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## Selective Interaction of a Water Soluble Naphthalenediimide with Single-Walled Carbon Nanotubes

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A water soluble naphthalenediimide (NDI) selectively interact with small diameter single-walled carbon nanotubes (SWCNTs), as demonstrated by Raman, along with absorption and emission spectroscopies.

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Carbon Nanotubes (CNTs) are amongst the more used nanomaterials of the last decades. They have been applied to different fields, including electronics, solar cells, catalysis and nanomedicine.<sup>1,2</sup> One of the main drawbacks for their use in most applications is the strong tendency to aggregate and the poor solubility in any solvent, organic or aqueous. Chemical functionalization is the best solution to make this material not only easier to manipulate and to handle,<sup>3</sup> but also more biocompatible.<sup>4</sup> However, covalent functionalization may modify the sp<sup>2</sup> character of the carbon framework and consequently can influence their properties.<sup>5,6</sup> Non-covalent approaches take advantage of supramolecular interactions, where the adsorption of organic and inorganic molecules on the surface of CNTs lead to stable suspensions.<sup>7</sup>

The possibility to recognize and sort selected types of CNTs is of prominent interest, since the electronic and optical properties strongly depend on their structural parameters (diameter and helicity).<sup>8</sup> As a consequence, a structural control of SWCNTs is required for their use, especially in electronic and optical applications. Although several methods for the selective synthesis of specific types of SWCNTs have been devised, there are still problems of size heterogeneity. Therefore, post growth separation approaches, such as density gradient ultracentrifugation,<sup>9</sup> electrophoresis,<sup>10</sup> chromatography<sup>11</sup> and molecule assisted selective extractions<sup>12–14</sup> are currently employed to minimize size dispersion. While the use of n-type semiconductors for selective adsorption on SWCNTs have been successfully reported,<sup>15,16</sup> here we discuss the non-covalent interaction of a water soluble naphthalenediimide derivative (NDII) with SWCNTs. The naphthalenediimides are the smallest n-type semiconductor analogs in the family of rylene.<sup>17</sup> Their shape and rich  $\pi$  system makes them as good candidates for the formation of interesting hybrid materials with SWCNTs. Only a few articles employing NDIs as surfactants for CNTs have been reported.<sup>18,19</sup> In this work, we have used a bis-cationic NDI (Scheme 1), which can interact strongly with the scaffold of SWCNTs. This interaction appears to be selective to some types of SWCNTs, by adsorbing on the smaller diameter nanotubes.

### Methods

NDII with Iodide as counter anion was synthesized as reported previously.<sup>20</sup> The bis-chloride derivative was synthesized by following the procedure that is reported in the Supplementary Material. The hybrid with SWCNTs was prepared by using the following procedure: 3 mg of NDII were solubilized in 5 ml of milliQ H<sub>2</sub>O. 3 mg of HiPco SWCNTs (batch n. HP27-078) were dispersed in 5 ml milliQ H<sub>2</sub>O with the assistance of sonication (30 min). The two solutions were mixed and the resulting suspension was sonicated for further 30 min, followed by magnetic stirring (2 h). The final mixture was filtered and washed several times with H<sub>2</sub>O. The solid was redispersed in D<sub>2</sub>O and



Scheme 1. Structure of NDII.

centrifuged at 1000 rpm for 1 h. A fraction (70%) of the supernatant solution was collected and directly used for the absorption and emission measurements. A fraction of the solution was deposited by spin coating on SiO<sub>2</sub> surface for Raman spectroscopy characterization.

### Results and Discussion

The first aim of this investigation was to focus on the solubilization of SWCNTs using NDII as a surfactant. As clear from Scheme 1, NDII comprises two functional parts: the aromatic core, which is the main part for the interaction with the sp<sup>2</sup> system of CNTs; and two cationic groups, to establish water solubility. In the absorption spectrum of NDII, well resolved maxima at 360 and 380 nm, with shoulders at 233 and 340 nm with extinction coefficient 15530 M<sup>-1</sup>cm<sup>-1</sup> (maximum at 380 nm) are clearly discernible (Figure 1). In the emission spectrum, two peaks are present at 393 nm and 411 nm upon excitation at 380 nm with low quantum yield of around 3% [quinine sulfate in 0.10 M H<sub>2</sub>SO<sub>4</sub> (literature quantum yield 0.54 at

