Dalton
Transactions

COMMUNICATION

Cite this: *Dalton Trans.*, 2014, **43**, 7379

Received 21st November 2013,
Accepted 12th February 2014

DOI: 10.1039/c3dt53291g

www.rsc.org/dalton

Hexahapto-lanthanide interconnects between the conjugated surfaces of single-walled carbon nanotubes

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We report the response of the electrical conductivity of semiconducting single-walled carbon nanotube (SWNT) thin films on exposure to metal vapors of the early lanthanides under high vacuum conditions. We attribute the strongly enhanced conductivities observed on deposition of samarium and europium to charge transfer from the metals to the SWNT backbone, thereby leading to the first examples of mixed covalent–ionic bis-hexahapto bonds [(η^6-SWNT)M(η^6-SWNT), where M = Sm, Eu].

The conjugated carbon allotropes – fullerenes, carbon nanotubes and graphene – exist as continuous arrays of trivalent carbon atoms. There is no simple route to their covalent interconnection which preserves the conjugation; thus the interconnection of benzenoid surfaces is an important problem in the realization of carbon electronics. We have recently introduced the use of organometallic hexahapto covalent bonding of transition metals to graphene surfaces in order to interconnect such delocalized systems without inducing structural rehybridization.[1] This new type of bonding is able to interconnect single-walled carbon nanotubes (SWNTs) and decreases the electrical resistance of thin film networks, particularly on formation of the (η^6-SWNT)Cr(η^6-SWNT) bond. While such bonds are expected to be covalent, the use of the highly electropositive lanthanides offers the possibility of hexahapto bonding combined with ionic character. In the present manuscript we report the electrical response of semiconducting (SC-) SWNT films on exposure to metal vapors of the early lanthanides (Ln) under high vacuum conditions and we show that there is a strong increase in the conductivity associated with all metals but only samarium (Sm) and europium (Eu) exceed the previously determined values of the first row transition metals. We suggest that the enhanced conductivities shown by Sm and Eu is due to charge transfer from metal to the SWNT backbone, thereby leading to the first examples of a mixed covalent–ionic bis-hexahapto bond.

The metal vapor synthesis (MVS) technique[2] has proved to be an extremely versatile method for the preparation of neutral organometallic complexes.[3,4] The use of the electron-gun furnace (or e-beam),[5,6] greatly expanded the range of evaporable metals and allowed the isolation of the first zerovalent bis-hexahapto-arene–lanthanide complexes [Ln(η^6-arene)$_2$].[7,8] We have shown that e-beam evaporation of very small amounts of transition metals on thin films of SWNTs under high vacuum conditions significantly enhances their conductivity.[1,9,10] It is well known that the nanotube junctions are the principle source of electrical resistance in such networks,[11–13] and given the known mobility of transition metals on graphitic surfaces and the geometric and electronic requirements for bis-hexahapto bond formation it is apparent that these nanotube complexes [M[(η^6-SWNT)$_2$, where M = transition metal] form spontaneously at the network junctions[1] in analogy with the low temperature reactions observed in the MVS experiments.[2–6]

An interesting outcome of the carbon nanotube studies is the finding that chromium gives rise to the highest conductivities,[9] in apparent validation of the 18 electron rule of organometallic chemistry.[14] We had expected that bis-hexahapto-metal bonds, which deviate from the 18 electron rule, might be associated with enhanced conductivities due to the accessibility of electronic configurations involving charge transfer, but in the cases examined to date there is no evidence for this type of bonding.[1,9,10] In the present Communication we explore the behavior of the early lanthanides and we report results suggesting that selected members of this series are able to access mixed covalent-ionic bonding when allowed to interact with the graphene surfaces of SWNTs under high vacuum conditions.

