Supplementary Information

Excitonic linewidth of organic quantum wires generated in reduced dimensionality matrices

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I   Thin films elaboration process

Thin films are elaborated within two steps : (a) functionalization of SiO_2 substrates and (b) evaporation of the diacetylene (DA) compound.

-(a) A nanostructured pattern of PTFE (poly-tetrafluoroethylene or teflon) fibres is fabricated using the friction transfer method. A PTFE rod is rubbed against a cleaned SiO_2 slide with a speed of $\sim$1 mm/s. Deposition is performed as thermalization of the substrate and PTFE rod is achieved. Optimized regular structures (corresponding to partial PTFE deposition with : 10 nm < fibre height < 30 nm and inter-fibre spacing equal to a fraction of micron) are obtained for the following conditions : T$\sim$210°C, P$\sim$100 g/mm^2. High regularity is typically maintained over a few tens of microns along the fibre direction.

-(b) Deposition by sublimation is performed under vacuum at a pressure of $3 \cdot 10^{-7}$ torr and crucible temperature around 110°C. The deposition rate is kept sufficiently low (typically 0.2-0.3 Å/s). The substrate holder is rotated around a vertical axis to ensure homogeneous deposition.

N.B. : Thumbnails correspond to Atomic Force Microscopy characterization images.
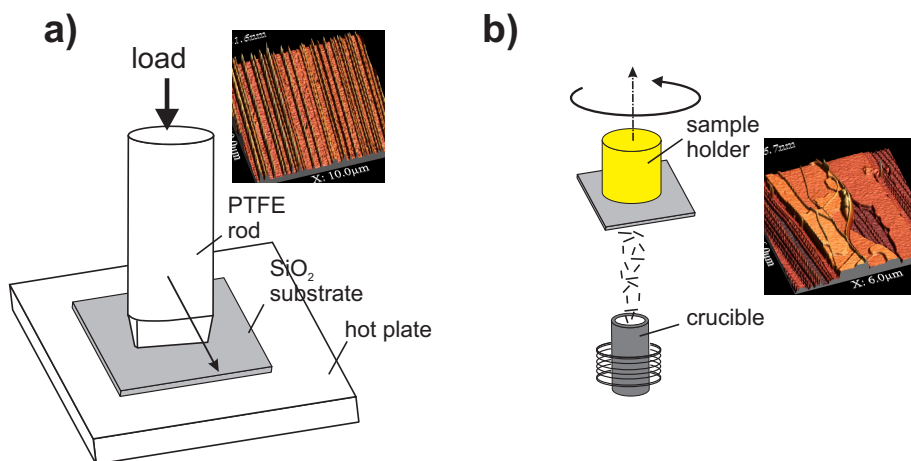
II   Derivation of $\Gamma_0(T)$

Poly-3BCMU chains are considered here as quasi-ideal 1D crystals supporting excitons as primary excitations. Following Rudin *et al.* [Rudin90] the absorption by the polymer chain of a phonon having the momentum $\overrightarrow{q}$ leads to a transition between a $k_i \sim 0$ exciton state to a $\overrightarrow{k}_f = \overrightarrow{k}_i + \overrightarrow{q}$ state of higher energy. Note that the initial state is generated at the bottom of the band ($k_i \sim 0$) in the optical transition because the momentum of the photon is infinitely smaller than the extension of the Brillouin zone. The linewidth, Γ_0 is thus written as a transition rate between the $k_i \sim 0$ and k_f states, averaged over all vector $\overrightarrow{q}$ (provided by the surrounding matrix) that may fit energy and momentum conservation in the transition.

For the lowest-lying 1S exciton states Γ_0 reads (using the Fermi Golden Rule) :

$$\Gamma_0 = \pi V \sum_\lambda \int d^3\overrightarrow{q}(2\pi)^{-3} N(q)|V_{1S,\lambda}(q)|^2 \delta(E_{1S}(\overrightarrow{k}_i) - E_\lambda(\overrightarrow{k}_f = \overrightarrow{q}) + \hbar\omega(\overrightarrow{q})) \tag{1}$$

