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Evidence of Hybrid Excitons in Weakly Interacting Nano-Peapods

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Computational details

All calculations presented here are based on density-functional theory (DFT) and employ many-body perturbation theory on top to describe the quasi-particle band structure and the excitation spectra.

For constructing the peapod unit cell, we considered the polymer to be located in the center of the nanotube parallel to its cylindrical axis. As polymer and nanotube are basically commensurate, the unit cell of the peapod contains only one benzene ring. Along the two perpendicular directions, we used vacuum distances of 8Å, which turned out to be sufficient to prevent interactions between neighboring replica.

The actual calculations consisted of four subsequent steps. First, ground state geometries of the subunits, *i.e* PPP and the (14,0) nanotube, as well as that of the combined system PPP@(14,0) were relaxed separately utilizing the package Quantum ESPRESSO.[1] Exchange-correlation effects were treated by the generalized gradient approximation (GGA) in the parametrization by Perdew-Burke-Ernzerhof.[2] We used a planewave basis with a kinetic-energy cutoff of 30 Ry. Brillouin zone integrations were carried out by using 8 k points. To account for van der Waals (vdW) interactions, we employed the vdW density functional[3] in a post-SCF manner as implemented by Nabok.[4]

For the relaxed geometries, self-consistent calculations were carried out by the full-potential linearized augmented planewave (LAPW) method, using the WIEN2K code.[5] Here, we used muffin-tin radii of 0.75 and 1.28 for hydrogen and carbon atoms, respectively. The basis size was defined by the cutoff parameter $K_{max} = 3.9$ Ry. As the Kohn-Sham levels of DFT do not reflect quasi-particle effects, the electronic bands needed for the last step were corrected based on quasi-particle band structures.

The quasi-particle band structures were calculated within the G_0W_0 approach using the planewave-based code ABINIT.[6] Instead of performing the summation over unoccupied states, we exploited the energy-effective scheme by Berger and coworkers.[7] To prevent interactions between neighboring replica of the peapod, we truncated the Coulomb potential according to a procedure of Ismail-Beigi.[8] The frequency dependence of the screened Coulomb potential was treated by a plasmon

pole model.[9] The self-energy was evaluated in 32 k points along the 1-dimensional Brillouin zone.

Band structures, from DFT and G_0W_0 for the isolated polymer and the combined system are shown in Figure 1.
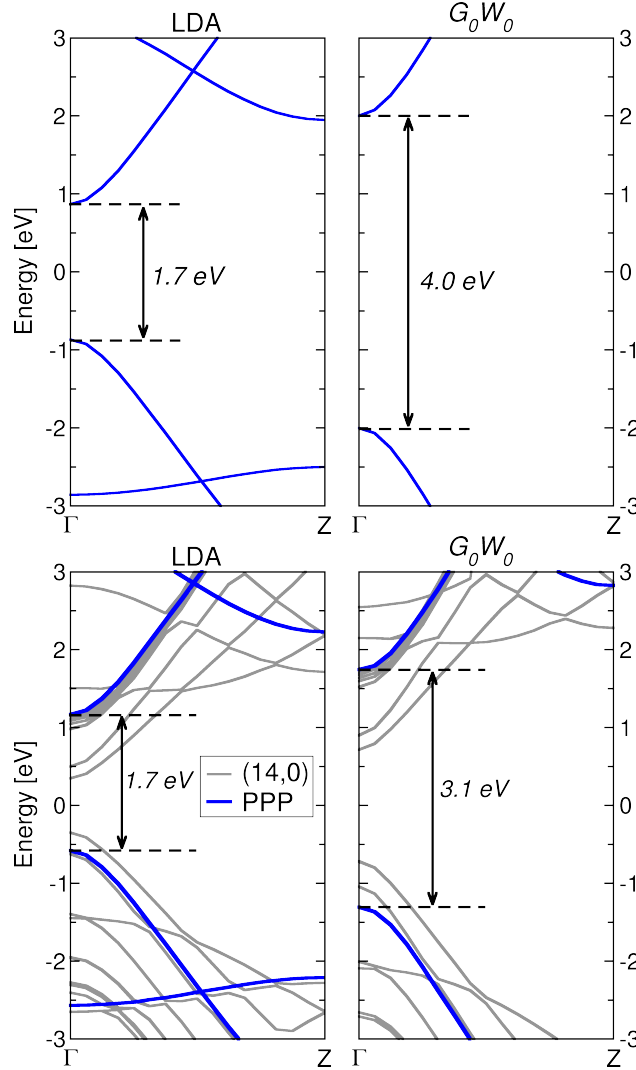

Figure 1: Comparison of DFT (left) and quasi-particle (right) band structures of isolated PPP (top) and the PPP@(14,0)-peapod (bottom). The blue color highlights the bands originating from PPP. The gray lines represent the bands stemming from the nanotube.

Comparing the quasi-particle band structure of the isolated polymer to its bands within the combined system, leads to the conclusion that the polymer band gap is reduced upon encapsulation by about 0.9 eV. This effect occurs due to the image-charge effect, *i.e.*, when a charge distribution is located in the vicinity of a polarizable surface. It is interesting to note that the band of the nan-

otube remains almost unaltered in the presence of PPP. Based on these results, we determine the quasi-particle corrections to the Kohn-Sham energies for the solution of the BSE. To do so, we use a scissor operator approach which introduces a constant, k-independent correction, Δ_c, to the conduction bands. We adopt values of $\Delta_c = 0.8$ eV for the tube and 1.4 eV for the polymer, respectively (taken at the Γ-point). This way, the so-corrected band structure includes also polarization effects.

