Effect of the orientation of nitro group on the electronic transport properties in single molecular field-effect transistors

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Supplementary Information

Details of thermal average calculation

In Fig. 4, we plot the relative total energy of the free NO2BDT molecule as a function of twist angle $\theta$. Then we fit the curve to a harmonic oscillator potential for $\theta$ ranging from 0° to 50°.

The amplitude of rotation can be written as the standard deviation of $\theta$,

$$
\sigma = \sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2},
$$

where $\langle \theta \rangle = \frac{\text{Tr}(e^{-\frac{H}{kT}})}{\text{Tr}(e^{\frac{H}{kT}})}$ is the thermal average.

Hamiltonian of the harmonic oscillator is written as:

$$
H = \frac{1}{2} \frac{\omega^2}{2I} \theta^2 + \frac{1}{2} I \dot{\theta}^2,
$$

where $I$ is the moment of inertia, $\omega = \sqrt{\kappa/2I}$ is the vibration frequency, $L = I \frac{d\theta}{dt}$ is the angular momentum.

Introduce the raising and lowering operators:

$$
\theta = \frac{\hbar}{\sqrt{2I\omega}} (b^+ + b), \quad L = i \frac{\hbar\omega I}{2} (b^+ - b),
$$

which satisfy the following commutation relations:

$$
[b, b^+] = bb^+ - b^+b = 1 \quad \text{and} \quad [b, b] = [b^+, b^+] = 0.
$$

Then we can obtain:
$H = \hbar \omega (b^+ b + \frac{1}{2})$.

The eigen equation is:

$$H |n\rangle = E_n |n\rangle,$$

where $|n\rangle$ is the eigenvector, $E_n = \hbar \omega (n + \frac{1}{2})$ is the eigenvalue.

Therefore,

$$\langle \theta \rangle = \frac{\text{Tr}(e^{\frac{-H}{kT}} \theta)}{\text{Tr}(e^{\frac{-H}{kT}})} = \frac{\sum_n \langle n | e^{\frac{-H}{kT}} \theta | n \rangle}{\sum_n \langle n | e^{\frac{-H}{kT}} | n \rangle},$$

$$\langle \theta^2 \rangle = \frac{\text{Tr}(e^{\frac{-H}{kT}} \theta^2)}{\text{Tr}(e^{\frac{-H}{kT}})} = \frac{\sum_n \langle n | e^{\frac{-H}{kT}} \theta^2 | n \rangle}{\sum_n \langle n | e^{\frac{-H}{kT}} | n \rangle}.$$  

Substitute $\theta = \sqrt{\frac{\hbar}{2I\omega}} (b^+ b)$ into the two equations above, and we can obtain:

$$\langle \theta \rangle = 0,$$

$$\langle \theta^2 \rangle = \frac{1}{I\omega^2} \langle H \rangle = \frac{\hbar \omega}{2} \coth\left(\frac{\hbar \omega}{2kT}\right).$$

When $kT \gg \hbar \omega$, $\langle \theta^2 \rangle \approx \frac{kT}{I\omega^2} = \frac{kT}{\kappa}$.  

At room temperature ($T = 300K$), $kT = 25.86\text{meV}$. $\kappa$ can be obtained from the curve fitting of Fig. 4, $\kappa = 0.154\text{meV/deg}^2$. Take into account these parameters above, we obtain:

$$\sigma = \sqrt{\langle \theta^2 \rangle - \langle \theta \rangle^2} = \frac{kT}{\kappa} = 12.96\text{deg}.$$