$E_\lambda(\overrightarrow{k})$ is the exciton energy for a state with internal quantum number λ and center-of-mass wave vector $\overrightarrow{k}$. In the effective mass approximation $E_\lambda(\overrightarrow{k})$ is given by :

$$E_\lambda(\overrightarrow{k}) = E_\lambda(\overrightarrow{k} \sim \overrightarrow{0}) + \hbar^2 k^2/2M \tag{2}$$

where M is the total mass of the exciton. $N(q)$ is the Bose occupation function for phonons :

$$N(q) = [\exp(\hbar\omega(q)/(k_B T)) - 1]^{-1} \tag{3}$$

Total momentum and energy should be conserved in the process, so, considering the polymer chain as an "ideal" 1D system, $\overrightarrow{k}_f = \overrightarrow{k}_i + \overrightarrow{q}$ where $\overrightarrow{q}$ is the momentum of the phonon which direction is that of the chain ($\overrightarrow{q} = \overrightarrow{q}_{//}$). Also energy conservation writes $E_{\lambda'}(k_f) = E_\lambda(k_i) + \hbar\omega(q)$ that is taken into account through the Dirac function in equation (1). The matrix element for exciton-phonon interaction is [Rudin90] :

$$V_{\lambda,\lambda'}(q) = \int d^3\overrightarrow{r}\,\phi_\lambda^*(r)\phi_{\lambda'}(r)[u^e(q)\exp(-i\overrightarrow{q}.\overrightarrow{r}\,m_e/M) - u^h(q)\exp(-i\overrightarrow{q}.\overrightarrow{r}\,m_h/M)] \tag{4}$$

with m_e and m_h the electron and hole masses. For the deformation-potential interaction with acoustic phonons (assumed to be the preponderant term here), $u^{e,h}(q)$ are given by :

$$u^{e,h}(q) = q^{1/2}(\hbar/2\rho v_S V)^{1/2} D_{e,h} \tag{5}$$

where v_S is the sound velocity along the polymer wire, $D_{e,h}$ are the deformation constants, V the sample volume (chain length, L, in the present case) and ρ is the mass per unit length of the polymer chain.

For the 1S ground state of the exciton with momentum $\overrightarrow{k}_i \sim \overrightarrow{0}$, energy conservation for one phonon absorption gives :

$$E_{\lambda'} + \hbar^2 q^2/2M - E_{1S} - \hbar\omega(q) = 0 \tag{6}$$

Real solutions of the previous equations require $E_{\lambda'} - E_{1S} < Mv_S^2/2$ a condition that is verified, for low energy acoustic modes, only for $\lambda' = $1S say for intraband transitions.

Here the integration is over the relative coordinate r for an exciton that is generated on a polymer chain so the integration in equation (4) reduces to a 1D integration, the product $\overrightarrow{q}.\overrightarrow{r} = q_{//}r$ being a scalar (the same approach was used for instance in [Nguyen11] to extract exciton dephasing time in carbon nanotubes). With $\phi_{1S,\lambda} = (\frac{2}{a_0})^{(1/2)}\exp(-r/a_0)$ with a_0 the exciton Bohr radius, we find :

$$V(q_{//}) = \left(\frac{\hbar q_{//}}{2\rho v_S L}\right)^{1/2}\left(\frac{D_e}{1 + (a_0 q_{//} m_e/2M)^2} - \frac{D_h}{1 + (a_0 q_{//} m_h/2M)^2}\right) \tag{7}$$

where L, the polymer chain length, replaces the volume term in (5). With $a_0 \sim 2$ nm [Lec02] and $v_S \sim 5500$ ms^{-1} (see main text) the terms $a_0 q_{//} m_{e,h}/2M = a_0 v_S m_e/\hbar$ remain small in front of unity so that (7) simplifies as :

$$V(q_{//}) = \left(\frac{\hbar q_{//}}{2\rho v_S L}\right)^{1/2}(D_e - D_h) \tag{8}$$

