A Crown-Ether Loop-Derivatized Oligothiophene Doubly Attached on Gold Surface as Cation-Binding Switchable Molecular Junction

Truong Khoa Tran, Kacem Smaali, Marie Hardouin, Quentin Bricaud, Maïténa Oçafrain, Philippe Blanchard, Stéphane Lenfant,* Sylvie Godey, Jean Roncali,* and Dominique Vuillaume**

Dedicated to the memory of Dr. Nuria Gallego-Planas

Molecular junctions and switches are a focus of considerable current interest as possible basic components of future molecular electronic devices.[1,2]

During the past decades molecular switches based on different concepts and mechanisms have been proposed, synthesized and investigated.[3] These include reversible bond breaking,[1,4,5] translocation of part of multi-component molecular assemblies,[6,7] proton transfer,[1,4,8] or reversible conformational changes of a system with geometry-dependent electronic properties.[9–11]

The interplay of the cation-binding properties of crown-ether and conformational changes has already been investigated. Thus, Shinkai used the photoisomerization of azobenzene units inserted in crown ether systems to modulate the cation binding properties of the cavity.[12] From a different viewpoint, we have shown that the cation-binding ability of a polyether loop attached at two fixed points of an oligothiophene chain can serve as driving force to generate changes in the geometry and hence electronic properties of the conjugated system.[13] A related approach has been also used for the synthesis of polythiophene-based sensors[14] and more recently for the control of the intramolecular photoinduced electron transfer in crown ether bridged oligothiophenes.[15]

In this context, we now report on the surface immobilization by double fixation on gold surface of a dithiol quaterthiophene derivatized with a polyether loop **1-SH** (**Scheme 1**). In recent years we have extensively studied the structural conditions and synthetic approaches allowing the horizontal double fixation of conjugated oligothiophenes as monolayers on gold surface.[16] After an analysis of the cation complexation properties of the related acetyl-protected dithiol molecule **1** in solution by UV-vis spectroscopy and cyclic voltammetry, the preparation of monolayers by double fixation of the oligothiophene chain on gold surface will be described, the structure and properties of these monolayers will be investigated using cyclic voltammetry, ellipsometry, water contact angle measurement, XPS and their electrical properties will be assessed by contacting the monolayer with a conducting eutectic GaIn drop. Finally, preliminary results on the cation binding properties of the monolayer and investigations on the use of the immobilized molecule as a switchable molecular junction will be presented and possible transport mechanisms will be discussed.

Compound **1** has been synthesized by deprotection/functionalization of the appropriately protected thiolate groups according to the already published method.[16b] The detailed synthesis of this molecule and of some parent compounds will

Dr. T. K. Tran, Dr. M. Hardouin, Dr. Q. Bricaud,
Dr. M. Oçafrain, Dr. P. Blanchard, Dr. J. Roncali
LUNAM, University of Angers
CNRS UMR 6200, MOLTECH-Anjou
Group Linear Conjugated Systems
2 Bd Lavoisier, 49045 Angers cedex, France
E-mail: Philippe.Blanchard@univ-angers.fr;
Jean.Roncali@univ-angers.fr
Dr. K. Smaali, Dr. S. Lenfant, Dr. S. Godey, Dr. D. Vuillaume
Institute for Electronics Microelectronics & Nanotechnology
CNRS, University of Sciences and Technologies of Lille
BP60069, Avenue Poincaré
59652 Villeneuve d'Ascq, France
E-mail: stephane.lenfant@iemn.univ-lille1.fr;
dominique.vuillaume@iemn.univ-lille1.fr
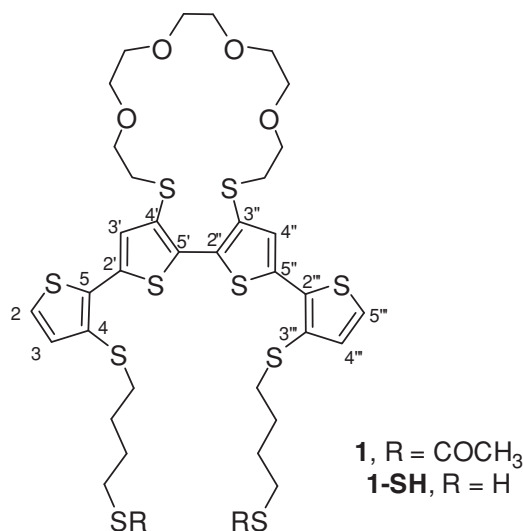
Scheme 1. Crown-ether quaterthiophenes **1** and **1-SH**.

