Supporting Information to: Super-localization of excitons in carbon nanotubes at cryogenic temperature.


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I. RAMAN MAPS

The almost mono-chiral (6,5) nanotubes are spin-coated on a quartz substrate marked with gold labels that allow for a reproducible scanning of the same sample area with different techniques including Raman scattering and PL. Since all nanotubes belong to the same chiral family (in agreement with a uniform RBM mode at 310 cm⁻¹), they are all equally excited at 633 nm and the Raman map directly reflects the nanotube distribution. Fig. S-1 shows the matching between PL and Raman maps.

II. TEMPERATURE INDUCED RECONFIGURATION OF THE TRAPS

A strong indication that the trapping of excitons along the nanotube axis is not due to deep structural defects but rather to soft inhomogeneities of the nanotube/matrix interface is given by the steady observation of a drastic change in the PL spectrum of a given nanotube when the sample is brought back to room temperature and cooled down again to 10 K (Figure S-2). This suggests a deep reconfiguration of the energy landscape along the nanotube. Thus, the exciton traps must have a typical binding energy lower than 25 meV, which is rather in favor of conformational changes in the polymer matrix at the interface with the nanotube.

III. SUPER-POISSONIAN NOISE CONTRIBUTION

Figure S-3 shows the time evolution of the PL intensity of one spectrally filtered line of a CNT. The time bin is 1s. The histogram of the intensity distribution is shown on the right panel together with the simulated Poissonian intensity distribution with identical mean count rate (blue), showing the super-Poissonian contribution in the data. The total variance of the experimental distribution is fitted to \( \sigma^2 = \epsilon^2 + N + \alpha N^2 \), where \( \epsilon \) is a background noise and \( \alpha \) is the super-Poissonian coefficient. Values for \( \alpha \) are tube dependent but are typically found between \( 10^{-2} \) and \( 10^{-1} \).

IV. LOCALIZATION ACCURACY

The super-localization techniques rely on the fact that a point-like emitter can be located with an arbitrary precision if the (diffraction limited) point image can be measured with an arbitrarily high signal-to-noise ratio. In the case of carbon nanotubes however, the super-Poissonian statistics of the emission sets a limit to this signal to noise ratio even for long integration time or large excitation power. The super-Poissonian contribution to the intensity fluctuations are estimated from the time-trace of the luminescence intensity of a CNT spectral line as discussed above. From fits on numerical simulations of Gaussian spatial intensity profiles with such noise, it is then possible to estimate the standard deviation on the position of the center of the spot as a function of the mean count rate and for several super-Poissonian coefficients (Fig. S-4.a). It turns out that the precision on the position of the emitter decreases with increasing non-Poissonian coefficient. In addition, the accuracy levels off for count rates larger than a threshold value related to the dark-count and to the non-Poissonian coefficient. In total, in our experimental conditions, the typical accuracy is on the order of 15 nm.

Fig. S-4.b shows the influence of the number of pixels in PL maps on the accuracy on the emitter position. In
Figure S-2. Series of PL spectra of the same individual nanotube recorded at 10 K with the same experimental parameters after a cycle of heating up to room temperature and cooling down again to 10 K. The pressure in kept below $1 \times 10^{-3}$ mbar during the whole cycle.

Figure S-3. (left) PL intensity of a spectral line of a CNT as a function of time (time bin 1s). The dashed lines show the $2\sigma$ limits of the count rate distribution. (Right) Histogram of the intensity together with Gaussian fit (black). Simulated Poissonian histogram for the same mean count together with a Gaussian fit (blue).

Contrast to the Poissonian case, where the best accuracy is obtained whatever the number of pixels ($N>2$ in each direction), in the presence of a non-Poissonian component in the noise, the precision is greatly enhanced when a larger number of pixels is used in the PL map. As a trade-off between noise and long term thermal or mechanical drift, we used $5 \times 5=25$ pixels.

Finally, this estimate of the super-localization accuracy was benchmarked against reproducibility measurements. By taking several consecutive maps of the same luminescence spot, we confirmed that the spot center localization accuracy is below 15 nm.

V. SPATIAL DISTRIBUTION OF THE TRAPS

In Figure S-5, we display additional maps of exciton trapping along the tube axis through super-localization measurements, together with the overall histogram of the distance between neighbouring traps. The mean of this distribution is 110 nm and the standard deviation is 100 nm. The inset shows the simulated trap distribution extracted from the random potential used to generate the spectra of Figure 4 of the main text. The distribution yields an average inter trap distance of 70 nm, shorter than the experimental one. However, assuming that a fraction of the order of 0.5 of the traps are overlooked in real experimental conditions (line overlap, low luminescence yield...), the apparent trap distribution becomes very similar to the experimental one.

