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Supporting Information

for

Further insights into the thermodynamics of linear carbon chains for temperatures ranging from 13 to 300 K

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Additional figures and calculations

Representative Raman spectra:

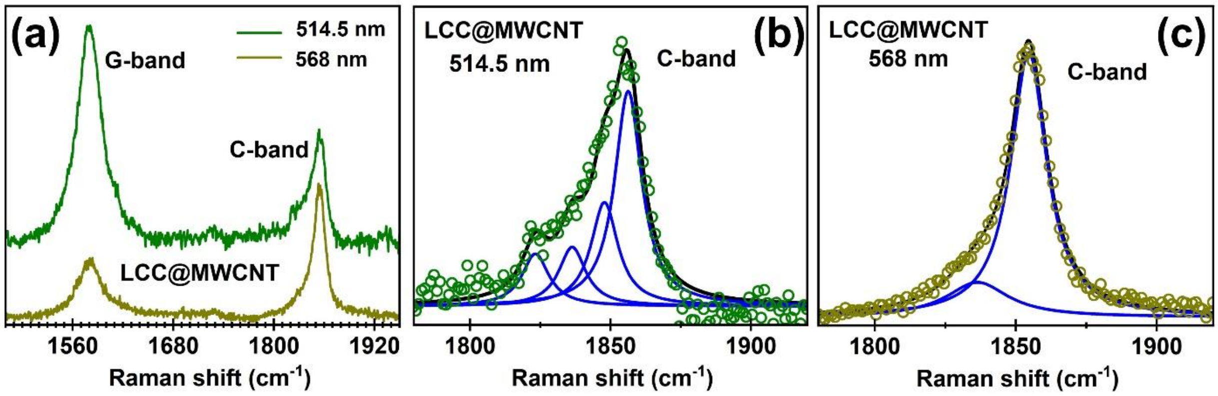

Figure S1: (a), (b) and (c) Representative Raman spectra obtained at 293 K using 514.5 nm and 568 nm lasers. In **(a),** the G-band from the host CNT is around 1580 cm^{-1} and the C-band is around 1850 cm^{-1}. **(b)** using 514.5 nm and **(c)** using 568 nm, show the C-band, where the open symbols are the experimental data, the black solid curve is the fitting result using Lorentzian curves (navy blue solid curves). LCC@MWCNT stands for LCC encapsulated by MWCNT.

Plots of the thermodynamic observable for the full set of LCC:

