

Effect of solvent and dispersant on the bundle dissociation of single-walled carbon nanotube

Silvia Giordani*, Shane D. Bergin, Anna Drury, Éimhín Ní Mhuircheartaigh, Manuel Ruther, Jonathan N. Coleman and Werner J. Blau

- School of Physics, Trinity College Dublin, Dublin 2, Ireland

ABSTRACT

Single-wall carbon nanotubes (SWCNT) are severely restricted in their applications, as they exist in rope-like bundles. Recently, J. Coleman et al. demonstrated a spectroscopic method to monitor bundle dissociation in low concentration NT-polymer composites.¹ The method relies on the measurement of the ratio of free-polymer to the nanotube-bound polymer in the SWCNT-polymer solutions via luminescent spectroscopy. A theory has been developed to transform this data into the bundle surface area, which is of course related to the bundle size. This method clearly shows that individual, isolated SWCNT are stable in low concentration dispersions.

The main aim of this work is to better understanding of the physics behind polymer – SWCNT interactions, the binding scheme, and the magnitude of the polymer – SWCNT binding energy. In an effort to broaden the understanding of the physical processes governing the NT de-bundling a wide range of suitable polymers and short-chain molecules have been examined. We found a strong dependence of the concentration at which individual NTs become stable with the nature of the dispersant molecule.

Keywords: Single-wall carbon nanotubes, polymers, fluorescence, microscopy, dispersion, de-bundling.

1. INTRODUCTION

Single-walled carbon nanotubes (SWCNT) have generated much interest in recent years due to their unique properties and huge potential for applications¹. However, some fundamental problems remain to be addressed. Not least is the fact that SWNT are almost always present in the form of bundles. These bundles can be quite large with diameters of 10-200 nanometers. It would be advantageous to have access to samples of dispersed individual nanotubes or, at the very least, to have some control over the bundle size. This is the case not only for fundamental studies where individual SWCNT are essential but for more applied studies such as composite research where uniform dispersions are required. While it is possible to obtain individual nanotubes by dispersion of SWCNT in surfactants followed by ultra-centrifugation, this is a very inefficient method with more than 99% of SWCNT being lost from the dispersion².

Several approaches have been reported to disperse CNT bundles via amide solvents^{3,4,5}, surfactants⁶, polymers^{7,8}, strong acids⁹, and surface functionalisation¹⁰.

In this work we focus on the dispersing effects of different polymers and short chain analogues along with different solvents. Using the simple model based on adsorption/desorption equilibrium developed in-house, by Coleman et al¹, we can calculate the concentration at which individual SWNT are observed for each system. Also, by studying the interactions of SWCNTs with a wide variety of dispersants, we aim to garner a solid understanding of the interactions involved in non-covalent functionalisation of SWCNTs, as well as the de-bundling process of the SWCNTs.

2. EXPERIMENTAL PROCEDURES

2.1. Sample preparation

The purified nanotubes used in this work were prepared by the Hipco process¹¹, supplied by Carbon Nanotechnologies Inc and used without further treatment. The solvents were purchased from commercial sources. The polymers used were poly[*m*-phenylenevinylene-co-(1,5-dioctyloxy-2,6-naphthylene vinylene)] (12 units average, $M_w/M_n \sim 4$), (PmNV) and poly[*m*-phenylenevinylene-co-(2,5-dioctoxy-*p*-phenylenevinylene)] (19 units average, $M_w/M_n \sim 5$), (PmPV). The shorter molecules were analogues, based on the repeat units of the polymers, and they were 2,5-dioctyloxy-1,4-dinaphthylvinylbenzene (pDNB), and 2,5-dioctyloxy-1,4-distyrylbenzene (pDSB). They were synthesised in house¹² and their molecular structures are shown in Figure 1.

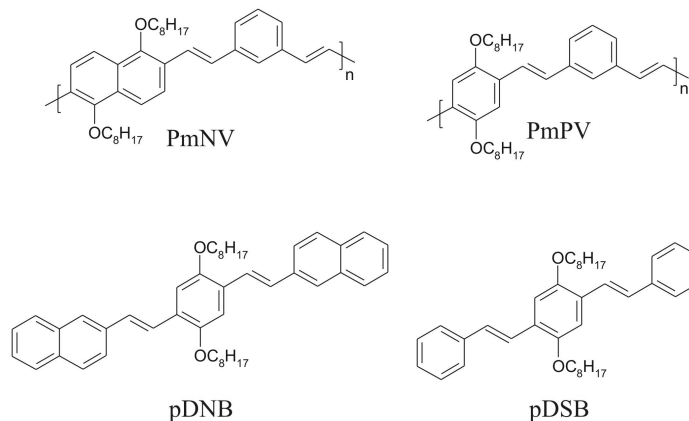


Figure 1. Molecular structures of the polymers and short-chained analogues studied.