1, R = COCH$_3$
1-SH, R = H

be reported elsewhere.[17] The identity and purity of compound **1** were established by ^{1}H and ^{13}C NMR spectrometry and HR mass spectrometry giving satisfactory results (see Supporting Information). Dithiol **1-SH** was prepared by reduction of the thioester groups of **1** using DIBAl-H.

Metal complexation in solution: The metal cation complexing properties of compound **1** have been analyzed by UV-vis spectroscopy and cyclic voltammetry. Preliminary tests using UV-vis absorption spectroscopy in the presence of various metal cations (Li^+, Na^+, Cs^+, Ba^{2+}, Sr^{2+}, Cd^{2+}, and Pb^{2+}) have shown that only Pb^{2+} is complexed by compound **1**. **Figure 1**a shows the UV-vis absorption spectrum of **1** in CH_3CN upon stepwise addition of substoichiometric amounts of Pb^{2+}. The initial spectrum shows two maxima at 279 and 380 nm. Addition of Pb^{2+} produces an intensification of the two absorption bands. These changes occur around an isosbestic point at 398 nm which suggests interconversion between two species. Addition of one equivalent of Pb^{2+} leads to a 5 nm hypsochromic shift of the 380 nm maximum. This blue-shift indicative of a decrease of π-conjugation of the quaterthiophene skeleton can be ascribed to an increase of the twist angle around the central $C(5')$-$C(2'')$ bond. As shown in Figure 1a, the blue-shift stops and the intensity of the two bands remains constant after addition of more than one equivalent of Pb^{2+} suggesting the formation of a 1:1 complex with Pb^{2+}.

Figure 1b shows the cyclic voltammogram (CV) of **1** upon complexation of Pb^{2+}. The initial CV of **1** exhibits two one-electron reversible oxidation waves corresponding to the successive formation of the radical-cation (E_{pa}^1 = 0.86 V) and dication (E_{pa}^2 = 0.99 V) of the quaterthiophene backbone. The addition of increasing amounts of Pb^{2+} to a solution of **1** produces a decrease in intensity of the first oxidation peak which completely disappears after addition of one equivalent of Pb^{2+}. The CV then exhibits a single two-electron reversible oxidation peak at 1.02 V. Thus, the first and second initial oxidation peaks undergo a 160 mV and 30 mV positive shifts, respectively. This result can be related to the existence of repulsive Coulombic interactions between Pb^{2+} and the radical cation or the dication of the quaterthiophene skeleton, and also to a decrease of the +*M* mesomeric effect of the two sulfur atoms in 4′ and 3″ positions due to the participation of their free electron pairs to the complexation of Pb^{2+}.[18] In addition, no more change is observed beyond one equivalent of Pb^{2+} which further supports the formation of a 1:1 complex between **1** and Pb^{2+}.