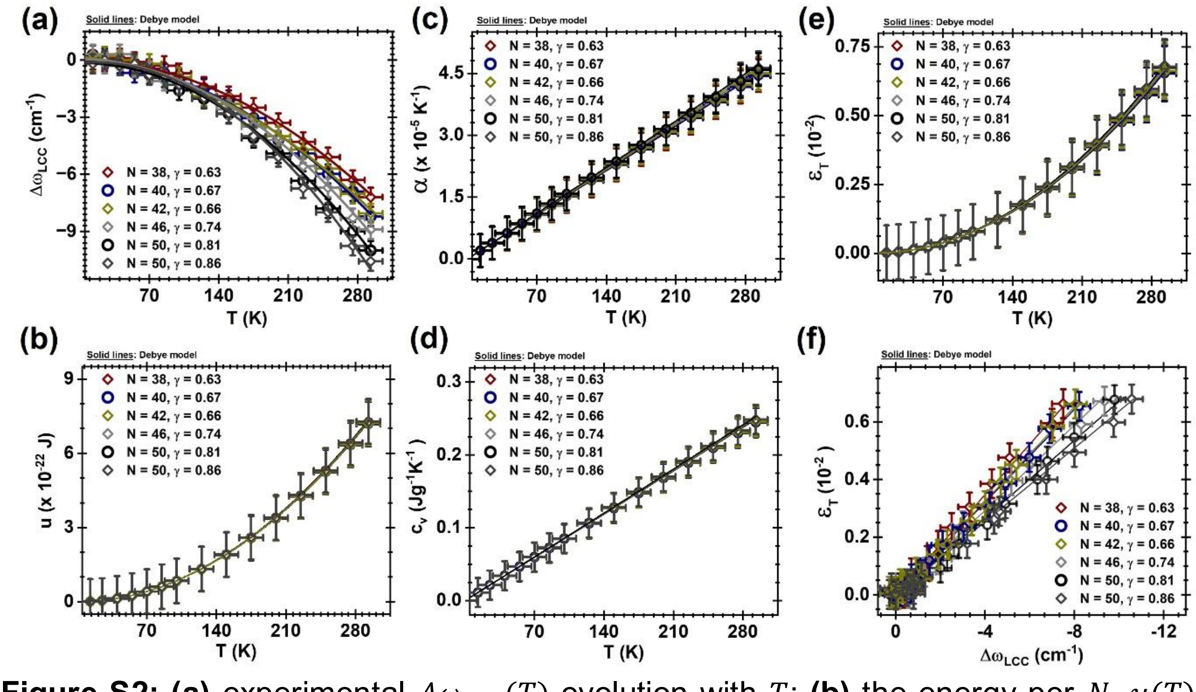

Figure S2: (a) experimental $\Delta\omega_{LCC}(T)$ evolution with T; **(b)** the energy per N, $u(T)$, presents a quadratic, universal, and unified behavior with T; **(c)** $\alpha(T)$ shows a linear universal behavior with T; **(d)** the heat capacity per N, $c_v(T)$, presents a linear, universal and unified behavior with T; **(e)** A T^2 universal dependence is observed for the thermal strain $\varepsilon_T(T)$; **(f)** Every LCC presents a distinct linear dependence of ε_T with $\Delta\omega_{LCC}(T)$.

The Debye model for LCC:

Under the Debye model formalism (from now on DMF), the canonical partition function for LCC is given by **[1]**:

$$lnZ = -N\frac{T}{T_{LCC}}\int_0^{\frac{T_{LCC}}{T}} ln[1-exp(-x)]dx, \qquad \textbf{(S1)}$$

where x=$\frac{\hbar\omega_{ph}}{k_bT}$=$\frac{T_{ph}}{T}$, ω_{ph} is the phonon frequency and T_{ph} is the phonon equivalent temperature. Upon integration by parts, **Equation S1** becomes:

$$lnZ \approx N\frac{T}{T_{LCC}}\int_0^{\frac{T_{LCC}}{T}} \frac{x}{e^x-1}dx. \qquad \textbf{(S2)}$$

For T<<T_{LCC}, $\frac{T_{LCC}}{T}$→∞ and **Equation S2** is simplified to:

$$lnZ \approx N\frac{T}{T_{LCC}}\int_0^{\infty}\frac{x}{e^x-1}dx = N\frac{T}{T_{LCC}}\left(\frac{\pi^2}{6}\right) = \frac{Nk_b\pi^2}{6\hbar}\frac{T}{\omega_{LCC}(T)}, \qquad \textbf{(S3)}$$

where $\int_0^{\infty}\frac{x}{e^x-1}dx = \frac{\pi^2}{6}$. As thoroughly described by Costa and collaborators **[1]**, the LCC's internal energy per N,$u(T)$, $c_v(T)$ and $\alpha(T)$ must contain one term representing the Debye approximation plus corrections involving derivatives of $\omega_{LCC}(T)$. This way $u(T)$ is:

$$u(T) = \frac{k_bT^2}{N}\frac{d(lnZ)}{dT} = \frac{k_b^2\pi^2}{6\hbar}\frac{T^2}{\omega_{LCC}(T)}\left[1-\frac{T}{\omega_{LCC}(T)}\frac{d\omega_{LCC}}{dT}\right], \qquad \textbf{(S4)}$$

Equation S4 leads to the heat capacity per N - $c_v(T)$:

$$c_v(T) = \frac{du}{dT} = \frac{(k_b\pi)^2}{3\hbar}\frac{T}{\omega_{LCC}(T)}\left\{1-2\frac{T}{\omega_{LCC}(T)}\frac{d\omega_{LCC}}{dT}+\frac{T^2}{\omega_{LCC}^2(T)}\left[\left(\frac{d\omega_{LCC}}{dT}\right)^2-\frac{\omega_{LCC}}{2}\frac{d^2\omega_{LCC}}{dT^2}\right]\right\}, \qquad \textbf{(S5)}$$

being $\alpha(T)$ given by:

$$\alpha(T) = \frac{-\delta}{2\Theta^2}\frac{c_v(T)}{a_{C-C}} = \frac{42(k_b\pi)^2}{3\hbar m a_{c-c}^2}\frac{T}{\omega_{LCC}^3(T)}\left\{1-2\frac{T}{\omega_{LCC}(T)}\frac{d\omega_{LCC}}{dT}+\frac{T^2}{\omega_{LCC}^2(T)}\left[\left(\frac{d\omega_{LCC}}{dT}\right)^2-\frac{\omega_{LCC}}{2}\frac{d^2\omega_{LCC}}{dT^2}\right]\right\}, \qquad \textbf{(S6)}$$

where a_{c-c}=1.37 Å is the average C-C distance, Θ=$\frac{m[\omega_{LCC}(T)]^2}{2}$, δ=$\frac{-21m[\omega_{LCC}(T)]^2}{a_{c-c}}$ and $\varepsilon = \frac{ma_{C-C}^2(\omega_{LCC}^0)^2}{72}$.

References:

[1] N. L. Costa et al., Thermodynamics of Linear Carbon Chains, Phys. Rev. Lett. 126, 125901 (2021).