Supplementary Material for: Incidence of Quantum Confinement on Dark Triplet Excitons in Carbon Nanotubes

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ABSTRACT

This supplementary materials is organized as follows. We presente the conventional rate equations for the fluorescence-phosphorescence system, which is relevant for the ODMR process. We present additional experimental data to support the identification of the wavelength resolved phosphorescence peaks, namely excitation profiles. We also present the detailed rate equations for the exciton energy transfer, or Förster exciton transfer process, which occurs in a small bundle of SWCNTs.

Rate equations for the ODMR process

The basic ODMR process is illustrated in Figure[1]. In the course of ODMR measurement, $S_0 \rightarrow S_1$ transition is pumped by a laser which causes a steady-state population of the triplet sublevels. The probability of the intersystem crossing is denoted by $k_{ISC}$. In the case of this example, the population rates ($p_u$) and decay rates ($k_u$) are not the same, therefore the relative populations of the sublevels are also different ($n_u$).

If one applies resonant microwaves, transitions are possible between any two sublevels e.g. $T_x$ and $T_z$, which have the largest population difference in this example. After the changes of the population caused by the resonant microwave, the $T_z$ state has more population, however, its decay rate remains the same i.e. the smallest (Figure[2]). It means that more electrons stay in the triplet state per unit time, therefore fewer electrons can deexcite to the ground state and can be excited again to the $S_1$ state. This process causes the decrease of the photoluminescence signal.[14]

The ODMR process on nanotubes is illustrated in Figure[2]. First, the absorption of light generates an exciton to the energy level proportional to the second optical transition, then it relaxes to the lowest possible excited state because of Kasha’s rule. Here, it can recombine and emit a photon with $k_{10}$ probability, which contributes to the fluorescence signal. This path is illustrated by the red arrow.
However, from $S_1$ state, it can cross over to the triplet states with $k_{ISC}$ decay rate. The deexcitation from this sublevels is denoted by the green arrow. If the system is irradiated by microwaves radiation, after aligning the differences between the sublevels with magnetic field, then the strength of the phosphorescence signal changes. It causes the increase (or decrease) of the population of the $S_0$ ground state. The strength of the fluorescence signal depends on the population of the ground state since the greater population let participate more nanotubes in the fluorescence cycle.

To study the change of the photoluminescence signal, we need to analyze the rate equation of the population of the states which are involved in the process. The total number of excitable electrons is denoted by $N$.

$$N = [S_0] + [S_1] + [S_2] + \sum_{u=0}^{3} [T_u]$$

(1)

Here, the population of the ground state is $[S_0]$, the excited singlet and triplet states are indicated by $[S_1]$, $[S_2]$ and $[T_u]$.

For the following calculation of the population dynamics of the five sublevels, we need to suppose a few conditions. First of all, that no spin-lattice relaxation occurs between the triplet states, which is possible at low temperatures, and they do not affect the population of the other two sublevels. Another condition, that due to the short lifetime of the $S_1$ and $S_2$ level, the population of these states is negligible.

$$N \approx [S_0] + \sum_{u=0}^{3} [T_u]$$

(2)

The differential equations of the population dynamics are described by the following equations:

$$\frac{d[S_0]}{dt} = -k_0[S_0] + k_1[S_1] + \sum_{u=0}^{3} k_u[T_u]$$

(3)
\[
\frac{d[S_1]}{dt} = k_0[S_0] - k_1[S_1] - \sum_{u=0}^{3} k_{ISC} P_u[S_1] = k_0[S_0] - k_1[S_1] - k_{ISC}[S_1] 
\]  
(4)

\[
\frac{d[T_u]}{dt} = k_{ISC} P_u[S_1] - k_u[T_u] 
\]  
(5)

Here, \( P_u \) denotes the relative populating probabilities \( (P_x + P_y + P_z = 1) \), from which the population rates of the sublevels are determinable: \( p_u = P_u k_{ISC} \). From the above equations, the population of the triplet states is calculated:

\[
[T_x] + [T_y] + [T_z] \sim \frac{p_x}{k_x} + \frac{p_y}{k_y} + \frac{p_z}{k_z} \sim n_x + n_y + n_z 
\]  
(6)

Figure 2: The principle of ODMR spectroscopy. Resonant microwave field (Mw) induces the change of the triplet sublevel population.

