Optical Spectra from Molecules to Crystals: Insight from Many-body Perturbation Theory

Caterina Cocchi\(^1\)\(^,\)\(^2\) and Claudia Draxl\(^1\)\(^,\)\(^2\)

\(^1\)Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany
\(^2\)European Theoretical Spectroscopic Facility (ETSF)

(Dated: February 26, 2015)

PACS numbers: 71.15.Mb, 71.35.Cc, 78.40.Me

Optical excitations in organic materials are strongly dominated by many-body effects [1–3]. Electron-electron interactions determine the electronic structure, and electron-hole (e-h) correlations rule the excitation process. A methodology that is able to consistently capture the features of molecular materials, from single molecules to their condensed phases, including organic crystals [4], adsorbate systems [5, 6], hybrid materials, and nanosstructures [7, 8], is an essential prerequisite to predict their excited-state properties. Many-body perturbation theory (MBPT) represents the state-of-the-art method to calculate optical excitations in solids [9]. The GW approach [10] gives quasi-particle (QP) energies and the solution of the Bethe-Salpeter equation (BSE) [11, 12] yields excitation energies and wavefunctions of the e-h pairs. Although, in principle, GW+BSE can be applied to any material, it is computationally too demanding for many systems of technological interest. Quantum chemistry offers powerful tools, such as Coupled Clusters (CC) and Configuration Interaction Singles and Doubles (CISD) [13], to accurately compute optical properties of molecules. Again, only small systems can be treated with these methods, due to their huge computational costs.

Since the turn of the century, time-dependent density-functional theory (TDDFT) has gained increasing popularity [14], due to its remarkable success in reproducing optical spectra of small molecules and clusters, with relatively low computational effort [15, 16]. However, TDDFT suffers from severe drawbacks when dealing with extended systems. The spurious long-range behavior of standard exchange-correlation kernels \((f_{xc})\) inhibits reproducing bound excitons in solids [20, 21]. For the same reason, TDDFT is unable to describe charge-transfer-like excitations in molecular complexes [22, 23]. To overcome these limitations, new kernels have been developed including many-body effects [24–26] and exhibiting the correct long-range behavior [27, 28]. Unfortunately, these improvements are mainly concerning specific classes of materials and/or excitations, and therefore do not often extend, in practice, the range of applicability of TDDFT.

The goal of this work is to understand the role of many-body effects in the optical excitations of molecular materials, from the gas-phase to crystals, and to clarify when and why TDDFT can be trusted. We adopt the adiabatic local-density approximation (ALDA) [29], as the simplest and most common kernel of TDDFT. While more sophisticated kernels can quantitatively improve the results [30, 31, 32], the physical picture is already clear from ALDA [33]. The success of TDDFT for isolated molecules is mainly ascribed to the dominance of the long-range part of the Coulomb kernel \(v\) over \(f_{xc}\) [34]. It blue-shifts the absorption onset above the Kohn-Sham gap, and re-distributes the oscillator strength (OS) to higher energies, providing a good approximation for the optical spectra [9]. We confront TDDFT with MBPT, with the aim to identify the most relevant contributions to the optical excitations and to understand to which extent TDDFT is able to reproduce them. To do so, we choose the family of oligothiophenes as prototypical example. Since only a few intense peaks characterize their UV-visible spectra [10], they are ideally suited for this study. We investigate thiophene oligomers with an even number of rings, up to 6, as well as the single thiophene ring, going from the isolated molecule to the crystal.

All calculations are performed with the exciting code [11], a computer package for density-functional theory and MBPT, implementing the all-electron full-potential augmented plane-wave method. The Kohn-Sham electronic structure is computed within the local-density approximation (LDA) [12]. The optical absorption spectra are obtained from linear-response TDDFT as well as from MBPT, in the framework of \(G_0W_0+\text{BSE}\) [34, 40]. In exciting, TDDFT and BSE are treated on the same footing [41], enabling a direct comparison between the results. Computational details are provided in the Supplemental Material (SM) [40].

