Tuning the photophysical properties of soluble single-wall carbon nanotube derivatives by co-functionalization with organic molecules

Fabrizio Cordella[a], Marco De Nardi[b], Enzo Menna[b,], Cécile Hébert[c], Maria Antonietta Loi[a,*]*

[a]*Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[b]*ITM-CNR and Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italy*
[c]*EPFL SB-CIME & IPN-LSME, Bâtiment MXC, Station 12, CH-1015 Lausanne, Switzerland*

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ABSTRACT

The photophysical characterization of three soluble derivatives of single-wall nanotubes (SWCNTs), functionalized with poly(ethylene glycol) (PEG), co-functionalized with PEG and aminofluorene and co-functionalized with PEG and aminoanthracene is reported. The peculiar excellent solubility of these derivatives allows, for the first time in covalently functionalized SWCNTs, the study of their excitation dynamics by monitoring the near-infra-red emission. Moreover, the aminoanthracene derivative shows higher photoluminescence efficiency in the visible range than the aminofluorene derivative, demonstrating the possibility to tune extensively the photophysical properties of these functionalized SWCNTs.

1. Introduction

Single-wall carbon nanotubes (SWCNTs) are very intriguing nano-scale objects that receive great interest in the scientific community for their outstanding mechanical, electronic and optical properties, mostly determined by their one-dimensional character [1,2], and for their potential applications in molecular electronics [3,4], sensing [5,6], optoelectronics [7,8], energy conversion [9–13] and biomedicine [14,15]. Great effort has been dedicated in the past decade to find the proper way to give them good processability and additional optical functionalities [16–20]. In fact either from the technological point of view or for the study of the fundamental physical properties it is crucial to find a procedure to separate them from bundles. For biological applications the functionalization and solubility of SWCNTs is a necessary property not only for an efficient cell up-tacking [14] but also to strongly reduce their cytotoxicity [21]. Moreover, in all applications related to biomedicine it is essential to localize the SWCNTs,

by means of fluorescent markers or by detection of their self-fluorescence, before and during the delivery of the active medicament to the biological target. Among the different approaches presented in the literature to make carbon nanotubes soluble we have recently shown that the co-functionalization of SWCNTs is a feasible way to obtain: (i) solubility up to 5 mg/ml in several organic solvents such as tetrahydrofuran (THF), $CHCl_3$, CH_2Cl_2 and water, by means of covalent functionalization with poly(ethylene glycol)amine (PEG-NH_2), and (ii) light emission in the UV–vis spectral range by co-functionalization with aromatic molecules [22,23]. Furthermore, hybrid systems based on SWCNTs and inorganic nanoparticles [24,25], phthalocyanine [26], porphyrin [27,28] and fullerene [29] have been recently demonstrated. The latter systems, combining the nearly ballistic charge transport properties of SWCNTs and the outstanding optical properties of organic materials are promising for application in optoelectronics, in particular in solar energy conversion. However, while in energy conversion systems an ultra fast electron transfer is

* Corresponding authors: Fax: +31 503638751 (M.A. Loi), +39 0498275660 (E. Menna).
E-mail addresses: Enzo.Menna@unipd.it (E. Menna), M.A.Loi@rug.nl (M.A. Loi).

required, for biomedical applications, where their traceability is required, a not or weakly quenched photoluminescence is necessary.

