Synthesis, characterization and photophysical properties of a SWNT-phthalocyanine hybrid†

Beatriz Ballesteros,[a] Stéphane Campidelli,[bc] Gema de la Torre,[a] Christian Ehli,[d] Dirk M. Guldi,*[d] Maurizio Prato*[b] and Tomas Torres*[a]

Received (in Cambridge, UK) 23rd February 2007, Accepted 17th April 2007
First published as an Advance Article on the web 10th May 2007
DOI: 10.1039/b702819a

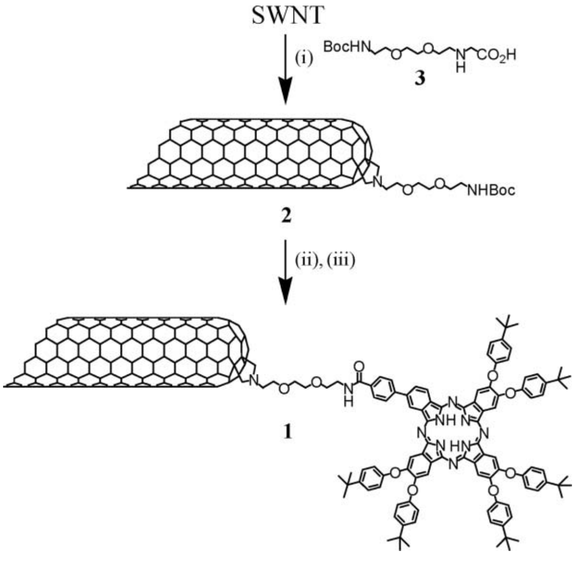
We report the synthesis, characterization and photophysical features of a new nanometer scale carbon nanostructure, that is, a single-wall carbon nanotube bearing phthalocyanine chromophores.

Carbon-based nanomaterials are currently under active investigation for producing innovative materials, composites and electronic devices of greatly reduced size.[1] In particular, single-wall carbon nanotubes (SWNTs) are one-dimensional nanowires that are either metallic or semiconducting. They readily accept charges, which can then be transported under nearly ideal conditions along the tubular SWNT axis.[2] The electrical conductivity, morphology and good chemical stability of SWNTs are promising features that stimulate their integration into electronic devices.

The combination of SWNTs with electron donors such as ferrocene,[3] porphyrins[4] or TTF[5] has been achieved, and has led to new materials giving rise—upon photoexcitation—to intraensemble electron transfer processes. Among the wide variety of electron donor moieties, phthalocyanines (Pcs),[6] which are synthetic porphyrin analogues, exhibit particularly intense absorption characteristics in the red/near-infrared spectral region, where porphyrins fail to absorb appreciably. Pcs have been extensively used as dyes, and more recently have also been integrated as excited electron donors into donor–acceptor systems, in combination with electron accepting fullerenes.[7]

Here, we report the synthesis, characterization and photophysical properties of SWNTs that were decorated with free base phthalocyanines (SWNT-H_2Pc, **1**). Covalent functionalization of carbon nanotubes with Pcs using amido linkages has also been reported by both us and others.[8] However, the resulting materials proved to be nearly insoluble in common organic solvents.

Scheme 1 summarises the synthesis of the SWNT-H_2Pc nanoconjugate (**1**). The functionalised carbon nanotubes **2** were prepared by 1,3-dipolar cycloaddition between amino acid **3**,[9] paraformaldehyde and purified HiPCO SWNTs[10] in DMF. After 5 d, the DMF-soluble material was separated from the reaction mixture by several sonication, centrifugation and filtration processes (see the ESI for experiment details†). The nanotubes were re-suspended in DMF, and removal of the N-*tert*butoxycarbonyl protecting groups (Boc) was achieved by bubbling gaseous HCl through the suspension. The corresponding ammonium chloride salt precipitated during the acid treatment, followed by filtration. Synthesis of **1** involved reaction of the ammonium chloride salt with phthalocyanine **4** in the presence of *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC), 1-hydroxybenzotriazole (HOBt) and ethyldiisopropylamine.