Integration in equation (1) is performed differently whether a 3D or a 2D bath is considered for phonons. Due to the 1D nature of the exciton, in both cases the total momentum in the direction parallel to the chain has to be conserved in the absorption process : for a phonon of wavevector $\overrightarrow{q}$ this will lead to the relation $\overrightarrow{k}_f = \overrightarrow{k}_i + \overrightarrow{q}_{//}$, where $\overrightarrow{q}_{//}$ is the component parallel to the chain axis. The energy conservation is then expressed by replacing $\overrightarrow{q}$ by $\overrightarrow{q}_{//}$ in the argument of the Dirac function of (1). The number of phonons with wavevectors that will match both momentum and energy conservation rules and likely to induce the transition will thus be higher in the 3D case (see figure below). In this rough model however, the "volume" of the chain, L, will not compensate the volume of the sample, so we will assume a proportionality relation
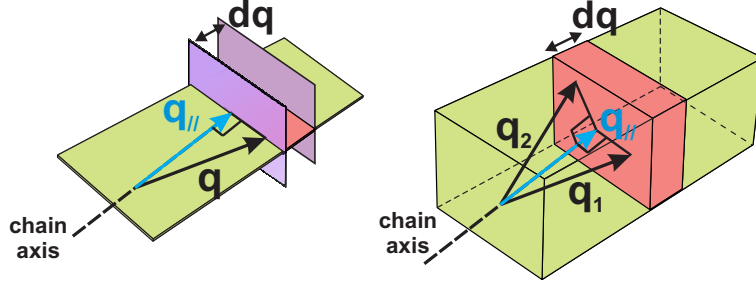
FIG. 1 – In a thin film (left side), the phonons of wavevectors $\overrightarrow{q}$ that contribute to the process are those having their projection onto the chain axis, $\overrightarrow{q_{//}}$ matching the conservation of momentum and energy rules. Right : for 3D matrix several wavevectors outside the same plane may contribute to the process.

only between Γ_0 and expression (1) having in mind that the temperature evolution is under focus in this work ; in particular the prefactor value will not be discussed. If we note $\overrightarrow{q} = \overrightarrow{q}_{//} + \overrightarrow{q}_{\perp}$, we find :

$$\Gamma_0 \propto \pi V \int d^3 \overrightarrow{q}\, (2\pi)^{-3} N(q) |V(q_{//})|^2 \delta(E_{1S} - E_\lambda(\overrightarrow{q_{//}}) + \hbar\omega(\overrightarrow{q_{//}})) \tag{9}$$

$q = (q_{//}^2 + q_\perp^2)^{1/2}$ and $q_{//} = 2Mv_S/\hbar$ (see equation (6)). Integration in (9) is done using the property of Dirac distributions that allows to link energy and momentum domains : $\delta(E = \hbar v_S q_{//}) = \frac{1}{\hbar v_S}\delta(q_{//})$. Also in cartesian coordinates for infinite systems one has :
- $\frac{d^3q}{(2\pi)^3} \rightarrow \frac{d^2q}{(2\pi)^2} = \frac{dq_\perp dq_{//}}{(2\pi)^2}$ for ideal films (without thickness), V being replaced by S, the film area ;
- $\frac{d^3q}{(2\pi)^3} = \frac{2\pi q_\perp dq_\perp dq_{//}}{(2\pi)^3}$ for 3D matrix.

The integration leads to :

$$\Gamma_{0,1S_{2D}}(T) \propto \frac{SM^2(D_e - D_h)^2}{L\pi\rho\hbar^2} \int_0^\infty dq' \frac{1}{e^{(\gamma(1+q'^2)^{1/2})} - 1} \tag{10}$$

and

$$\Gamma_{0,1S_{3D}}(T) \propto \frac{VM^3 v_S(D_e - D_h)^2}{L\pi\rho\hbar^3} \int_0^\infty dq' \frac{q'}{e^{(\gamma(1+q'^2)^{1/2})} - 1} \tag{11}$$

with $\gamma = 2Mv_s^2/k_B T$ and $q' = q_\perp/q_{//}$.

[Rudin90] Rudin, S. ; Reinecke, T.L. ; Segall, B. Temperature-dependent exciton linewiths in semiconductors. *Phys. Rev. B* **1990**, 42, 11218-11231.

[Nguyen11] Nguyen, D.T. ; Voisin, C. ; Roussignol, Ph. ; Roquelet, C. ; Lauret, J.S. ; Cassabois, G. Phonon-induced dephasing in single-wall carbon nanotubes. *Phys. Rev. B* **2011**, 84, 115463.

[Lec02] Lécuiller, R. ; Berréhar, J. ; Ganière, J.D. ; Lapersonne-Meyer, C. ; Lavallard, P. ; Schott, M. Fluorescence Yield and Lifetime of Isolated Polydiacetylene Chains : Evidence for a One-dimensional Exciton Band in a Conjugated Polymer. *Phys. Rev. B* **2002**, 66, 125205.