In Fig. 1 we show the optical spectra of bithiophene (2T), quarterthiophene (4T) and sexithiophene (6T). For
the smallest oligomer, 2T, the ALDA spectrum is in excellent agreement with the \( G_0 W_0 + \text{BSE} \) result. The UV-visible region is dominated by a strong peak, polarized along the long (\( x \)) axis of the molecule [47], and governed by the transition between the highest-occupied molecular orbital, HOMO (H), and the lowest-unoccupied one, LUMO (L). Our finding is in agreement with experiments [48–50] and with quantum-chemistry results [47, 51, 52]. As the size of the oligomer increases, discrepancies between the \( G_0 W_0 + \text{BSE} \) and ALDA spectra emerge in both the energy of the first peak and in the overall spectral shape.

In order to understand the source of this disagreement, we inspect in detail the results from MBPT concerning the first excitonic peak. This analysis is summarized in Table I. Two types of many-body effects come into play: the QP correction to the electronic structure (\( \Sigma - V_{xc} \)) and the e-h interaction. Like the fundamental gap computed from LDA (\( E^{\text{LDA}}_{\text{gap}} \)) and \( G_0 W_0 \) (\( E^{\text{G}_0 W_0}_{\text{gap}} \)), also \( \Sigma - V_{xc} \), which corresponds to their difference, decreases with increasing oligomer length. Its effect is to blue-shift the absorption onset in absence of e-h correlation and local-field effects (LFE). From the solution of the BSE, the exciton binding energies (\( E_b \)) are computed; for simplicity, we define \( E_b \) as the difference between the excitation energy and \( E^{G_0 W_0}_{\text{gap}} \). Due to its bound and localized character, the lowest exciton in 2T has a large binding energy of almost 3 eV (Table I). The peak position arises from a partial cancellation between \( \Sigma - V_{xc} \) and \( E_b \). We label this difference \( \Delta_{MBPT} = (\Sigma - V_{xc}) - E_b \), which is usually a positive quantity. This compensation should be mimicked by ALDA, in order to correctly yield the absorption features. The ALDA kernel indeed blue-shifts the absorption onset compared to \( E^{G_0 W_0}_{\text{gap}} \). By considering \( \Delta TDDFT = E^{ALDA} - E^{G_0 W_0}_{\text{gap}} \), where \( E^{ALDA} \) is the first peak energy, we can quantitatively compare the results of the two methodologies. The closer \( \Delta TDDFT \) is to \( \Delta_{MBPT} \), the better the agreement obviously is. In 2T, \( \Delta TDDFT \approx \Delta_{MBPT} \), ALDA mimics almost perfectly the blue-shift caused by the QP correction and the red-shift due to exciton binding. As the size of the oligomer increases, the spread between \( \Delta TDDFT \) and \( \Delta_{MBPT} \) becomes larger [54].

The BSE helps to clarify the shortcomings of ALDA. To this extent, we analyze the nature of the low-energy excitations in terms of single-particle contributions, namely, whether they stem from one transition or from a combination of two or more. Excitation energies from BSE are obtained by diagonalizing the Hamiltonian \( H^{\text{BSE}} = H^{\text{diag}} + 2H^x + H^\text{dir} \) (see SM for details [46]). In this case (singlet spectrum, solid blue line in Fig. 1), the first intense exciton of 6T is due to a mixing of \( H \rightarrow L \) (74%) and \( H-1 \rightarrow L+1 \) (20%) transitions. A similar result (see SM [46]) is obtained also for the triplet, when the exchange term (\( H^x \)), and hence LFE, are neglected, i.e., \( H^{\text{BSE}} = H^{\text{diag}} + H^\text{dir} \). From this we can assert that e-h correlation effects, given by \( H^\text{dir} \), crucially determine the composition of the first exciton in 6T. Fig. 1 also shows the spectrum obtained from an effective approximation to the e-h interaction term (\( H^{\text{BSE}} \), shaded area). This corresponds to considering only the \( \mathbf{G} = \mathbf{G}' = 0 \) term of \( H^\text{dir} \) (including a q-independent screened e-h interaction). The Hamiltonian then becomes \( H^{\text{BSE}} = H^{\text{diag}} + h_0 \), where \( h_0 \) is the \( \mathbf{G} = 0 \) term of \( H^\text{dir} \). The exchange term \( H^x \) vanishes, as it contains only the short-range part of the bare Coulomb potential \( \tilde{v} = v - v_0 \), \( v_0 \) being the \( \mathbf{G} = 0 \) component of \( v \). Excitations resulting from \( H^{\text{BSE}} \) consist of pure single-particle transitions due to \( H^{\text{diag}} \), which are rigidly red-shifted by the “zero-order” e-h interaction from \( h_0 \) [55]. In the \( H^{\text{BSE}} \) spectrum of 6T, in addition to the intense peak at 2 eV, given by \( H \rightarrow L \), a weak peak at about 3 eV stems from the \( H-1 \rightarrow L+1 \) transition [46]. The same feature appears also in the ALDA spectrum (orange line). This analogy, supported by the insight from the BSE results (dominance of \( H^\text{dir} \)), confirms that the local and frequency-independent \( f_{\text{xc}}^{\text{ALDA}} \) cannot properly account for correlation effects. In smaller molecules like 2T and 4T, the OS in the corresponding energy range is concentrated only in the first peak, which is indeed largely dominated by \( H \rightarrow L \) [47]. We conclude that the agreement between BSE and ALDA in the small oligomers is determined by the single-particle character of the first intense peak. As the size of the molecule increases, correlation effects become more relevant: TDDFT can only reproduce the energy of the first excitation but not a correct
∆