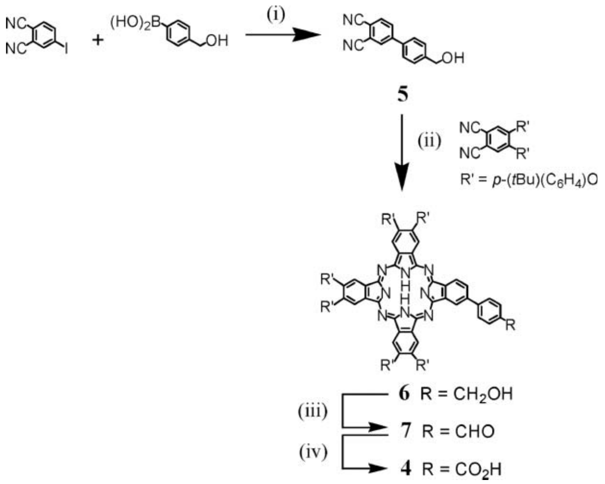
Scheme 1 *Reagents and conditions*: (i) Amino acid **3**, paraformaldehyde, DMF, 120 °C, 5 d; (ii) HCl gas, DMF, rt, 1 h; (iii) H_2Pc **4**, EDC, HOBt, ethyldiisopropylamine, DMF, rt, 5 d.

The carboxyphenyl-substituted phthalocyanine **4**, on the other hand, was synthesized in four steps starting from 4-(hydroxymethyl)phenylphthalonitrile (**5**) (see ESI†) and 4,5-*tert*-butylphenoxyphthalonitrile[11] (Scheme 2). The statistical tetramerization reaction of **5** and 4,5-*tert*-butylphenoxyphthalonitrile in the presence of lithium led to the (hydroxymethyl)phenyl-substituted phthalocyanine **6**. The latter was then oxidised with MnO_2 to yield the formylphenylphthalocyanine **7**. In the final step, phthalocyanine **4** was obtained by the oxidation of **7** using sulfamic acid and sodium chlorite. All Pcs (**4**, **6** and **7**) are new and were fully characterised by UV-vis, ^{1}H NMR and IR spectroscopies,

---

[a] *Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain. E-mail: tomas.torres@uam.es*
[b] *INSTM, Unit of Trieste, Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa, 1, I-34127 Trieste, Italy. E-mail: prato@units.it*
[c] *Laboratoire d'Electronique Moléculaire, Service de Physique de l'Etat Condensé (CNRS URA 2464), CEA Saclay, F-91191 Gif sur Yvette Cedex, France. E-mail: stephane.campidelli@cea.fr*
[d] *Institute of Physical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany. E-mail: guldi@chemie.uni-erlangen.de*

† Electronic supplementary information (ESI) available: Techniques, synthesis and analytical data. See DOI: 10.1039/b702819a



Scheme 2 *Reagents and conditions*: (i) $Pd(PPh_3)_4$, K_2CO_3, THF, H_2O, reflux, 24 h; (ii) Li, 1-pentanol, 150 °C, 18 h; (iii) MnO_2, $CHCl_3$, 60 °C, 5 h; (iv) NH_2SO_3H, $NaClO_2$, THF, H_2O, rt, 3 h.

MALDI-TOF mass spectrometry and elemental analysis (see ESI†).

The nanotube derivatives **1** and **2** were characterized by standard analytical techniques, such as UV-vis-NIR, thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and atomic force microscopy (AFM). The photophysical properties of **2** and reference phthalocyanine **4** have been also investigated by steady-state and time resolved fluorescence, as well as by femtosecond transient absorption.

TGA of compounds **1** and **4** are shown in Fig. S1†. SWNT-H_2Pc nanoconjugate **1** gives rise to a weight loss of about 27% at 600 °C. However, at this temperature, the phthalocyanine is not completely decomposed (see Fig. S1†), with 38% of its original mass still remaining. If we assume a similar behaviour in **1**, we roughly approximate the real amount of functional groups to be around 43%; this would correspond to 1 functional group per 190 carbon atoms.

TEM confirmed the presence of SWNT in our samples. Two representative images of nanoconjugates **1**, shown in Fig. S2†, reveal high aspect ratio objects that appear throughout the scanned regions. The mean length of these objects is typically in the order of several microns, and their diameters range between a few nanometers and several tens of nanometers. **1** has also been investigated by AFM. The samples were prepared by spin coating on a silicon wafer from a DMF solution. The pictures in Fig. 1 reveal the presence of thin bundles of nanotubes, well dispersed on the substrate, and terminated by individual SWNTs. The line profile below the right-hand picture shows the typical height of the objects on the surface, with bundles of nanotubes having diameters ranging from 3 to 20 nm.