The dispersive capabilities of each molecule were investigated using the fluorescence-based technique with the solutions being made, in chloroform, according to Coleman's work. A stock solution of each polymer / molecule was made, with concentration of 0.25mg/ml. Similarly, a SWCNT stock solution, 0.25 mg/ml, was made using HiPCO SWCNTs and was subject to 2 mins sonication using a high-power sonic tip (200 Watts at 20%). Two identical solutions of each polymer / molecule, in chloroform, were made. To one solution of each polymer, was added pure HiPCO SWCNTs, such that the polymer-SWCNT mass ratio was 2:1. Each solution was then diluted, serially, on the order of twenty times to give a broad range of CNT concentrations (10^{-2} mg/ml – 10^{-8} mg/ml). Each solution was sonicated for 1 minute using a high power sonic tip and then allowed to stand for 24 hours to come to equilibrium. No sedimentation was observed over this period. It should be noted at this point that unfunctionalised SWNT such as those used here cannot be effectively dispersed in Chloroform. Mixing of SWNT and chloroform in the absence of polymer / molecule results in the aggregation and sedimentation of the nanotube material within minutes.

Three main factors governed the choice of molecules and polymers to be examined. Firstly, the molecule / polymer had to be strongly fluorescent so it could be clearly detected at the lower end of the concentration range. Secondly, it had to display minimal self-aggregation, i.e. its maximum emission peak remained at the same wavelength across the concentration range. Finally, it had to disperse SWCNTs in an organic solvent.

The absorbance spectrum of each polymer / molecule was recorded using a UV-Vis spectrometer and the emission of each solution was recorded using LS-55 Perkin Elmer luminescence spectrometer.

2.2. Spectroscopic Technique

Recently, J. Coleman et al.¹ investigated the binding kinetics and SWNT bundle dissociation in low concentration polymer – SWCNT dispersions. A new spectroscopic technique was developed to probe the polymer – SWCNT adsorption/desorption kinetics. This method allowed the measurement of the fraction of unbound polymer as a function of concentration, in polymer – SWCNT solutions. This was found to be highly non-linear. A model was constructed based on adsorption/desorption equilibrium. This model was capable of computing the binding energy, per molecule, of

the polymer to the SWCNT. It also monitored the surface area of the SWCNT bundles as a function of SWCNT concentration, thus producing solid evidence (confirmed by AFM images) that lowering the concentration of polymer-functionalised SWCNTs, with sonication, leads to individual SWCNTs in solution.

3. RESULTS AND DISCUSSION

3.1. Effect of the dispersant

Photoluminescence (PL) measurements were performed on all molecules and composite solutions. The excitation and emission wavelengths vary with the molecules / polymers investigated and are reported in Table 1 for clarity.

	Excitation Wavelength (nm)	Emission Wavelength (nm)
PmPV	398	454
PpNV	400	470
pDSB	388	445
pDNB	400	460

Table 1. Spectroscopic details of the polymers and short-chained analogues studied.

Figure 2 and 3 show the photoluminescence of PmPV and pDSB in chloroform respectively. Three different concentrations have been selected and the spectra before and after the addition of HiPco SWCNT reported. It should be noted that upon the addition of the SWCNT to both PmPV and pDSB quenching occurred and no shift occurred in the PL spectra.