III   Additional comments

III.1   Role of localized and interface modes

In typical heterostructures (layered semiconductor structures or embedded structures) the presence of heterointerfaces has two main consequences : acoustic mode localization and existence of interface modes. The acoustic phonon states and spectra will then depend on the geometry of the structures (through boundary conditions) as well as the relationships among elastic parameters [Mitin]. The elastic constants of a

monomer crystal and a polydiacetylene crystal are nearly identical except in the chain direction. The replacement of weak van der Waals bonding with strong covalent bonds along the polymer backbone leads to an increase in Young's modulus of nearly one order of magnitude [Young]. An isolated embedded chain is thus a highly anisotropic structure of high stiffness along its main axis that will modify the elastic properties in its immediate vicinity.

In a single PDA chain the carbon conjugated backbone is mostly responsible for the elastic properties and the section area of such a structure is hardly measurable. At least an effective radius in the nanometer range may be defined. As a consequence studies for embedded bulk cylindrical wires have to be considered cautiously. In wires dilatational and flexural confined modes have a longitudinal component and are those that may couple to excitons. Every dispersion curve of these modes has a finite cutoff frequency. The important point is that the lowest mode has the wavelength $\lambda_c \sim R$ with R the wire radius, that is localized modes are relatively short-wavelength and high frequency vibrations [Mitin][Nishi94]. Correspondingly the cutoff frequency λ_c is a fraction of THz and $h\nu_c$ compares to $k_B T$ at $T \sim$10 K. Occupation numbers of higher energy modes are thus rapidly beyond unity.

The region of existence of interface (dilatational) modes drastically depends on the combination of material parameters by way of two quantities, the ratio of longitudinal bulk sound velocities and the ratio of mass densities ρ_{poly}/ρ_{mono} [Nishi94]. Calculations show that the interface modes of the wire-surrounding system occur only for a combination of materials which also supports interface modes at a planar interface of the same materials. The region contracts with decreasing qR and vanishes at the critical wave number $q_0 R \sim$4.2. For radius in the nanometer range, existing modes will again be of relatively small wavelength. In the studied case, $\rho_{poly}/\rho_{mono} \sim$1 within a few percent; in this particular case interface mode exist for any $q > q_0$ but only for a given ratio of the longitudinal sound velocities which itself is close to unity. As $v_{poly}/v_{mono} = \sqrt{c_{poly}/c_{mono}} \sim$2.7 with c the appropriate elastic constant [Young], the system should not support phonons bound to the wire. It is finally important noting that the region of existence of the interface modes is very poorly dependent of the transverse velocities and that given some refinements a similar picture is predicted for flexural interface modes.

The elastic-continuum approach is used to obtain the previous results meaning that the length scales characterizing the elastic waves should significantly exceed the lattice constants of materials. Here the cell parameter, $b \sim 4.9$ Å in the monomer crystal, is also the length of the repeating unit in the polymer along the chain axis. $\lambda_c \sim R$ clearly questions the validity of the approach. The extrapolation of the model to low R values seems to point the minor role that confined or interface modes play. However the actual situation asks for a more rigorous description based on a microscopic treatment of lattice vibrations.

[Mitin] Mitin, V.V.; Kochelap V.A.; Stroscio, M.A. Quantum Heterostructures : Microelectronics and Optoelectronics, Cambridge University Press, 1999.

[Young] Young, R.J. in Mechanical and Structural Properties of Polydiacetylenes, pp 335-362, in Polydiacetylenes : Synthesis, Structure and Electronic Properties, Proceedings of the NATO Advanced Research Workshop on Polydiacetylenes, D. Bloor and R.R. Chance Eds, 1984.

[Nishi94] Nishiguchi, N. Confined and interface acoustic phonons in a quantum wire. *Phys. Rev. B* **1994**, 50, 10970-10980.