VI. TRAP WIDTH AND PHONON WINGS ANALYSIS

Based on the non-Ohmic exciton-phonon coupling model developed in [1, 2], we obtained the size of the center-of-mass exciton envelope function $\sigma$ from a fit of the PL profile including the phonon wings (Figure S-6). Basically, the exciton size is inversely proportional to
the spectral width of the phonon side-bands. This stems from the energy/momentum conservation in the phonon assisted exciton recombination and yields a cut-off Stokes shift for the phonon side-band of $h v_s / \sigma$ where $v_s$ is the acoustic phonon velocity. We consistently get values of $\sigma$ between 4 and 6 nm, in agreement with previous reports. Note that this value is consistent with the modeling presented in the main text and in the section below. In fact, when fitting by a Gaussian the square modulus of the ground state wave-functions in each trap, we obtain an average exciton size of 5.5 nm.

VII. EXCITATION SPECTROSCOPY

We provide additional examples of PLE spectra for quasi-resonant (figure S-8) and phonon side-band (figure S-7) excitation.

VIII. MODELING

In a first attempt to model the exciton creation, diffusion and recombination in the nanotubes, we used a model where a few localized traps are distributed along the nanotube axis. The energy baseline corresponds to the free exciton. This model gives a sizable contribution of the free exciton to the PL spectra and a strong contribution of the free exciton to all PLE spectra, in contrast to the experimental data (Figure S-9).

Next, we used a totally random potential landscape $V(x)$, defined by its correlation function $C(x') = \frac{1}{V(x)V(x+x')}$. We chose a Gaussian correlation function

$$C(x') = (\Delta E)^2 \exp \left( -\frac{x'^2}{2\delta_x^2} \right).$$

To obtain such a potential, we add Gaussian white noise in the Fourier domain of $V(x)$:

$$V(x) = \Delta E \sqrt{\frac{l_{coh}}{2\sqrt{2\pi}}} \int dk \ e^{ikx} e^{-k^2l_{coh}^2/4}(r_1(k)+i r_2(k)),$$

(1)

where $r_1$ and $r_2$ are Gaussian random variables with unitary standard deviation, and null mean value. In order to have a real-valued potential $V(x)$, $r_1$ is even with $k$ and $r_2$ is odd. Correlations reads : $r_1(k)r_1(k') = \delta(k-k')+\delta(k+k')$, $r_2(k)r_2(k') = \delta(k-k')-\delta(k+k')$ and $r_1(k)r_2(k') = 0$. The values of $\Delta E$ and $l_{coh}$ are adjusted in order to have a FWHM of 40 meV in the distribution of the local minima of energy, and a mean distance between neighbour wells of 70 nm. We found that $\Delta E = 20$ meV and $l_{coh} = 16$ nm match these conditions. Numerically, the distribution was obtained following the method given in [3].

The exciton binding energy being typically 10 times larger than the confinement energy, the electron-hole interaction is treated first and the role of the random potential is accounted for in the effective mass approximation for the exciton center of mass. We solved numerically the 1D Schrödinger equation associated to this potential, using a mass of $0.2 \times m_0$ associated to the exciton center of mass. The numerical resolution of the Shrödinger equation is done by finding the eigenvector (wavefunctions) and the eigenvalues (energies) of the following $n \times n$ matrix (where $n$ is the number of points along the tube axis, corresponding to a discretization step $\delta x = 0.1$ nm ; in
Figure S-5. (a-b) Additional examples of the measurement of exciton trapping along the nanotube axis by means of superlocalization technique together with polarization diagrams indicating the local orientation of the nanotube. The representation of the nanotube is only a guide for the eyes. (c) Histogram of the spatial distance between nearest neighbors. The bin corresponds to the experimental resolution. Inset: simulated trap distribution for the random potential used in Figure 5 (main text) and assuming that about 50% of the trap states are not detected in experimental conditions.

Figure S-6. Selection of PL lines of a CNT at 10 K where the phonon side bands are well resolved. Fits of these PL profiles to the non-Ohmic model as developed in [1, 2] (red lines). The width $\sigma$ of the exciton center-of-mass envelope deduced from these fits is indicated in black (Gaussian envelope). Note that the lesser agreement with the blue wing is due to partial overlap with neighbour lines.

Figure S-7. Photoluminescence excitation spectrum of each emission line of a single CNT at 15 K, together with the PL spectrum (black) obtained for non resonant excitation (1.59 eV) and with the absorption spectrum (measured on an ensemble, dashed blue). This nanotube is the same as in Figure 3 of the main text but additional lines are investigated.

The simulation we used $n = 10000$):

$$H = -\frac{\hbar^2}{2m^*} \begin{pmatrix} -2 & \delta & \delta^2 \\ \delta & 2 & \delta \\ \delta^2 & \delta & 2 \end{pmatrix} + V,$$

where $A$ is the square matrix with $-2$ value on the diagonal and $+1$ on the first superdiagonal and subdiagonal.
This matrix corresponds to discrete version of the operator $\frac{\partial^2}{\partial x^2}$. The matrix $V$ is diagonal with values corresponding to $V(x)$. The eigen quantum levels are shown in Figure 4 of the main text. The wave function is displayed only in places where it takes significant values.