In the presence of microwave field, which saturates the triplet sublevel transitions, the population and the decay rates change in first approximation:

\[
p'_x = \frac{1}{2}(p_x + p_z)
\]

\[
p'_y = p_y
\]

\[
p'_z = \frac{1}{2}(p_x + p_z)
\]  
(7)

\[
k'_x = \frac{1}{2}(k_x + k_z)
\]

\[
k'_y = k_y
\]

\[
k'_z = \frac{1}{2}(k_x + k_z)
\]  
(8)
And the population of the triplet state under continuous illumination of microwave field is:

\[ [T_x]' + [T_y]' + [T_z]' \sim \frac{p_x + p_z}{k_x + k_z} + \frac{p_y}{k_y} + \frac{p_z + p_x}{k_z + k_x} \]  

(9)

The fluorescence intensity is related to the \([S_0]\), therefore the change of the signal is proportional to the change of the population of the \(S_0\) state, which one can express using the condition that the population of the \(S_1\) state is negligible (Eq. (2)).

\[
\Delta[S_0] = [S_0]' - [S_0] = -(\sum_{u=0}^{3} [T_u]' - \sum_{u=0}^{3} [T_u]) = -\Delta(\sum_{u=0}^{3} [T_u])
\]  

(10)

Equation (10) indicates that a decrease of triplet population leads to the increase of the PL signal. This is easy to understand if one thinks through that the molecules, which are trapped in long-living triplet states, are liberated and can participate in the fluorescence cycle again. With ODMR spectroscopy this change can be measured. This measurement is realized in practice by applying an amplitude modulated (or chopped) strong microwave and the resulting optical signal is detected using a lock-in detection.

\[
\Delta(\sum_{u=0}^{3} [T_u]) \sim \frac{1}{k_x + k_z} (n_x - n_z)(k_x - k_z)
\]  

(11)

**Additional experimental data**

**Excitation energy profiles**

In Figures 3, ODMR and PL spectra are shown, however, in this case the data are presented as a function of excitation wavelength. We find that the chirality peaks, which belong to different nanotubes, are detected at the same wavelength whereas their intensities are different. As consequence of this observation is that we indeed detect the change of the fluorescence signal during the ODMR measurement.

In Figures 4, the cross section of the ODMR map are shown at different emission wavelengths. We chose the wavelength where the strength of the fluorescence peak is the strongest and compare it with the excitation spectrum where the phosphorescence sideband of the peak is observable. We present this comparison for the largest chirality peaks and we can see that the phosphorescence peaks can be excited at the same wavelength than the fluorescence ones.

We measured the spectra in 6 nm steps, which limits the resolution of this type of data.
The fluorescent and phosphorescent transition energies in SWCNTs

We can identify the different peaks on the ODMR maps as belonging to the different SWCNT chiralities. Positions of the fluorescence peaks and the phosphorescence sidebands are determined from Figure 1, the simultaneously measured PL and ODMR map.

In Table 1, data of the larger peaks are collected such as the \((n,m)\) indices and the family which they belong to. The literature values, the excitation and emission wavelength, are presented in the work of Weisman and Bachilo. Note that there is a difference between these data and the actual chirality peaks, which is caused by the temperature difference and a different surfactant used. The calculated data show the PL peak positions at 300 K and our measurements are taken at 77 K. The measured roomtemperature values are read from the 300 K PL map.

