

## Tuning of metallic vs semiconducting selectivity in the reaction of diazonium with SWNT to enhance CNTFETs performances

*Grégory Schmidt, Salomé Gallon, Stéphane Esnouf,  
Jean-Philippe Bourgoïn and Pascale Chenevier*

*Service de Physique de l'Etat Condensé (CNRS URA 2464)  
CEA Institute Radiation Matter of Saclay  
91191 Gif sur Yvette (France)  
[gregory.schmidt@cea.fr](mailto:gregory.schmidt@cea.fr)*

Nanoelectronics applications of single wall carbon nanotubes are strongly impeded by the fact that synthesized carbon nanotubes (NT) have heterogeneous electronic properties (metallic and semiconducting). It is possible to separate metallic and semiconducting (m- and sc-) NT by a number of methods among which chemical functionalization with diazoniums. Despite the importance of the diazonium coupling route, the mechanism is still mostly unknown and has been the subject of very few studies [1,2]. Indeed, diazonium reactivity has proved rich and complex, which renders the mechanism elucidation difficult. Nevertheless, only a proper mechanistic understanding of the reaction can bring tools to fine tune the reaction, hence allowing the necessary fine balance between functionalization yield and preserved conductivity [3], or an increase in m- vs sc-NT selectivity up to high enough levels for separation purposes.

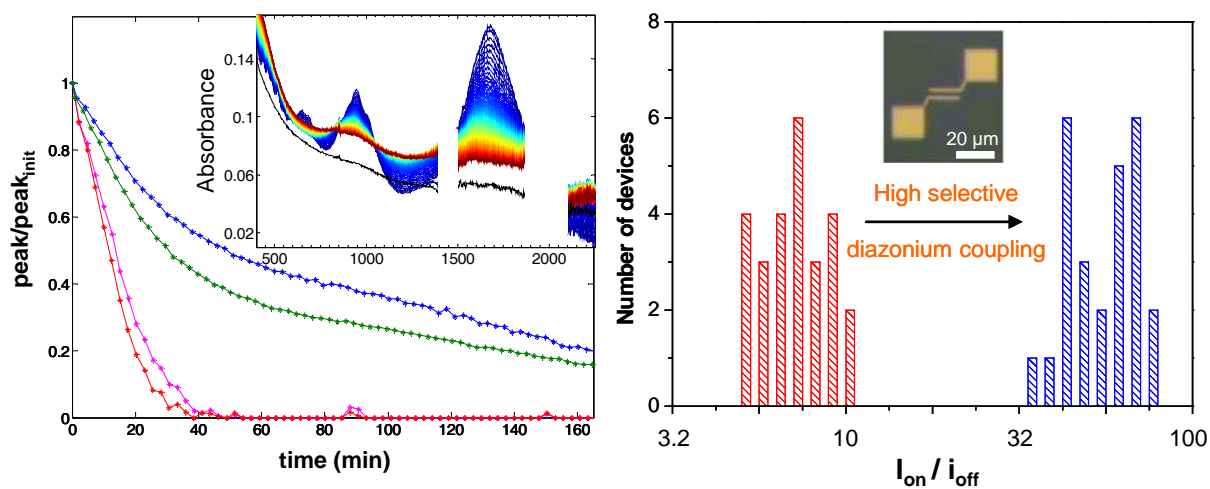
We investigated the mechanism of the reaction [4] using kinetic follow up by spectroscopy and electron spin resonance (ESR). A free radical chain reaction is evidenced without ambiguity. Metallic NT are shown to play an unexpected catalytic role. The step determining the selectivity toward metallic NT is identified by a Hammett correlation. A mechanistic model is proposed that predicts reactivity and selectivity as a function of diazonium electrophilicity and metallic to semiconducting CNT ratio.

Thanks to the detailed understanding of the mechanism, we propose a method to significantly increase the selectivity of diazonium coupling to metallic NT. We increase the selectivity from **4** with the best electrophilic diazonium to **13** with our method [5]. This improved method impacts dramatically the electrical performances of carbon nanotube field effect transistors (CNTFETs). Indeed, the fine tuning of the reaction parameters allows achieving NT transistors with preserved high on state current and high current modulation even for reduced channel lengths.

### References:

- [1] C. A. Dyke, M. P. Stewart, F. Maya, J. M. Tour, *Synlett*. **2004**, 155.
- [2] M. L. Usrey, E. S. Lippmann, M. S. Strano, *J. Am. Chem. Soc.* **2005**, 127, 16129.
- [3] L. An, Q. A. Fu, C. G. Lu, J. Liu, *J. Am. Chem. Soc.* **2004**, 126, 10520.
- [4] G. Schmidt, P. Chenevier, et al. *Chemistry A Eur. J.* **2009**, 15, 2101-2110.
- [5] G. Schmidt, P. Chenevier, French Patent n°0950757, **2009**.

## Figures:



Kinetics (left) of absorption peak decrease (m-NT at 688nm, red, and sc-NT at 940nm, blue) for the reaction of SWNT with Bromo-benzenediazonium (Br-BDT) in aqueous solution. The inset (left) shows absorption peak decrease during the reaction performed with intervals of 1 min. Compared the statistic of modulation on several devices for unreacted and high selective functionalized NT (right).