Prolonged spontaneous emission and dephasing of localized excitons in air-bridged carbon nanotubes – Supplementary Information

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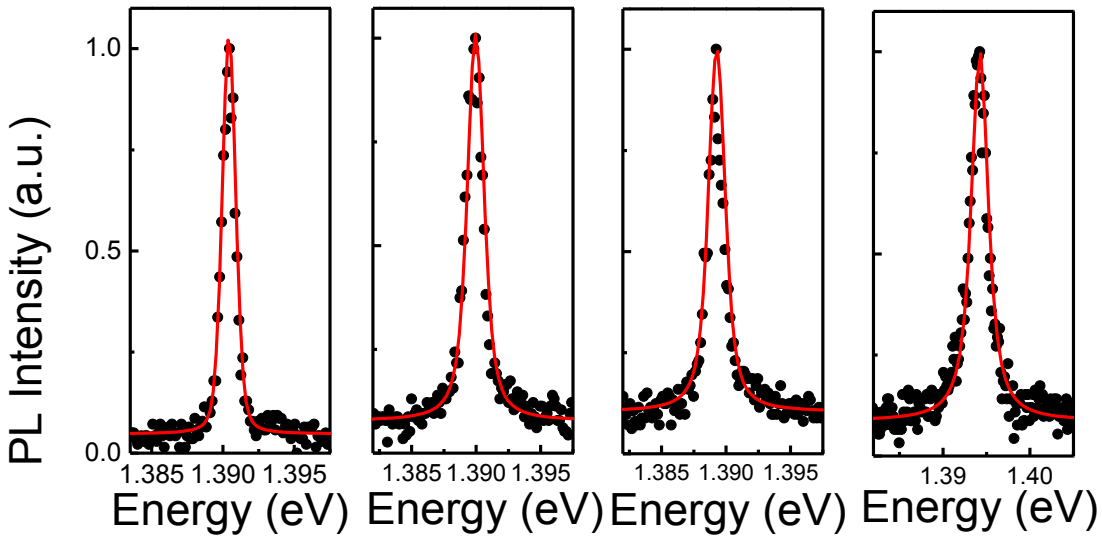
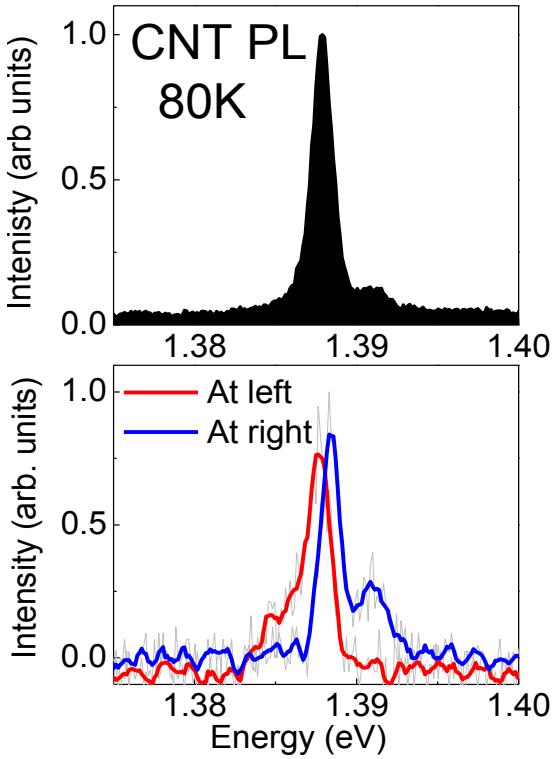
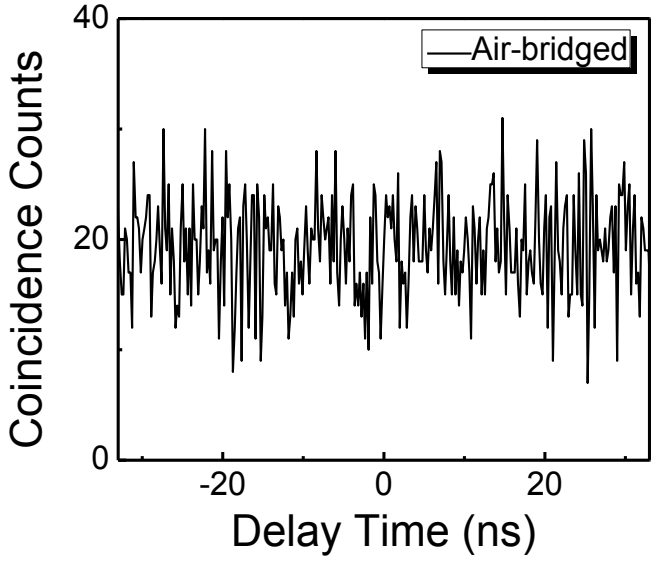