In this communication, we report on the photophysical characterization of three soluble derivatives of SWCNTs, functionalized with PEG (SWCNT-PEG), co-functionalized with PEG and aminofluorene (SWCNT-AF) and co-functionalized with PEG and aminoanthracene (SWCNT-AA) which show a large tunability of the photophysical properties. We first show that the peculiar excellent solubility of these derivatives, reducing the inter-tube interactions and consequently the nanotubes photoluminescence (PL) quenching allows us to study the SWCNT excitation dynamics by monitoring the near-infra-red (N.I.R.) emission, for the first time measured in covalently functionalized SWCNTs. The N.I.R. emission lifetimes measured in the derivatives are compatible with those of isolated pristine tubes strongly indicating the unaltered physical properties of these compounds. Finally, we study the photophysical properties of the two co-functionalized nanotubes. The aminofluorene derivative systems show a strong quenching of the visible light emission, demonstrating an efficient electron transfer to the nanotubes backbone with a rate constant of about $5 \times 10^{10}\,\mathrm{s}^{-1}$. Conversely, the aminoanthracene derivative shows a much weaker PL quenching, indicating the possibility to tune the functionalized nanotubes properties in order to have either efficient energy conversion systems or good light emission in the visible spectral range. The motivation for the different behavior of the aminofluorene and aminoanthracene functionalized tubes is to be found in the energy levels alignment and in the different orientation of the transition dipole of the two organic molecules respect to the SWCNT.

2. Experimental

The three SWCNTs derivatives were synthesized from HiPco nanotubes through an oxidation–amidation route. In particular, carboxylic groups resulting from acidic oxidation [30] were activated through $SOCl_2$ treatment and then allowed to react with excess of poly(ethylene glycol) monoamine (PEG-NH_2, molecular weight = 5000) in the case of SWCNT-PEG, together with 2-aminofluorene or 2-aminoanthracene in the case of co-functionalized derivatives SWCNT-AF and SWCNT-AA respectively [22]. Only the functionalized soluble fractions of SWCNT derivatives were extracted by means of sonication and centrifugation cycles. On the other hand, the presence of isolated un-functionalized tubes in solution was ruled out through a control experiment consisting of the same synthetic procedure, but omitting the $SOCl_2$ activation. Such test did not yield any soluble product, as checked through both gravimetric and spectroscopic analysis [22].

HR-TEM images were acquired using a CM300-UT operating both at 300 and 200 kV on dried samples dispersed onto holey carbon film.

For the optical measurements SWCNT-PEG, SWCNT-AF and SWCNT-AA were dispersed in THF and, after low power bath sonication for about 15 min, diluted to reach a homogenous solution. The samples were excited at 400 nm or at 370 nm by using the second harmonic of a self mode-locked Ti:Sapphire laser delivering 150 fs pulse train @ 76 MHz repe-

tition rate. Typical excitation power densities were around $30\,\mathrm{W\,cm}^{-2}$ for N.I.R. measurements, and $300\,\mathrm{mW\,cm}^{-2}$ for the study of the exciton recombination dynamics of the organic molecule. The excitation beam was in both experiments roughly 150 μm in diameter. The PL was collected in transmission geometry and spectrally dispersed in an imaging spectrometer. For the UV–vis measurements the spectrometer was coupled with a Hamamatsu synchroscan streak-camera equipped with N5716-03 tube (time resolution around 2ps) and with EM-CCD digital camera (for time integrated spectra). The SWCNTs N.I.R. emission was detected by using a second Hamamatsu synchroscan streak-camera equipped with N5716-02 tube (time resolution around 2 ps) and with an Andor iDus InGaAs detector array (for time integrated spectra).