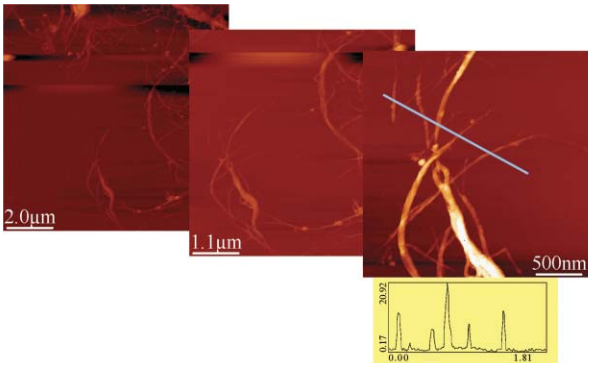


Fig. 1 AFM images of SWNT-H_2Pc nanoconjugate **1** prepared by spin coating on a silicon wafer from a DMF solution.

Next, the SWNT-H_2Pc nanoconjugate **1** was probed in a number of photophysical experiments. In this context, an important test emerges around its absorption characteristics. In particular, the absorption spectra in THF reveal only features that correlate with SWNT, despite the strong absorption cross-sections of H_2Pc in the visible region of the solar spectrum. Extinction coefficients as high as 2×10^5 M^{-1} cm^{-1} are found in the 700 nm region (Fig. 2, top). It is reassuring that, upon photoexcitation at 680 nm, a steady-state fluorescence spectrum evolves that is reminiscent of that seen for H_2Pc (**4**), namely, a fluorescence maximum at 706 nm. This confirms unmistakably the presence of H_2Pc in SWNT-H_2Pc (Fig. 2, bottom). When relating the fluorescence intensity of SWNT-H_2Pc (**1**) to that of H_2Pc (**4**)—with identical ground state absorption at the excitation wavelength—a significant quenching of the fluorescence is derived (~100). An obvious rationale for this trend implies the presence of electroactive SWNT.

Time-resolved fluorescence measurements further confirmed the trend of electronic interactions between photoexcited H_2Pc and SWNT. While a long lived fluorescence—with a lifetime of 4.3 ns—was seen for **4** in the range of the 700 nm fluorescence maximum, in SWNT-H_2Pc, the major component (78%) of fluorescence decay was 57 ps.‡

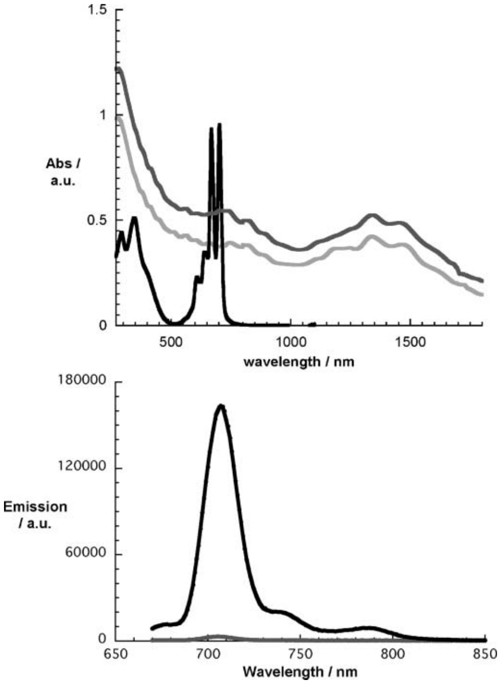


Fig. 2 Top: Absorption spectra of the pristine SWNT (pale grey), SWNT-H_2Pc (**1**) (dark grey) and H_2Pc (**4**) (black). Bottom: Steady-state fluorescence spectra of **1** and **4** in THF at room temperature with matching absorptions at the excitation wavelength (*i.e.*, 680 nm).

