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Electrical-field-induced structural change and charge transfer of lanthanide–salophen complexes assembled on carbon nanotube field effect transistor devices

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ABSTRACT

The application of a negative gate voltage on a carbon nanotube field effect transistor decorated by a binuclear Tb(III) complex leads to the generation of a negatively charged mononuclear one, presenting an electron density transfer to the nanotube and ambipolar behaviour.

Carbon nanotubes are very promising 1D materials in many general fields, such as mechanics,¹ optics^{2,3} and electronics.⁴

Combining the unique transport properties of single-walled carbon nanotubes (SWNT) and those of organic or inorganic materials led to several breakthroughs in the last few years. In particular, SWNTs can act as sensors (gas, biomolecules, organic and inorganic compounds)^{5,6} in different kinds of devices, such as Carbon Nanotube Field Effect Transistors (CNFET).^{4,7} In such devices, the gate-monitored transport property through the semiconducting nanotube is highly sensitive to its close environment. The functionalization of the nanotube by molecules induces a change in the transport allowing us to probe the assembled molecules.^{2,6,8} Recently, a supramolecular spin valve was designed and used as a magnetic probe thanks to the coupling of the magnetic properties of a rare earth complex with the electronic ones of CNFET.⁹

In this communication, we report on the solid-state structural transformation of the binuclear lanthanide–salophen-based complex [Tb₂(salophen)₃] (**1**) (where H₂salophen is disalicylidene-1,2-phenylenediamine) induced by the electrical field of the CNFET device. Rare earth complexes built using Schiff-base scaffold possess interesting optical and magnetic properties. Salophen was chosen as a base unit for the design

of the lanthanide complex because it possesses a delocalized p system, which can lead to non-covalent p-stacking inter- actions with the SWNT.

The [Tb₂(salophen)₃] binuclear complex is obtained via the reaction of Tb(NO₃)₃ and H₂salophen in the presence of triethylamine with a slight modification of the reported pro- cedure (see ESI[†]).^{10,11} Crystals suitable for structural studies were grown and the structure

was solved.[‡] The molecular arrangement consists of a binuclear triple-decker-like complex. The two Tb(III) ions have different surroundings: one has 8 bonds, 4 with a peripheral salophen and four with the bridging one, while the other Tb atom has only 7 bonds, four with the other peripheral salophen and only two with the bridging one. The seventh atom in the coordination sphere belongs to an ethanol molecule (Fig. 1 and S1, see ESI[†]). Prior to the transport studies, **1** and **1**/HiPCO-SWNT was characterized by electronic and photoluminescence studies that showed the absence of an interaction between the complex and the nanotubes (Fig. S2 and S3 see ESI[†]).

The transistors used in this study were obtained as we already reported (Fig. S4 and S5 see ESI[†]).¹² Current (I_{ds}) versus gate voltage (V_g) characteristics shows the expected p-type FET behaviour (ON state at V_g < 0) with a very good I_{ON}/I_{OFF} ratio between five and seven decades (Fig. S5, ESI[†]). The usual large hysteresis is the result of charge injection from the carbon nanotube to the nearby region. The measures are realized with a 2 V bias and V_g is swept from –20 V to + 20 V.

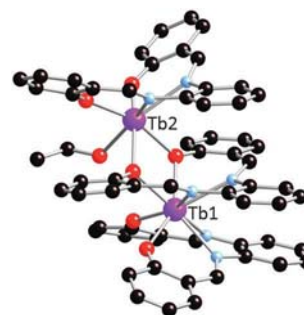


Fig. 1 A view of the structure of binuclear complex **1** showing the two different coordination spheres of the Tb(III) ions.

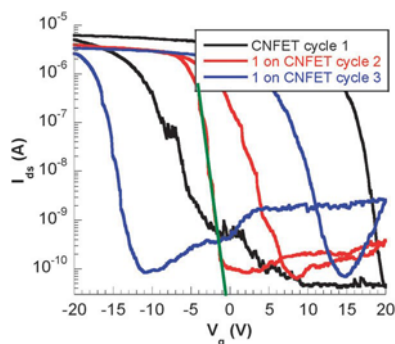


Fig. 2 I_{ds} vs. V_g characteristics for a CNFET device before (black curve) and after the presence of **1** (red). The blue curve corresponds to a second cycle of the gate voltage. The curves are recorded within a bias of 2 V.