Preparation, characterization, and metal complexation properties of monolayers of **1-SH***:* Monolayers of **1-SH** were prepared under a controlled argon atmosphere by immersion of gold bead electrodes[16] during 48 h in a millimolar solution of compound **1-SH** in CH_2Cl_2. The resulting electrodes were then rinsed with CH_3CN before CV analysis. Reproducible monolayers were obtained when dithiol **1-SH** was freshly generated and chromatographed to prevent the possible formation of multilayers of disulfide compounds.[16,19] The CV of monolayer of **1-SH** exhibits only one broad reversible oxidation peak at 1.05 V/SCE. As already observed for a parent 4T derivative containing ferrocene,[16b] this single oxidation wave includes in fact the two successive one-electron oxidation steps of 4T. The occurrence of a single oxidation wave suggests a broadening of the individual waves due to intermolecular interactions as
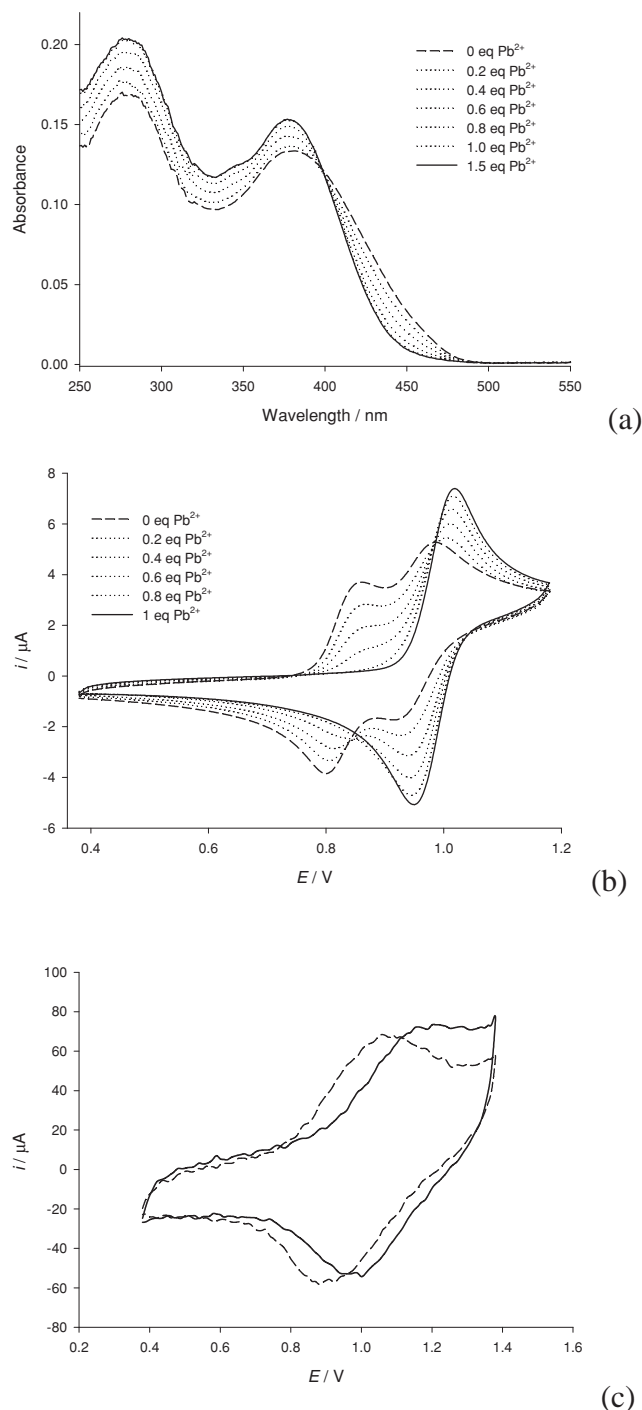

(a)

(b)

(c)

Figure 1. (a) Changes in the UV-vis spectrum of **1** (1×10^{-5} M) in CH_3CN *vs* number of Pb^{2+} eq. added as perchlorate. (b) CV of **1** (0.5 mM in 0.10 M Bu_4NPF_6/CH_3CN, scan rate 0.1 V s^{-1}, Pt working electrode, ref. SCE) in the presence of increasing amounts of Pb^{2+} added as perchlorate by increments of 0.2 equivalent. (c) CVs of a monolayers of **1-SH** on a gold bead electrode in 0.10 M Bu_4NPF_6/CH_3CN in the absence (dotted line) and in the presence (solid line) of $Pb(ClO_4)_2$·$3H_2O$ (5 mM), scan rate 20 V s^{-1}, ref. SCE.

observed in the CV of oligo- and polythiophenes.[20] The intensity of peak currents varies linearly with scan rate as expected for a surface-confined electrochemical reaction. These