3. Results and discussion

Fig. 1a shows the schematic representation of SWCNT-PEG and of the two co-functionalization products SWCNT-AF and SWCNT-AA. These three derivatives were synthesized from HiPco SWCNTs through the widely used oxidation–amidation route (see Section 2 for more details). The soluble functionalized SWCNT derivatives were extracted by means of sonication and centrifugation cycles. The presence of isolated un-functionalized tubes in solution was ruled out through a control experiment (see Section 2). As previously published, TGA, Raman and NMR characterization demonstrated the loading of the aromatic molecule in the complex and its covalent attachment [22]. The maintenance of the radial breathing mode (RBM) in the Raman spectra, which is typical of the non-treated SWCNTs, confirms that the functionalization procedure introduces a limited amount of defects in the nano-
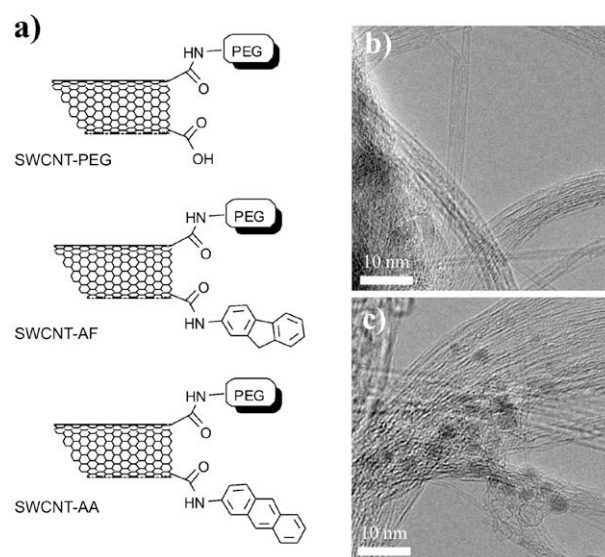

Fig. 1 – (a) Schematic representation of the SWCNTs functionalized with poly(ethylene glycol) (SWCNT-PEG) and co-functionalized with PEG and aminofluorene (SWCNT-AF) and with PEG and aminoanthracene (SWCNT-AA). (b) and (c) HR-TEM images of SWCNT samples after and before the purification treatment, respectively.

tubes structure, and that electronic and physical properties of the SWCNTs are not altered during the whole treatment [22].

Bundles and ropes as well as isolated nanotubes can be found in our dried SWCNTs as can be seen from the images showed in Fig. 1b. The HR-TEM images confirm that the nanotubes have not been damaged by the preparation treatment and that the metallic particles present in the pristine SWCNTs (Fig. 1c) have been successfully removed by the purification procedure, allowing a truthful spectroscopic characterization. It is important to note that HR-TEM of SWCNT-PEG has not been reported because the presence of the PEG molecules strongly degraded the quality of the images.

As already mentioned the functionalization has as most important consequence to make the SWCNTs soluble, i.e., to separate them from the bundles that are spontaneously formed by the pristine SWCNTs due to the extremely strong inter-tube interactions. When the single tubes are isolated, well resolved peaks appear as typical features in the optical absorption and PL spectra [31]. The absorption spectrum of SWCNT-PEG is reported in Fig. 2a, showing several well resolved peaks that indicate the presence of isolated tubes in solution. Another evidence of the separation of the tubes is the N.I.R. emission, that is generally measurable only for samples where isolated tubes are present, due to the very effective exciton quenching in bundles. The nanotubes emission spectrum in the VIS-N.I.R. region (reported in Fig. 2b, only for

SWCNT-PEG) is quite similar for the three derivatives in solution. It shows a broad band centered at around 750 nm and two weaker peaks at around 800 and 1000 nm. The PL in this spectral region is tentatively attributed to the lowest excitonic transition in small diameter semiconducting nanotubes [31,32] excited off-resonance with 400 nm pump laser pulses [33,34].

Fig. 2c displays the PL decay of SWCNT-PEG spectrally integrated between 750 and 850 nm. The emission shows an initial fast decay followed by a much slower component, well described by a bi-exponential fitting function with time constants $\tau_1 = 45$ ps and $\tau_2 = 430$ ps.

Similar decay time constants have been reported in the literature for well dispersed SWCNTs in aqueous solutions [35]. It is worth notice that our experiments allow to study the excitation dynamics in ensemble of nanotubes with different diameters and chiralities. We also found that the PL dynamics depend on the emission spectral range (see Fig. 2c and d) and thus on the nanotube diameter. The characteristic time constants of the PL spectrally integrated between 950 and 1050 nm (Fig. 2d) are $\tau_1 = 5$ ps and $\tau_2 = 60$ ps, that is around 8 times shorter than the emission at 800 nm (Fig. 2c). A similar multi-exponential and diameter-dependent photoluminescence lifetime has been recently reported also in resonantly excited SWCNTs and has been attributed to intrinsic effects, like non-radiative decay toward dark exciton states and/or extrinsic factors such as structural defects, impurities and inter-tube interactions [35].

