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Carbon nanotubes as substrates for molecular spiropyran-based switches

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Abstract
We present a joint theory–experiment study investigating the excitonic absorption of spiropyran-functionalized carbon nanotubes. The functionalization is promising for engineering switches on a molecular level, since spiropyrans can be reversibly switched between two different conformations, inducing a distinguishable and measurable change of optical transition energies in the substrate nanotube. Here, we address the question of whether an optical read-out of such a molecular switch is possible. Combining density matrix and density functional theory, we first calculate the excitonic absorption of pristine and functionalized nanotubes. Depending on the switching state of the attached molecule, we observe a red-shift of transition energies by about 15 meV due to the coupling of excitons with the molecular dipole moment. Then we perform experiments measuring the absorption spectrum of functionalized carbon nanotubes for both conformations of the spiropyran molecule. We find good qualitative agreement between the theoretically predicted and experimentally measured red-shift, confirming the possibility for an optical read-out of the nanotube-based molecular switch.

(Some figures may appear in colour only in the online journal)

1. Introduction

The adsorption of molecules onto the surface of carbon nanostructures is becoming a focus of current research [1–14]. The functionalization of graphene and carbon nanotubes (CNTs) consisting of a single atomic layer is a promising strategy to create new hybrid systems with distinct and externally controllable properties. In particular, the functionalization of CNTs with photochrome molecules, such as spiropyrans and azobenzenes, has sparked great interest in both fundamental research and technological application, since these hybrid nanostructures can be exploited for engineering switches on a molecular level as well as high-efficiency photo-detectors with a tunable wavelength range [15, 2, 6, 8, 9, 11–14]. The first experiments have been realized illustrating the successful covalent and non-covalent functionalization of CNTs with spiropyran molecules [2, 6, 12]. In particular, Guo et al have shown that spiropyran molecules can be used to externally and reversibly switch the conductance of a CNT transistor [6].

There are few theoretical studies investigating the properties of CNTs functionalized with photochrome molecules [9, 11, 16]. However, the key for designing and engineering novel devices based on hybrid nanostructures is a better microscopic understanding of the interaction between the adsorbed molecule and the substrate nanotube. In a previous work addressing the change in absorption spectra of spiropyran-functionalized CNTs, we investigated different functionalization regimes. Our calculations revealed a red-shift of transition energies in the range of some tens of meV depending in particular on the molecular dipole moment and its orientation [14]. In this work, we present a joint theory–experiment study investigating the excitonic absorption of spiropyran-functionalized CNTs. We have...
extended the theoretical model by performing \textit{ab initio} calculations based on the DFT package SIESTA, including the recently implemented van der Waals exchange–correlation functional. We perform a full geometrical relaxation of the adsorbed molecules at the surface of the CNT and obtain the dipole moment of the entire hybrid nanostructure including its orientation with respect to the CNT axis. The resulting theoretical absorption spectrum of functionalized CNTs is compared with corresponding experimental observations.

2. Theoretical approach

In this work, we focus on non-covalently functionalized CNTs, where the influence of the attached spiropyran molecule on the electronic structure of the substrate CNT is small, i.e. the band structure and the wavefunction remain approximately unchanged [4]. As a result it is sufficient to investigate the behavior of a pristine CNT located in a static dipole field induced by the attached molecules. Our approach is based on a combination between density matrix (DM) and density functional theory (DFT). The DM formalism is exploited to microscopically determine the excitonic absorption coefficient \( \alpha(\omega) \) for an arbitrary functionalized CNT. The DFT is applied to perform a geometrical relaxation of the adsorbed molecule on the surface of the substrate nanotube and to determine the functionalization parameters, such as the dipole moment, the dipole orientation, and the molecule distance from the CNT surface. These parameters are needed for the calculation of \( \alpha(\omega) \) within the DM theory. Note that in this work we study the nanotube–molecule interaction for a relatively small molecule density on the surface of the CNT making sure that there are no inter-molecular overlap effects.

The spiropyran molecules can be reversibly switched between the open merocyanine (MC) and the closed spiropyran (SP) conformation. The corresponding ring-opening/ring-closing process is driven by visible and ultraviolet light, respectively [15] (see figure 1(a)). It induces a significant change of the molecular dipole moment enabling an externally stimulable coupling between the excitons in the CNT and the external dipole moment. As a result, depending on its conformation, the attached molecule accounts for a distinguishable and measurable change of the carrier mobility and the optical transitions in the substrate CNT.