monolayers exhibit a good electrochemical stability and no variation of the CV was observed after 200 cycles between 0.50 and 1.10 V/SCE at 1 V·s^{-1}. The surface coverage Γ of molecules **1-SH** has been determined by using gold planar electrode of 0.2 cm^2 and integration of the voltammetric peak after correction for double-layer charge.[21] A typical value of 1×10^{-10} mol cm^{-2} (i.e., 0.6×10^{14} molecules/cm^2) was obtained for Γ, in agreement with the formation of a monolayer on gold. The complexation properties of Pb^{2+} by monolayers of **1-SH** have been analyzed by cyclic voltammetry. The CV of monolayers of **1-SH** have been recorded repeatedly and alternately in a solution of 0.1 M Bu$_4$NPF$_6$/CH$_3$CN in the absence or presence of Pb(ClO$_4$)$_2$ (5 mM) (Figure 1c). A significant positive shift of 90 mV of the oxidation wave is observed for each CV cycle recorded in the presence of Pb^{2+}. This result shows that the monolayer of **1-SH** is sensitive to the presence of Pb^{2+} in solution. Monolayers of **1-SH** for ellipsometry, wettability, XPS and current/voltage analysis have been prepared on evaporated gold layer (200 nm) on silicon wafers recovered by a 10 nm adhesion layer of titanium. Thickness measurement of the monolayers by ellipsometry, gave a value of 14 ± 2 Å. This value is in good agreement with a monolayer formation and with the height of 18 Å calculated for **1-SH** in a geometry expected for a double fixation, as deduced from MOPAC 3D software and assuming a S-Au distance of about 2 Å (see Supporting Information).[22] The relatively low values of water contact angle for monolayers of **1-SH** (θ_{H2O} = 74° ± 2°) show that these surfaces present a hydrophilic character consistent with the presence of the oxyethylene chains on the top of the surface.[23] The water contact angles and monolayer thicknesses are not much affected by Pb^{2+} complexation. For a monolayer of **1-SH** immersed in a 5 mM solution Pb(ClO$_4$)$_2$·3H$_2$O in CH$_3$CN for 48 h and rinsed with CH$_3$CN, we have measured θ_{H2O} = 71° ± 2° and a thickness of 16 ± 2 Å. This feature indicates that the integrity of the monolayer is globally preserved upon Pb^{2+} complexation. The survey of XPS spectrum (not shown here) of the **1-SH** monolayer shows the presence of the different atoms of the molecule: carbon (peak C1s), oxygen (peak O1s), sulfur (peaks S2s and S2p) and lead (peak Pb4f) after complexion. The C1s spectrum shows (**Figure 2**a) two components at 285.5eV (main peak) and 287 eV (shoulder). The main peak is attributed to C–C in good agreement with results published for monolayers grafted on gold.[24] The shoulder peak is attributed to C–O,[25] with an experimental area peak ratio C–C/C–O of 3.3 (expected value of 26/8 = 3.25). The S2s and O1s peaks appear at 228.4 eV and 532.9 eV, respectively, without significant variation after Pb^{2+} complexation.

The high-resolution XPS spectrum of the S2p region of monolayers of **1-SH** shows two doublets (Figure 2b). The peaks at 162.5 eV and 163.7 eV of the lower energy doublet S2p$_{3/2,1/2}$ of monolayers can be assigned to the thiol chemisorbed on the Au surface (S-Au bond).[24a,26] The other doublet S2p$_{3/2,1/2}$ at 164.3 and 165.5 eV corresponds to the other sulfur atoms of compound **1-SH** (S—C bond). Comparison of the areas of these two doublet signals leads to an estimated S—C/S-Au ratio of 3.8 ± 1 which is close to the theoretical value expected for a double fixation (S—C/S-Au = 4). Thus, XPS results confirm that most of **1-SH** molecules are doubly fixed on the gold surface.
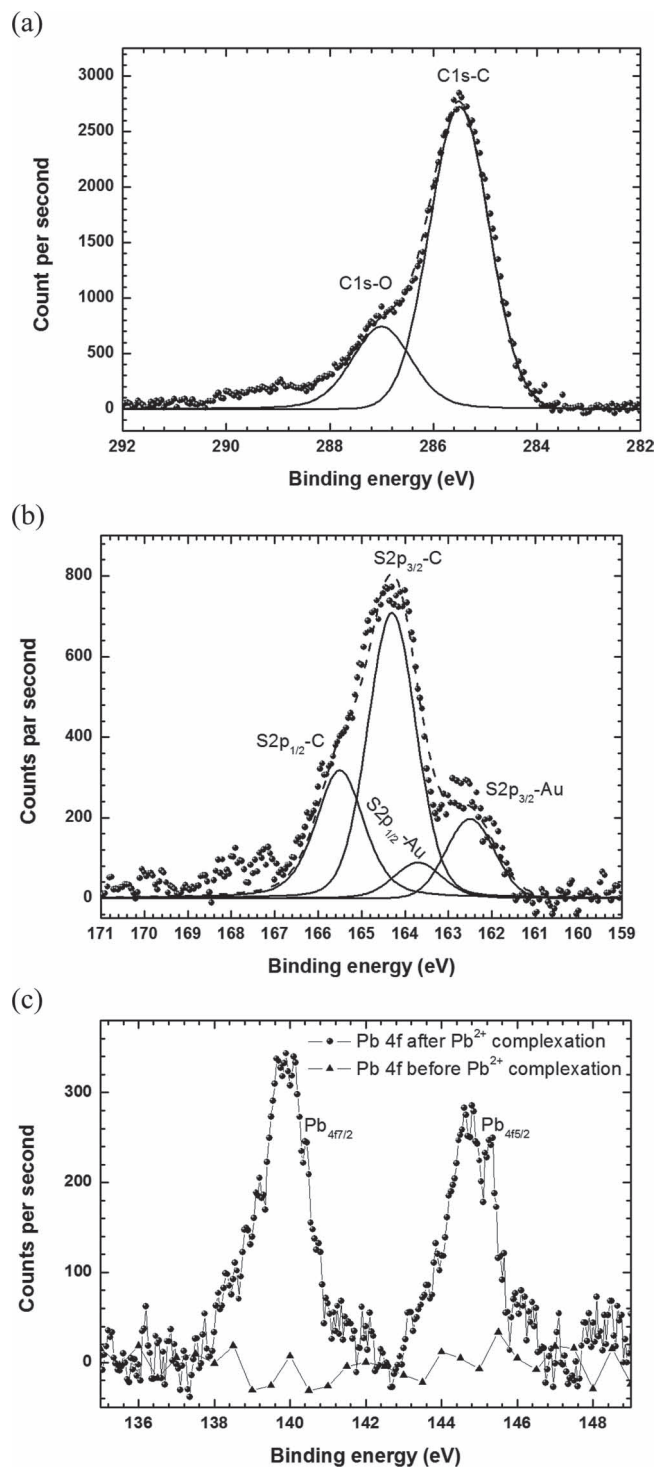