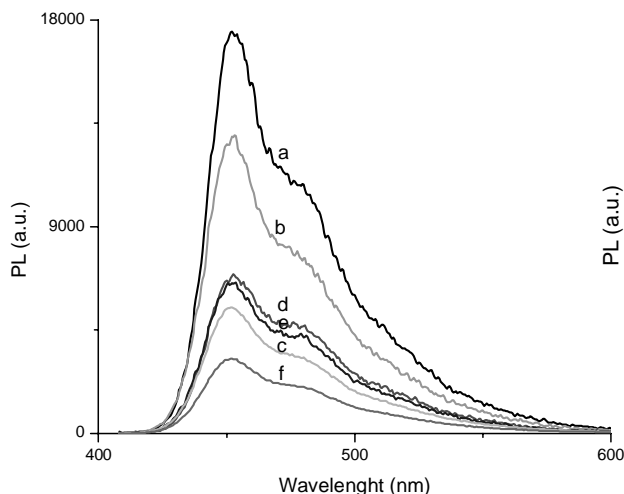


Figure 2. Photoluminescence spectra of PmPV in chloroform before (a, b, c) and after (d, e, f), the addition of SWCNT respectively. (a, d = $1.2 \times 10^{-2} \text{ kg/m}^3$, b, e = $5.3 \times 10^{-3} \text{ kg/m}^3$ and c, f = $2.3 \times 10^{-3} \text{ kg/m}^3$).

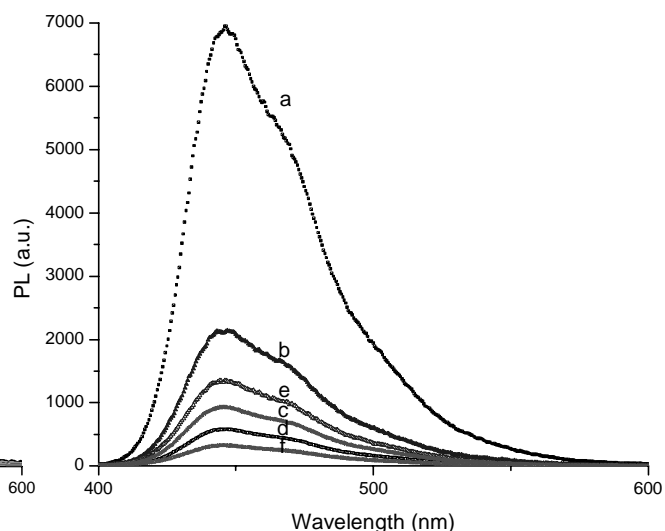


Figure 3. Photoluminescence spectra of pDSB in chloroform before (a, b, c) and after (d, e, f), the addition of SWCNT respectively. (a, d = $3.1 \times 10^{-6} \text{ M}$, b, e = $7.7 \times 10^{-7} \text{ M}$ and c, f = $3.2 \times 10^{-7} \text{ M}$).

For each molecule investigated, for each concentration, the integrated PL was lower in the composite solution compared to the equivalent polymer / molecule solution, as it can be clearly seen in Figures 4 and 5 (for the polymer PmPV and the short molecule pDSB respectively). The PL of both the composite solutions and the polymer / molecule solutions increase with concentration. At high concentration the PmPV molecules aggregate significantly when compared with the pDSB molecules.

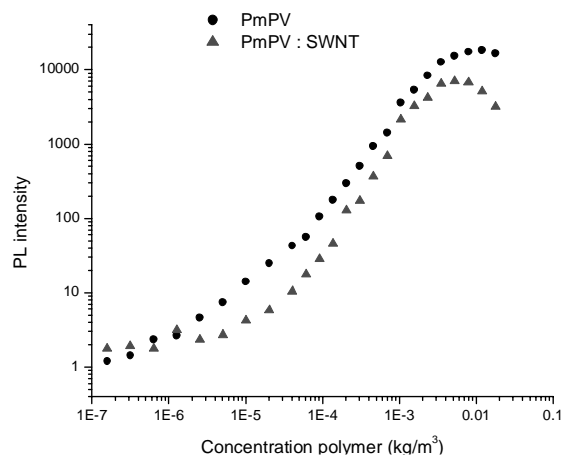


Figure 4. The photoluminescence intensity of PmPV before (circles) and after the addition of HiPCO SWNT (triangles) as a function of concentration.

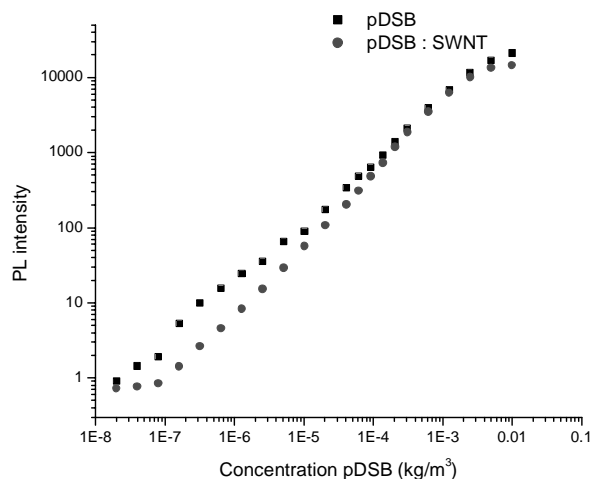


Figure 5. The photoluminescence intensity of pDSB before (squares) and after the addition of HiPco SWNT (circles) as a function of concentration.