The first step in our approach is the description of the many-particle Hamilton operator

\[ H = H_0 + H_{c,t} + H_{c,c} + H_{c,d}, \]

which determines the dynamics of the carrier system in the CNT. It consists of: (i) the free-carrier part \( H_0 = \sum \hat{\epsilon} \hat{c}_l^\dagger \hat{c}_l \) with the electronic band structure \( \epsilon_l \) [17, 18] and the ladder operators \( \hat{a}_l^\dagger \) and \( \hat{a}_l \), which create and annihilate an electron in the state \( I = (k, \lambda) \) consisting of the momentum \( k \) along the CNT axis and the subband index \( \lambda \); (ii) the coupling with the optical field \( H_{c,t} = i \hbar \sum_{l} \hat{c}_l^\dagger \hat{c}_l \cdot \lambda(t) \hat{a}_l^\dagger \hat{a}_l \) with the optical matrix element \( M_{l_1,l_2} \) [19, 18, 20] and the vector potential \( \lambda(t) \); (iii) the carrier–carrier interaction \( H_{c,c} = \frac{1}{2} \sum_{l_1,l_2} \lambda_{l_1,l_2} \hat{v}_{l_1,l_2}^\dagger \hat{v}_{l_1,l_2} \hat{a}_l^\dagger \hat{a}_l \) with the Coulomb matrix element \( \lambda_{l_1,l_2} \) [21, 20, 30]; and (iv) the CNT carrier coupling to the external molecular dipole moment

\[ H_{c,d} = \sum_{l_1,l_2} g_{l_1,l_2} \hat{a}_l^\dagger \hat{a}_{l_2}, \]

with the carrier–dipole coupling element

\[ g_{l_1,l_2} = \langle \Psi_l(\mathbf{r}) | e \phi_0(\mathbf{r}) | \Psi_{l_2}(\mathbf{r}) \rangle \]

with the zone-folded tight-binding wavefunctions \( \Psi_l(\mathbf{r}) \) and the potential \( \phi_0(\mathbf{r}) = \frac{d(\mathbf{r}-\mathbf{R}_d)}{4\pi\varepsilon_0 |\mathbf{r}-\mathbf{R}_d|^3} \). This external dipole field depends on the molecular dipole moment \( d \), its orientation \( \alpha \) with respect to the CNT axis, and its distance \( R_d \) from the CNT surface (see figure 1(a)). These parameters are determined by \textit{ab initio} calculations performed within the SIESTA package [23, 24] including the recently implemented van der Waals exchange–correlation functional [25]. The calculation of the microscopic dipole moment of a fully relaxed spiropyran- and merocyanine-functionalized CNT is based on a recent technique within the Clar sextet rule [26]. Here, the edges of the CNT are hydrogenated following the recipe given by the Clar sextet rule in such a way that the electronic structure of a finite CNT converges fast with the CNT length to the case of an infinite CNT. First, a Clar unit...
cell is built by optimizing the number of aromatic rings. Then, the finite-size CNT is obtained by repetition of this unit cell. Finally, the edges of the resulting CNT are hydrogenated. In general, a Clar unit cell differs considerably from the regular CNT unit cell. Such an approach has proved to be much more accurate for modeling the electronic structure of CNTs than typical hydrogen terminations or capped CNTs [26].

In contrast to the previously published work [14], where only the dipole moment of an isolated molecule was considered, this new approach allows us to additionally obtain the dipole moment induced in the CNT together with the change in the dipole of the adsorbed molecule. More details will be given in a future publication [27]. Using a Clar sextet-terminated nanotube with a length of 48 Clar unit cells (corresponding to a length of around 180 Å) in a supercell with a square lateral section (perpendicular to the nanotube) of 120 Å times 120 Å, we obtain \( d_{\text{MC-CNT}} = 16.6 \) D for merocyanine- and \( d_{\text{SP-CNT}} = 7.3 \) D for spiropyran-functionalized CNTs. The corresponding orientation of the dipole moment with respect to the CNT axis is given by \( \Theta_{\text{MC-CNT}} = 5.6^\circ \) and \( \Theta_{\text{SP-CNT}} = 22.0^\circ \), respectively. The distance of the attached molecule to the CNT surface is determined by the van der Waals radius.