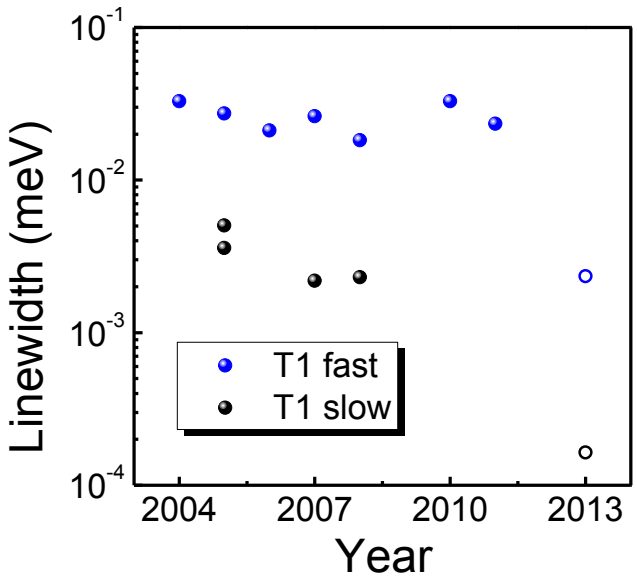
Supplementary Figure S1: Normalized exciton emission spectra for individual air-bridged SWCNTs. Four examples of the E_{11} exciton transition of (6,4) chirality SWCNTs recorded at 9 K are shown, which fit well to Lorentzian lineshapes with no visible asymmetry at lower energies, in contrast to earlier reports. Previous studies reported asymmetric exciton lineshapes with linewidth of about 3.5 meV for surfactant dispersed SWCNTs grown by the CoMoCat technique, which were attributed to an intrinsic non-Markovian dephasing mechanism of excitons and acoustic phonons [33]. Such an asymmetry was also reported for air-bridged SWCNTs displaying rather large linewidth of 10 meV and attributed to the Van Hoove singularities in the density of states [34]. After the discovery that the optical emission in SWCNTs stems from excitons [2] it became clear that the lineshape is not related to the Van Hoove density of states. While contributions from exciton acoustic phonons to the lineshape are expected, we find that the lineshape is symmetric to a high degree and is with values down to 220 μeV also significantly narrower than previous work [2, 34]. We further quantified the residual degree of asymmetry on the lineshape by fitting a Doniach Sunjic lineshape to the data, yielding the asymmetry parameter α. For the four spectra we find rather small values of α=0.024, α=0.023, α=0.026, and α=0.01, respectively, suggesting for all intents and purposes, a symmetric lineshape.