The figure shows distinct peaks with variable signal strength. However, it is noted that not all \((n,m)\) pairs can be assigned to a chirality peak. First of all, we know that zig-zag nanotubes \((m = 0)\) do not have a photoluminescence signal. The explanation of this effect is currently unknown. On the other hand, the distribution of the diameters follows a Gaussian function, therefore nanotubes with larger diameter are not present in the sample.

The dipolar broadening in SWCNTs

The van Vleck formula describes the broadening of a spectral line due to the dipole-dipole interactions between like spins as:
Chirality peak has a maximum at 1281 nm emission wavelength. Its sideband is observable at 1323 nm.

\[
\Delta B^2 = \frac{1}{(\gamma T_2)^2} \approx 5\mu_0^2 g^2\mu_B^2 S(S+1) \frac{1}{d^2}
\]

where \(\Delta B\) is the second moment of the linewidth that is associated with the spin-spin relaxation time, \(T_2\), \(\mu_0\) is the vacuum permeability, \(\mu_B\) is the Bohr magneton, \(S\) is the spin value. This formula is a simplification of the exact calculation for an arbitrary crystal structure, and it is valid for randomly oriented crystallites with a cubic lattice constant, \(d\). This is clearly oversimplified for the SWCNT, it however serves as a good basis to obtain an order of magnitude estimate of the dipolar linewidth.

For \(S = 1\) and \(d = 10\) nm, Eq. (12) gives \(\Delta B = 0.023\) mT.

### Rate equations for the exciton energy transfer process

In Table 3, the emission and excitation wavelength and energies of a bundle peak marked by B are presented. The table also shows the nanotubes which take part in the creation of the peak. The data are read from the PL map (Figure 1).

This additional peak appears only on the PL map and is completely absent on the ODMR map. Further considerations are required to explain this observation.

An exciton jumps to another nanotube in a bundle, it emits a photon with \(E'_{11}\) energy, or it is transferred to the triplet state and does phosphorescence radiation with \(k'_T\) decay rate. Regardless of which process

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Figure 4: (8, 7) chirality peak has a maximum at 1281 nm emission wavelength. Its sideband is observable at 1323 nm.
occurs, the nanotube reaches the \( S'_0 \) ground state and the nanotube, from which the exciton originates, also reaches the \( S_0 \) ground state upon transferring the exciton.

For a one-nanotube ODMR process the ODMR signal is a consequence of the triplet population change due to the microwave irradiation. For the bundle peak in principle both the \( T \) and \( T' \) states can be populated, i.e. a strong ODMR signal would be expected. The first observation is that the bundle peak intensity itself is unaffected by the \( T' \) state population as the \( S'_1 \) population only depends on the exciton transfer process (that process "pumps" the \( S'_1 \) population). In principle a phosphorescent peak near the bundle peak would be observable but it overlaps with other signal we are therefore unable to resolve it.

The remaining question is why the \( T \) population does not affect the bundle peak. In our opinion, the only possible explanation of the experimental result is that the \( T \) state is not populated at all for the bundle PL process. It means that the exciton transfer to the neighboring tube in a bundle is preferred as compared to an internal conversion process, either from the \( S_2 \) or from the \( S_1 \).

Following the above qualitative considerations, we give a more quantitative discussion. We can investigate the population dynamics of the two nanotubes. First of all, we can determine the number of the
Table 1: Positions of the fluorescence (F) and phosphorescence (Ph) peaks at 77 K as determined from the ODMR map.

| Family | Literature value | F (300 K) | F (77 K) | Ph (77 K) |
|--------|------------------|-----------|-----------|-----------|
|        | λ<sub>exc</sub>  | λ<sub>em</sub> | λ<sub>exc</sub> | λ<sub>em</sub> | λ<sub>exc</sub> | λ<sub>em</sub> |
| (n,m)  | (nm)             | (nm)      | (nm)      | (nm)      | (nm)      | (nm)      |
| (10,2) | 22               | 731       | 1041      | 742       | 1071      | 748       | 1038      | 748       | 1078 |
| (9,4)  | 22               | 716       | 1087      | 727       | 1118      | 730       | 1088      | 730       | 1130 |
| (8,6)  | 22               | 711       | 1159      | 724       | 1190      | 724       | 1169      | 724       | 1209 |
| (8,7)  | 23               | 721       | 1250      | 736       | 1282      | 727       | 1281      | 727       | 1323 |