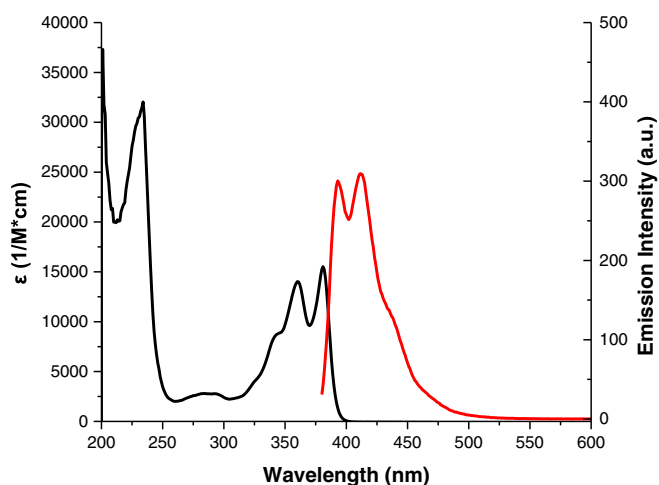
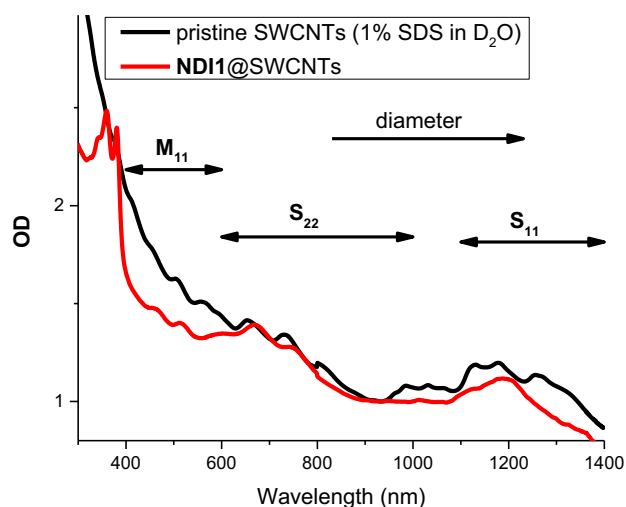


Figure 1. Absorption spectrum (black) and emission spectrum (red) of NDII (0.6 mM) in D<sub>2</sub>O upon 380 nm excitation.

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**Figure 2.** UV/Vis/nIR spectrum of **NDII**@SWCNTs in D<sub>2</sub>O, along with the spectrum of the pristine SWCNTs in 1% SDS in D<sub>2</sub>O.

360 nm) as the standard]. Notably, once **NDII** is combined with SWCNTs, no shift at absorption/emission bands are noticed, but the fluorescence of **NDII** is enhanced as a result of the interactions with the scaffold of SWCNTs (Supplementary Material, Figure S3-S4). This effect is not common for the interaction of molecular chromophores with carbon nanotubes, though some examples exist in which the reason for this enhancement is the aggregation induced emission.<sup>21-24</sup> Nevertheless, this particularly interesting point needs to be studied more in depth for full comprehension.

The UV/Vis/nIR spectra of **NDII**@SWCNTs were recorded in homogeneous conditions and show the successful interaction of **NDII** with the nanotubes (Figure 4). For comparison, pristine SWCNTs were dispersed in D<sub>2</sub>O with the assist of 1% sodium dodecyl sulfate (SDS). This spectrum displays the absorption features of the transitions between the van Hove singularities in the density of states (DOS) of metallic (M) and semiconducting (S) nanotubes. In addition, the three regions are characteristic for the SWCNTs: M<sub>11</sub> transitions at wavelengths 300–600 nm, S<sub>22</sub> transitions, between 600 and 1000 nm and S<sub>11</sub> transitions, at wavelengths larger than 1000 nm.<sup>25,26</sup>