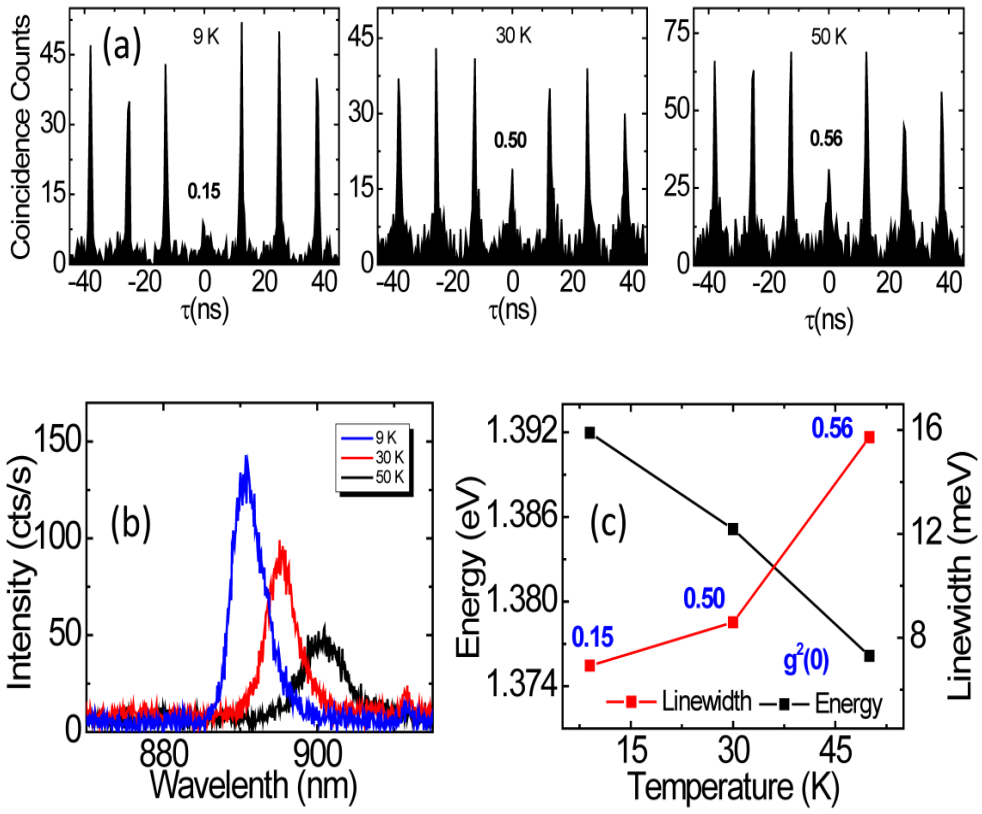
Supplementary Figure S2: Illustration of the spectral filtering for the spectral diffusion measurements of air-bridged SWCNTs. The top graph is the full PL spectrum recorded at 80 K from an individual SWCNT which has a FWHM of 1.7 meV (1.1 nm). The bottom graph shows the PL spectra after the light was coupled into an optical fiber, which was connected to a tunable 1 nm bandpass filter before reaching APDs, resulting in the filtered spectra with bandpass detuning to the left (red spectrum, sent to APD1) and to the right (blue spectrum, sent to APD2). We note that in this example the PL linewidth is about 20% narrower than for the experiment reported in Figure 3 in the main text (FWHM of 2.2 meV or 1.4 nm), but the spectra are still distinct. Therefore, the 1 nm bandpass filter creates a conditional probability at the detectors which should lead to the observation of bunching, if spectral diffusion contributes to the linewidth, and if the spectral diffusion time is slower than the timing jitter of the APDs.



Supplementary Figure S3: Photon correlation trace for the air-bridged SWCNT under continuous wave excitation. Another reason why the correlation trace for the air-bridged tubes in Figure 3c of the main text might not show bunching from residual SD could be that it is masked by photon antibunching from localized quantum dot like excitons, in particular since some SWCNTs do show antibunching under pulsed excitation. In order to test this hypothesis we recorded photon correlation measurements for the same SWCNTs with a 40 nm broad bandpass filter that passes the entire PL spectrum. The result is a flat coincidence trace as shown, which was recorded for 1.5 hrs at 9 K**.** Even if the light emitted by the SWCNT would be antibunched it would be hard to be detectable since the APD timing jitter is about 210 ps and the exciton emission has a fast component of about 30 to 200 ps for the first order of magnitude (see Figure 3 in main text). We therefore conclude that antibunching does not mask the SD experiments.