It is important to observe that Auger-like singlet–singlet annihilation processes can be neglected at the excitation power used in our experiment [36]. The fact that the SWCNTs emission is measurable is a strong indication of the good solubility of the tubes [37,38] and of the low amount of side-wall defects possibly induced during the functionalization procedure. This is indeed the first time that the N.I.R. emission and its dynamics are reported for functionalized SWCNTs.

The PL decays in the near-infra-red of SWCNT-AF and SWCNT-AA are displayed in Fig. 3a and b. The dynamics is longer compared with the one of SWCNTs functionalized only with PEG, measured at the same wavelength (Fig. 2c) and is well described by a bi-exponential fitting function with time constants $\tau_1 = 55$ ps, $\tau_2 = 670$ ps and $\tau_1 = 95$ ps, $\tau_2 = 1200$ ps for the aminofluorene and the aminoanthracene functionalized SWCNTs, respectively. A more delocalized emitting excitonic state could explain this longer decay time in the two co-functionalized derivatives with respect to the PEG-functionalized system. However, the very different decay times of SWCNT-AA and SWCNT-AF could be also be ascribed to a different solubility of the two systems. The nanotubes with an higher degree of dispersion exhibiting a longer decay time. The very similar PL emission spectra for SWCNT-AF and SWCNT-AA in the N.I.R. demonstrate that the electronic properties of carbon nanotubes are not strongly altered by the covalent co-functionalization.

The functionalization with PEG allows making SWCNTs soluble and luminescent in the N.I.R. spectral range, however, also the tagging with visible light emitting molecules is necessary to trace the SWCNTs in biomedical applications. Fig. 4 shows the PL spectrum and decay of SWCNT-AF and the PL dynamics of the pristine chromophore (aminofluorene, AF)
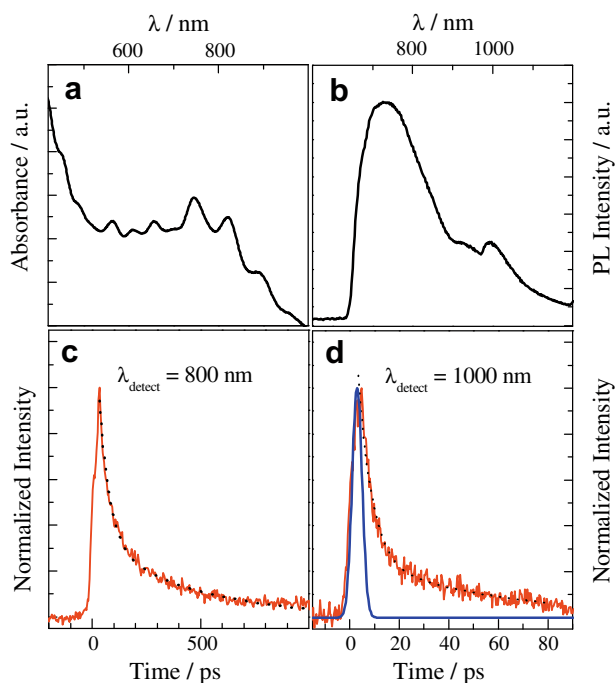