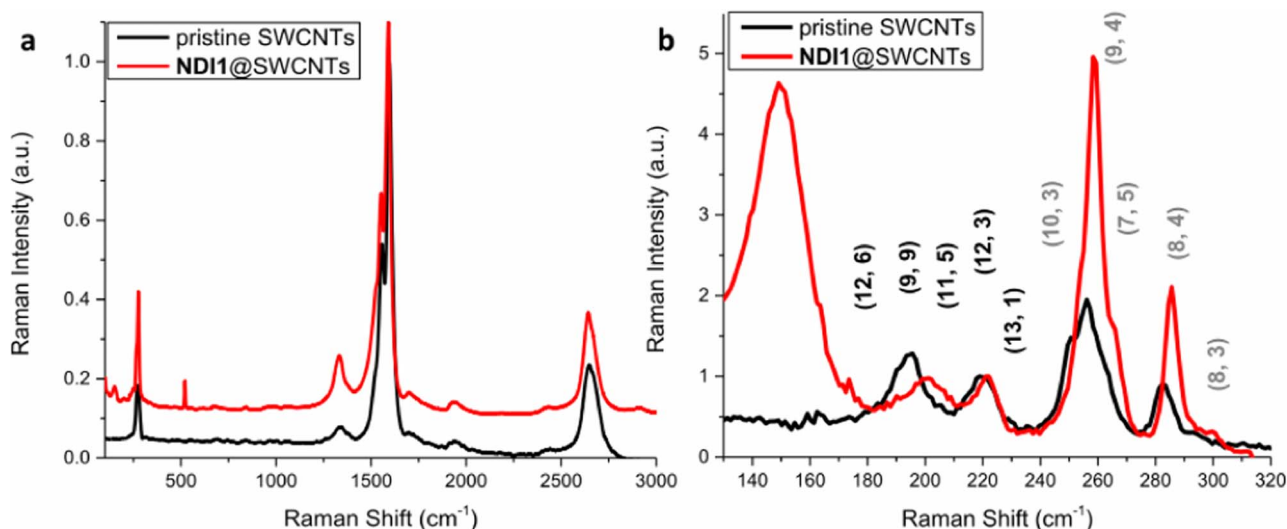
By comparing the **NDII**@SWCNTs spectrum with the one of the two starting materials, the features of both components in the hybrid material are evident. Whereas no considerable shifts take place on

the **NDII** features (Supplementary Material, Figure S5),<sup>18</sup> several changes are evident in the SWCNT part. In the near infrared region, the intensity of the features is relatively lower, while some of these bands have disappeared (Figure 2).<sup>27</sup> On the other hand, we notice an enhancement of the peaks at 748, 670, 512 and 463 nm. This is a piece of evidence that **NDII** interacts with SWCNTs, but not with all the tubes. Based on literature data, this result is an evidence of selective interaction with small diameter tubes (Figure 2).<sup>28-31</sup> In addition, the amount of **NDII** that is used is in the range of 0.05 wt% (for the SDS 1 wt% was used). This indicates that **NDII** as a very good dispersant for the SWCNTs. This difference in the amount of surfactant used probably lies in the presence of an extended aromatic core, which enhances the interactions between the **NDII** and the nanotubes and as a consequence increases the dispersibility power.<sup>32</sup>

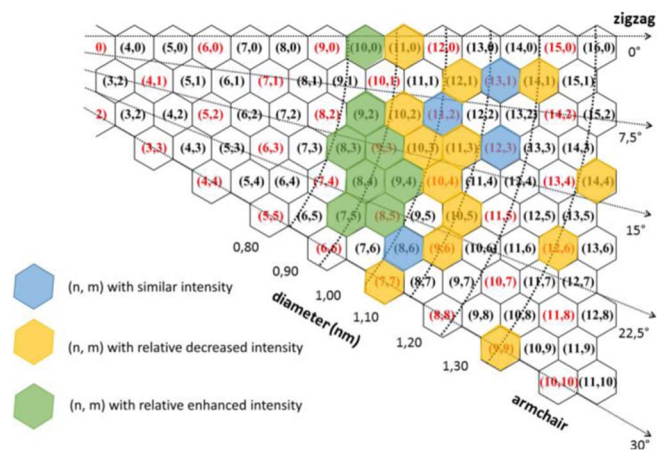
To confirm these initial results, we used Raman spectroscopy, a powerful technique for the characterization of SWCNTs. The suspension of **NDII**@SWCNT was deposited on SiO<sub>2</sub> and the Raman spectrum was recorded at 10 distinct points with three different excitation wavelengths (532 nm, 633 nm and 785 nm).

Some of the peaks correspond to **NDII** (Figure 3a, Figure S6).<sup>33</sup> The RBM region, associated with the debundling, as well as with different diameter and chirality, is characteristic of SWCNTs.<sup>34,35</sup> The RBM regions were normalized to a resonance signal at different wavenumbers, specifically 220 cm<sup>-1</sup> (633 nm excitation, Figure 3b–Figure S11), 185 cm<sup>-1</sup> (532 nm excitation, Figure S7–S8) and 258 cm<sup>-1</sup> (785 nm excitation, Figure S12–S13), at which the effect of change in intensity due to debundling is low. In the case of **NDII**@SWCNTs, the Raman spectra generally shows an increase in the RBM signals intensity in the low-frequency region, where small-diameter chiralities appear (especially around 240–300 cm<sup>-1</sup>).<sup>8,36</sup> In particular, when exciting at 532 nm, the normalized RBM signals shows an even more pronounced intensity enhancement at increasing wavenumbers. In this region the small diameter nanotubes resonate. This increase can be assigned to two different effects: first, the debundling effect, and second, the enrichment in the mixture of the small diameter SWCNTs. In addition, the spectrum recorded at an excitation wavelength of 633 nm (Figure 3b), at which both metallic and semiconducting tubes are revealed, confirms the increased intensities at wavenumbers above 240 cm<sup>-1</sup>, typical of the smaller diameter nanotubes.