Once we have determined the Hamilton operator including the matrix elements and the functionalization parameters, we can apply the Heisenberg equation of motion [28] and derive many-particle Bloch equations for arbitrary hybrid nanostructures [14]. They consist of a coupled system of differential equations for the occupation probabilities \( \alpha_k = \langle \alpha_{k} \rangle \) and the microscopic polarization \( \mathbf{p}_k = \langle \mathbf{a}_k \rangle \), which is a measure for the transition probability between the valence (\( \lambda = v \)) and the conduction band (\( \lambda = e \)) (see figure 1(b)). Since we are interested in describing a linear absorption spectrum, the driving field is considered to be small, resulting in a negligible change of the occupation. As a result, the optical response is determined only by the microscopic polarization, i.e.

\[
\alpha(\omega) \propto \omega \Im \chi(\omega) \propto \sum_k M_{\nu c}(k) \Im[p_k(\omega)] / \omega |A(\omega)|.
\]

(3)

However, due to the coupling between the excitons in the CNT and the external molecular dipole moment the microscopic polarization \( \mathbf{p}_k \) is determined by non-diagonal transitions \( \sigma^\nu c_{k_1 k_2} \equiv \langle \mathbf{a}^\nu_k \mathbf{a}^c_{k_2} \rangle \), which account for the momentum transfer \( (k_1 - k_2) \) due to the spatial inhomogeneity (see figure 1(b)). The dynamics of \( \sigma^\nu c_{k_1 k_2} \) is given by

\[
\dot{\sigma}^\nu c_{k_1 k_2} = -i (\hbar \epsilon_{k_1 k_2} - i \gamma) \sigma^\nu c_{k_1 k_2} + \sum_{k'} \langle \mathbf{g}_{k k'} \rangle^\nu c \langle \mathbf{g}_{k' k} \rangle^c \sigma^\nu c_{k' k_2},
\]

(4)

where \( \epsilon_{k_1 k_2} = (\epsilon_{k_2} - \epsilon_{k_1}) - \sum_k V_{\text{e-e}}(k', k_1, k_2) \) is the band gap energy renormalized due to the repulsive electron–electron contribution \( V_{\text{e-e}}(k', k_1, k_2) \) and where \( \Omega_{e}(t) = \frac{\sigma_{\text{MC}}(k)A(t) \delta_{k_1 k_2}}{\sum_{k'} V_{\text{e-h}}(k', k_1, k_2) p_{e}(t)} \) is the Rabi frequency renormalized due to the attractive electron–hole interaction \( V_{\text{e-h}}(k', k_1, k_2) \). For more details on the analytic calculation of the Coulomb matrix elements \( V_{\text{e-e}}(k', k_1, k_2), V_{\text{e-h}}(k', k_1, k_2) \) using tight-binding wavefunctions and applying a regularized Coulomb potential see [29, 21, 30]. In the limiting case of \( k_1 = k_2 \), (4) contains the contribution of the microscopic polarization \( p_k = \sigma^c_{k_2} \), which turns out to be crucial for the dynamics of \( \sigma^\nu c_{k_1 k_2} \). The phenomenological parameter \( \gamma \) in (4) influences the peak width in the absorption spectrum accounting for the dephasing by scattering contributions beyond the Hartree–Fock approximation [14].

3. Experimental approach

In order to non-covalently attach the spiropyran-based switch to the CNT sidewall, we exploit a compound already used in [31]. It consists of a pyrene fragment (which has been proven to efficiently stick on the nanotube sidewalls [32]) attached as an anchoring group to the spiropyran moiety via a flexible linker. The structure of the compound as well as its chemo-physical characterization can be found in [31]. CoMoCAT nanotubes, produced by SouthWest NanoTechnologies (SWCNT, SG 76) and all belonging to the same production batch were used for this experiment. The tubes have a diameter of 0.9 ± 0.3 nm and a high aspect ratio (1000). Tetrahydrofuran (THF) suspensions of our switching compound were prepared setting the molarity to 5 \( \mu \)M. The solution was transparent and exhibited no absorption in the visible. This implies that for THF at room temperature the switch was stable in the ring-closed spiropyran form. As a matter of fact, for the solvent used at room temperature there is no need for visible light illumination in order to induce the mero-to-spiro back-isomerization, as the kinetics of the thermally driven back-isomerization takes place over a timescale comparable to the light induced one [31]. Therefore, in the experiment performed in this work, we left the sample in the dark in order to induce the mero-to-spiro back-isomerization. In order to compare with theory and get the spectra of ‘pristine’ tubes, we exploited 4-(1-pyrenyl)butyric acid (PBA; CAS n.3443-45-6), which shares the same properties as our switching compound, apart from the obvious lack of a spiropyran switching moiety attached to its end.