Figure 2. (a) C1s region of the XPS spectrum of 1-SH monolayer before exposure to Pb^{2+}. (b) S2p region of the XPS spectrum of 1-SH monolayer before exposure to Pb^{2+}. (c) XPS spectra of the Pb4f region before and after Pb^{2+} complexation.

After Pb^{2+} complexation by the **1-SH** monolayer, the energy values of the four components of the S2p peak are not significantly modified (less than 0.2 eV). In addition, we also observed (Figure 2c) the presence of Pb4f peaks at 139.8 eV and 144.9 eV

for the doublet Pb4f$_{7/2,5/2}$ (Figure 2c).[27] The Pb/C ratio of 4×10^{-3} determined by XPS shows that around 13% of Pb^{2+} is still present in the monolayer.

Electronic transport properties: Current-voltage (I–V) are measured on Au-molecule-metal junctions by contacting the top surface of the monolayer with an eutectic gallium-indium (eGaIn) drop (see Experimental section).[28] Typical I–V curves before and after complexation of Pb^{2+} are shown in **Figure 3**a. For the pristine monolayer, a very low current (slightly higher than the sensitivity of our amp-meter of ca. 0.01 pA) is measured between -1 V and +1 V. The I–V curves display a rather symmetrical behavior for negative and positive voltages (i.e., the ratio $I_{V<0}/I_{V>0}$ is always around 1, see Supporting Information). Applying the transition voltage spectroscopy (TVS) technique,[29] i.e., plotting the same data as $\ln(I/V^2)$ *vs.* $1/V$ (Figure 3b),[30] we get a positive and negative transition voltage V_T (i.e., the voltage at which $\ln(I/V^2)$ is minimum) at +1.09 ± 0.02 V and −1.09 ± 0.02 V. The SAMs with Pb^{2+} show a rather different behavior, with a huge increase of the current at low bias (a ratio up to 280 at around 1.15 V and 1.6×10^3 at −1.2 V). We also note a slight asymmetrical behavior with higher current

at negative than at positive bias (with a max ratio of about 9). Then, at higher bias (< −2V and > 2V) the two I–V curves overlap. TVS (Figure 3b) show a decrease of V_T, which are −0.52 ± 0.04 V and +0.86 ± 0.04 V, these asymmetric values (in absolute values) reflecting the asymmetrical I–V behavior already mentioned.[31] Recent discussions in the literature pointed out how it can be possible to relate V_T with the energy position of the LUMO or HOMO levels in the junctions and with the voltage division factor γ, a parameter that describes the degree of symmetry or asymmetry of the molecular orbitals in the junction (−0.5 ≤ γ ≤ 0.5, γ = 0 being the case of a symmetrical coupling of the molecular orbitals between the two electrodes).[30,31] Following the analytical model of Bâldea[31b] (Equations 6 and 7 therein), we determine the energy level ε_0 of the molecular orbital involved in the electrical transport (with respect to the Fermi energy of the electrodes), and γ, directly from the measured V_{T+} and V_{T-}. For the pristine **1-SH** junction, we get ε_0 = 0.96 eV, and γ = 0. After Pb^{2+} complexation, ε_0 decreases to 0.56 eV and $\gamma = \pm 0.1$ depending whether ε_0 corresponds to the LUMO or the HOMO, respectively. With this simple analysis it is not possible to discriminate which molecular orbital is involved in the transport. A more detailed analysis and comparison with ab-initio calculations will be reported elsewhere.[17]

