Electronic Supplementary Information

A tailored RAFT copolymer for the dispersion of single walled carbon nanotubes in aqueous media

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Materials and instrumentation

HiPco SWCNTs were purchased from UNIDYM (lot#P2150) and the solvent N,N-dimethylformamide was a Tokyo Chemical Industry product for spectroscopy. Sonication was performed using a bath sonicator Elmasonic S10 H (0.23 W cm^{-2}, 37 kHz).Absorption spectra were recorded with a Perkin-Elmer λ950 spectrophotometer. The luminescence measurements were made in cuvettes with path length of 1 cm. Photoluminescence maps were recorded with an Edinburgh Instruments FLS920 spectrofluorimeter. Samples were excited with a 450 W Xe lamp and the detector was a liquid-nitrogen-cooled germanium detector and preamplifier (Northcoast Scientific Corp. Model EO-817L). A Northcoastmuon filter (Model 829B) was used as an electronic signal filter; the signal was sent to a lock-in amplifier (Standford Research Systems, Inc. Model SR510) to enhance the S-N ratio of the weak NIR emission bands. Centrifugations were performed using an ALLEGRA 64R centrifuge from Beckman Coulter (rotor F1202, fixed rotor angle). AFM imaging was performed using a Nanoscope Multimode 8 (Bruker, Santa Barbara, USA) equipped with a 15 μm piezoelectric scanner. The AFM was operated in tapping mode and in peak-force tapping mode.