III.2 Dimensionality considerations

We stress here the idea that "2D" bath is achieved in the prepared films. Scattering using a phonon having a non zero component in the $\perp$ direction (the direction perpendicular to the film plane also corresponds to the **a** crystallographic axis of the DA crystal) is possible if energy and momentum conservation rules allow to connect two states in the exciton band (absorption process); for a phonon of momentum $\overrightarrow{q}$ two conditions are required : **(i)** $\overrightarrow{k}_f = \overrightarrow{k}_i + \overrightarrow{q}_{//}$ (see below for notations) and **(ii)** equation 6 should be satisfied with q replaced by $q_{//}$. Calculations are then performed again when going progressively from the monolayer situation (ideal 2D bath) to multilayered structures (N is the number of layers; note that the unit cell contains two molecules in the **a** direction and the film thickness is $aN/2$). Modes with $q_\perp \neq 0$ are then

taken into account through a discrete summation over authorized $q_\perp$ values in the confined structure :

$$\Gamma(T) \propto \sum_{q_\perp} \int_0^\infty dq' \frac{1}{e^{[\gamma(1+q'^2+(q_\perp/q_0)^2)^{1/2}]} - 1} \ , \ q_0 = 2Mv_S/\hbar \text{ and } q_{\perp max} = \frac{2\pi}{a} \tag{12}$$

where, in the isotropic approximation, discrete values of $q_\perp$ have to be considered : $q_{\perp,p} = p \times \frac{2\pi}{a} \times \frac{1}{N/2}$ with $p = 1, ..., N/2$.

Figure 2 shows $\Gamma(T)$ evolution with N. A difference with the "purely" 2D case is rapidly observed *ie* typically for $N > 10$.
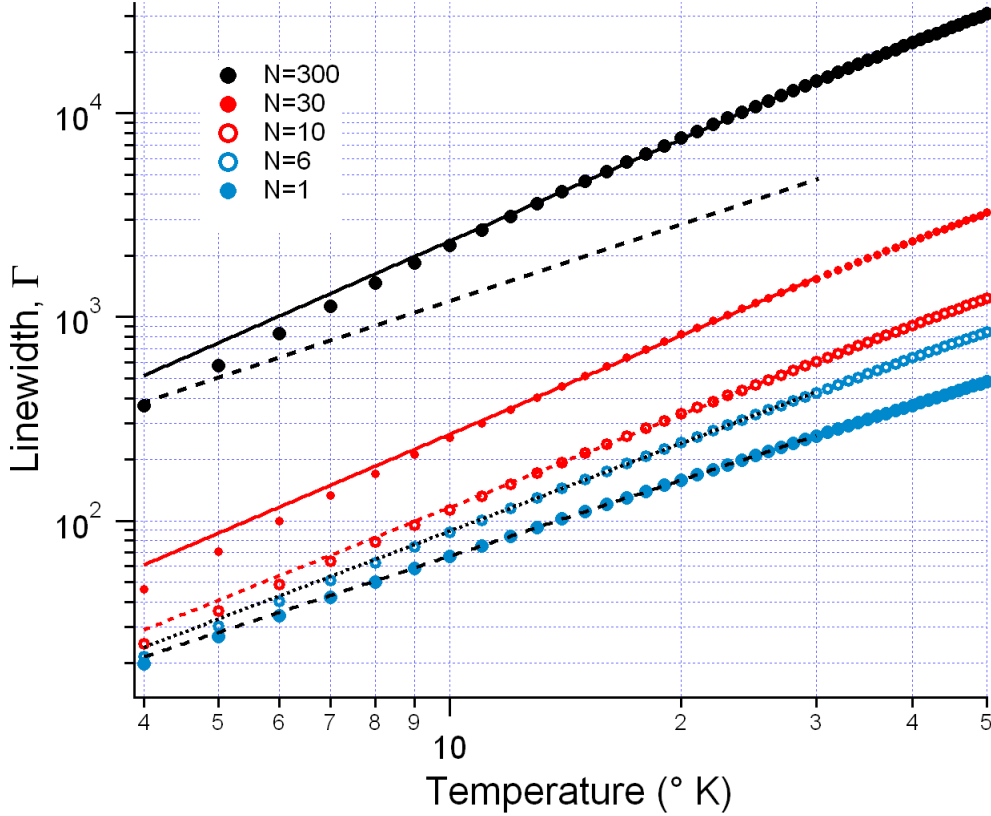

FIG. 2 – Temperature dependence of linewidth as a function of film thickness (4 K - 50 K range). N is the number of layers considered in the simulation. Solid lines are indicative fits according to a power law $\Gamma(T) = aT^\alpha$. For comparison the fit obtained for $N = 1$ is displayed close to the $N = 300$ curve (dashed line).

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