2.04  0.28  1.66
2.08  6.66  2.70  5.44  1.14  1.91  4.21  2.30  2.91  6.82  3.91

1.18  1.38  0.56  4.63  9.47  4.84  2.22  1.02  7.14  3.78  6.31
1.77  5.63  7.17  3.75  5.80  0.79  2.70  0.73  2.37
4.59  9.85  5.26  0.01  1.14  7.69  3.81  5.77  4.65  2.19  4.09
4.42  8.34  3.92  1T crystal
4.63  9.47  4.84  1T expanded crystal
4.59  9.85  5.26  1T molecule

TABLE I: Energies relevant for the analysis of excitations in all systems considered in this work: Fundamental gaps, obtained by LDA and \( G_0 W_0 \) and their difference (\( \Sigma - V_{xc} \)); exciton energies of the first triplet (\( E_{\text{triplet}} \)) and singlet (\( E_{\text{singlet}} \)) peak as well as from an approximation to the e-h interaction (\( E_{\mu_{\text{BSE}}} \), see text); \( \Delta^{\text{MBPT}} = (\Sigma - V_{xc}) - E_b \) for the first bright exciton from BSE; \( \Delta^{\text{TDDFT}} = E^{\text{ALDA}} - E_{\text{gap}} \), with \( E^{\text{ALDA}} \) being the first peak energy from TDDFT. Exciton binding energies are given in parenthesis. All energies are expressed in eV.

To better identify the source of this disagreement, we further analyze the spectra in Fig. 3 (upper panel), including also triplet excitations. The \( H_0^{\text{BSE}} \) (turquoise shaded area) and triplet (green line) spectra resemble each other in shape, but they are shifted in energy. We recall that in both cases \( H_0^{\text{BSE}} \) does not include the exchange term \( H^x \). Hence, \( H_0^{\text{BSE}} \) and triplet differ only by the treatment of the screened e-h interaction: in the former case, it is \( \mathbf{q} \)-independent, while in the latter one the full dielectric tensor is included (see Ref. \[55\] and SM for further details \[46\]). The \( H_0^{\text{BSE}} \) and triplet results are also similar concerning the excitation character. In both cases, the first peak stems entirely from H \( \rightarrow \) L (see SM \[46\]). From this we conclude that, no matter

FIG. 2: (Color online) BSE and ALDA spectra of the 1T molecule (top), expanded crystal (middle), and crystal (bottom), as shown on the right. Solid lines represent the average over the three Cartesian components. In the top panel, dotted (dashed) curves indicate the \( xx \) (\( yy \)) component of \( \text{Im} \) \( \varepsilon_{\text{M}} \) from BSE. LDA and \( G_0 W_0 \) gaps are indicated by dashed lines. A Lorentzian broadening of 0.1 eV is applied to all the spectra.
contrast to the previous example of 6T, where e-h interactions play the dominant role. In 1T, LFE are not only responsible for the redistribution of the OS to higher energies, but also for the order and composition of the lowest excitons [46]. Again, ALDA cannot account for these many-body effects, inaccurately describing the first two peaks and slightly overestimating the absorption onset (see $\Delta_{\text{MBPT}}$ and $\Delta_{\text{TDDFT}}$ in Table I). As shown in Fig. 3a (bottom panel), the main effect of the ALDA kernel (orange line), compared to the independent-particle approximation (IPA, see SM [46], shaded gray area), is to blue-shift the energy of the first two peaks and to redistribute the OS to higher energies. Overall, TDDFT results reflect the discrete spectrum of molecular levels. Therefore, above the onset (7 – 10 eV), ALDA captures transitions between such localized single-particle states, in better agreement with BSE than the regime dominated by strongly bound excitons.