The metal deposition experiments were performed on 8 nm thick films of semiconducting (SC-) SWNTs. Films were prepared on an alumina membrane disk by vacuum filtration and

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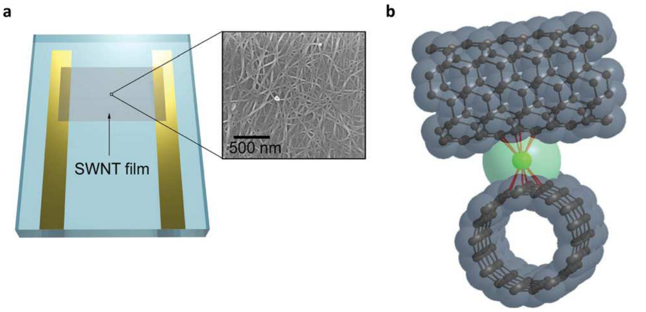

Fig. 1 Network of single-walled carbon nanotubes (SWNTs) and the bonding of a lanthanide atom at a SWNT junction. (a) SWNT film mounted on gold contacts for e-beam deposition of lanthanides; inset shows an SEM image of SWNT film. (b) Schematic of two SWNTs bridged by a lanthanide atom.

sliced into 4 mm × 2 mm rectangles, which were mounted on substrates with gold contacts *via* silver paste (Fig. 1).[9] After annealing at 573 K for 3 hours, the substrates were transferred into a cryo-pumped Temescal BJD 1800 e-beam evaporator equipped with custom fittings to allow the measurement of the *in situ* film resistance. The conductivity (σ) of the pristine SC-SWNT films was $\sigma = 2$ S cm^{-1}.

In each set of experiments the metal was deposited continuously on the carbon nanotube films until a thickness of 2 nm was obtained.[9,15] It is important to note that the deposition of 2 nm of lanthanide metals on a blank channel without a SWNT film did not result in a measurable resistance ($R > 100$ Mohm), thereby indicating that this amount of deposited metal is not sufficient to form a continuous conducting metal film.

Fig. 2 displays the conductivity of SC-SWNT films during atomic vapor deposition of lanthanum (La), neodymium (Nd), samarium (Sm), europium (Eu), and gadolinium (Gd) and it is apparent that all of the metals elicit a strong response in the film conductivities. The first point of interest is the stability of the bis-hexahapto-lanthanide complexes: whereas Nd and Gd form isolable complexes with 1,3,5-tri-*t*-butylbenzene (Bz*) of formula [Ln(η^6-Bz*)$_2$],[8,16] the other metal complexes showed the following degradation temperatures: Eu (200 K), Sm (225 K), and La (273 K).[8,16] Similarly, experimental estimates of the mean metal–arene bond enthalpies [*D*(M–arene) for the process M(η^6-arene)$_2$ → M° + 2 arene] indicate values of 32 kcal mol^{-1} (Eu), 37 (Sm), 57 (Nd), 69 (La), and 69 (Gd).[17] Our experiments show that all of the Ln(η^6-SWNT)$_2$ complexes are thermally stable in high vacuum and heating the samples to 400 K did not degrade the materials as evidenced by the electrical conductivities.

Based on a frontier molecular orbital treatment of the electronic structure of graphene at the Dirac point we have suggested that graphene and SWNTs should be excellent ligands for hexa-hapto-transition metal complexes,[1,18] in agreement with the present findings. The previous results obtained on Cr are included in Fig. 2 for comparison and it is apparent that the conductivity enhancements shown by the lanthanides fall into two groups, one of which includes metals that exceed the conductivities shown by the transition metals studied to date.[9,10] The rapid saturation of the conductivity in the case of Cr is attributed to the kinetically favorable formation of the (η^6-SWNT)Cr(η^6-SWNT) bond.[1,9]

The electronic structure of the Ln(η^6-arene) and Ln(η^6-arene)$_2$ complexes have received detailed experimental and theoretical examination[8,16,17,19–22] and the most widely accepted model for hexa-hapto-lanthanide complexation relies on the generation of the 5d^1 6s^2 electronic configuration at the metal center thereby requiring a consideration of the 4f^n 6s^2→4f^{n-1} 5d^1 6s^2 promotion energy.[8,19,20] In Fig. 3 we have plotted the conductivity enhancements as a function of the 4f^n 6s^2→4f^{n-1} 5d^1 6s^2 transition energies and it may be seen that there is an excellent correlation; thus Sm and Eu require about 2 eV to produce the requisite electronic structure for bis-hexahapto bonding and on this basis we have generated the orbital interaction diagram for Eu and Gd shown in Fig. 4.

