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Remanent polarization in a cryptand-polyanion bilayer implemented in an organic field effect transistor

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We investigate the possibility to maintain an electric polarization in an organic bilayer via ion trapping, i.e., without any external bias. In the cryptand-polyanion bilayer, ions of specific size can be strongly coordinated with organic macrocyclic molecules. Cations move from the polyanion layer to the cryptand layer upon applying a bias and are trapped in this layer. As a result, the voltage dependence of the polarization displays a hysteresis. The bilayer is then advantageously used as an electronic insulating layer in an organic field effect transistor. The ions trapping and de-trapping can be followed by the amplitude of the threshold voltage (V_{th}) shift as well as its temporal evolution. © 2012 American Institute of Physics. [doi:10.1063/1.3677663]

A main research direction in organic electronics comes from the opportunities to combine electrons and ions as charge carriers in electrochemically active conjugated materials. This is used advantageously to produce low operating voltage devices such as light emitting devices,¹ electrochromic displays,² and transistors.³ Organic electronics offers many possibilities beyond conventional electronics because chemists can implement functions in molecules and materials. Here we are interested in artificial macrocyclic molecules that have the ability to complex selectively metal ions with compatible dimensions. Cyclic polyethers, such as crown ethers, are ionophores and they have already been demonstrated for sensing specific ions in solid contact ion selective electrodes (SCISE).⁴ Crown ethers have been covalently attached to conjugated polymers, such as polythiophene.⁵ The optical properties of those functional polymers in solution change upon complexation with specific cations.⁶ Besides SCISEs, macrocyclic ionophores have not been used in combination with other organic materials to achieve electronic devices with new functions.

In this letter, we investigate the polarization of a bilayer composed of one layer of macrocyclic organic ligands, such as cryptands, and one layer of a polyanionic electrolyte. The complexation of the mobile cations with the macrocycle is expected to produce a remanent polarization in the bilayer. Further, we investigate the possibility to integrate this bilayer as a gate insulator in an electrolyte-gated organic field effect transistor (OFET) to achieve a shift of threshold voltage by applying low programming voltages.

In host-guest chemistry, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8] hexacosane (cryptand 2.2.2, Fig. 1) is known as a host molecule forming a stable complex with a guest potassium cation (K^+) (binding constant in water at 25 °C $\text{Log } K_a = 5.4$),⁷ because of the good matching between the size of the ions (diameter = 0.266 nm) and the diameter of the inner cavity of the macrocycle ($\varnothing = 0.26\text{--}0.32$ nm).⁸

Here, the cryptand molecules are blended in a poly(methyl methacrylate) (PMMA, Fig. 1) matrix to create

an ionic trapping layer (ITL) (thickness = ~ 25 nm). Various amounts of cryptand 2.2.2 are considered (0 wt. %, 6 wt. %, 28 wt. %, 50 wt.%) in the ITL. The bilayer is composed of an additional ionic conducting layer (ICL) (thickness = ~ 80 nm) made of a solid polyelectrolyte, potassium polystyrene sulfonate (PSSK, Fig. 1). The organic bilayer is sandwiched between two metal electrodes (inset Fig. 2(a)). In order to demonstrate that K^+ cations can migrate from the ICL into the ITL and effectively be trapped, the impedance of the device is measured in the range [10^{-2} – 10^6 Hz] (Figs. 2(a) and 2(b)). Without cryptand 2.2.2 or with a low (6 wt. %) concentration of the macrocycle, the organic blends are purely capacitive with a phase angle Φ of the impedance close to -90° at frequencies below 10^4 Hz. The lack of resistive character indicates that ions are immobile, hence preventing the creation of electric double layers of high capacitance at the electrode surface. Indeed small effective capacitances (less than $0.3 \mu\text{F}/\text{cm}^2$) at 10 mHz are measured. The potassium cations do not penetrate into the ITL due to the low ionic conductivity of PMMA. For high concentration cryptand 2.2.2 (up to 28 wt. % and 50 wt. %), Φ approaches -45° at low frequencies (10 mHz) indicating a slow migration of cations within ITL even for very low AC potential ($0.5 V_{\text{rms}}$). This is further supported by the increase of capacitance up to $2 \mu\text{F}/\text{cm}^2$ and $10 \mu\text{F}/\text{cm}^2$ at 10 mHz, for a cryptand content of 28 wt. % and 50 wt. %, respectively. This reflects the formation of electric double layers at the Ti electrode/PMMA-cryptand and Ti electrode/PSSK interfaces. Our hypothesis is that the PMMA-cryptand blend is composed of cryptand-rich domains throughout which the cations are mobile and can reach the Ti electrode.