The color code shows the strength of the coupling to light. According to the textbook separation of relative and center-of-mass variables, it can be shown that the oscillator strength $f_i$ of the dipolar interaction with an incoming electromagnetic field is proportional to the square of the integral of the envelope wavefunction over the nanotube length: $f_i \propto \int |\psi_i(x)|^2 dx$. Therefore, excited states which have a more pronounced oscillatory component are much less coupled to light than the ground states (for each trap). In addition their weaker average population at low temperature (Boltzmann factor) yields a negligible contribution of the excited states to the PL spectra.

In contrast, excited states play a key role in the quasi-resonant PLE spectra and explain the sharp and specific lines. In the low-temperature PLE simulations, the excitons generated on each excited states (at a rate proportional to the oscillator strength) are supposed to relax down to the lower ground state cascading in the local energy gradient. This relaxation is supposed to be much faster than the PL lifetime.

When raising the temperature the exciton are not completely trapped in local energy minima any longer and diffusion along the tube axis has to be taken into account. However, the typical inter-level spacing for confined states is on the order of 10 meV (Figure 4). Thus, it is not possible to evaluate the diffusion of the exciton using the continuous external potential $V(x)$ because the energy levels accessible to the exciton are discrete at the scale of $k_BT$. The usual approach in this case is to use instead the Bohm quantum potential [4]. In this framework, the potential $U(x)$ felt by quantum particle is given by the energy of the quantum state having the highest density of probability at each position $x$ along the nanotube axis (Figure S-10).

Next, the diffusion of the exciton along the nanotube is computed by solving numerically the diffusion equation [5]:

$$\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial x^2} - \frac{1}{\tau} N - \frac{\partial (A(x)N)}{\partial x}, \quad (3)$$

where $N(x,t)$ is the exciton density, $D$ is the diffusion coefficient and $\tau$ is the exciton lifetime. A drift term $\partial_x (AN)$ is used to describe the non-uniform potential. In the limit of infinite lifetime, the steady state exciton density $N_s$ should follow a Boltzmann distribution, which leads to $A(x) = \frac{D}{N_s} \frac{\partial N_s}{\partial x}$. In the discrete description, $A$
The exciton population is defined on each position with the highest density of probability is shown by a thicker line. Their corresponding eigen energies are used to generate the new potential $\mathbf{U}(\mathbf{x})$.

diffusion constant $D$ is tuned in order to have a diffusion length of 200 nm at room temperature [7].

In the simulations, excitons are launched one by one in a random initial position. The diffusion length is obtained by calculating the average distance travelled by the exciton in a lifetime. We found that a value of $D = 900 \text{ nm}^2\text{ps}^{-1}$ yields $<L> \approx 200 \text{ nm}$ at 300 K. We stress that the diffusion length is smaller than ($<L_{flat}> = \sqrt{2DT} = 300 \text{ nm}$). This is a consequence of the rough energy profile that reduces the excursion length in the exciton random walk. By changing the temperature and the lifetime $\tau$ in the simulations, (Figure S-11), we find that the diffusion length is well approximated by :

$$<L> \approx \sqrt{2D_{eff}(\mathbf{T})\tau} + L_0/\sqrt{12} \hspace{1cm} (9)$$

The effective diffusion coefficient is given by an Arrhenius law $D_{eff} = D_0 \exp(-E/kT)$ [8], with an intrinsic value of the diffusion coefficient $D_0 = 1100 \text{ nm}^2/\text{ps}$ and $E = 30 \text{ meV}$ [9]. The offset term $L_0/\sqrt{12}$ is negligible at high temperature but becomes dominant at low temperature. This term corresponds to the average distance between traps $L_0 = 70 \text{ nm}$.

The PL spectrum is calculated from the integral over time of the exciton population at each position. Each position along the nanotube is associated to a PL line at an energy given by the local value of the exciton energy and an intensity proportional to the oscillator strength $f_i$ calculated for the local quantum state associated to this energy. Numerically, we use equation (5) and let the population evolve for five lifetimes.

Finally, we validated the statistical parameters of the model by summing up the PL spectra obtained at 10 K for a set of 10000 realizations of the random potential. We compared this average spectrum to the experimental one obtained by summing up the spectra of 20 different nanotubes (Figure S-12a). We observe that both the
lineshape and the spectral width are in good qualitative agreement between simulations and experiments (number of peaks, asymmetry of the line, ...).

![Figure S-12. Average low temperature spectra. The black curve corresponds to the sum of 20 spectra taken at 10K. The blue curve is the mean of 10000 simulated spectra at 0 K.]