Characterization of the polymers

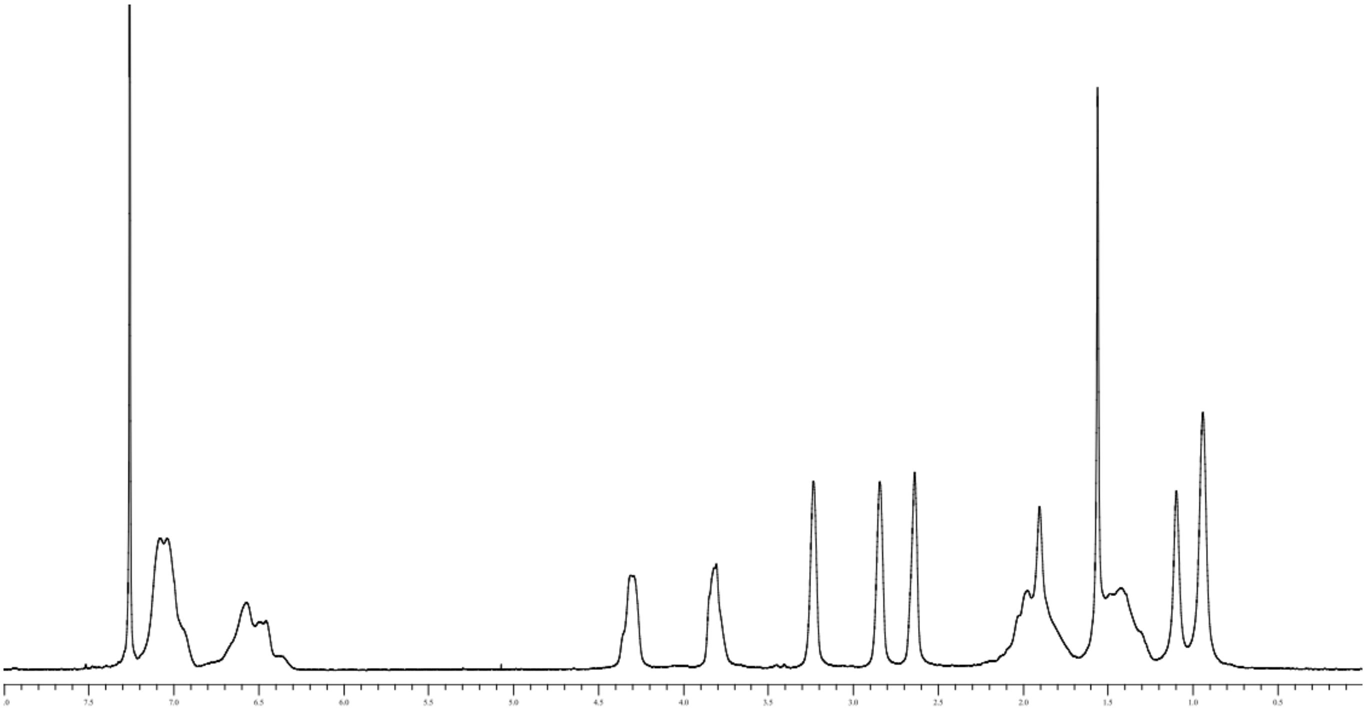

Fig. S1. ^{1}H NMR of PGMA-*b*-PSt in $CDCl_3$.

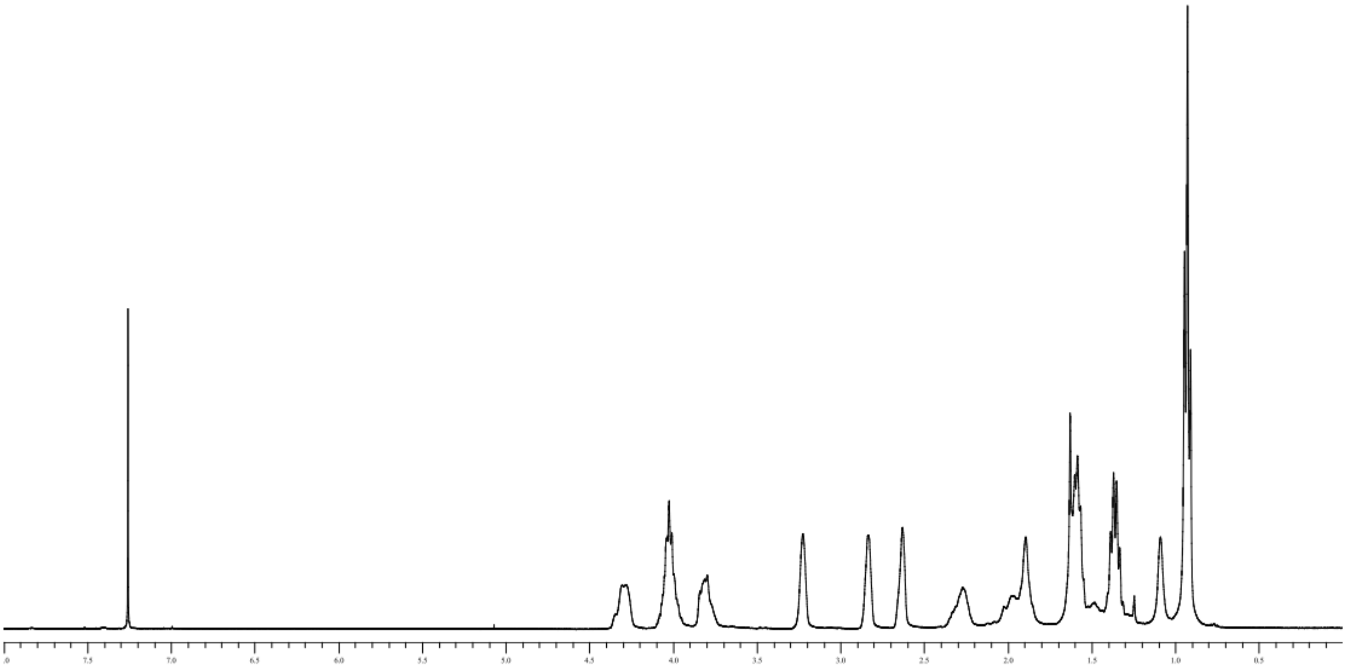

Fig. S2. ^{1}H NMR of PGMA-*b*-PBA in $CDCl_3$.

