Supporting information: Photostability of single-walled carbon nanotubes/polymer core-shell hybrids as Telecom Wavelength Emitters

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Synthesis of the core-shell structures

CNT@PFO/PS. The solution of L-SWNTs was prepared by sonicating the nanotubes in 4% wt sodium cholate (SC) solution for 1.5 h with an ultrasonic tip (Sonics Vibra-CellTM VCX-500) followed by ultracentrifugation at 150 000 g for 1 h. The supernatant was recovered and used for the reaction. 100 μL of PFO solution (1 mg/mL) in CH_2Cl_2 was added to SWNTs in SC (4 mL). The mixture was sonicated for 10 min. at the maximum power of a sonic bath (2.5 liters Fisherbrand, model FB 11201), then at 50% of the maximum power of the sonic bath for 10 min to obtain a clear solution. Poly(9,9-di-n-octylfluorenyl-2,7-diyl) was purchased from Aldrich((ref 571652, Mw $\geq$20000). 100 μL of a solution of styrene/DVB (9/1) (30 % in wt) in CH_2Cl_2 was added. The mixture was sonicated for 20 min at the maximum power of the sonic bath and stirred for 72h to obtain a clear solution. An aqueous solution of ammonium persulfate (40 μL 43 % in wt) and 7 drops of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were added to the aqueous nanotubes solution. The mixture was stirred for one night. After the reaction the nanotubes were filtered through a 0.2 μm PTFE membrane, washed with water, ethanol, acetone and then THF. CNT@PFO/PS core-shell systems were re-dispersed in THF in the sonic bath.

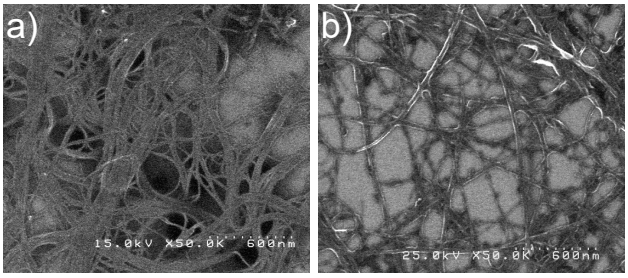

FIG. S1: SEM images of a) CNT@PS/PS and b) CNT@PFO/PS core-shell structures

CNT@PS/PS. The solution of L-SWNTs was prepared by sonicating the nanotubes in 4% wt sodium cholate (SC) solution for 1.5 h with an ultrasonic tip (Sonics Vibra-CellTM VCX-500) followed by ultracentrifugation at 150 000 g for 1 h. The supernatant was recovered and used for the reaction. 100 μL of polystyrene solution (1 mg/mL) in CH_2Cl_2 was added to SWNTs in SC (4 mL). The polystyrene average Mw is 35 000 (Aldrich 331651) . The mixture was sonicated for 5 min at the maximum power of a sonic bath (2.5 liters Fisherbrand, model FB 11201), then at 50% of the maximum power of the sonic bath for 10 min to obtain a clear solution. This step (addition and sonication) was repeated twice. 100 μL of a solution of styrene/DVB (9/1) (10 % in wt in CH_2Cl_2 was added. The mixture was sonicated for 20 min at the maximum power of a sonic bath and stirred for 72h to obtain a clear solution. An aqueous solution of ammonium persulfate (30 μL 20 % in wt) and 4 drops of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were added to the aqueous nanotubes solution. The mixture was stirred for one night. After reaction the nanotubes were filtered through a 0.2 μm PTFE membrane, washed with water, ethanol, acetone and then THF. CNT@PS/PS core-shell systems were redispersed in THF in the sonic bath.

SEM characterization

Figure S1 shows SEM images of some core-shell hybrids deposited on a silicon substrate. Both scale bars are 600 nm. The images has been recorded with a Hitachi S-4500 Scanning Electron Microscope. Figure S1a) displays a SEM image of a CNT@PS/PS sample while figure S1b) shows a typical image for the case of CNT@PFO/PS. In both images one can observe tubular structures that are compatible with laser nanotubes wrapped with the polymer shell layer. For the CNT@PFO/PS structures, some clusters can be observed on the tubular structures. This observation is compatible with the AFM measurements reported in the main text.