As already pointed out by Coleman et al. in the case of the polymer/SWCNT composite solutions, the polymer molecules exist in two forms, free polymer and polymer that is bound to the SWNT. For bound polymer chains, the PL efficiency is expected to be extremely low as any photo-generated singlet excitons preferentially decay non-radiatively through the fast vibrational manifold of the nanotubes¹³. Thus any observed PL from the polymer/SWCNT solutions is due to the free polymer only. (N_F = amount of free polymer). Measuring the PL of the polymer-only solution represented the total amount of polymer present (i.e. N_{Total}). It should be noted that $N_{Total} = N_{Bound} + N_{Free}$. Thus the ratio of PL intensity for a polymer/SWCNT solution to that of a polymer solution of equivalent concentration is a measure of the fraction of free polymer molecules in the composite solution at that concentration.

For all concentrations, the fraction of free polymer was calculated from the intensity ratio. Due to constant polymer adsorption/desorption from the nanotubes, this fraction of free polymer is not expected to be constant over the concentration range studied. Indeed this plot is highly non-linear with respect to concentration, but approaches 1 at very low concentrations indicating that most molecules are unbound at low concentration. The same argument can be extended to the short-chain analogues studied in this work.

Each polymer / molecule examined generated the same kind of non-linear response, but differed slightly. Figure 6 and 7 show the results obtained with the polymer PmPV and the short-analogue pDSB. These graphs, along with the results for PmNV and pDNB were transformed to plot the 'characteristic concentration' versus concentration of SWCNTs, as represented in Figure 8. The characteristic concentration, which describes the physics of the system, is directly proportional to the surface area of the SWCNT bundle, as described by Coleman et al.

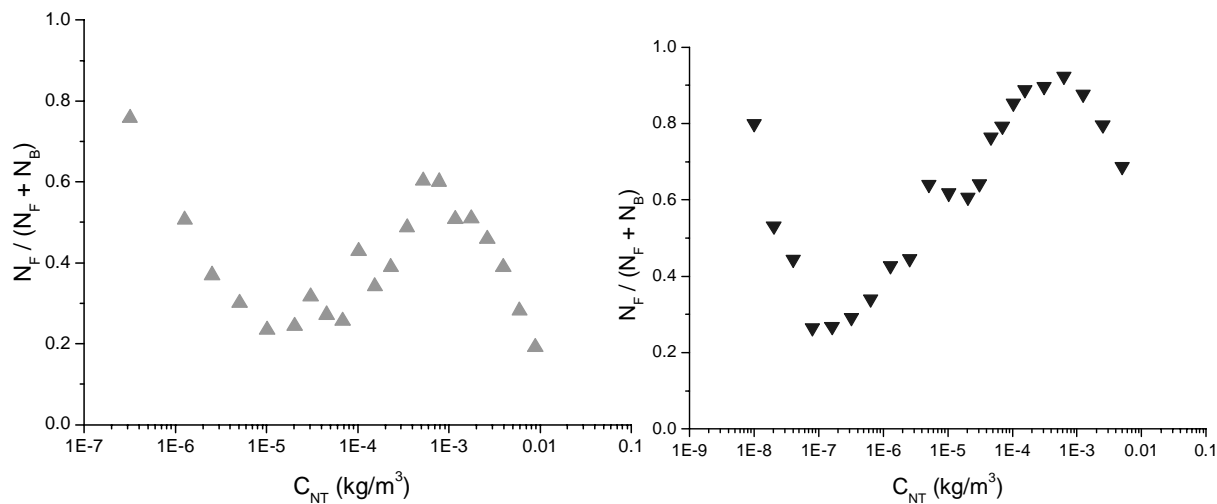


Figure 6. Graph of the fraction of free molecule as a function of SWNT concentration for PmPV.

Figure 7. Graph of the fraction of free molecule as a function of SWNT concentration for pDSB.