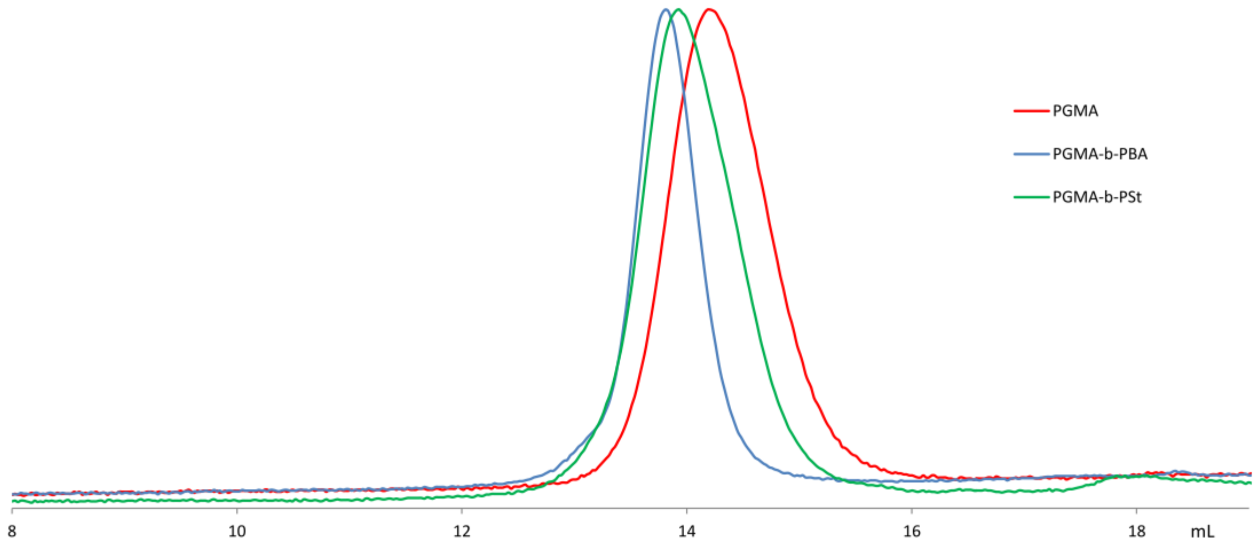

Fig. S3. GPC traces of PGMA macroRAFT (red line), PGMA-*b*-PMMA (green line), PGMA-*b*-PBA (blue line), PGMA-*b*-PSt (yellow line).

Analysis of the absorption spectra

The analysis of the absorption spectra may provide a rough comparative estimation of the amount of SWCNT dispersed in the two samples. This is obtained by assessing the so-called dispersion efficiency and resonant ratio (RR). The dispersion efficiency is estimated by measuring the absorbance at a selected wavelength and the value obtained can be related to the SWCNTs concentration by the Lambert-Beer law. This method is somewhat rough due to the uncertainties on the extinction coefficients of SWCNTs. The resonant ratio aims at assessing the relative weight of the absorbance background, affording a rough estimation of the extent of debundling.[1] The resonant area is the ratio between the total area of the absorption spectrum and a linear background area, as exemplified in Fig. S1a. In particular, the RR is obtained by dividing the resonant area (Fig. S1a, in red) and the non resonant background area (Fig. S1a, in grey). The RR reflects, qualitatively, the ability of the polymer to disperse SWCNTs. High values of RR indicate a better dispersion capability, namely a lower background in comparison to signal. The resonant ratio of **1.SWCNT** and **2.SWCNT** was calculated between 950 nm and 1340 nm, in order to highlight the E_{22} transition only, and is reported in the right panel of Fig. S1. Such comparison underpins the stronger capability of **1** to debundle SWCNTs compared to **2**. To estimate RR, absorption spectra were recorded with samples prepared in parallel, following the procedure described in the main text.