The situation becomes even more problematic for TDDFT when intermolecular interactions come into play. To extend our analysis in this direction, we go systematically to the 1T crystalline phase, by considering the experimental crystal structure [53] as well as a model system with lattice vectors scaled by a factor 1.25 (expanded crystal) [46]. The corresponding spectra are shown in Fig. 3b (bottom and middle panels). Large values of $E_{\text{gap}}$, and hence of $\Sigma - V_{\text{xc}}$, and of $E_{\text{b}}$ are obtained from MBPT (Table I), due to the small size of the molecular constituents. A number of intense bound excitons appear in the spectra of both crystal structures. These are signatures of the strong e-h interaction in organic crystals, also beyond the first few excitations. This is also confirmed by the spectra shown in Fig. 3b (upper panel). By comparing the triplet (green line) and $H_{\text{BSE}}^*\text{BSE}$ (turquoise shaded area) results, we observe a large difference between their absorption onsets, resembling the situation in the molecule. Moreover, the double-peak structure of the triplet only appears when the e-h interaction term ($H_{\text{dir}}^\text{e-h}$) is fully taken into account. Also LFE play an important role. The singlet spectrum (blue line) is blue-shifted by over 2 eV compared to the triplet and the OS of the low-energy peaks is drastically reduced. Given this complexity, it is not surprising that TDDFT presents serious problems in correctly yielding the spectra. ALDA slightly underestimates the absorption onset (Table I) and gives only two peaks in the respective energy regime as seen in Fig. 3b (bottom panel). Similarly, two intense peaks appear also in the IPA spectrum (gray shaded area), $\sim$ 1 eV below the ALDA onset (orange line). In both spectra, the continuum starts at about 8 eV, in a region where BSE features bound excitonic peaks. This confirms once again that ALDA reproduces only “IPA-like” excitations, and thus cannot quantitatively capture the spectral features of molecular crystals.

In summary, through a systematic analysis of the optical absorption features in oligothiophenes, we have demonstrated that many-body effects play a decisive role in molecular materials. For the crystal structures, TDDFT turns out to be an inadequate approach, being unable to reproduce bound excitons and drastically underestimating the continuum onset. In large oligomers, as shown for the case of 6T, correlation effects turn up in terms of e-h interaction, evidenced by mixed excitations. Conversely, in the single thiophene ring, the low-energy excitations are driven by LFE. Neither scenario is captured by TDDFT. ALDA results are in excellent agreement with BSE merely in the case of 2T, where the first intense peak stems from one vertical transition. From this we conclude that ALDA can be trusted only for molecular systems characterized by optical excitations with mainly single-particle character. Kernels treating the exchange interaction on a higher level cannot be expected to cure this situation.

Lucia Reining and Kieron Burke are gratefully acknowledged for stimulating discussions. C. D. thanks Hardy Gross for asking the question which inspired this work. This work was partly funded by the German Research Foundation (DFG), through Collaborative Research Centers SFB-658 and SFB-951.