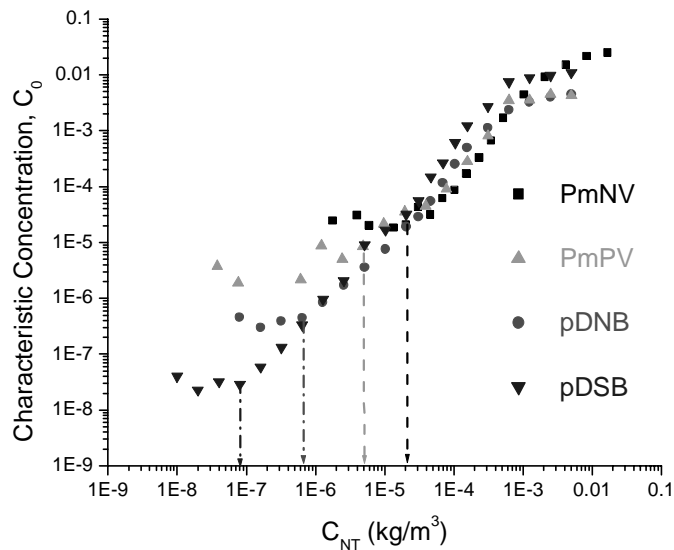


Figure 8. Characteristic Concentration as a function of SWNT concentration for all molecules/polymers

It can be clearly seen that as the SWCNT concentration decreases, the characteristic concentration, and thus the bundle surface area, falls proportionally. This clearly indicates that the bundles are breaking up, until they are stable as individual SWNTs, represented by the plateau. According to this data, individual SWNTs are stable at a much lower composite concentration when using the short-chain analogues, when compared with the longer polymers.

3.2. Effect of the solvents

The different solvents investigated were Chloroform, N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF). The results obtained with the short-analogue pDSB / SWCNT solutions in the different solvents are shown in Figure 9. The solid black lines represent response of an individual-SWCNT system as deduced from Coleman's model, fitted for the results obtained in chloroform and in NMP. In the case of the chlorinated solvent the experimental data deviates from this curve at SWCNT concentrations higher than 1×10^{-7} mg/ml indicating that bundles occur above this limit. In the case of the amide solvents the response does not deviate from the solid curve, indicating that individual SWCNTs or small bundles of SWCNTs are present up to the limit of the experiment.

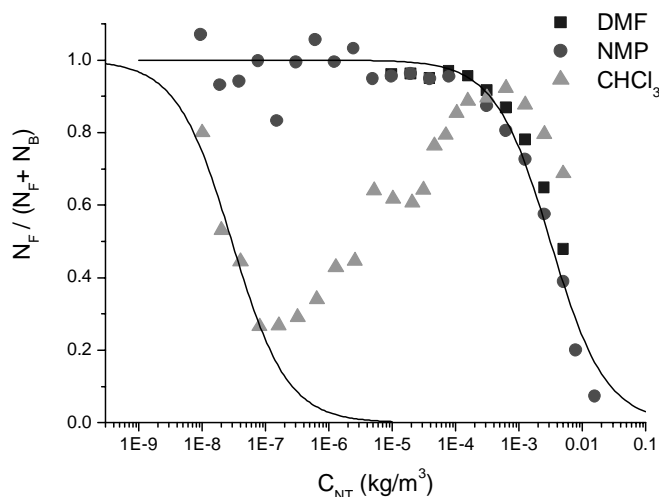


Figure 9. Graph of the fraction of free molecule as a function of SWNT concentration for pDSB in the different solvents.

3.3. Transmission Electron Microscopy

Preliminary TEM results are seen to agree with the spectroscopic results. Low-resolution images of solutions of DSB: HiPco SWNT on holey carbon grid were taken at concentrations of 0.0025 kg/m^3 in NMP and in CHCl_3 (Figure 10). The diameters distributions of the SWCNTs present in both solvents are presented in Figure 11 (CHCl_3 top, NMP bottom). There is a clear shift in the bundle size distribution, to smaller bundles, in the amide solvent versus the chlorinated solvent. The dominant feature is the presence of small SWCNT bundles at relatively high SWCNT concentrations in the case of the amide solvent.

