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COMMUNICATION

Ternary Memory Module Using Low-Voltage Control over Optical Properties of Metal-Polypyridyl Monolayers†

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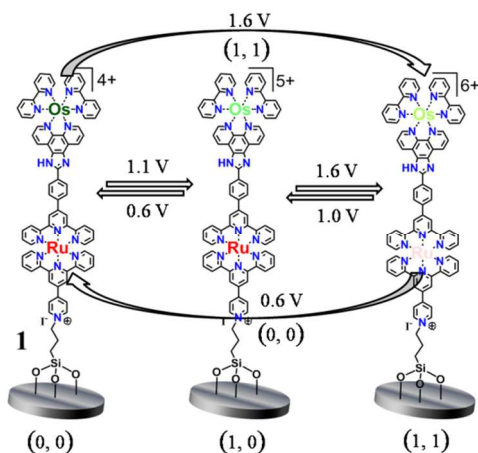
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Accepted 00th January 2014Anup Kumar^a, Megha Chhatwal^a, Prakash Chandra Mondal^a, Vikram Singh^a, Alok Kumar Singh^a, Domenico A. Cristaldi^b, Rinkoo D. Gupta^{c*} and Antonino Gulino^{b*}

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Ternary memory module has been designed as a function of precise voltage command. The monolayer based module displays perpetual stability and non-hysteretic reversibility for multiple scans (10^2). Ternary-state readout provides a vision to integrate next generation of “smart electro-optical devices” viable for multi-state memory.

Smart surfaces¹ find potential impetus for advanced memory storage/processing² via commutable redox-states. In this context, distinct redox-states are highly recommended for realization of multi-memory enabled molecular devices.³ Notably, the control over multi-redox states⁴ potentially ensures rapid information storage/transfer for molecular-memory. In this aspect, spectro-electrochemical control over a hetero-redox-centred monolayer is highly imperative and rarely exploited thus far.⁵ Herein, we assessed the electro-optical tuning of the especially designed hetero-bimetallic complex based monolayer (**1**) comprising two redox-active data saving bits (Ru^{2+} and Os^{2+}) and a conductive imidazole aromatic spine (scheme 1).



Scheme 1: Representation of electro-optical tuning of **1-I-TO** monolayer under precise potential command.

The siloxane-based monolayers of **1** were fabricated on the Si(100)/ITO-coated glass substrate by adopting a previously reported method.⁶ The integrity of molecules on surface was verified with a combination of surface analysis techniques such as X-ray photo-electron spectroscopy (XPS), semicontact atomic force microscopy (AFM), optical transmission and electrochemistry. The surface morphology investigated by AFM revealed a homogeneous monolayer (Figure S1, left). The root mean square roughness of the monolayer was typically around 0.9 nm with a height distribution centred on 2.8 nm (Figure S1, right). The molecular characterization of the **1-Si(100)** monolayer was carried out by XPS.⁷

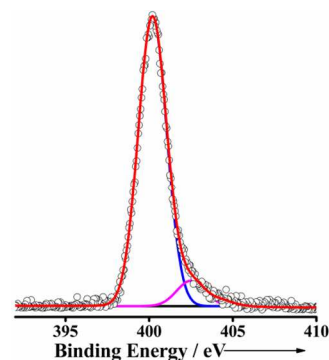


Figure 1. Monochromatized Al-K α excited XPS at 45° photoelectron take-off angle for **1-Si(100)** monolayer in the N 1s binding energy region. The experimental spectral data points (open circles) are fitted with two dominant Gaussians at 399.8 (red line) and 402.3 (magenta line) eV.

As a general observation, the atomic concentration analyses, performed at all the investigated photoelectron take-off angles, has shown that the substrate signals increase and the monolayer signals decrease on going from low (5°) to high (80°) angles. Moreover, atomic concentration analyses always indicated the Os 4f, Ru 3p and N 1s signals in the 1:1:15 intensity ratios, once

corrected for the relevant atomic sensitivity factors. Spectral fitting of the N 1s signal reveals the presence of two components in the 1:15 ratio (Figure 1). These two peaks lie at 399.8 and 402.3eV. As a consequence, the component at 399.8 is assigned as a whole to all polypyridyl nitrogens of **1**. The higher energy component is consistent with the quaternized nitrogen of a pyridine moiety.⁸ Figure S2 shows the Os 4f spin-orbit components at 51.0 and 53.8eV, consistent with the Os(II) oxidation state. In analogy, Ru 3p levels lying at 462.4 and 486.6eV are consistent with the presence of Ru(II) state (Figure S3).⁹

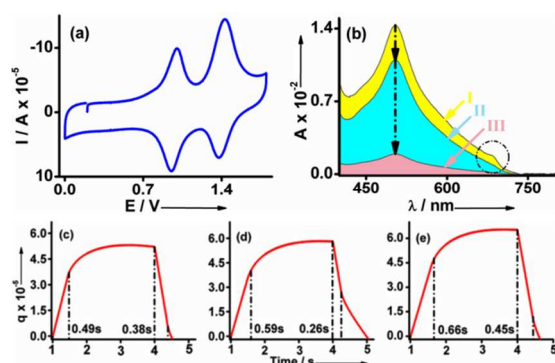


Figure 2: Cyclic voltammogram of the as-synthesized **1-ITO** monolayer at 1.0Vs^{-1} (vs. Ag/AgCl, 20mM $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$) (a), Spectro-electrochemical switching of **1-ITO** monolayer ($3.0 \times 0.8\text{cm}$) using triple-step potential 0.6, 1.1, and 1.6V (b), Chronocoulometry experiment at 0.6-1.1V (c), 1.0-1.6V (d) and 0.6-1.6V (e) for 3s.