There are uncertainties associated with the construction of this orbital correlation diagram but as much as possible we have followed the previous literature regarding the electronic structure of lanthanide complexes,[8,16,17,19–22,25–27] theoretical analyses of organometallic bonding to SWNTs and graphene,[23,24,28] and frontier molecular orbital theory.[1] We have closed the gap between the highest occupied and lowest unoccupied arene molecular orbitals (HOMO and LUMO,

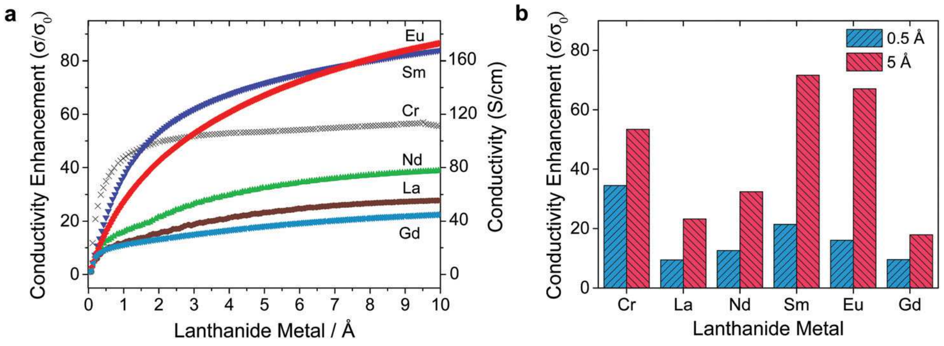

Fig. 2 Effect of lanthanide deposition on the conductivities of SC-SWNT films. (a) Conductivity enhancement of semiconducting single-walled carbon nanotube (SC-SWNT) films of thickness, t = 8 nm, as a function of metal deposition. (b) Conductivity enhancement of SC-SWNT films after the deposition of 0.5 Å and 5 Å of lanthanide metal.

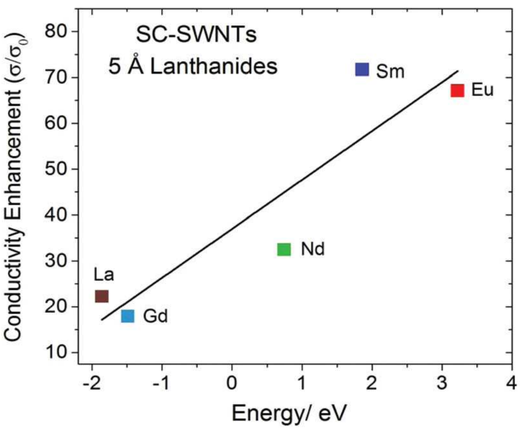

Fig. 3 Enhancement of carbon nanotube conductivity as a function of the $4f^n\ 6s^2 \rightarrow 4f^{n-1}\ 5d^1\ 6s^2$ transition energies of the lanthanides. Conductivity enhancement of SC-SWNT films of 8 nm thickness after deposition of 5 Å La, Gd, Nd, Sm and Eu; the conductivity values are given relative to the initial conductivity (σ_o) of the pristine SC-SWNT film.

respectively) in Fig. 4, in recognition of the small energy gap between the valence and conduction bands of SC-SWNTs,[29] while retaining the usual arene symmetry labels, which are expected to correlate with the symmetries of the SWNT bands at selected points in momentum space.[1]

The orbital energy correlation diagram for gadolinium is standard for the Ln(η^6-benzene)$_2$ complexes;[8,16,17,19–22] in the case of Gd(η^6-benzene)$_2$ there are two low energy metal states: $^9E_{2g}$ ($4f^7 5d^3$ Gd configuration) and $^{11}A_{2g}$ ($4f^7 5d^2 4s^1$ Gd), with $^9E_{2g}$ as the likely ground state.[19,20] The half-filled 4f orbitals remain completely localized on the metal atoms and will not be considered further; thus the bonding is principally dependent on the interaction of the arene π-orbitals and metal 5d orbitals. In the present case the L (ligand)→M (metal) component comprises the a_{1g} SWNT π-orbitals which lie near the bottom of the valence band (VB) and the 5d and 6s metal orbitals of the same symmetry, but the more important contribution originates from the e_{1g} interaction between the metal d_{XZ}, d_{YZ} orbitals and the SWNT π-orbitals which lie near the top of the VB and are well positioned to interact strongly with the metal.[1,10]

The reverse electron donation involving the M→L interaction is at least as important as the L→M component of the bonding,[8,16,17,19–22] and in the present case takes on particular significance.