In the final step, the Bethe-Salpeter equation (BSE) for the electron-hole two-particle Green function was set up and diagonalized leading to optical spectra and electron-hole wave functions. Again, the Coulomb potential was truncated,[8] and a vacuum separation of 8 Å turned out to be sufficient to converge exciton energies within 0.2 eV. We found 96 **k**-points along the Brillouin zone and a cut-off of 15 Ry to be sufficient for both computing the microscopic dielectric matrix as well as the electron-hole interaction matrix elements. Unoccupied states up to 5 Ry above the Fermi level were taken into account. For setting up the BSE Hamiltonian, 4, 16, and 18 conduction and valence states for were required for PPP, the CNT, and the peapod, respectively, to obtain converged spectra in the energy range of 0 to 5 eV. For comparison, optical spectra within the independent particle approximation (IPA) were computed by neglecting the direct and exchange electron-hole matrix elements in the BSE Hamiltonian. Details of the BSE implementation can be found in Ref.[10]

Another important quantity obtained from the BSE approach is the exciton wavefunction. To visualize this six-dimensional object depending on the position vectors of electron and hole (Fig. 2c in the main text), we fixed the hole coordinate at the respective center of the polymer, nanotube, and peapod. The isosurfaces are depicted at 10% of the maximal / minimal values of the wavefunction.

Experimental details

The preparation of peapods was adopted from our previous papers.[11,12] Briefly, 6P@CNT was synthesized through sublimation of 6P in the presence of purified single wall CNTs in a sealed vessel, followed by extensive washings with solvent and thermal treatments at reduced pressure to remove the molecules adsorbed on the external CNT walls.

We note that the nanotubes used in this study were initially a mixture of metallic and semi-conducting ones. Due to the cleaning process, the metallic population was, however, strongly suppressed.

For the optical measurements, all samples were dispersed in dimethylformamide (DMF) by mild sonication for one minute. Photoluminescence excitation (PLE) spectra were recorded with a Perkin-Elmer LS 50B spectrometer. For time-resolved and steady-state photoluminescence (PL) measurements, the solutions were excited by a 150-fs-pulsed Kerr-mode-locked Ti:sapphire laser, frequency doubled at about 380 nm and the steady-state PL emission was measured with a silicon CCD detector. The time-resolved PL was recorded by a Hamamatsu streak camera working in synchroscan mode. All measurements were performed at room temperature, and the spectra were calibrated for the instrumental response.

References

(1) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I. et al. QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys. Condens Matter* **2009**, *21*, 395502.

(2) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation for the Exchange-Correlation Hole of a Many-Electron System. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(3) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* **2004**, *92*, 246401.

(4) Nabok, D.; Puschnig, P.; Ambrosch-Draxl, C. noloco: An Efficient Implementation of van der Waals Density Functionals Based on a Monte-Carlo Integration Technique. *Comp. Phys. Commun.* **2011**, *182*, 1657.

(5) Blaha, P.; Schwarz, K; Madsen, G. Kvasnicka, D; Luitz, J WIEN2k: An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties. **2001**.

(6) Gonze, X.; Amadon, B.; P.-M.Anglade,; Beuken, J.-M.; Bottin, F.; Boulander, P.; Bruneval, F.; Caliste, D.; Caracas, R.; Cote, M. et al. ABINIT: First-Principles Approach to Material and Nanosystem Properties. *Comput. Phys. Comm.* **2009**, *180*, 2582.

(7) Berger, J. A.; Reining, L.; Sottile, F. *Ab initio* Calculations of Electronic Excitations: Collapsing Spectral Sums. *Phys. Rev. B* **2010**, *82*, 041103.

(8) Ismail-Beigi, S. Truncation of Periodic Image Interactions for Confined Systems. *Phys. Rev. B* **2006**, *73*, 233103.

(9) Godby, R. W.; Needs, R. J. Metal-insulator Transition in Kohn-Sham theory and Quasiparticle Theory. *Phys. Rev. Lett.* **1989**, *62*, 1169.

(10) Puschnig, P.; Ambrosch-Draxl, C. Optical Absorption of Semiconductors and Insulators Including Electron-Hole Correlations: An *ab-initio* Study within the LAPW Method. *Phys. Rev. B* **2002**, *66*, 165105.

(11) Loi, M. A.; Gao, J.; Cordella, F.; Blondeau, P.; Menna, E.; Bártová, B.; Hébert, C.; Lazar, S.; Botton, G.; Milko, M.: Ambrosch-Draxl C. Encapsulation of Conjugated Oligomers in Single Wall Carbon Nanotubes: Towards Nano-Hybrids for Photonic Devices. *Adv. Mater.* **2010**, *22*, 1635-1639.

(12) Gao, J.; Blondeau, P.; Salice, P.; Menna, E.; Bártová, B.; Hébert, C.; Leschner, J.; Milko, M.; Ambrosch-Draxl, C.; Loi, M. A. Electronic Interactions between "Pea" and "Pod": The Case of Oligothiophenes Encapsulated in Carbon Nanotubes. *Small* **2011**, *7*, 1807-1815.