The cyclic voltammogram of **1-ITO** monolayer showed two reversible redox waves at $E_{1/2} = 0.97$ and 1.38V attributed to $\text{Os}^{2+/3+}$ and $\text{Ru}^{2+/3+}$ redox couples respectively (Figure 2a).¹⁰ The redox waves have followed the characteristics of typical surface-confined molecules. The peak current densities (I_{pa} and I_{pc}) increase linearly with the scan rate (Figure S4).¹¹ Further, the peak separation (ΔE) of order $< 20\text{mV}$ was observed at lower scan rates followed by a gradual enhancement at higher scan rates due to iR -drop and/or the influence of heterogeneous electron-transfer kinetics on surface.¹² The operational stability of the **1-ITO** monolayer under the potential domain (0.0-1.8V) was judged by running the continuous read-write cycles (10^2) (Figure S5). Consequently, cyclic voltammogram displayed slight variation (*ca.* 8%) for initial conditioning scans, which could be assigned to deactivation/reordering of molecular components.⁶ Additionally, UV-vis and mass spectra of the electrolytic solution after 10^2 cycles revealed absence of any complex and implies the desired robustness of system against the imposed voltage domain. The UV-vis spectrum of the **1-ITO** monolayer showed characteristic singlet and triplet metal-to-ligand charge transfer bands ($^1\text{MLCT}$ and $^3\text{MLCT}$) centred at $\lambda_{max} = 503$ and 687nm respectively. These two bands revealed a bathochromic shift ($\Delta\lambda$) of 8 and 40 nm respectively, *w.r.t.* solution measurements due to the formation of pyridinium salt.¹³ The footprint (from UV-vis) / surface coverage (from CV), estimated as $\sim 90\text{-}110\text{ \AA}^2/\text{molecule}$, indicated a compact film, which is in agreement with

previous reports.¹⁴ Interestingly, the optical identity of **1** *i.e.*, singlet and triplet MLCT bands were tuned to exhibit three distinct absorbance states on varying the electrical input and thereby supporting the viability of **1** as multiple charge/information storage module. For instance, the $^1\text{MLCT}$ band ($\lambda_{max} = 503\text{nm}$) revealed a hypochromic shift (on/off ratio, 1.4:1 on ITO, 1.7:1 in solution) along with the vanishing of $^3\text{MLCT}$ ($\lambda_{max} = 687\text{nm}$) on applying a voltage-range of 0.6-1.1V (Figure 2b). This spectral perturbation can be assigned to the exclusive oxidation of Os^{2+} in **1**.^{1b} However, the observed low on/off ratio could be due to the substantial contribution of Ru^{2+} in $^1\text{MLCT}$ and to the considerable distance of Os^{2+} from ITO surface ($\sim 30\text{ \AA}$ estimated using the Chem3D Pro energy minimization model).^{4a} Further, on imposing the potential range of 1.0-1.6V, the absorbance of the $^1\text{MLCT}$ further reduced (on-off ratio 5:1), attributed to the oxidation of both (Ru^{2+} and Os^{2+}) redox-species in **1**.⁴ Notably, rapid response time was observed for this charge based bit-storage/ release (*i.e.*, 0.49s/0.38s for $\text{Os}^{2+/3+}$, 0.59s/0.26s for Os^{3+} and $\text{Ru}^{2+/3+}$) as depicted in Figures 2c, 2d respectively. Noticeably, the **1-ITO** monolayer can produce three-state absorbance changes *i.e.*, **I** (Absorbance threshold = 0.014, Os^{2+} and Ru^{2+}), **II** (Absorbance threshold = 0.010, Os^{3+} and Ru^{2+}) and **III** (Absorbance threshold = 0.002, Os^{3+} and Ru^{3+}) under the applied potential of 0.6, 1.1 and 1.6V respectively. Moreover, overall optical changes could be produced in a single-step by applying a wider potential range (0.6-1.6V) in $\sim 0.7\text{s}$ (Figure 2e). The spectral deviation was estimated as $\sim 6\text{-}10\%$ for three experiments using same set-up (Figure S6). The transduction of the voltage input into precise optical readout has been demonstrated in solution also (Figure S7, 8, 9).