Table 2: Singlet-triplet gap of single-walled carbon nanotubes.

| Diameter d (nm) | Excitation E<sub>22</sub> (eV) | F E<sub>11</sub> (eV) | Ph E<sub>T</sub> (eV) | S-T gap ΔE<sub>ST</sub> (meV) |
|-----------------|---------------------------------|------------------------|-----------------------|-------------------------------|
| (10,2)          | 0.87231                         | 1.65842                | 1.19509               | 1.15074                       | 44.35                          |
| (9,4)           | 0.90342                         | 1.69932                | 1.14017               | 1.09973                       | 40.44                          |
| (8,6)           | 0.953                           | 1.7134                 | 1.06026               | 1.02605                       | 34.21                          |
| (8,7)           | 1.01837                         | 1.70633                | 0.96914               | 0.9412                        | 27.94                          |

excitable electrons.

\[ N = [S_0] + [S_1] + [S_2] + [S_1'] + [S_2'] + \sum_{u=0}^{3} [T_u'] \approx [S_0] + [S_1'] + \sum_{u=0}^{3} [T_u'] \]  

Here, we take into account that \([S_1], [S_2]\) and \([S_1']\) are negligible since the lifetime of these states are shorter.

Because in bundles, the exciton always jumps to the acceptor nanotube, the population of the ground state of the donor nanotube only depends on the \(k_{exc}\) excitation probability and is not affected by the decay rates of the excited states.

\[ \frac{d[S_0]}{dt} = -k_{exc}[S_0] \]  

The transition between the tubes are described by \(k_{IT,1}\) and \(k_{IT,2}\), because from these data we cannot decide from which excited state the transition occurs: \(S_1\) or \(S_2\). We assume that the two processes, the internal conversion and the jump between the nanotubes, compete with each other on the \(S_2\) excited state.

\[ \frac{d[S_1]}{dt} = k_{IC}[S_2] - k_{IT,1}[S_1] \]  

\[ \frac{d[S_2]}{dt} = k_{exc}[S_0] - k_{IC}[S_2] - k_{IT,2}[S_2] \]

For the following differential equations, we assume that excitons on the second nanotube drop out from the photoluminescence cycle and they can only get to the acceptor tube from the donor tube.

\[ \frac{d[S_0']}{dt} = k'_{PL}[S_1'] + \sum_{u=0}^{3} k'_u[T_u'] \]
Table 3: The optical excitation and emission energy for the peak denoted as B.

|   | (n,m) | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $E_{22}$ (eV) | $E'_{11}$ (eV) |
|---|------|----------------------|---------------------|--------------|--------------|
| B | (9, 4) | (7, 6) | 730 | 1140 | 1.699 | 1.086 |

\[
\frac{d[T_u]}{dt} = k'_{ISC}P_u[S'_1] - k'_u[T_u]
\] (18)

\[
\frac{d[S'_1]}{dt} = k_{IT,2}[S_2] + k_{IT,1}[S_1] - \sum_{u=0}^{3} k'_{ISC}P'_u[S'_1] - k'_PL[S'_1] =
\]
\[
= k_{IT,2}[S_2] + k_{IT,1}[S_1] - (k'_{ISC} + k'_PL)[S'_1]
\] (19)

The intensity of the bundle peak depends on the population of the $S'_1$ state, where the fluorescence radiation occurs from. It is clear that $[S'_1]$ is not affected by $k'_u$ decay rates and the change of the population of the triplet sublevels, which occurs under continuous microwave irradiation. These considerations thus explain why the bundle peak is absent on the ODMR map.

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