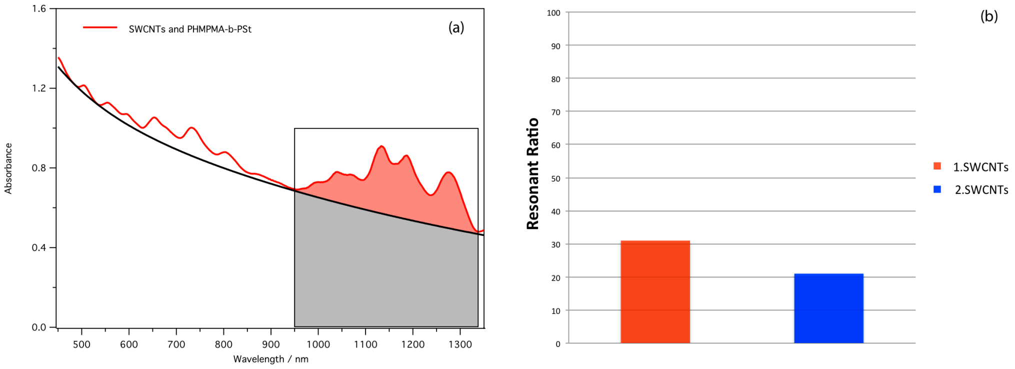

Fig. S4. a) Absorption spectrum of **1.SWCNT** with the resonant area (red) and non-resonant background (gray); b) Comparison between the resonant ratio of **1.SWCNT** (red) and **2.SWCNT** (blue).

Details on the sample preparation and characterization

The last centrifugation step brings about changes only for the samples of **1.SWCNT**. Only in this case the supernatant persisted as a stable dispersion for several days, displaying the typical well resolved absorption spectra and photoluminescence maps of highly dispersed samples by polymer wrapping(though of lower intensity if compared with an uncentrifuged sample, Fig. S2). On the other hand, the precipitate of the **1.SWCNT** sample requires a 30 min sonication step to re-disperse the SWCNT. The sample thus obtained, however, is not stable for more than one day and the photophysical characterization affords poorly resolved absorption and emission features (Fig. S2b-d); this suggests that the sample is primarily made of SWCNTs only, with negligible amounts of polymer.This trend is not observed with the sample of**2.SWCNT**, because there are no relevant differences between the precipitate sample and supernatant of the centrifuged sample.