$^*$ Electronic address: caterina.cocchi@physik.hu-berlin.de

[1] K. Hummer, P. Puschmig, and C. Ambrosch-Draxl, Phys. Rev. Lett. 92, 147402 (2004).
[2] N. Sai, M. L. Tiago, J. R. Chelikowsky, and F. A. Reboredo, Phys. Rev. B 77, 161306 (2008).
[3] P. Cudazzo, M. Gatti, and A. Rubio, Phys. Rev. B 86, 195307 (2012).
[4] M. Schwoerer, H. C. Wolf, and W. D. Brewer, Organic
SUPPLEMENTAL MATERIAL

Optical Spectra from Molecules to Crystals: Insight from Many-body Perturbation Theory

Caterina Cocchi\textsuperscript{1, 2} and Claudia Draxl\textsuperscript{1, 2}

\textsuperscript{1}Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany
\textsuperscript{2}European Theoretical Spectroscopic Facility (ETSF)\textsuperscript{∗}

\textsuperscript{∗}Dated: February 25, 2015

PACS numbers: 71.15.Mb, 71.35.Cc, 78.40.Me

The Supplemental Material is organized as follows. In the first section, we summarize the formalism to compute the macroscopic dielectric function from time-dependent density-functional theory (TDDFT) and many-body perturbation theory (MBPT). This paragraph is intended to provide all the ingredients to interpret the results presented in the main text. For exhaustive reviews on the topics, see e.g. Refs. [1–3]. For details about the implementation of TDDFT and MBPT in the \textit{exciting} code [4], we refer to Ref. [5]. In the second section we present the computational details of our calculations. Finally, we report additional information on the nature of the lowest-energy excitations of isolated thiophene oligomers, in terms of single-particle transitions.

THEORETICAL BACKGROUND

Time-dependent Density-functional Theory

The basic approach to compute optical absorption spectra from TDDFT is the solution of the Dyson-like equation for the dynamic polarizability $\chi$:

$$\chi = \chi_0 + \chi_0(v + f_{xc})\chi,$$

where $\chi_0$ is the Kohn-Sham (KS) response function, $v$ is the long-range bare Coulomb potential, and $f_{xc}$ is the exchange-correlation (xc) kernel. In the adiabatic local-density approximation (ALDA), $f_{xc}^{ALDA}$ is local and static [6, 7]. From the solution of Eq. 1, the inverse of the dielectric tensor $\epsilon$ is computed. In reciprocal space, $\epsilon$ reads:

$$\epsilon_{G,G'}(q,\omega) = \delta_{GG'} - v_{G}G_{G'}(q)\chi_{G,G'}(q,\omega).$$

The optical absorption spectra are obtained from the imaginary part of the macroscopic dielectric function, $\epsilon_M$, given by:

$$\epsilon_M(\omega) = \lim_{q \to 0} \frac{1}{q \tilde{\epsilon}(q,\omega)}.$$

When $f_{xc} = 0$ in Eq. 1, the dynamic polarizability $\chi$ is computed within the random-phase approximation (RPA). In the independent-particle approximation (IPA), $v = f_{xc} = 0$, hence $\chi = \chi_0$.

Many-body Perturbation Theory

MBPT is applied here in the flavor of $G_0W_0$, to account for the quasi-particle (QP) correction to the Kohn-Sham (KS) electronic structure, and the Bethe-Salpeter equation (BSE) to compute optical excitations [8]. The solution of the BSE comes from the diagonalization of the eigenvalue problem $H^{BSE}A^\lambda = E^\lambda A^\lambda$, for the effective two-particle Hamiltonian $H^{BSE}$:

$$H^{BSE} = H^{diag} + 2\gamma_xH^x + \gamma_{ddir}H^{dir}.$$

The \textit{diagonal} term $H^{diag}$ accounts for single-particle transitions:

$$H^{diag}_{ek\varepsilon ek'} = (\varepsilon_{ek} - \varepsilon_{ek'})\delta_{\varepsilon\varepsilon'}\delta_{kk'}.$$
By including only this term into $H^{BSE}$, the IPA spectrum is obtained. The repulsive exchange term $H^x$, which reads:

$$H^x_{vck,v'c'k'} = \int d^3r \int d^3r' \phi_{vk}(r)\phi^*_{vk}(r)\bar{v}(r,r')\phi_{v'c'k'}(r')\phi^*_{v'c'k'}(r'),$$

represents the counterpart of the Coulomb term $v$ in the TD-DFT kernel (Eq. 1). However, in Eq. 6, only the short-range bare Coulomb potential $\bar{v} = v - v_0$ appears, which accounts for local-field effects (LFE). $v_0$ is the long-range term of $v$. Finally, the direct term $H^{\text{dir}}$ reads:

$$H^{\text{dir}}_{vck,v'c'k'} = - \int d^3r \int d^3r' \phi_{vk}(r)\phi^*_{vk}(r')W(r,r')\phi_{v'c'k'}(r')\phi^*_{v'c'k'}(r).$$