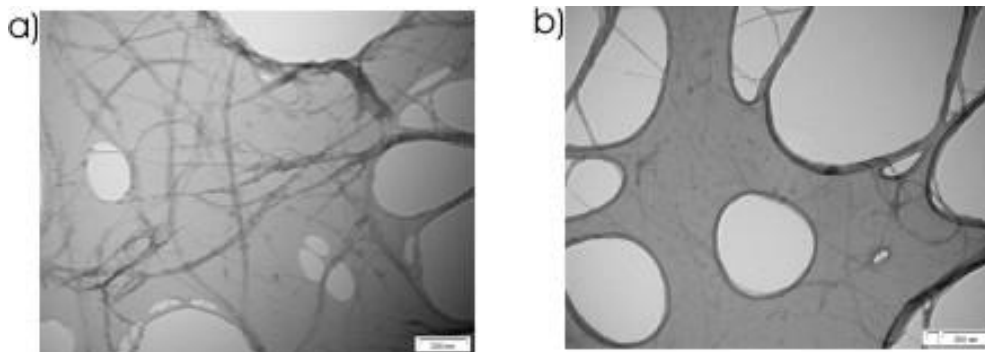


Figure 10. TEM images of pDSB : SWNT in Chloroform (a) and NMP (b).

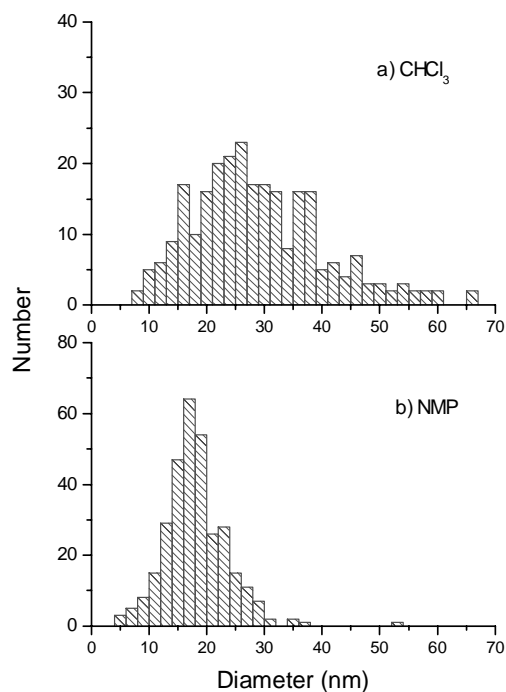


Figure 11. Diameter Distribution in Chloroform (a) and NMP (b).

4. CONCLUSIONS

Stable dispersions of SWCNTs have been obtained and characterised via the use of non-covalent functionalisation with conjugated luminescent polymer and short molecules. Isolated SWNT are stable at low concentrations. The small molecules have been shown to solubilise and de-bundle SWNT in chloroform at lower concentration compared to the polymers. However, using amide solvents, the concentration at which isolated nanotubes are stable was found to increase by about five orders of magnitude.

Quantitative analysis of these dispersions is well under way with initial results comparing well with those reported in the literature. Future work aims to understand the physics of each system, in an effort to optimise the dispersivity of the SWCNTs.

ACKNOWLEDGMENTS

The authors wish to acknowledge financial support from the European Union, the Irish Higher Education Authority, Enterprise Ireland, and Intel.

REFERENCES

1. J.N. Coleman, S. Maier, A. Fleming, S. O'Flaherty, A. Minett, M.S. Ferreira, S. Hutzler, W.J. Blau, *J. Phy. Chem. B.*, 108, 3446, 2004.
2. M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. P. Ma, R. H. Hauge, R. B. Weisman, R. E. Smalley, *Science* **2002**, 297, 593-596.

3. C.A. Furtado, J.A.C.S. **2004**, 126, 6095 – 6105
4. K.D. Ausman, J. Phys. Chem. B, **2000**, 104, No. 38, 8911 – 8915
5. B.J Landi, J. Phys. Chem. B **2004**, 108, 17089 – 17095
6. S.M. Bachilo, Science, **2002**, 298, 2361 – 2366
7. A. Star, Angew. Chem. Int. Ed. **2001**, 40, No.9
8. D.W.Steuerman, J. Phys. Chem B **2002**, 106, 3124 – 3130
9. A. Penicaud, P. Poulin, A. Derre, J.A.C.S. **2005**, 127, 8 – 9
10. A. Koshio, M. Yudasaka, Nano Lett., **2001**, 1 (7), 361 – 363
11. Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, 313, 91.
12. S. Giordani et al. in preparation
13. a) Ago, H.; Shaffer, M. S. P.; Ginger, D. S.; Windle, A. H.; Friend, R. H. *Phys. Rev. B.* **2000**, 61, 2286. b) Wery, J.; Aarab, H.; Lefrant, S.; Faulques, E.; Mulazzi, E.; Perego, R. *Phys. Rev. B.* **2003**, 67, 115202.