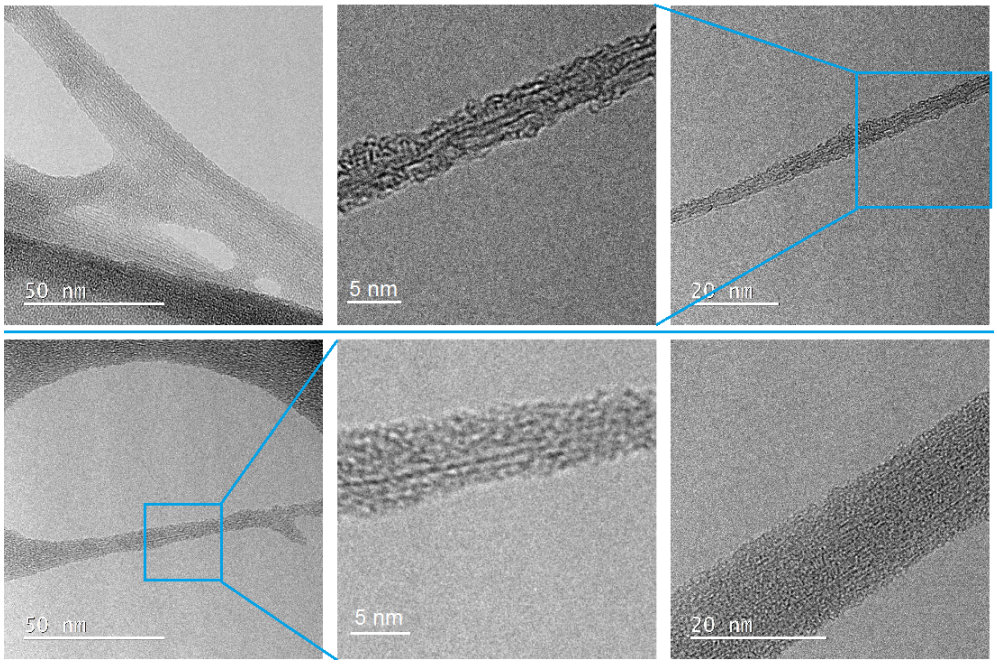

FIG. S2: TEM images of thin bundles and individual nanotubes covered by layers of PFO and PS polymers: (top) CNT@PS/PS ; (bottom) CNT@PFO/PS core-shell structures. Images recorded at 200 kV.

TEM characterization

The morphology of some CNT@PFO/PS and CNT@PS/PS hybrids have been also investigated by transmission electron microscopy (figure S2). The nanotubes hybrids have been dispersed in ethanol, deposited on copper TEM grid (Lacey carbon films, 300 mesh) and imaged with a Zeiss Libra 200 MC equipped with an electrostatic CEOS monochromator, an in-column Ω filter and a Gatan ultrascan 1000 CCD camera. The microscope was operated at 200kV and the monochromator set to obtain a 0.4 eV energy dispersion and reduce the chromatic aberration. Probe current was kept as low as possible to reduce beam damage. The images of CNT@PFO/PS and CNT@PS/PS show the presence of thin bundles or individual tubular objects that are covered by a layer of amorphous materials; this amorphous layer is likely due to the presence of PFO and polystyrene shell. It is worth mentioning that the polymers form a thin and well-distributed layer around the nanotubes supporting our description of the core-shell hybrids.

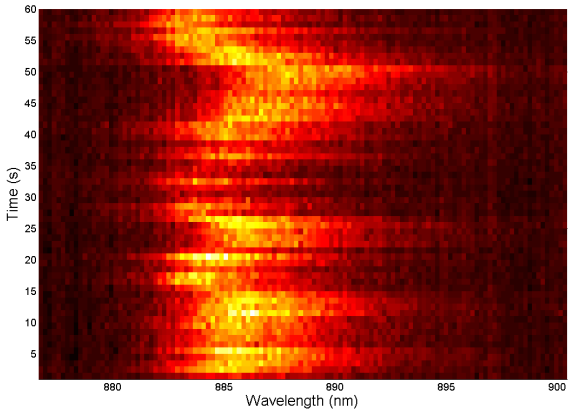

FIG. S3: Temporal evolution of the spectra of a single CoMoCat nanotube on polylysine recorded at 5K with a 1s integration time. The mandel parameter is Q=230 and the standard deviation of the emission energy is 1.97 meV.

CoMoCat nanotubes

Figure S3 displays a temporal trace of a single CoMoCat (6, 5) nanotube recorded at 5K. The nanotube is deposited on polylisine according to the procedure reported in reference [1]. It shows a lot of blinking with a Mandel parameter Q=230 and a lot of spectral diffusion with a standard deviation of the central energy of the line of 1.97 meV.