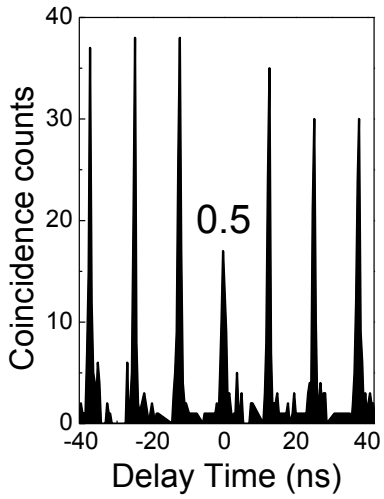


Supplementary Figure S4: Contribution to spectral linewidth from the spontaneous emission lifetime. In general, both T_1 and T_2 can contribute to the spectral linewidth via the well-known relation $\boldsymbol{\Gamma = \hbar/T_1 + 2\hbar/T_2}$ where T_2 typically dominates the contribution to the linewidth. Our lifetime measurements in Figure 3 of the main text reveal however a fast component which is resolution limited, implying that T_1 could be much faster. To quantify this we compared the known values from Refs. [5, 7, 12, 20, 33, 44-47] recorded with much higher temporal resolution as compared to our case and sorted them by publication year on the x-axis. Open data points in 2013 are this work. T_1-fast typically varies between 20 to 40 ps (but not faster) in surfactant dispersed CNTs. This corresponds to a spectral linewidth of only 20 to 40 μeV. While T_1 does not contribute more than 2% to the linewidth for polymer SWCNTs or for air-bridged SWCNTs from the 10 min growth, it contributes up to 20% for the narrowest linewidth of 220 μeV for the 2 min growth. We have therefore included the influence of T_1 for the linewidth values calculated from the interferometric dephasing time measurements and compared those corrected values to the spectral linewidth resulting in the ΔE values plotted in Figure 5e.



Supplementary Figure S5: Temperature dependence of photon antibunching, photoluminescence, and linewidth for an individual polymer embedded SWCNT. It is well known that quantum dot like states can form randomly along one-dimensional SWCNTs as is evident from Coulomb blockade effects in low-temperature electron transport experiments [48, 49]. These random confinement potentials along the tube axis can also give rise to spatial localization of optically excited excitons. This is most evident from recent low-temperature experiments showing pronounced photon antibunching of the spectrally filtered exciton emission [17, 18]. Since the exciton binding energy is about 400 meV larger than kT at room temperature one would expect quantum light signatures to survive up to room temperature. Another important factor is however the energetic depth of the localization potential which could give rise to exciton delocalization at elevated temperatures and thus a loss of quantum light signatures. In order to investigate the thermalization behavior of quantum-dot like excitons in SWCNTs we carried out photon antibunching studies at elevated temperatures using surfactant dispersed SWCNTs embedded in a

polystyrene cavity to enhance the light extraction [18]. Panel (a) shows the second order correlation function $g^{(2)}(\tau)$ for three different temperatures for a (6,4) chirality SWCNT, which has been recorded under pulsed excitation at 10 μW pump power. At 9 K we observe substantial antibunching with $g^{(2)}(0) = 0.15$ followed by a degrading of the single photon signature at 30 K with $g^{(2)}(0) = 0.5$, which further increases to $g^{(2)}(0) = 0.56$ at 50 K. Panel (b) shows the corresponding PL spectra which display a remarkable redshift of the peak energy (black squares) from 890 nm at 9 K to 900 nm at 50 K. This corresponds to a shift in emission energy of 15 meV as is shown in panel (c). The magnitude and direction of the shift is comparable to previous experiments with surfactant dispersed SWCNTs [33]. In that work, it was pointed out that the redshift cannot be reproduced in a non-Markovian model assuming coupling of excitons to the stretching mode phonons, and was thus attributed to environmental changes such as exciton delocalization. Our data set correlates the spectral redshift to a degradation of the single photon purity strongly supporting the idea of delocalization of quantum-dot like excitons at elevated temperatures in SWCNTs. We note that we have not been able to follow the thermalization behavior for this particular SWCNT up to higher temperatures since it exhibited at 80 K a sudden blue shift event and a strong diminishing of the PL intensity. Similar behavior was observed recently by Finnie and Levebre and attributed to molecular deposition and subsequent deep level formation under optical excitation [10].



Supplementary Figure S6: Photon antibunching of an air bridged SWCNT. In order to show that localized quantum-dot like exciton states can also be present in air bridged SWCNTs at cryogenic temperatures, we recorded the second-order autocorrelation function for a (6,4) chirality SWCNT under pulsed optical excitation. The data are recorded at 9K for 1 hr and by pumping into a phonon sideband at 780 nm displaying nonclassical light emission with $g^{(2)}(0) = 0.5$. We remark that the majority of the investigated air-bridged SWCNTs do not display photon antibunching, while they all display a prolonged T_1 time of several ns in agreement with the absence of the PAIEI mechanism.

Supplementary References

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