The low lying conduction band (CB) of the SWNTs suggests that the electropositive nature of the lanthanides will allow the $5d_{XY}$, $5d_{X^2-Y^2}$ orbitals to make a very strong donation of electron density into the e_{2g} orbitals near the bottom of the CB of the SWNTs. We further suggest that in case of Eu and Sm, because of the high promotion energy associated with the valence $5d^1\ 6s^2$ configuration of the metal, the 5d orbitals will be moved up in energy to the point that electrons are released into the CB of the SC-SWNTs. This electronic structure rationalizes the large conductivity difference between Gd and Eu and the fact that the conductivities of Eu and Sm exceed those of all other lanthanides and transition metals examined to date. Given the tendency of the electropositive lanthanides to form the trivalent and divalent oxidation states[30–33] it is reasonable to assume that ionic bonding should be relevant in members of this series.

The stability of the Ln(η^6-SWNT)$_2$ complexes establishes the graphitic surfaces of the SWNTs as excellent ligands in bis-hexahapto coordination compounds and the conductivity of

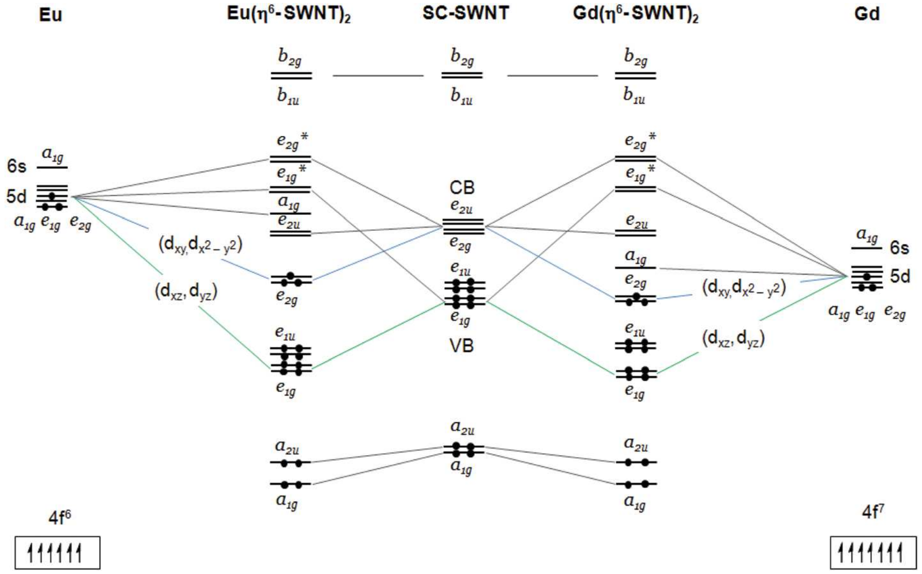

Fig. 4 Orbital correlation diagram for the interaction of the semiconducting single-walled carbon nanotube (SC-SWNT) ligands with gadolinium (Gd) and europium (Eu). The schematic diagram includes those orbitals which are germane to the present discussion; complete, quantitative treatments of orbital energy levels of the M(η^6-arene)$_2$ complexes, where M = transition metal and lanthanide and arene = benzene, SWNT, and graphene fragment are available in the literature.[17,20–24]

the M(η^6-arene)$_2$ bond highlights the ability of this linkage to seamlessly interconnect the conjugated surface of SWNTs and graphene to extend their dimensionality. The strongly enhanced conductivity of Sm(η^6-SWNT)$_2$ and Eu(η^6-SWNT)$_2$ supports the idea that these complexes exhibit the first instances of mixed covalent-ionic bonding in bis-hexahapto-metal complexes.

Acknowledgements

This work was supported by NSF under contract DMR-1305724. The carbon nanotube film preparation was sponsored by the Defense Microelectronics Activity (DMEA) under agreement number H94003-10-2-1003. M.L.M. acknowledges support through the U.S. Department of Education GAANN award P200A120170.

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