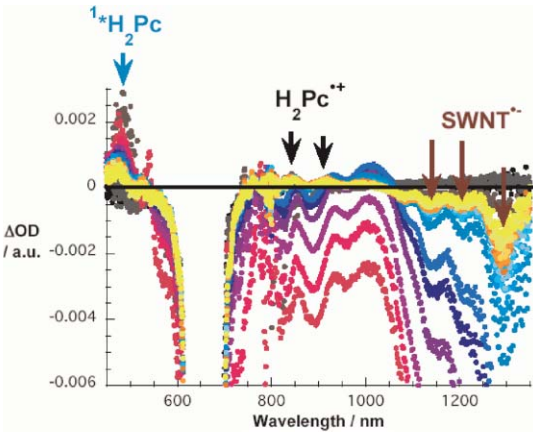


Fig. 3 Differential absorption spectrum (NIR) obtained upon femtosecond flash photolysis (660 nm) of SWNT-H_2Pc (**1**) in nitrogen-saturated THF with time delays between 0 and 50 ps at room temperature.

Decisive insights into the nature of the electronic interactions came from transient absorption measurements, which were performed with H_2Pc (**4**) and SWNT-H_2Pc (**1**) following photoirradiation of the H_2Pc ground state features around 680 nm. In the H_2Pc reference, we saw immediately, with the conclusion of the excitation, the following spectroscopic features: maxima at 485/800 nm and minima around 700 nm. However, the singlet excited state transient was surprisingly stable. In fact, within the time window of our experimental set-up (1.6 ns), it barely showed any decay at all. From the fluorescence lifetime data, we must infer an intersystem crossing to the triplet manifold somewhere around 4 to 5 ns.

When looking at **1**, the transient absorption characteristics that were seen during the initial stage (*i.e.*, up to 1 ps) were identical to those summarized above for **4** (Fig. 3). This observation is critical, since it corroborates the selective formation of the H_2Pc singlet excited state. However, after this initial stage, the spectroscopic and kinetic features differ substantially from **4**, which lack any SWNT. Kinetically, for example, a much faster singlet decay evolves. In fact, 45 ps is a good reflection of the fluorescence lifetime. Spectroscopically, the transients—with maxima at 845 and 920 nm, and minima at 642, 650 and 688 nm—bear no resemblance to any H_2Pc excited state (*i.e.*, singlet or triplet). Particularly important is the maximum at 920 nm, which corresponds to the signature of the one-electron oxidized H_2Pc radical cation.

In the context of radical ion pair formation, we turned to the NIR region, where the most prominent electron transfer changes are known to occur for SWNT. Here, the following features—a maximum at 995 nm, and minima at 1080, 1136, 1204, 1290 and 1395 nm—prompt the reductive charging of SWNT. Important in this context is the blue-shift of the minima relative to their ground state maxima and excited state minima at 1150, 1215, 1315 and 1435 nm. Implicit are new conduction band electrons—injected from photoexcited H_2Pc.[4b,12] Extending the measurements to nanosecond time scales allowed determination of the radical ion pair stability, with a major component of 305 ns.

In conclusion, we have described the synthesis of a new series of free base phthalocyanines and the attachment of one of them to SWNTs. The properties of the SWNT-H_2Pc nanoconjugate **1** have been studied, and we demonstrated that phthalocyanine can interact photophysically with the nanotube side walls.

This work was carried out with partial support from the University of Trieste, MUR (prin prot. 2006034372 and Firb RBNE033KMA), EU (RTN network "WONDERFULL"), SFB 583, DFG (GU 517/4-1), FCI and the Office of Basic Energy Sciences of the U. S. Department of Energy. Funding from MEC (CTQ2005-08933/BQU) and Comunidad de Madrid (S-0505/PPQ/000225) is also acknowledged.

Notes and references

‡ The minor component (22%), on the other hand, had a 4.3 ns lifetime.

1 (*a*) *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, ed. M. S. Dresselhaus, G. Dresselhaus and P. Avouris, Springer-Verlag, Berlin, 2001; (*b*) *Carbon Nanomaterials*, ed. Y. Gogotsi, CRC Press, Boca Raton, FL, 2006; (*c*) *Carbon Nanotechnology: Recent Developments in Chemistry, Physics, Materials Science and Device Applications*, ed. L. Dai, Elsevier Science, Amsterdam, 2006; (*d*) *Carbon Nanotubes—Science and Applications*, ed. M. Meyyapan, CRC Press, Boca Raton, FL, 2005; (*e*) *Carbon Nanotubes: Properties and Applications*, ed. M. J. O'Connell, CRC Press, Boca Raton, FL, 2006.

