

Optical properties of one-dimensional graphene polymers: the case of polyphenanthrene

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We investigate from first principles the effect of many-body corrections on the optoelectronic properties of polyphenanthrene (PPh), a prototype system for carbon-based ladder polymers and 1D nanographenes with *cis*-polyene edges. We show that the inclusion of many-body effects is essential to correctly describe both quasiparticle bandstructure and optical response. Consistently with the reduced dimensionality of the system, the inclusion of electron–hole interaction leads to strongly bound excitons which dominate the spectra. A complete characterization of the low-energy excitonic states is carried out, together with their optical activity. In particular, we find a dark exciton below the first optically active one, which is expected to crucially affect the luminescence efficiency.

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1 Introduction

Carbon-based nanoscale materials play a crucial role for both fundamental nanoscience and nanotechnology applications. In particular, the aromatic network obtained when carbon atoms arrange in a honeycomb structure is responsible for the unique electronic and optical properties encountered in systems such as conjugated polymers [1], C-nanotubes [2] and, more recently, graphene nanoribbons [3–6].

Going from oligomers to one-dimensional polymeric chains to the two-dimensional graphene, one can find several supramolecular structures with very different features, significantly dependent on size, edge structure and termination (see, e.g., Refs. [7–9]). Polyacene (*trans*-polyene-edge) and polyphenanthrene (*cis*-polyene-edge) are among the most studied prototypes for such systems. Characterized by different edge structures, they show strikingly different electronic properties. While the first has a small gap induced by second-order Peierls distortion, polyphenanthrene (PPh) is a large gap semiconductor [8]. Moreover, increasing the number n of *cis*-polyene chains, the PPh(n) structures show an oscillating behaviour of the bandgap [8, 10, 11], suggesting the opportunity to tailor their optoelectronic properties by controlling the width.

Very few calculations including many-body effects were performed on oligoacenes [12–14], where a significant role is played by the 3D herring-bone-like arrangement of molecular units. The polymer case, such as 1D PPh chains, was instead addressed within the single-particle approximation only [8]. However, isolated polymer chains are an excellent model to understand the peculiar properties of organic systems obtained from dilute solutions and many body effects are expected to play a key role in low dimensional systems due to enhanced electron–electron correlation. In this paper we discuss the effect of many-body interactions on the electronic and optical properties of PPh by means of an *ab initio* state-of-

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the-art method based on many-body perturbation theory. On one hand, the single-particle Kohn–Sham gap strongly underestimates the quasi-particle (QP) ‘true’ one. On the other hand, the QP band-structure alone does not yield reliable information on the optical properties, for the description of which is necessary to include the electron–hole interaction.

2 Method

The calculation of the quasi-particle electronic properties is performed in two steps. First, we calculate the Kohn–Sham band-structure and eigenfunctions of the relaxed atomic structure within the density functional theory (DFT) in the local density approximation (LDA) [15]. For these calculations, we use the DFT-LDA implementation present in the PWscf package [16, 17]. In the second step, we use the GW approximation [18] to evaluate the self-energy corrections to the LDA dispersion. We carry out a non self-consistent calculation (G_0W_0), where the LDA wavefunctions are used as good approximations for the QP wavefunctions and the screening is treated within the plasmon-pole approximation [19].

The electron–hole interaction is included on top of the QP description by solving the Bethe–Salpeter (BS) equation [20]. Here, the static screening in the direct term is calculated within the random-phase approximation (RPA) and the BS hamiltonian is solved in the Tamm–Dancoff approximation, i.e. only the resonant part is included [21]. Only light polarized along the principal axis (z) is considered in our calculations, since for polarization perpendicular to the z -axis the optical absorption is known to be strongly suppressed in 1D systems (see, e.g., Refs. [22, 23]). All GW -BS calculations are performed with the code SELF [24, 25].

3 Results and discussion

Figure 1a depicts the PPh quasiparticle bandstructure, while its optical absorption spectrum is shown in Fig. 2a. The GW correction opens the LDA energy gap at Γ by 2.95 eV, bringing E_{gap} to the value of 5.45 eV. It is worth noting that, in order to simulate an isolated system in the supercell approach, is not sufficient to introduce a certain separation between images, as for LDA calculation only, because of the long-range nature of the screened Coulomb interaction in both GW and BS schemes. Hence, we introduce a box-shaped truncation of the Coulomb potential in our calculations in order to avoid non-physical

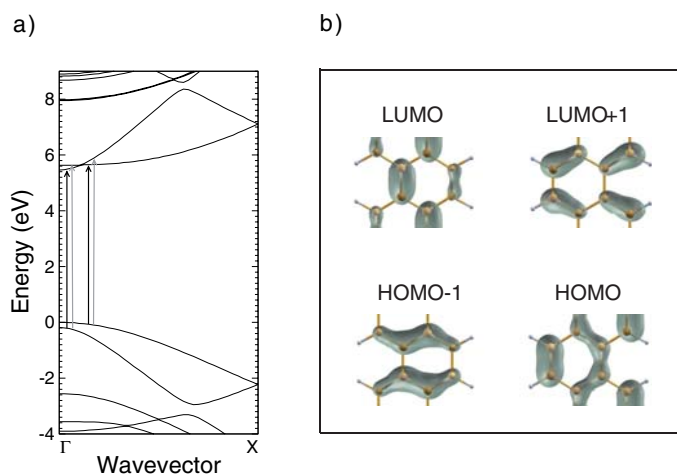


Fig. 1 (online colour at: www.pss-b.com) a) Quasiparticle bandstructure of PPh. Vertical arrows indicate the interband transitions giving rise to the lowest-energy excitonic states (see Fig. 2). Black arrows stand for the optically allowed transitions, while grey arrows for the dipole forbidden ones. b) Charge density plot for the single-particle Kohn–Sham states which mainly contribute to the lowest-energy optical features. All the states are plotted at $k = \Gamma$, in the PPh unit cell.