Fig. 2 – (a) Absorption spectrum of SWCNT-PEG solution in THF, (b) time integrated emission spectrum of SWCNT-PEG solution under excitation with 400 nm laser pulses, (c) photoluminescence decay spectrally integrated between 750 and 850 nm, and (d) Photoluminescence decay spectrally integrated between 950 and 1050 nm. The solid black line is the fit to the experimental data using a bi-exponential function. The instrument response is displayed in panel (d) by the blue line.
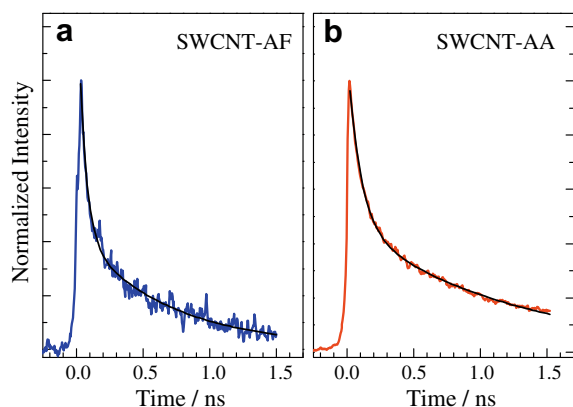
Fig. 3 – (a) Photoluminescence decay of SWCNT-AF and (b) SWCNT-AA spectrally integrated between 750 and 850 nm. The solid black line is the fit to the experimental data.

in solution. The AF PL is strongly quenched (more than 90%) in the SWCNT derivative, as can be seen from the comparison of the PL time decays showed in Fig. 4b. The initial 20 ps decay (see inset in Fig. 4b) is followed by a long-living component with time constant around 2 ns which is very similar to the PL lifetime of pristine AF. The fast PL decay indicates an efficient non-radiative process that competes with the radiative recombination in SWCNT-AF, whereas the long-living component can be attributed to the non interacting molecules present in solution. It is important to underline that the dynamics of the PL is the same for each spectral component.

The observed phenomenology can be well described in terms of photoinduced electron transfer as suggested by other authors [24–28], even if our experimental results do not allow to completely rule out the energy transfer process between the blue emitting organic molecule and the low band gap semiconducting SWCNT.

After absorption of a near-UV laser pulse the exciton population is created in the AF moiety. The excited-state, after fast non-radiative relaxation to the lowest excitonic state, can relax back to the ground state and recombine emitting photons, or alternatively an electron can be transferred from the molecule toward the SWCNT. Because of the large energy level displacement between the two moieties the driving force inducing the electron transfer process is expected to be very strong, as confirmed by the fast PL decay of SWCNT-AF in the visible spectral range. On the other hand, the PL of samples with different SWCNT-AF concentration (not shown here) showed very similar decay times, indicating that other quenching processes, ascribed for instance to aminofluorene aggregation, can be neglected. The rate of charge separation can be estimated from the relation: $k_{CS} = (1/\tau)_{hybrid} - (1/\tau)_{AF}$, where τ_{hybrid} and τ_{AF} are the PL lifetime of the co-functionalized SWCNTs and the pristine AF molecule, respectively. By assuming that the electron transfer is responsible for the initial fast PL decay we found that $k_{CS} \approx 5 \times 10^{10}$ s^{-1}. This high charge separation rate indicates that the intra-complex electron transfer is very efficient in this system compared to similar SWCNTs based materials reported in the literature [29].

While this ultrafast charge transfer could be interesting for photovoltaic and sensing applications, it is however detrimental for tagging and optical localization of the nanotubes within biological entities. A quite different landscape is found when studying the emission properties of the aminoanthracene (AA) derivative.

The PL spectrum of SWCNT-AA in the visible range is reported in Fig. 5a, whereas Fig. 5b shows the PL decay of the complex compared with the emission decay of the pristine
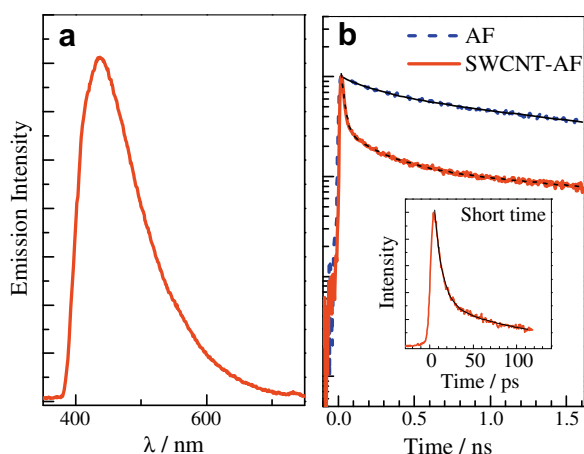