The general trend of the **NDII** on SWCNTs is observed in Figure 4, where the above discussion is summarized. Blue and green hexagons represent the signals with constant or increased intensity, while the yellow ones correspond to the ones with decreased intensity. The general trends show an enrichment of diameters below 1.1 nm.



**Figure 3.** a. Raman Spectrum of **NDII**@SWCNTs in comparison with the spectrum from the pristine SWCNTs (excitation wavelength: 532 nm). b. RBM region from the Raman spectra of **NDII**@SWCNTs in comparison with the pristine SWCNTs (excitation wavelength 633 nm).



**Figure 4.** Summary of enrichment based on the Raman measurements for the NDII@SWCNTs.

From the Raman spectra, we can also observe the consequences of the electronic communication between NDII and SWCNTs. This manifests as a shift of the 2D mode from  $2648 \pm 2 \text{ cm}^{-1}$  in the pristine SWCNTs, to  $2641 \pm 2 \text{ cm}^{-1}$  for NDII@SWCNTs (Supplementary Material, Figure S9). This can be due to a partial charge transfer from the electron donating SWCNTs to the electron acceptor NDII.<sup>18</sup>

### Conclusions

In conclusion, we used a cationic, water soluble naphthalenediimide for the solubilization of SWCNTs. The interaction between the two components was characterized by means of Raman and optical spectroscopies. The successful supramolecular interaction leads to a selective dispersion and enrichment of SWCNTs in aqueous solutions, which is characterized by a small diameter distribution. In addition, a strong electron interaction between NDII and the SWCNTs is evidenced. The present work shows the utility of this n-type semiconductor for the construction of new photoelectronic devices.