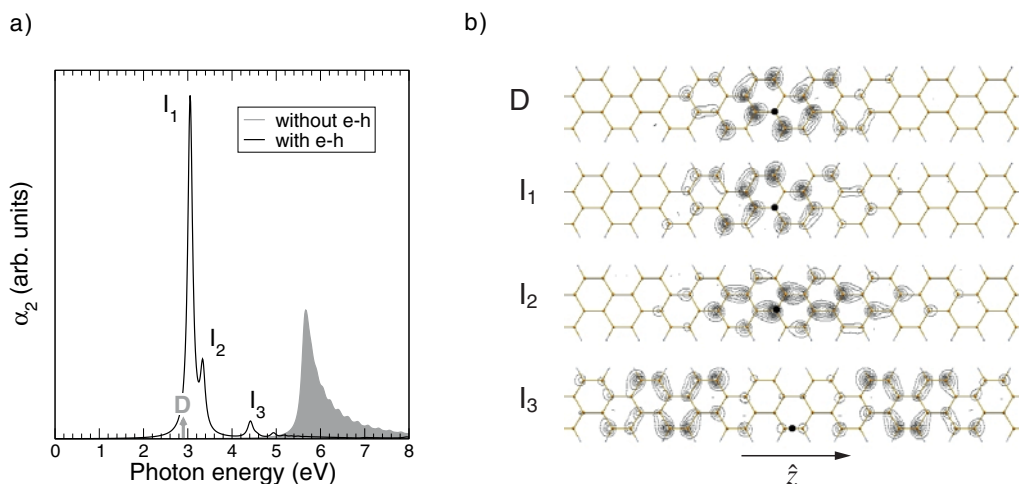


Fig. 2 (online colour at: www.pss-b.com) a) Optical absorption spectrum of PPh. The solid black line represents the spectrum with electron–hole interaction, while the single-particle spectrum is in grey. A Lorentzian broadening is introduced in the calculations. b) In-plane spatial distribution of the electron for a fixed hole position (black dot), corresponding to the lowest-energy excitonic states. The spatial density is averaged over the direction orthogonal to the ribbon plane.

interactions between image charges [26, 27]. Here, for a separation distance of 35 a.u., the untruncated potential leads to a reduction of the QP gap of about 8% with respect to the case of cut-off potential. This gap opening is accompanied by an overall stretching of the valence (conduction) bands of about 15% (10%), similar to those found for GNRs [6].

In the absence of e–h interaction, such a bandstructure would result in the optical absorption spectrum depicted in grey (Fig. 2a), characterized by prominent 1D van Hove singularities. In the low-energy window, the main contributions to the asymmetric peak at 5.65 eV come from the optically allowed interband transitions [black arrow in Fig. 1a] between the last two valence and the first two conduction bands (depicted in Fig. 1b at $k = \Gamma$). The inclusion of excitonic effects (Fig. 2a, solid black line) dramatically modifies both the peak position and absorption line-shape, giving rise to individual excitonic states below the onset of the continuum, with binding energies of the order of the eV. The I_j series of excitonic peaks originates from linear combinations of optically allowed transitions between the same four bands [Fig. 1b], with larger weights in k -space near the Γ point. The binding energy of the main optically active exciton (I_1), calculated as the difference between the peak position and the QP gap, is 2.53 eV. In addition to the I_j series, the mixing of the dipole forbidden transitions between these bands (grey arrows in Fig. 1a) is responsible for an optically inactive exciton (D) lying about 0.1 eV below the main bright one. The D state thus provides a competing path for non radiative decay of optical excitations, which could affect the luminescence yield of the system.

A further insight in the effects of electron–hole interaction is provided by the evaluation of the resulting spatial correlations. In Fig. 2b, we plot the in-plane probability distribution of the electron for a fixed hole position (black dot), corresponding to the lowest excitonic states. While the electron distribution extends over the whole ribbon width, the modulation of the exciton wavefunction $|\psi(r_e; r_h)|^2$ along the z -axis is entirely determined by the Coulomb interaction; the spatial extensions are inversely proportional to the binding energies and vary from 8 (D) to 27 (I_3) Å. Moreover, while D , I_1 and I_2 have symmetric envelope functions, that of I_3 is antisymmetric with a nodal plane at the hole position ($z = z_h$) [28]. This explains why the oscillator strength of I_3 is fairly small, even if this excitonic state is made up of dipole allowed transitions. Similar effects have been found also for C -nanotubes [29] and conjugated polymers [22].

4 Conclusions

In conclusion, we have shown that the optical properties of PPh reflect the peculiar signature of 1D systems, since bound exciton states appear in the optical absorption spectra below the continuum of transport states, and the corresponding van Hove singularity associated to a non-interacting 1D electron gas is suppressed. Our results demonstrate a sizeable binding energy for PPh: this feature can be interpreted as a combined effect of the reduced dimensionality and of the maximum electronic gap experienced by this prototype system within the PPh(n) oscillating series.

The present analysis can be combined with a more extensive characterization of further PPh(n) systems [6], which is expected to provide an interpretation of polymer width as a tunable parameter to control the optoelectronic performance of nanographene-based real devices.

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tion band states with energies up to 15 eV above the valence band. An optical window of 12 eV around the gap is considered for the calculation of the absorption spectrum.

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