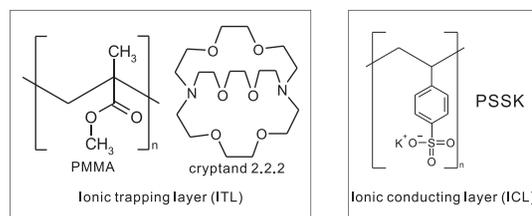


FIG. 1. Chemical structures of PMMA, cryptand 2.2.2 in ITL, and PSSK in ICL.

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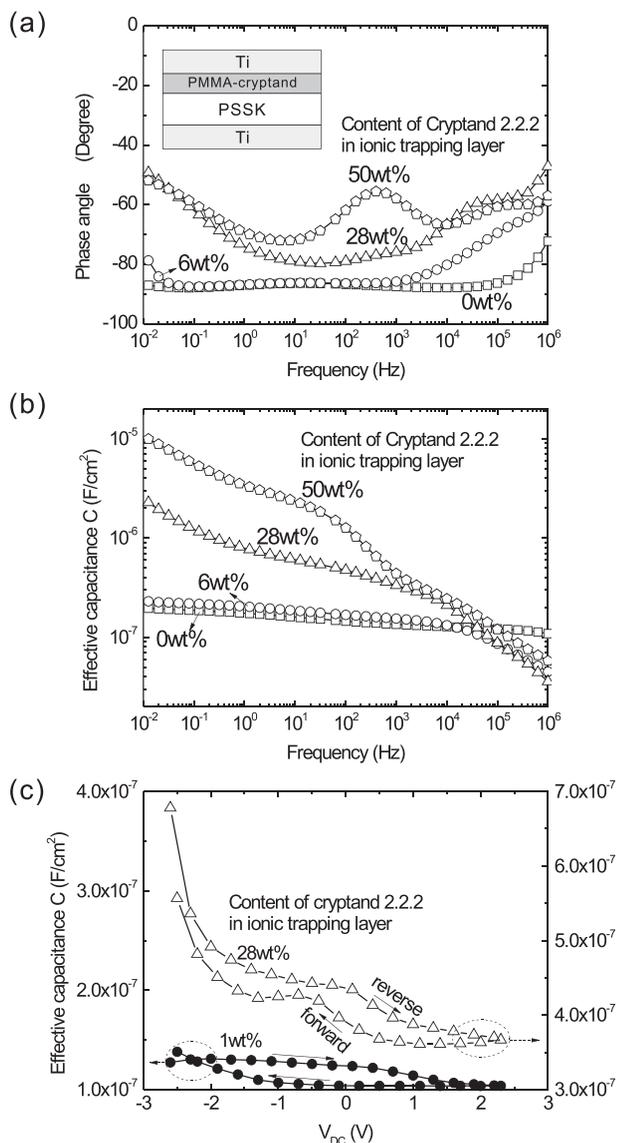


FIG. 2. (a) Phase angle versus frequency of ionic trapping bilayer capacitor (applied AC voltage: $0.5 V_{rms}$). Inset: the ionic trapping element included in a capacitor structure. (b) Effective capacitance versus frequency of ionic trapping bilayer capacitor (applied AC voltage: $0.5 V_{rms}$). (c) C-V characteristics at 1 kHz (applied AC voltage: $0.01 V_{rms}$). The impedance measurements were performed in ambient by Alpha high-resolution dielectric analyzer (Novocontrol GmbH).

Further, we estimated the evolution of the capacitance versus the applied voltage. Interestingly, the capacitance displays a hysteresis loop (Fig. 2(c)). In other words, the capacitance values measured at the reverse sweep (from -2.6 V to $+2.3$ V) are relatively higher than those at the forward sweep (from $+2.3$ V to -2.6 V). This observation implies that the polarization of the bilayer is remanent. The cations move into the ITL (increased capacitance) during the forward sweep and partially remain in the ITL (trapped), so that the high capacitance is maintained in the backward sweep. Note that the larger the amount of cryptand, the larger the capacitance becomes at negative bias. Hence, a relatively high concentration of cryptand in the ITL provides both the formation of electric double layers of high capacitance and a hysteresis behavior.