In conclusion, we clearly demonstrate that the Pb^{2+} complexation by a **1-SH** molecule moves one of the molecular orbitals close to the Fermi energy of the electrodes, inducing a significant increase (up to 1.6×10^3) of the current at low bias, while only about one Pb^{2+} atom is captured per 7-8 molecules. The distortion of the molecular conformation after Pb^{2+} complexation also leads to an asymmetrical molecular coupling in the junction with the two electrodes as evidenced by the rectification behavior.
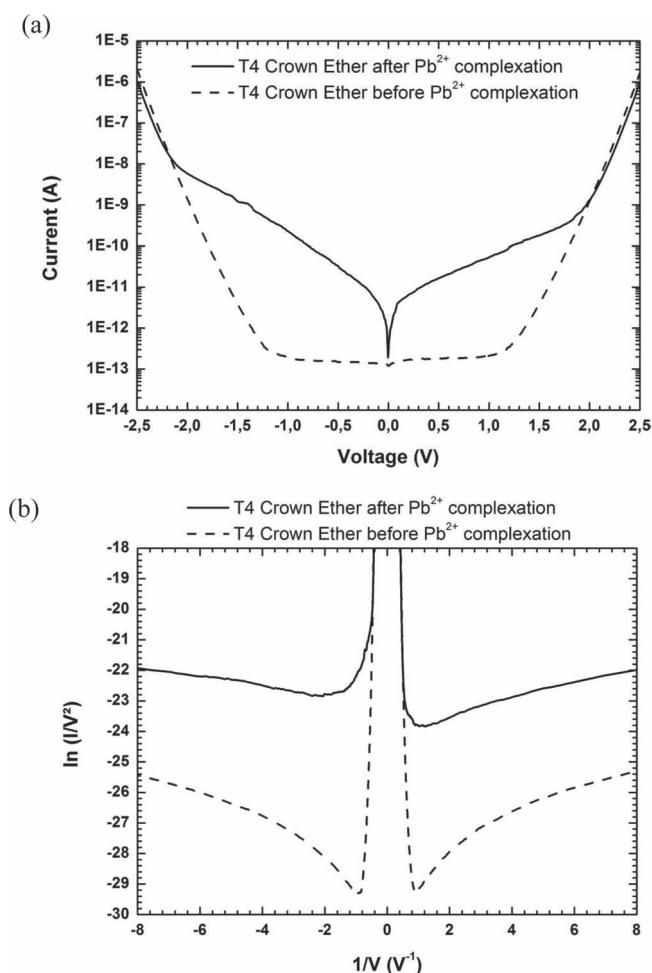

Figure 3. Typical I–V curves (averaged over 5 measurements) for the Au/molecules/eGaIn junction before and after Pb^{2+} complexation. (b) TVS plots of the same data as in Figure 3a.

Experimental Section

Gold substrates consist of 200 nm Au film thickness, evaporated onto silicon wafers covered by titanium or chromium sublayer (10 nm) deposited under ultrahigh vacuum. Electrochemical experiments were carried out with a PAR 273 potentiostat-galvanostat in a three-electrode single compartment cell. We measured the water contact angle with a remote-computer controlled goniometer system (DIGIDROP by GBX, France). We recorded spectroscopic ellipsometry data in the visible range using an UVISEL (Jobin Yvon Horiba) Spectroscopic Ellipsometer equipped with a DeltaPsi 2 data analysis software. XPS measurements were performed with a Physical Electronics 5600 spectrometer fitted in an UHV chamber with a residual pressure of 2×10^{-10} Torr. We performed current-voltage measurements by eutectic GaIn drop contact (eGaIn 99.99%, Ga:In; 75.5:24.5 wt% from Alfa Aesar). I–V curves were acquired with an Agilent semiconductor parameter analyzer 4156C with an ultimate sensitivity of 0.01 pA. More details in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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