This term includes the screened Coulomb potential $W_{G,G'}(q) = e_{G,G'}^{-1}q_{G,G'}(q)\nu_{G,G'}(q)$, which represents the attractive electron-hole ($e-h$) interaction. The coefficients $\gamma_x$ and $\gamma_c$ in Eq. 4 allow to switch on and off the exchange and the direct terms. Depending on the values of these coefficients, the singlet ($\gamma_x=\gamma_c=1$, corresponding to Eq. 4) and triplet ($\gamma_x=0$ and $\gamma_c=1$) spectra are computed. In the latter case, the BSE Hamiltonian reads:

$$H^{BSE}_0 = H^{\text{diag}} + H^{\text{dir}}.$$  

We need to pay particular attention when only the $G = G' = 0$ term of $H^{BSE}_0$ is considered [9]. In this case, the exchange term $H^x$ vanishes, by definition of $\bar{v}$ (see Eq. 6). The resulting BSE Hamiltonian is:

$$H^{BSE}_0 = H^{\text{diag}} + h_0,$$

where $h_0$ is the $G = G' = 0$ term of $H^{\text{dir}}$:

$$h^{\text{dir}}_{0vck,v'c'k'} = -\frac{2}{(2\pi)^2} \frac{6\pi^2}{\Omega} \frac{4\pi}{\epsilon(q=0)} \delta_{cc'}\delta_{vv'}.$$  

For the derivation of Eq. 10, see Ref. [9]. It is evident from Eq. 10 that $h_0$ is constant for all diagonal elements of $H^{\text{dir}}$ and represents an effective “zero-order” $e-h$ interaction. As such, it produces a rigid shift of the excitation energies, without affecting the oscillator strengths. Thus, the spectrum obtained by diagonalizing $H^{BSE}_0$ corresponds to the result of the IPA, red-shifted by the binding energy given by $h_0$.

The imaginary part of the macroscopic dielectric function from BSE reads:

$$\text{Im } \epsilon_M = \frac{8\pi^2}{\Omega} \sum_\lambda |t_\lambda|^2 \delta(\omega - E_\lambda),$$

where $\Omega$ is the unit cell volume. The coefficients $t_\lambda$ are associated with the BSE eigenvectors $A^\lambda$ and the momentum matrix elements:

$$t_\lambda = \sum_{vck} A^\lambda_{vck}(|ck|\hat{p}|ck)\epsilon_{ck} - \epsilon_{ck}.$$  

The $A^\lambda_{vck}$ coefficients correspond to the amplitude of the excitons. They carry information about the weight of the vertical transitions, between each valence-conduction band pair $|ck| \rightarrow |ck|$, which build up the excitons.

**COMPUTATIONAL DETAILS**

The crystal structure of the thiophene (1T) crystal is taken from Ref. [10]. The system has an orthorhombic unit cell, with lattice vectors $a_0=9.76$ Å, $b_0=7.2$ Å, and $c_0=6.67$ Å. Two molecules are included in the unit cell. The expanded crystal is obtained by scaling the lattice vectors $a_0$, $b_0$, and $c_0$ by a factor 1.25. The crystal structures are not relaxed. The electronic and optical properties of the isolated molecules 1T, bithiophene (2T) and quarterthiophene (4T) are computed in orthorhombic supercells, including at least 7 Å of vacuum in each lattice direction, in order to prevent unphysical interactions between the replicas. In the case of sexthiophene (6T), 6 Å of vacuum in each direction are considered. The internal coordinates of each molecule are relaxed, by adopting a threshold of 0.025 eV/Å for the forces acting on the atoms. All the resulting geometries are flat.
TABLE S1: Analysis of the single-particle transitions contributing to the first peak of 2T, 4T and 6T. Results of $H_0^{BSE}$ (Eq. 9), triplet (Eq. 8) and singlet (Eq. 4) are shown.