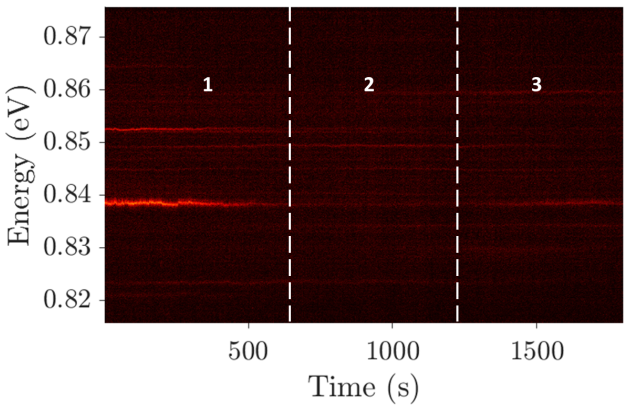

FIG. S4: Temporal evolution of the spectra of single nanotubes in a PS matrix, before the heating process, recorded at 5K with a 1s integration time.

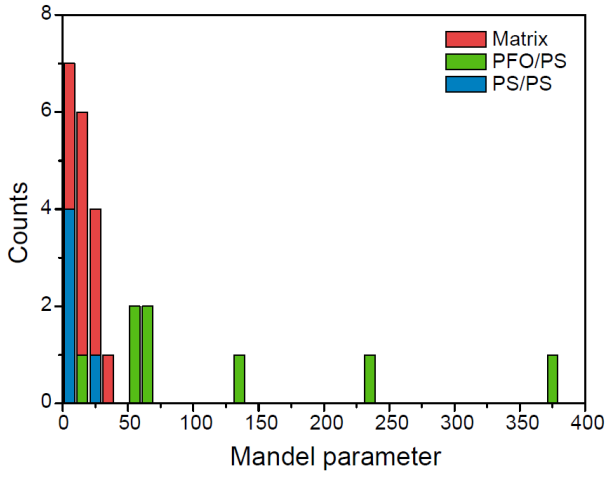

FIG. S5: Histograms of the Mandel parameter calculated for CNT@PFO/PS (green), CNT@PS/PS (blue) and CNT@Matrix (red).

Influence of the heating process on the stability of the emission of single nanotubes in the Polystyrene matrix.

Figure S4 displays a temporal evolution of the emission of a single nanotube acquired just after the fabrication of the sample. Both the intensity and the central energy of the line are changing over time. In particular, the photoluminescence is disappearing on hundreds of seconds time-scale and can be recovered on the same time-scale. This behavior is typical of what is observed on every nanotubes in this sample. Figure 2(c) of the main paper shows traces recorded on the same sample after 45 min of heating at 350 K under vacuum in the chamber of the cryostat. The emission is much more stable both in intensity and energy. This observation highlights the importance of the sample preparation process to get stable emission of single nanotubes in a matrix.

Statistics of Mandel parameter.

Figure S5 shows histograms of the Mandel parameters obtained for the different samples. The CNT@Matrix and the CNT@PS/PS show very peaked distributions of Mandel parameters centred around Q=5. On the contrary, CNT@PFO/PS exhibit much more dispersed values of Q varying from ∼15 to ∼375.

Allan deviations of CNT@Matrix

Figure S6 displays all the Allan deviation curves recorded for the CNT@Matrix sample after the annealing procedure. The curves are relatively flat close to a τ^0 slope as for the core-shell structures (see main text). Here also the values of the Allan deviation show a dispersion over one order of magnitude from $\sim 9.10^{-6}$ to $\sim 2.10^{-4}$ reflecting the diverse local environments felt by the nanotubes in the polystyrene matrix.

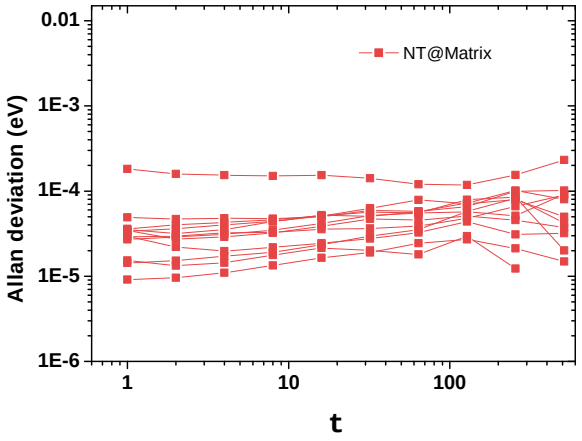

FIG. S6: Allan deviation of nanotubes/PFO embedded in a polystyrene matrix.