The hybrids were produced by the evaporation of a 5 μ L drop of a solution of **1** in dichloroethane (DCE) deposited on the CNFET surface. Since our systems consist of transistors built on diluted mats of SWNT with gaps between the two electrodes of up to 5 μ m, the impact of any molecule assembled non-covalently on the CNFET conduction is mainly attributable to an interaction with the channel or its direct environment (dielectric surface, but not the channel-electrodes interface).^{4,12} Three voltage cycles leading to I_{ds} vs. V_g plots were performed (Fig. 2): (i) for the bare transistor (first cycle, black), (ii) directly after the evaporation of the solution of **1** (second cycle, red) and (iii) a few minutes after the second cycle (third cycle, blue).^y The first cycle corresponds to a p-type semiconductor nanotube with no ambipolar behavior, as is expected for a device in ambient air atmosphere. For the second cycle, as gate voltage is swept to positive values, the ON/OFF threshold voltage V_{th} shifts from 1.1 to -0.9 V (Fig. 2) and the subthreshold swing $S_w = [dV_g/d\log(I)]$ (green slope on Fig. 2.) increases in comparison to that of the bare device. Both of these effects contribute to reduce the width of the hysteretic character. This is attributed to a modification of the charge trapping process occurring at the SWNT-dielectric interface that is responsible for the hysteretic behaviour.⁴ It suggests that **1** does not interact electronically with the nanotube, but forms a layer of randomly organized molecules that partially isolate the conduction channel from its environment: it acts as a screen for the charge trapping phenomenon, thus decreasing the width of the hysteresis curve. This is consistent with the UV-visible and photoluminescence studies that **1** does not interact electronically with the nanotube (Fig. S3, see ESI^w).

Finally, for the third cycle (blue curve) the aspect of the characteristic changes significantly again, showing many features that indicate the occurrence of an electronic interaction between a new molecular species and the nanotube. The width of the hysteresis loop has been restored to become similar to that of the bare device (as well as S_w), which is in line with the disappearance of the screening centres. The V_{th} strongly decreases ($\Delta V = -12.6$ V) in comparison to that of the bare transistor, as it is usually observed for non-covalently assembled molecules responsible of an electron density transfer phenomenon from the molecule to the SWNT.¹² In addition to those changes, a small ambipolar character appears for the positive values of V_g . In summary, the application of a negative

gate voltage (Fig. S6, see ESI^w),^z that produces an important holes current flow, modifies the layer of deposited molecules by deeply changing the nature of their interaction with the device. The charge transfer phenomenon suggests that the nature of the complex itself is modified, leading to a new entity able to assemble non-covalently on the surface of SWNT. It is important to note that the gate voltage was cycled several times after the third cycle and no noticeable change in the characteristics of the transistor was furthermore observed showing the stability of the new species.

The nature of the new species can be inferred by examining the structure of **1** and its behaviour in solution. **1** can be described as formed by the species $[\text{Tb}(\text{salophen})_2]^-$ and $[\text{Tb}(\text{salophen})]^{+}$ linked together by two Tb–O bonds (Fig. 1). Costes et al. have already shown the presence of an equilibrium in solution between these two charged species and **1**.^{10,11} Indeed, the chelating effect within the two new species is large enough to ensure their stability. We assume that the applied bias creates an electrical field in the close vicinity of the nanotube that produces enough energy to break **1** at its weakest bonds, i.e. the coordination Tb–O bonds with the central salophen ligand, leading to the new charged species. Indeed, the non-symmetrical binuclear complex must have an electrical dipole sensitive to the field generated by the applied bias. Furthermore, the driving force of such a phenomenon can be attributed to the electrostatic interaction between the holes (positive charges) flowing through the nanotube upon the application of a negative gate voltage and the negative charge of the $[\text{Tb}(\text{salophen})_2]^-$ entity. In order to confirm our hypothesis that the formed species is indeed the $[\text{Tb}(\text{salophen})_2]^-$ complex, we synthesized it by mixing a stoichiometric amount of salophen and $\text{Tb}(\text{NO}_3)_3$ in dimethylsulfoxide (DMSO) in the presence of CsCl .^{10,13} Even though single crystals suitable for structural studies were not obtained, the full characterisation of the powder confirmed the synthesis of the targeted complex that has the following formula $\text{Cs}[\text{Tb}(\text{salophen})_2] \cdot 0.3\text{DMSO}$ (**2**) (Fig. 3 top, see ESI^w).