CoMoCAT tubes were added to the solution with a starting concentration of 0.01 g \( \text{l}^{-1} \). We treated the mixture with a tip sonicator (Bandelin SonoPlus HD 2070) at a power of 60 W and cycles of 0.5 s. After 1 h the suspensions were centrifuged (Hettig Mikro 220R centrifuge) at 3500g at 27 °C for 60 min. The collected supernatant was used for the experiments. The UV light source for inducing the dipole switching dynamics was a hand-held UV lamp emitting at 365 nm. UV/vis measurements were performed with a Thermo-Fisher Evolution Array Spectrophotometer, wavelength range 270–1100 nm.

4. Excitonic absorption spectra

First, we apply the theoretical approach to determine the excitonic absorption coefficient \( \alpha(\omega) \) for the exemplary...
pristine (10, 0) zigzag CNT. Then, we calculate the spectrum of the same nanotube after the functionalization with spiropyran- and merocyanine molecules, respectively. The Bloch equation in (4) is evaluated within the Runge–Kutta algorithm to obtain the temporal dynamics of the microscopic polarization \( p_k(t) \) and the non-diagonal transitions \( \sigma_{k'k}^\alpha(t) \). Once we have these quantities, we can easily determine \( \alpha(\omega) \) from \( \sigma_{k'k}^\alpha(t) \) as a function of the momentum transfer \( k' \). This behavior reflects the dumbbell-like shape of the dipole potential. As a result, to obtain a maximal red-shift in the absorption spectrum, it would be advantageous to influence the orientation of the molecular dipole moment in the direction perpendicular to the CNT axis.

Next, we experimentally measure the absorption spectrum of the produced sample of CNTs (see section 3) before and after the functionalization with spiropyran molecules (figure 4(a)). For pristine CNTs (i.e. coated with PBA) we observe a symmetric Lorentz-shaped peak at 1.68 eV, suggesting an excitonic transition. Within a photoluminescence excitation map, we identify the (9, 4) nanotube to correspond to the transition energy in the nanotube functionalized with spiropyran molecules reflecting the large dipole moment. The strength, and in particular the shape, of the coupling element also depend on the dipole orientation \( \alpha \) with respect to the CNT axis (see figure 1(a)). The dashed lines in figure 3 show the two limiting cases of parallel (\( \alpha = 0^\circ \)) and perpendicular (\( \alpha = 90^\circ \)) orientations. For molecular dipole moments with (\( \alpha = 0^\circ \)), we observe that the coupling is zero for processes with vanishing momentum transfer, whereas for (\( \alpha = 90^\circ \)) the coupling reaches its maximal value for \( k = 0 \). This behavior reflects the dumbbell-like shape of the dipole potential. As a result, to obtain a maximal red-shift in the absorption spectrum, it would be advantageous to influence the orientation of the molecular dipole moment in the direction perpendicular to the CNT axis.
of the absorption peak during the switching dynamics can be monitored in real-time over a period of time. Figure 4(b) shows the temporal evolution of the red-shift, when ultraviolet light is switched on and off inducing the isomerization between the spiropyran and merocyanine form. After the light is switched off and the sample is located in the dark, back-isomerization is initiated and the red-shift starts to decrease again. It takes around 100 s, until the molecule is completely switched back into the closed spiropyran form.

5. Conclusions

In summary, we have theoretically and experimentally investigated the absorption spectrum of spiropyran-functionalized carbon nanotubes. We observe a red-shift strongly depending on the conformation of the attached molecule: for the open merocyanine form, which is characterized by a large dipole moment, we observe a red-shift of the energetically lowest transition energy by about 50 meV. This shift reflects the interaction between the excitons in the carbon nanotube and the external molecular dipole field. In contrast, in the case of the closed spiropyran form, the absorption spectrum is only slightly red-shifted, reflecting the smaller molecular dipole moment. This suggests the possibility of an optical read-out of a spiropyran-based molecular switch. Our theoretical predictions are in good qualitative agreement with experimental results confirming the predicted red-shift in the absorption spectra of functionalized nanotubes. Furthermore, our calculations show that the observed red-shift strongly depends on the dipole moment and the dipole orientation. As a result, the nanotube–molecule coupling can be optimized with regard to an optical read-out by aligning the molecular dipole moment perpendicular to the nanotube axis, which yields the strongest dipole-induced substrate–molecule coupling.

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References

[16] Lim S and Park N 2009 Appl. Phys. Lett. 95 243110