2 (*a*) A. Javey, J. Guo, Q. Wang, M. Lundstrom and H. Dai, *Nature*, 2003, **424**, 654; (*b*) S. Latil, S. Roche and J.-C. Charlier, *Nano Lett.*, 2005, **5**, 2216.

3 D. M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci, N. Tagmatarchis, D. Tasis, E. Vázquez and M. Prato, *Angew. Chem., Int. Ed.*, 2003, **42**, 4206.

4 (*a*) H. Li, R. B. Martin, B. A. Harruff, R. A. Carino, L. F. Allard and Y.-P. Sun, *Adv. Mater.*, 2004, **16**, 896; (*b*) S. Campidelli, C. Sooambar, E. Lozano-Diz, C. Ehli, D. M. Guldi and M. Prato, *J. Am. Chem. Soc.*, 2006, **128**, 12544; (*c*) Z. Guo, F. Du, D. Ren, Y. Chen, J. Zheng, Z. Liu and J. Tian., *J. Mater. Chem.*, 2006, **16**, 3121.

5 M. A. Herranz, N. Martín, S. Campidelli, M. Prato, G. Brehm and D. M. Guldi, *Angew. Chem., Int. Ed.*, 2006, **45**, 4478.

6 (*a*) G. de la Torre, C. G. Claessens and T. Torres, *Chem. Commun.*, DOI: 10.1039/b614234f; (*b*) *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2003; (*c*) G. de la Torre, P. Vázquez, F. Agulló-López and T. Torres, *Chem. Rev.*, 2004, **104**, 3723; (*d*) Y. Asano, A. Muranaka, A. Fukasawa, T. Hatano, M. Uchiyama and N. Kobayashi, *J. Am. Chem. Soc.*, 2007, **129**, 4516.

7 (*a*) A. Sastre, A. Gouloumis, P. Vázquez, T. Torres, V. Doan, B. J. Schwartz, F. Wudl, L. Echegoyen and J. Rivera, *Org. Lett.*, 1999, **1**, 1807; (*b*) M. E. El-Khouly, O. Ito, P. M. Smith and F. D'Souza, *J. Photochem. Photobiol., C*, 2004, **5**, 79; (*c*) D. M. Guldi, J. Ramey, M. V. Martínez-Díaz, A. de la Escosura, T. Torres, T. Da Ros and M. Prato, *Chem. Commun.*, 2002, 2774; (*d*) D. M. Guldi, A. Gouloumis, P. Vázquez, T. Torres, V. Georgakilas and M. Prato, *J. Am. Chem. Soc.*, 2005, **127**, 5811; (*e*) A. de la Escosura, M. V. Martínez-Díaz, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2006, **128**, 4112; (*f*) B. Ballesteros, G. de la Torre, T. Torres, G. L. Hug, G. M. A. Rahman and D. M. Guldi, *Tetrahedron*, 2006, **62**, 2097; (*g*) T. Fukuda, S. Masuda and N. Kobayashi, *J. Am. Chem. Soc.*, **129**, 5472.

8 (*a*) G. de la Torre, W. Blau and T. Torres, *Nanotechnology*, 2003, **14**, 765; (*b*) Z.-L. Yang, H.-Z. Chen, L. Cao, H.-Y. Li and M. Wang, *Mater. Sci. Eng., B*, 2004, **106**, 73; (*c*) H.-B. Xu, H.-Z. Chen, M.-M. Shi, R. Bai and M. Wang, *Mater. Chem. Phys.*, 2005, **94**, 342.

9 K. Kordatos, T. Da Ros, S. Bosi, E. Vázquez, M. Bergamin, C. Cusan, F. Pellarini, V. Tomberli, B. Baiti, D. Pantarotto, V. Georgakilas, G. Spalluto and M. Prato, *J. Org. Chem.*, 2001, **66**, 4915.

10 E. Vázquez, V. Georgakilas and M. Prato, *Chem. Commun.*, 2002, 2308.

11 S. E. Maree and T. Nyokong, *J. Porphyrins Phthalocyanines*, 2001, **5**, 782.

12 D. M. Guldi, G. M. A. Rahman, C. Ehli and V. Sgobba, *Chem. Soc. Rev.*, 2006, **35**, 471.