Note that, the presence of three distinct optical states **I**, **II**, and **III** could be exploited for integration of interchangeable binary and ternary memory states as a function of applied voltage.^{2b, 15} To mimic the memory elements, oxidation and reduction under each redox wave can be considered as writing “1” and erasing “0” of data by assuming the principle of binary logic.¹⁶ Thus, binary memory states could be constructed by applying a broad potential range (0.6-1.6V), capable of writing/erasing the data at duo redox moieties at single command for processing of multibits (“00”-“11”) of same information. However, successive knocking at redox moieties *viz.* “00”, “10” and “11” might construct a commutable ternary memory state under variable voltages.^{2a}

Both reversibility and stability are important parameters for a device-quality monolayer. Thus, the **1-ITO** monolayer was amperometrically subjected to switching potentials (0.6, 1.1 and 1.6V, 3s) for repetitive cycles and the corresponding absorbance change at $\lambda_{max} = 503\text{nm}$ was monitored as function of time (Figure 3). A minimal signal loss (*ca.* 10%) was observed after attaining 100 cycles for all states *i.e.*, **I**, **II**, and **III** using the same monolayer, probably due to minor leaching of molecules from surface under the potential stress. However, significant signal loss ($\Delta A = \sim 45\%$) was observed on scanning at potentials $> 2.0\text{V}$ and $< 0.0\text{V}$. The redox states *i.e.*, **II** and **III** were stable under the nitrogen atmosphere for 5 min, whereas regained state **I** under air within 50 and 70s respectively, due to reduction by adventitious moisture under the

open circuit conditions.¹⁷ In addition, XPS after attaining 100 cycles revealed atomic concentration values close to those of the starting monolayer (within the experimental errors $\pm 5\%$).

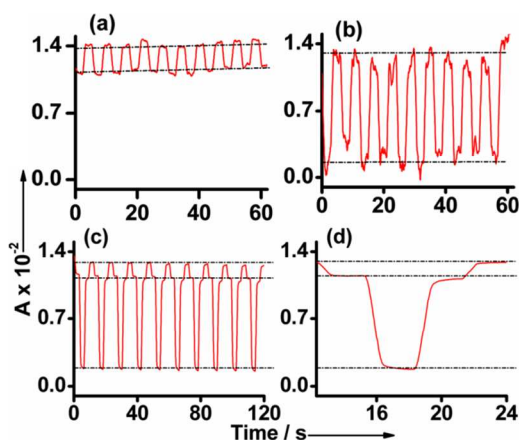


Figure 3: Chrono-absorptometry switching experiment at $\lambda = 503$ nm for Os^{2+} (a, 0.6-1.1V), Ru^{2+} and Os^{2+} (b, 0.6-1.6V), successive knocking at each metal centre (c, 0.6-1.1-1.6-1.0V) with magnified view of single cycle (d), for 3 min in 20mM TBAP in acetonitrile.

Further, most of the electronic devices suffer from the loss of functioning because of the mechanical heat released during prolonged-work schedules. Thus, stability and functioning at elevated temperature was judged by heating the module at 200°C for 50 h and also by stepping-up the temperature from 25 to 250°C in a programmable fashion with time interval of 1h. No significant UV-vis signal and switching magnitude loss was observed for the monolayer after the heat treatment (Figure S11). Hence, the module successfully displays the tendency to store and hold the data under/after mechanical heat.

Conclusions

In summary, the 1-ITO monolayer was exploited for ternary/binary data storage with non-destructive optical identity owing to its excellent stability and reversibility. The robustness of the system enabled it to overcome both potential stress and mechanical heat. The commutable binary and/or ternary state has demonstrated accurate control of voltage over optical threshold and can offer potential alternative to real devices such as DRAM, SRAM and FLASH memory. Indeed, intact functioning under long term potential stress and at elevated temperature is attractive for future electronics.

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Notes and references

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†A tribute to Late Dr. Tarkeshwar Gupta.

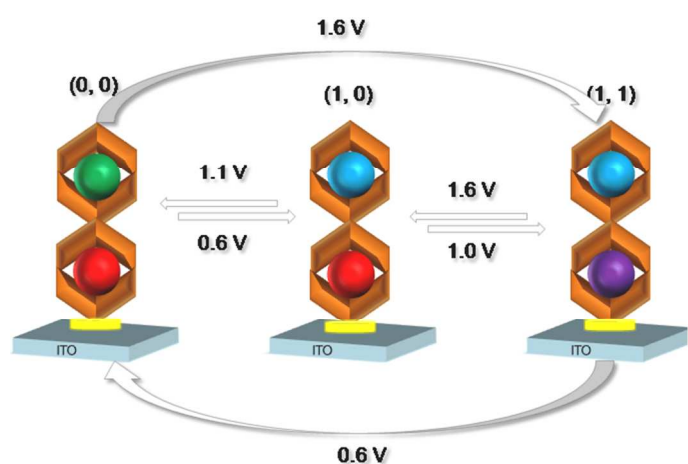
Electronic Supplementary Information (ESI) available: Experimental details, characterization, electrochromic result in solution. See DOI: 10.1039/b000000x/.

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Graphical Abstract

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Resettable ternary memory module is proposed *via* commutable redox states.