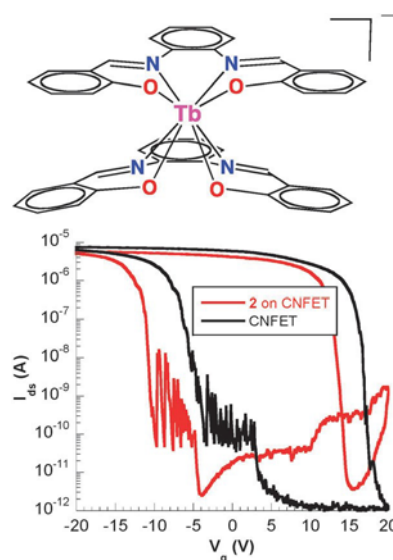


Fig. 3 A schematic view of the structure of **2** (top) and I_{ds} vs. V_g characteristics for a CNFET device before (black curve) and after (red curve) the assembly of **2**, the bias is 2 V (bottom).

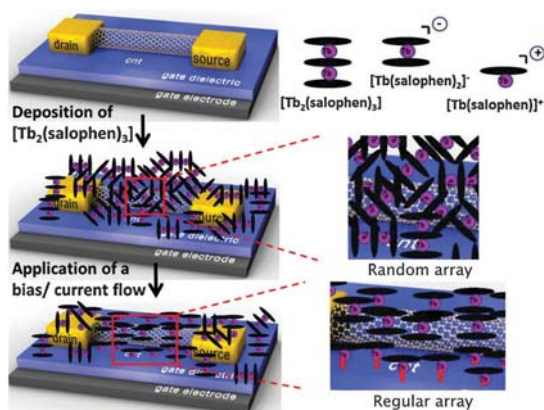


Fig. 4 A scheme of the global mechanism occurring during the deposition of the $[\text{Tb}_2(\text{salophen})_2]$ complex and the application of a bias. The bonds between the $[\text{Tb}(\text{salophen})]^+$ complexes and the SiO_2 surface are symbolized by red bold lines: Tb–O.

The crystal structure of a similar complex ($\text{Ce}(\text{salophen})_2$) has already been reported.¹⁴

In order to study the characteristics of **2** when assembled on the CNFET device, the same experiment as for **1** was carried out. Complex **2** behaves exactly as **1** after the third cycle in the first experiment. The width of the hysteresis loop is conserved, V_{th} shifts to a negative gate voltage value ($\Delta V = -6.6$ V) in comparison to the bare device and more importantly the same weak ambipolar character appears (Fig. 3). All of these characteristics are direct evidence that the molecular species obtained after the third cycle in the first experiment is indeed complex **2** (compare the blue curve of Fig. 2 to the red one of Fig. 3). We have checked that the addition of the pure $\text{H}_2\text{salophen}$, salophen^{2-} or $\text{Tb}(\text{NO}_3)_3$ on a CNFET device does not lead to the behaviour of complex **2**, which is an indirect confirmation of our hypothesis.

We have demonstrated that the application of a bias together with a negative gate voltage induces enough energy in the vicinity of the nanotube belonging to a field-effect transistor to lead to a structural modification of the rare-earth binuclear complex. This modification is driven by the stabilizing electrostatic interaction between the positively charged nanotube of the FET for negative V_g and the negative complex **2** (Fig. 4, see ESI^w). We prepared the whole series of binuclear complexes with $\text{Dy}(\text{III})$, $\text{Gd}(\text{III})$ and $\text{Ho}(\text{III})$. They all present exactly the same transport characteristics as **1** (Fig. S7, ESI^w), which is direct evidence of the mechanism we propose, where the structure and the molecular architecture of the molecules play the main roles in the observed behaviour. Theoretical studies are needed to get a better insight into the origin of the electron transfer between **2** and the nanotube and particularly on the role of complex **1** that acts as a charge scatter modifying the charge trapping process occurring at the SWNT-dielectric interface.

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Notes and references

z CCDC 883777 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.ac.uk/data>.

y Prior to this experiment, it was checked that pure DCE does not change the characteristics of the device.

Z In order to confirm that the change in the nature of the molecular species occurs at negative gate voltage, we performed the same experiment on a different device by cycling V_g only in the -20 to -8 V interval within a bias of 2 V. We indeed observed that after the first cycle, the I_{ON} value drops and is stabilized at the third cycle (Fig. S6, ESI^w).

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