Supporting Information for “Optical Identification of a DNA-Wrapped Carbon Nanotube: Signs of Helically Broken Symmetry” by S. E. Snyder, S. V. Rotkin

Model details

The cause of helical symmetry breaking of the nanotube is a combination of the Coulomb potentials of the partial charges of the atoms of single stranded DNA and the electrons on the SWNT itself, moving in the field of the DNA.

Table 1 shows partial atomic charges for a specific DNA base. Since many atomic charges are small and partially cancel the effects of nearby charges, we often approximate the effect of (A) all atomic charges with (B) regularly spaced point charges having the same net charge as an ionized phosphate group from CHARMM\[14]\.

TABLE I: Partial charges (in units of the elementary charge) on the cytosine base (from Ref. [14]).

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Charge</th>
<th>Atom type</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.50</td>
<td>H5</td>
<td>0.07</td>
</tr>
<tr>
<td>O1P</td>
<td>-0.78</td>
<td>C2</td>
<td>0.52</td>
</tr>
<tr>
<td>O2P</td>
<td>-0.78</td>
<td>O2</td>
<td>-0.49</td>
</tr>
<tr>
<td>O5’</td>
<td>-0.57</td>
<td>N3</td>
<td>-0.66</td>
</tr>
<tr>
<td>C5’</td>
<td>-0.08</td>
<td>C4</td>
<td>0.65</td>
</tr>
<tr>
<td>H5’</td>
<td>0.09</td>
<td>N4</td>
<td>-0.75</td>
</tr>
<tr>
<td>H5”</td>
<td>0.09</td>
<td>H41</td>
<td>0.37</td>
</tr>
<tr>
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<td>H42</td>
<td>0.33</td>
</tr>
<tr>
<td>H4’</td>
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<td>C2’</td>
<td>0.14</td>
</tr>
<tr>
<td>O4’</td>
<td>-0.50</td>
<td>H2”</td>
<td>0.09</td>
</tr>
<tr>
<td>C1’</td>
<td>0.16</td>
<td>O2’</td>
<td>-0.66</td>
</tr>
<tr>
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<td>H2’</td>
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</tr>
<tr>
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<td>C3’</td>
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<td>0.05</td>
<td>H3’</td>
<td>0.09</td>
</tr>
<tr>
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<td>0.17</td>
<td>O3’</td>
<td>-0.57</td>
</tr>
<tr>
<td>C5</td>
<td>-0.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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The unscreened potential on the surface of a nanotube is compared for both models in Figure 1. In solution, the charges are additionally screened by water molecules and counterions. We included this effect phenomenologically by adjusting the field of the DNA, though a microscopic model would be desirable to compute the exact perturbation potential.

It is a nontrivial problem to make a choice of the unit cell of the complex; a commensurate one dimensional periodic structure does not exist for every (helically symmetric) DNA potential and given SWNT symmetry. The SWNT lattice itself may possess spiral symmetry incommensurate with the DNA. Here we limit ourselves to commensurate structures where the angle of the DNA wrap is chosen such that one wind (or more winds) covers an integer number of nanotube lattice constants. For noncommensurate wrappings, it is always possible to find a commensurate wrapping with a wrapping angle that is infinitesimally close to the noncommensurate one.

We used a real-space, orthogonal, tight-binding Hamiltonian (see for example, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Carbon Nanotubes, (Imperial College Press, 1998))

$$\hat{H}_o = \sum_{ij} \gamma a_i^\dagger a_j,$$  \hspace{1cm} (A.1)

where $\gamma \simeq 2.9$ eV is the hopping integral (characteristic energy scale of the model) and the sum is taken over nearest neighbor carbon atoms in the supercell of the hybrid structure. The perturbation operator is chosen as

$$\hat{V} = \sum_i V(i)a_i^\dagger a_i = \sum_i e\varphi^{\text{act}}(i)a_i^\dagger a_i,$$  \hspace{1cm} (A.2)

where the sum over $i$ runs over all atoms of the supercell and the acting electrostatic potential at the lattice site, $\varphi^{\text{act}}$, is calculated self-consistently. The quantum mechanical charge density $\rho$ is determined by states below the Fermi level.

$$\delta \rho(\vec{x}) = \delta \langle e a_i^\dagger a_i \rangle = e \sum_{\lambda \leq \lambda_F} \left( |\psi_{\lambda}(\vec{x})|^2 - |\psi_{\lambda}(\vec{x})|^2 \phi - |\psi_{\lambda}(\vec{x})|^2 0 \right),$$  \hspace{1cm} (A.3)

The Fermi level is always in the middle of the band gap in all cases presented in this Communication to ensure charge neutrality of the SWNT. The total potential is given by the sum of two components

$$V = e\varphi^{\text{act}} = e(\varphi^{\text{xt}} + \varphi^{\text{ind}}) = e \left( \varphi^{\text{xt}} + \int \frac{\delta \rho(\xi)}{|\vec{x} - \xi|} d\xi \right),$$  \hspace{1cm} (A.4)
where $\varphi^{xt}$ is the unscreened potential due to DNA charges, and the induced (screening) potential $\varphi^{ind}$ is calculated as the Poisson integral.

Equations (A.2-A.4) are solved iteratively to yield the self-consistent polarization charge density and resulting self-consistent induced potential.