The choice of a polyanionic layer is crucial since the anions are immobile and the cations can be trapped into the ITL to keep a polarization in the capacitor. If the anions were small and mobile, they would also move into the ITL and the capacitance would not show the hysteresis. The polyanion is also crucial when it comes to integrate the peculiar polarization of the bilayer into a device easily addressable in a circuit: a transistor. Recently, polyanions have been identified as attractive insulating layer in OFETs,⁹ since it provides low operating voltage and fast transistors.¹⁰ The reason is that the polyanions are immobile and cannot migrate into the positively charged organic semiconducting channel, thus avoiding the slow response of an electrochemical transistor.

The bilayer structure is integrated into the architecture of a polyelectrolyte-gated OFET, given in inset in Fig. 3(a). Gold (Au) patterns, manufactured through standard vacuum-evaporation and photolithography, are formed on a silicon wafer to serve as drain and source electrodes. On top of these two bottom contacts, a stack of several organic layers are spin-coated. First, regio-regular poly(3-hexylthiophene) (P3HT) (0.2 wt. % in chloroform) is spin-coated to form a 12 nm-thick semiconducting layer. Second, a 200 nm-thick ICL made of PSSK (2.5 wt. % in a mixture of deionized water and 1-propanol) is spin-coated on the P3HT layer. Finally, a solution of PMMA and cryptand 2.2.2 (1/0.38% (w/w) in toluene) is spin-coated on PSSK to form a 25 nm-thick ITL. The orthogonality of the solvents used in the different layers allow forming a well defined multilayer without

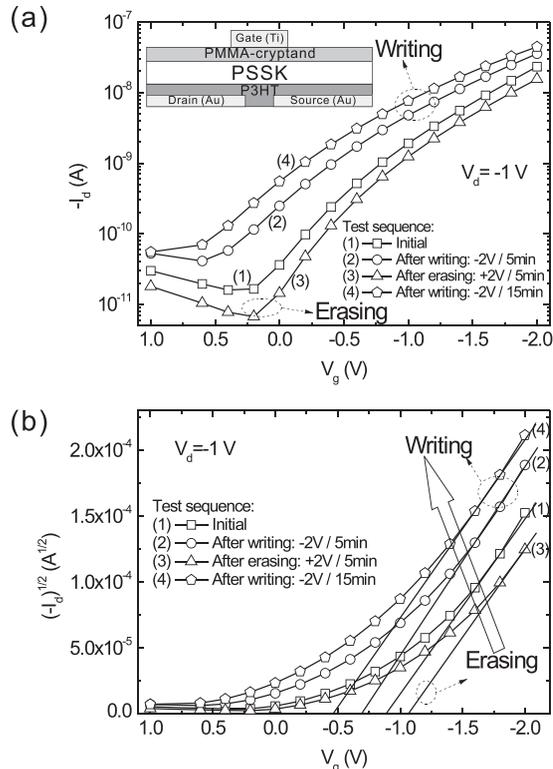


FIG. 3. (a) The transfer characteristic of the OFET with the ITL (channel length: $4 \mu\text{m}$, channel width: $500 \mu\text{m}$). Inset: the OFET incorporating the ionic trapping bilayer capacitor. (b) The square root of $-I_d$ versus V_g of the OFET with the ITL. The characteristics of the device were measured in a sequence of (1), (2), (3), (4) in a vacuum chamber (less than 6×10^{-3} Torr at room temperature) by Keithley 4200-SCS semiconductor parameter analyzer.

intermix at the interfaces. The transistor is finalized by vacuum depositing a titanium gate electrode.

Fig. 3(a) shows the transfer characteristics of the OFET with the ITL (28 wt. % cryptand 2.2.2 in the ITL). The transfer curves are obtained following the application of a gate bias in the chronological programming sequences: (1) no bias (initial condition, curve with square symbols) (2) a write-voltage of -2 V for 5 min (circles), (3) an erase-voltage of $+2$ V for 5 min (triangles), and (4) a write-voltage of -2 V for 15 min (pentagon). We estimated the threshold voltage from the a plot of $(-I_d)^{1/2}$ versus V_g , see Fig. 3(b), and extracted the hole mobility to about 1.45×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ assuming a capacitance of about $2 \mu\text{F}/\text{cm}^2$. During the writing step, V_{th} shifts towards positive voltage by 0.6 V (from -1.07 V to -0.47 V) while the hole mobility remains constant. Note that the bias stress effect leads to a threshold voltage shift in an opposite direction. Hence the displacement of the threshold voltage observed in the programming sequence of gate potentials is not a bias stress effect.