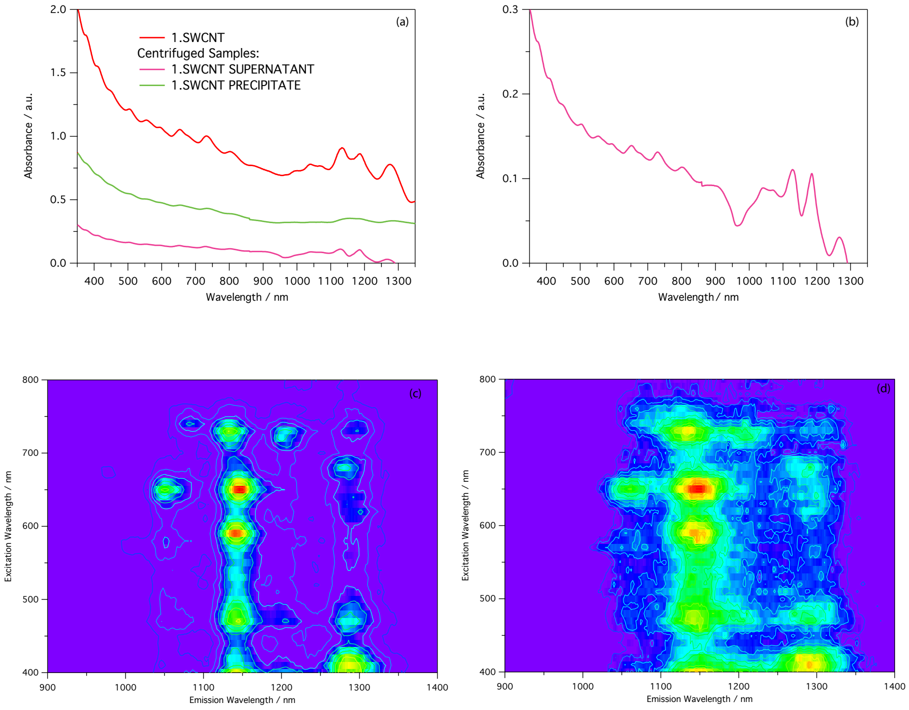

Fig. S5. a) Comparison between the absorption spectra of **1.SWCNT** as centrifuged and uncentrifuged samples. For the latter are reported both the spectra of the surnatant and of the precipitate. b) Magnification of the highly resolved and background free absorption spectra of the supernatant. (c) and (d) are the photoluminescence maps of the centrifuged samples of **1.SWCNT** as, respectively,surnatant and precipitate.

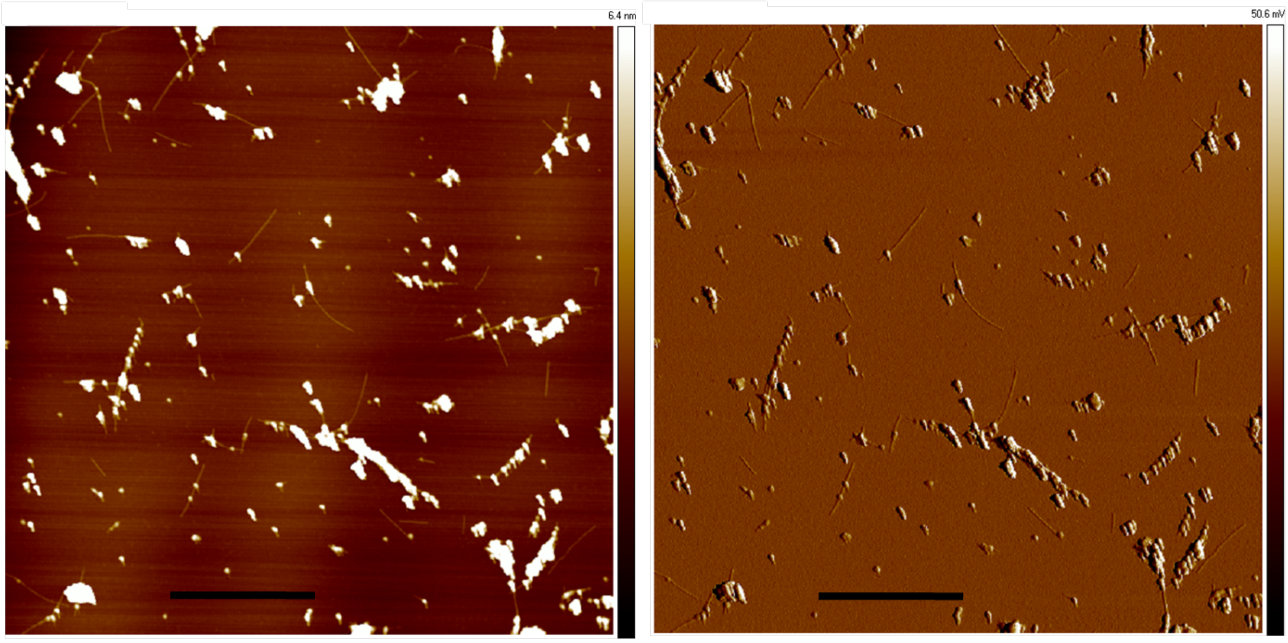

Fig. S6. AFM peak force mode of height (left) and peak force error (right) images of **1.SWCNT** deposited on mica supports after centrifugation (supernatant fraction), deposited on mica. Scale bars are 1 μm in length.

1 M. Gubitosi, J. V. Trilo, A. A. Vargas, N. V. Pavel, D. Gazzoli, S. Sennato, A. Jover, F. Meijide and L. Galantini, *J. Phys. Chem. B*, 2014, **118**, 1012.