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### References

1. M. Melchionna, S. Marchesan, M. Prato, and P. Fornasiero, *Catal. Sci. Technol.*, **5**(8), 3859 (2015).

2. A. Bianco, K. Kostarelos, C. D. Partidos, and M. Prato, *Chem. Commun. (Cambridge, United Kingdom)*, (5), 571 (2005).
3. N. Karousis, N. Tagmatarchis, and D. Tasis, *Chem. Rev.*, **110**(9), 5366 (2010).
4. H. Ali-Boucetta, A. Nunes, R. Sainz, M. A. Herrero, B. Tian, M. Prato, A. Bianco, and K. Kostarelos, *Angew. Chem. Int. Ed.*, **52**(8), 2274 (2013).
5. Z. Syrgiannis, M. Melchionna, and M. Prato, in *Encyclopedia of Polymeric Nanomaterials*, S. Kobayashi and K. Müllen, eds., p. 1–8, Springer Berlin, Heidelberg, (2014).
6. Z. Syrgiannis, A. Bonasera, E. Tenori, and M. Prato, *Curr. Org. Chem.*, **20**(6), 632 (2016).
7. C. Backes and A. Hirsch, in *Chemistry of Nanocarbons*, p. 1–48, John Wiley & Sons, Ltd, (2010).
8. H. Katura, Y. Kumazawa, Y. Maniwa, I. Umezumi, S. Suzuki, Y. Ohtsuka, and Y. Achiba, *Synth. Met.*, **103**(1–3), 2555 (1999).
9. M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, and M. C. Hersam, *Nat. Nanot.*, **1**(1), 60 (2006).
10. W. Obitayo, S. Luo, Z. Xiao, T. Liu, and J. Guan, *RSC Advances*, **4**(70), 37070 (2014).
11. B. S. Flavel, K. E. Moore, M. Pfohl, M. M. Kappes, and F. Hennrich, *ACS Nano*, **8**(2), 1817 (2014).
12. A. F. M. M. Rahman, F. Wang, K. Matsuda, T. Kimura, and N. Komatsu, *Chem. Sci.*, **2**(5), 862 (2011).
13. M. Tange, T. Okazaki, and S. Iijima, *J. Am. Chem. Soc.*, **133**(31), 11908 (2011).
14. F. Tshimitsu and N. Nakashima, *Nat. Commun.*, **5** (2014).
15. C. Ehli, C. Oelsner, D. M. Guldi, A. Mateo-Alonso, M. Prato, C. Schmidt, C. Backes, F. Hauke, and A. Hirsch, *Nat. Chem.*, **1**(3), 243 (2009).
16. A. Mateo-Alonso, C. Ehli, K. H. Chen, D. M. Guldi, and M. Prato, *J. Phys. Chem. A*, **111**(49), 12669 (2007).
17. F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, and D. Schmidt, *Chem. Rev.*, **116**(3), 962 (2016).
18. K. Dirian, S. Backes, C. Backes, V. Strauss, F. Rodler, F. Hauke, A. Hirsch, and D. M. Guldi, *Chem. Sci.*, **6**(12), 6886 (2015).
19. Z. Hu, G. D. Pantoş, N. Kuganathan, R. L. Arrowsmith, R. M. J. Jacobs, G. Kociok-Köhn, J. O'Byrne, K. Jurkschat, P. Burgos, R. M. Tyrrell, S. W. Botchway, J. K. M. Sanders, and S. I. Pascu, *Adv. Funct. Mater.*, **22**(3), 503 (2012).
20. L. Chen, Y.-M. Zhang, L.-H. Wang, and Y. Liu, *J. Org. Chem.*, **78**(11), 5357 (2013).
21. W. Z. Yuan, H. Zhao, X. Y. Shen, F. Mahtab, J. W. Y. Lam, J. Z. Sun, and B. Z. Tang, *Macromolecules*, **42**(24), 9400 (2009).
22. X. Zhang, Z. Chi, H. Li, B. Xu, X. Li, W. Zhou, S. Liu, Y. Zhang, and J. Xu, *Chem. Asian J.*, **6**(3), 808 (2011).
23. J. Liu, Y. Zhong, J. W. Y. Lam, P. Lu, Y. Hong, Y. Yu, Y. Yue, M. Faisal, H. H. Y. Sung, I. D. Williams, K. S. Wong, and B. Z. Tang, *Macromolecules*, **43**(11), 4921 (2010).
24. S.-Y. Ju, W. P. Kopcha, and F. Papadimitrakopoulos, *Science*, **323**(5919), 1319 (2009).
25. J. G. Duque, C. G. Densmore, and S. K. Doorn, *J. Am. Chem. Soc.*, **132**(45), 16165 (2010).
26. N. K. Subbaiyan, S. Cambré, A. N. G. Parra-Vasquez, E. H. Háröz, S. K. Doorn, and J. G. Duque, *ACS Nano* (2014).
27. D. Wunderlich, F. Hauke, and A. Hirsch, *J. Mater. Chem.*, **18**(13), 1493 (2008).
28. E. H. Haroz, J. G. Duque, X. Tu, M. Zheng, A. R. Hight Walker, R. H. Hauge, S. K. Doorn, and J. Kono, *Nanoscale*, **5**(4), 1411 (2013).
29. R. Haggemueller, S. S. Rahatekar, J. A. Fagan, J. Chun, M. L. Becker, R. R. Naik, T. Krauss, L. Carlson, J. F. Kadla, P. C. Trulove, D. F. Fox, H. C. DeLong, Z. Fang, S. O. Kelley, and J. W. Gilman, *Langmuir*, **24**(9), 5070 (2008).
30. B. Gebhardt, F. Hof, C. Backes, M. Müller, T. Plocke, J. Maultzsch, C. Thomsen, F. Hauke, and A. Hirsch, *J. Am. Chem. Soc.*, **133**(48), 19459 (2011).
31. J.-C. Blancon, M. Paillet, H. N. Tran, X. T. Than, S. A. Guebrou, A. Ayari, A. S. Miguel, N.-M. Phan, A.-A. Zahab, J.-L. Sauvajol, N. D. Fatti, and F. Vallée, *Nat. Commun.*, **4** 2542 (2013).
32. R. M. F. Fernandes, B. Abreu, B. Claro, M. Buzaglo, O. Regev, I. Furó, and E. F. Marques, *Langmuir*, (2015).
33. H. Shinohara, Y. Yamakita, and K. Ohno, *J. Mol. Struct.*, **442**(1), 221 (1998).
34. R. Graupner, *J. Raman Spectrosc.*, **38**(6), 673 (2007).
35. L. M. Ericson and P. E. Pehrsson, *J. Phys. Chem. B*, **109**(43), 20276 (2005).
36. M. S. Strano, *J. Am. Chem. Soc.*, **125**(51), 16148 (2003).