The behavior of the transistor is in agreement with the capacitance hysteresis observed in the bilayer capacitor. When writing ($V_g = -2$ V for 5 min), potassium cations migrate from the polyelectrolyte into the ITL. Some ions reach the gate electrode and form an electric double layer; some are trapped in the cryptand macrocycles. After the writing scheme, the ITL becomes positively charged and the ICL is negatively charged which leads that accumulation of holes becomes easier at the ICL-semiconductor interface. Hence, the V_{th} of device is reduced after writing. To erase the device, a positive gate voltage is applied; which forces trapped potassium cations to move back to the polyelectrolyte, leading to an increasing in the V_{th} .

The kinetic of trapping and de-trapping of ions is evaluated by testing the time evolution of the transistor characteristics. We monitored the drain current while the gate was electrically open (floating the gate) after erasing ($+2$ V/5 min) and after writing (-2 V/10 min), respectively, during a period of 30 min, see Fig. 4. After erasing the device, a very small drain current (“0” state, the solid curve) can flow through the channel. After writing, since K^+ cations are trapped in the ITL, a small electric field is then set up at the ICL-semiconductor interface, which accumulates holes and partially opens the channel. In such a situation, the drain current is switched to a higher current level (“1” state, the dashed curve). Right after writing, the “1” state current is about 30 times larger than the “0” state current, and then decays to about 40% larger than “0” state current after 15 min, i.e., a difference in current about 3 pA.

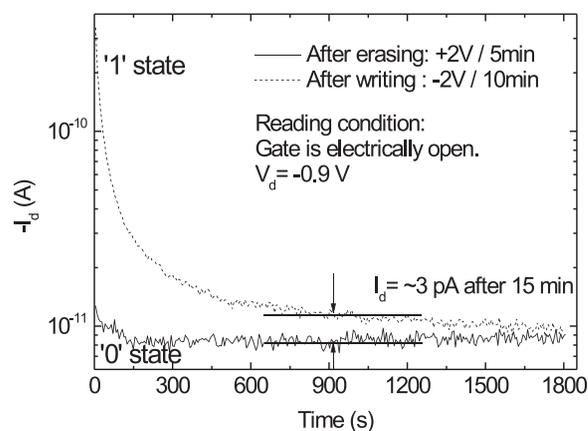


FIG. 4. The time evolution of $-I_d$ in 30 min measured in vacuum (sampling interval: 6 s).

In summary, we have demonstrated that a bilayer composed of a polyelectrolyte layer and a layer with cryptand macrocycles possesses a remanent electric polarization. This peculiar polarization is implemented in a polyelectrolyte-gated OFET, which results in specific threshold voltage shifts by applying low programming voltages (± 2 V).

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- ¹Q. Pei, G. Yu, C. Zhang, Y. Yang, and A. J. Heeger, *Science* **269**(5227), 1086 (1995).
- ²P. Andersson, R. Forchheimer, P. Tehrani, and M. Berggren, *Adv. Funct. Mater.* **17**(16), 3074 (2007).
- ³J. H. Cho, J. Lee, Y. Xia, B. Kim, Y. He, M. J. Renn, T. P. Lodge, and C. Daniel Frisbie, *Nature Mater.* **7**(11), 900 (2008).
- ⁴G. C. Ochoa and J. C. Aguilar-Cordero, *Electroanalysis* **23**(7), 1736 (2011).
- ⁵M. J. Marsella and T. M. Swager, *J. Am. Chem. Soc.* **115**(25), 12214 (1993).
- ⁶A. Boldea, I. Levesque, and M. Leclerc, *J. Mater. Chem.* **9**(9), 2133 (1999).
- ⁷X. Zhang, R. M. Izatt, J. S. Bradshaw, and K. E. Krakowiak, *Coord. Chem. Rev.* **174**(1), 179 (1998).
- ⁸T. K. Katsuhiko Ariga, *Supramolecular Chemistry—Fundamentals and Applications* (Springer, Heidelberg, Germany, 2006).
- ⁹E. Said, X. Crispin, L. Herlogsson, S. Elhag, N. D. Robinson, and M. Berggren, *Appl. Phys. Lett.* **89**(14), 143507 (2006).
- ¹⁰L. Herlogsson, M. Cölle, S. Tierney, X. Crispin, and M. Berggren, *Adv. Mater.* **22**(1), 72 (2010).