Comparison Allan deviations vs time traces

Figure S7 shows two time traces and their respective Allan deviation curves for each sample: CNT@PFO/PS; CNT@PS/PS and CNT@Matrix. The qualitative assessment in terms of emission energy stability is well reproduced by the quantitative Allan deviation analysis.

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[1] A. Högele, C. Galland, M. Winger and A. Imamoğlu, *Physical Review Letters*, 2008, **100**, 217401.

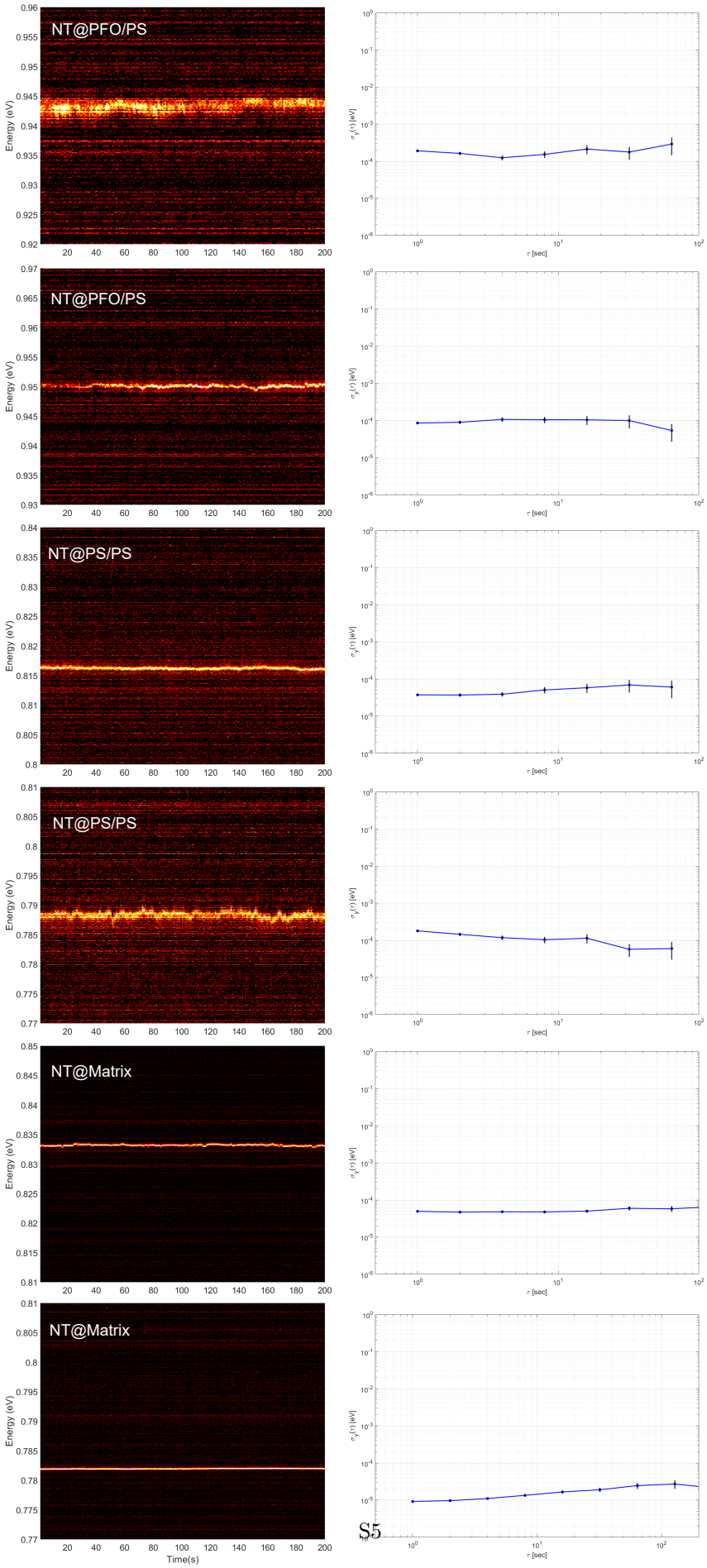

FIG. S7: Typical time traces and respective Allan deviation curves.