the deprotonated form of **1** is susceptible to oxidation by ambient dioxygen, whereas that of **2** is not.

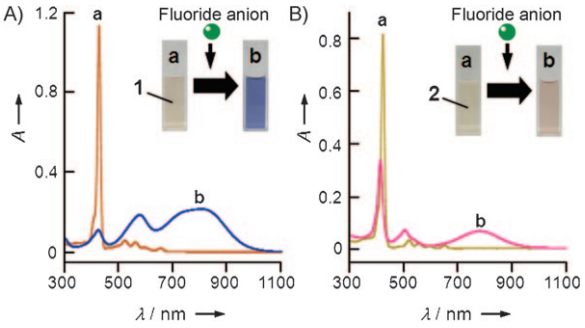


Figure 3. Changes in electronic absorption spectra upon addition of F^- to 10^{-5} M solutions of **1** (A) and **2** (B) in CH_2Cl_2.

An initial step towards fabricating a memory device involved using an organogelator, L-glutamide-derived lipid,[16] as an addressable matrix. Figure 4 shows a photograph of **1**-containing organic gel, in which "F" is written by using a solution of fluoride anions. OFF and ON states can be clearly detected because of their differing emission intensities. This illustrates the possibility that combination with an appropriate medium leads to a multi-bit memory device.

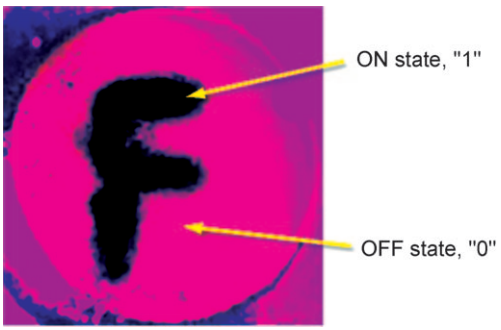


Figure 4. Photograph (under UV lamp at 365 nm) of **1**-containing organic gel, in which "F" was written by the solution of F^-. The organogelator and **1** were dissolved in a mixture of C_6H_6 and CH_2Cl_2 (4:1) at 40 °C and then cooled to room temperature to form a gel in the bottom of a vial with a diameter of 2 cm. "F" was written by using a microsyringe.

In conclusion, we have demonstrated fluoride-writable memory systems using simple porphyrin derivatives based on the relative oxidisability of these porphyrins in the presence of fluoride anions. Subtle structural modification at the porphyrin *meso* substituents enabled us to achieve both volatile and nonvolatile modes. In both cases, OFF and ON states exhibited large differences in fluorescence emission intensity (Figure 1C and D), which has great potential as a read-out signal for memory systems.

Experimental Section

Synthesis of 1 and 2: Porphyrin **1** was prepared by the condensation of pyrrole with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in propionic acid at reflux as previously reported.[12] Porphyrin **2** was prepared by a similar method by using a mixture of the appropriate benzaldehydes. Thus, pyrrole (6.7 g, 0.1 mol) was added to a mixture of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (11.7 g, 0.05 mol) and benzaldehyde (5.3 g, 0.05 mol) in propionic acid (500 mL) at reflux. Heating at reflux was continued for three hours. Subsequently, the reaction mixture was reduced to half its volume by distillation and allowed to cool. Methanol (300 mL) was added to the mixture and it was allowed to stand until a purple precipitate had formed (~2 days). The precipitate was filtered, washed with methanol and subjected to gel permeation chromatography (BioBeads SX-1) eluting with dichloromethane. Since only the least soluble porphyrins (i.e., *meso*-tetraphenylporphyrin, 5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10,15,20-triphenylporphyrin, and **2**) had precipitated from the reaction mixture upon addition of methanol, isolation of **2** was simplified and it was collected as the first band eluting from the GPC column. Fractions containing only **2** were combined, the solvent was evaporated and the solid was recrystallised from dichloromethane/methanol to give **2** as a purple microcrystalline solid (245 mg, 1.1%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 20°C): $\delta = 8.94$ (4H, d; pyrrolic β-H), 8.84 (4H, d; pyrrolic β-H), 8.24 (4H, m; phenyl-H), 8.06 (4H, s; hydroxyphenyl substituent Ar-H), 7.78 (6H, m; phenyl-H), 5.61 ppm (2H, s; phenol-O*H*), 1.64 (36H, s; *tert*-butyl-H); MALDI-TOF-MS (dithranol): *m*/*z*: 871.8 $[M+H]^+$. The isomeric identity of the compound was confirmed by observing the splitting pattern of the pyrrolic protons (see Figure S1 in the Supporting Information).

Memory cycling: Memory cycling of **1** and **2** was carried out as follows: 1) a 10^{-5} M solution of **1** in dichloromethane was prepared from a 5×10^{-4} M stock solution. 2) A large excess of tetra-*n*-butylammonium fluoride (>100 equiv) was added to that solution (*Writing*). 3) The solution obtained was washed with water until its colour was constant. The solution was evaporated then diluted to its initial concentration (*Retention*). 4) L-Ascorbic acid was dispersed in the solution (20 mg mL^{-1}) and stirred at room temperature for several days. Residual L-ascorbic acid was removed by syringe filtration (pore diameter: 0.2 μm) (*Erasing*). In the case of **2** only procedures 1) to 3) were applied. UV/Vis spectra of the solutions of **1** and **2** obtained after each procedure were measured in a 2.0 mm path length quartz cell. Fluorescence spectra for each solution after dilution (to $c = 10^{-6}$ M) were also measured in a 10 mm path length quartz cell. For all measurements excitation wavelengths were 426 nm for **1** and 423 nm for **2**. The intensity changes of the emission (659 nm for **1**; 655 nm for **2**) were monitored during repeated memory cycles.

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Keywords: fluoride · molecular devices · oxoporphyrinogen · porphyrinoids · switching

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