Fig. 4 – (a) Time integrated emission spectrum of SWCNT-AF solution (THF) under 370 nm laser excitation and (b) photoluminescence decay of pristine aminofluorene (AF) molecule (dash blue line) and SWCNT-AF (solid red line) spectrally integrated over the molecule emission region (450 ÷ 550 nm). The inset shows the Photoluminescence decay of SWCNT-AF in the initial 140 ps after excitation. The solid black line is the fit to the experimental data.
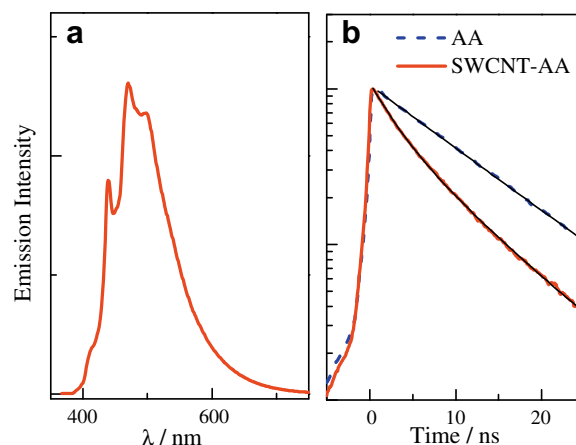

Fig. 5 – (a) Time integrated emission spectrum of SWCNT-AA in solution (THF) under 370 nm laser excitation, (b) photoluminescence decay of pristine AA molecule (dash blue line) and SWCNT-AA (solid red line) spectrally integrated over the molecule emission region (450 ÷ 550 nm). The solid black line is the fit to the experimental data.

AA molecule in solution. The PL decay of the isolated AA molecule is monoexponential with a lifetime about 10.6 ns, while in the SWCNT derivative it shows a bi-exponential behavior with time constants of 2.8 and 9 ns and an average lifetime less than two times smaller ($A_1\tau_1+A_2\tau_2 \sim 6$ ns) with respect to the one of the pristine molecule. Also in this case the spectrum is not changing shape in function of the time. This strong difference in the dynamics of the excitation in the two derivatives can be attributed either to a different energy level displacement between the carbon nanotubes and the two chromophores or to a diverse transition dipole orientation of the two molecules in the complex with respect to the SWCNTs [39,40]. In both cases the final result is to modulate the efficiency of the PL quenching process.

4.   Conclusions

In conclusion, we reported on the photophysics of the excitations in soluble SWCNTs covalently functionalized with PEG and organic chromophores. The excellent solubility provided by the PEG functionalization, reducing the inter-tube interactions and the emission quenching by the metallic tubes, allowed us, for the first time in functionalized nanotubes, to study the exciton recombination dynamics. The simultaneous functionalization with PEG and aminofluorene or aminoanthracene gives a new functionality to these soluble derivatives. The strong PL quenching of the aminofluorene chromophore demonstrated an efficient electron transfer from the organic molecule to SWCNTs taking place in a time scale shorter than 10 ps with a rate constant around 5×10^{10} s^{-1}. At the opposite, the SWCNTs co-functionalized with aminoanthracene show a much weaker PL quenching, demonstrating that aminoanthracene is a good fluorescence marker for biomedical application of SWCNTs. Finally, the electron transfer from organic molecules to nanotubes could be modulated or suppressed by opportune choice of the organic chromophore and possible spacer to be linked to the SWCNT.

Acknowledgements

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