Figure 2 shows a comparison of perpendicular absorption coefficients for the self-consistent induced potential and the non-self-consistent case. The self consistent potential is screened, resulting in a smaller shift of the peak of newly allowed transitions due to the DNA wrap. Since the absorption spectrum is qualitatively the same for both cases, non-self-consistent calculations were used for absorption plots in this Communication.
Absorption and luminescence calculation

The absorbed power density (per unit volume, per unit time) is found as

$$Q_{abs} = \frac{1}{V} \frac{2 \pi e^2 \hbar^2}{m_0^2 \omega^2} \mathcal{E}_m^2 \sum_{i,f} f(E_i) [1 - f(E_f)] \times$$

$$\times \frac{\Gamma \left| \langle f|\mathbf{J} \cdot \mathbf{e}|i \rangle \right|^2}{[(E_f - E_i - \hbar \omega)^2 + \Gamma^2]}$$

(A.5)

following the textbook V. L. Bonch-Bruevich and S. G. Kalashnikov, *Physics of Semiconductors (Fizika poluprovodnikov)*, Moscow, "Nauka," 1990. Here $V$ is the integration volume, $m_0$ is the free electron mass, $\mathcal{E}_m$ is the amplitude of the electric field of the photon with frequency $\omega$, $f(E)$ is the Fermi-Dirac function, $\Gamma$ is the inverse lifetime, and the matrix element $\langle f|\mathbf{J}|i \rangle$ is

$$\langle f|\mathbf{J}|i \rangle = \int \psi_f^* e^{i \mathbf{J} \cdot \mathbf{e}} \nabla \psi_i d^3 x,$$

(A.6)

which can also be rewritten as the operator of the dipole moment (see, for example, M. O. Scully and M. S. Zubairy, *Quantum Optics*, Cambridge University Press, 1997 for a similar derivation):

FIG. 2: Calculated absorption coefficient for perpendicularly polarized light vs. absorbed photon energy for the bare (7,0) nanotube (orange) and DNA-wrapped (7,0) nanotube (dashed black).
Here the electron and the hole are on the surface of a cylinder of the radius $R$.

We know that the absorption coefficient is related to the dynamic conductivity $\alpha = 4\pi\sigma/(cn)$ where $n = \sqrt{\epsilon}$ is the refraction coefficient. The dynamic conductivity is, in turn, related to the absorbed power density as: $\sigma = Q_{\text{abs}}/(E_i^2/2)$. This allows us to write the partial absorption coefficient (up to a numerical coefficient) as follows:

$$
\alpha_{\pm}(\hbar \omega, k) \propto \sum_i \sum_f q^2 \left| \langle \psi(k, m_f, \lambda_f) | \vec{p} \cdot \vec{e}_\pm | \psi(k, m_i, \lambda_i) \rangle \right|^2 \frac{m_0 \omega}{\hbar} \\
\times \frac{f(E_i(k, m_i, \lambda_i)) [1 - f(E_f(k, m_f, \lambda_f))]}{(E_f(k, m_f, \lambda_f) - E_i(k, m_i, \lambda_i) - \hbar \omega)^2 + \Gamma^2}.
$$

(A.8)

For simulating the luminescence we used the partial coefficient for stimulated radiation which is given by the same expression as the partial absorption coefficient with replacement of the indexes of the final and initial states. The spontaneous emission coefficient is related to the stimulated emission one via the Einstein relation and is derived from the principle of detailed balance, $Q_{\text{abs}} - Q_{\text{sp}} - Q_{\text{stim}} = 0$.

For this Communication we assumed that the distribution functions are degenerate Fermi-Dirac functions; explicitly, the values 1 and 0 for the initial and final states were used for the valence and conduction band states respectively (for absorption). As for the other mechanisms resulting in finite lifetime of the nonequilibrium charge carriers, we treat them phenomenologically. Both the emission and absorption response function are approximated by the sum (integral) of the Lorentzians with the fixed half-width given by the parameter $\Gamma$. We assume that this approximation is valid for the calculated absorption, though a realistic emission coefficient would need actual lifetimes as well as a realistic distribution function which is likely peaked at the edge of the band. However, calculation of the lifetime or the distribution function is beyond the scope of this paper. Thus, the simulated emission coefficient overestimates the emission probability for higher energies, but accurately reproduces the band edge. The conclusions of the paper are based on the appearance of new peaks, which means that only the band edge matters. Therefore, none of the results of the Communication depend on the assumed flat distribution function.
Comparison of hybrids with different geometry

We found that the strength of the perturbation is proportional to the total charge of DNA in the supercell as well to the SWNT radius. Thus the typical splitting of the subbands scales as $\propto R^4$ and becomes stronger for tubes of larger radius (Figure 3). We found that chiral symmetry breaking is also present for wraps with different angles (Figure 4), with circular dichroism and absorption peak splitting clearly observed. The radial or angular shift of the wrap is found to be unimportant (Figure 5). Therefore, we propose that the wrapping always may be detected via optical methods. We suggest, however, to study the absorption of light in circular or perpendicular polarization, since the absorption of light polarized along the SWNT axis may be almost the same with or without the wrap. Note that figures below are for the case of right circularly polarized incident light.

FIG. 3: Calculated absorption coefficient for right circularly polarized light vs. photon energy for bare (n,0) nanotube (blue) and DNA-wrapped (n,0) nanotube (red) for 4 different SWNT radiiuses: (5,0), (7,0), (8,0) and (10,0) SWNTs (we do not present data on the metallic nanotubes). Insets show geometry of the wrap.
FIG. 4: Calculated absorption coefficient for right circularly polarized light vs. photon energy for bare $(7,0)$ nanotube (blue) and DNA-wrapped $(7,0)$ nanotube (red) for three different angles of the wrap.

FIG. 5: Calculated absorption coefficient for right circularly polarized light vs. photon energy for bare $(7,0)$ nanotube (blue) and DNA-wrapped $(7,0)$ nanotube (red) for three different positions of the wrap on the SWNT: (Left) atom centered, (center) with an axial shift, (right) with an angular shift (rotation).