|          | 2T          | 4T          | 6T          |
|----------|-------------|-------------|-------------|
| $H_0^{BSE}$ | H → L (100%) | H → L (100%) | H → L (100%) |
| triplet   | H → L (96%)  | H → L (89%)  | H → L (59%) |
|           |             |             | H-1 → L+1 (27%) |
| singlet   | H → L (84%)  | H → L (89%)  | H → L (74%) |
|           |             |             | H-1 → L+1 (20%) |

For the experimental (expanded) crystal, a $4 \times 4 \times 4$ ($2 \times 2 \times 2$) k-point mesh is adopted for ground-state, TDDFT and MBPT calculations. 100 empty states are included to compute the dynamical response function $\chi$ in TDDFT and BSE calculations. This corresponds to at least 10 eV above the HOMO of the isolated molecules, and to at least 20 eV above the top of the valence band for the 1T crystals. The exciton binding energies ($E_b$) from BSE are computed as the difference between excitation energies and the gap computed from $G_0W_0$ ($E_{gap}^{G_0W_0}$). As such, bound excitons present negative values of $E_b$. The QP correction to the KS electronic structure is obtained within the $G_0W_0$ approximation. A scissors operator equal to the difference between $E_{gap}^{G_0W_0}$ and the KS gap is applied to the KS eigenvalues, as a starting point for the solution of the BSE. In the $G_0W_0$ calculations, the dynamically screened Coulomb potential $W_0$ is computed within RPA, including 100 empty states. For the solution of the BSE, 500 empty states are taken to compute the screened Coulomb interaction, which corresponds to at least 8 eV above the LUMO. The adopted computational parameters ensure accuracy of 0.05 eV for the peaks in the spectra.

COMPOSITION OF THE LOWEST-ENERGY EXCITATIONS OF OLIGOTHIOPHENE MOLECULES

In Table S1 we show the composition of the first peak of the respective nT molecules, with n=2, 4, 6. In 2T and 4T, the first peak is almost a pure transition from the HOMO (H) to the LUMO (L), in both triplet and singlet. In contrast, in 6T, when the full $H^{dir}$ term is included in $H^{BSE}$ (Eq. 8, triplet), a non-negligible contribution to the first peak comes also from the H-1 → L+1 transition. The physical picture does not change for the singlet, when also the exchange term $H^x$ is included in the Hamiltonian (Eq. 4). This provides a clear indication that the e-h interaction, through $H^{dir}$, is responsible for the nature of the first exciton in 6T, given by a mixing of two single-particle transitions.

In Table S2 we present the composition, in terms of single-particle transitions, of the first and second peak of the 1T molecule, obtained from $H_0^{BSE}$ (Eq. 9), triplet (Eq. 8), and singlet (Eq. 4). The polarization directions are referred to the axes of the molecule in Fig. 2 of the main text. When $H_0^{BSE}$ (Eq. 9) is diagonalized, the first peak is given by the H → L transition, polarized along the x axis of the molecule. The second excitation comes from H-1 → L and is polarized along the y axis. In the triplet spectrum, the character of the first two excitations does not change significantly compared to the results from $H_0^{BSE}$. Only when the exchange term $H^x$ is also included (singlet), the scenario changes. A non negligible contribution from the H → L+3 transition sums up to H-1 → L in the y-polarized exciton, which becomes the lowest-energy one. The x-polarized exciton is the second in energy in the singlet, and it remains dominated uniquely by the H → L transition.

|          | 1st peak | 2nd peak |
|----------|----------|----------|
| polarization | composition | polarization | composition |
| $H_0^{BSE}$ | $x$ | H → L (100%) | $y$ | H-1 → L (100%) |
| triplet   | $x$ | H → L (99%) | $y$ | H-1 → L (98%) |
| singlet   | $y$ | H-1 → L (60%) | $x$ | H → L (84%) |

H → L+3 (30%)

TABLE S2: Analysis of the first and second peak in the excitation spectrum of the 1T molecule. The polarization direction and the composition in terms of single-particle transitions are provided for the results of $H_0^{BSE}$ (Eq. 9), triplet (Eq. 8) and singlet (Eq. 4).
Electronic address: caterina.cocchi@physik.hu-berlin.de

[1] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002).
[2] J. R. Chelikowsky, L. Kronik, and I. Vasiliev, J. Phys. Condens. Matter. 15, R1517 (2003).
[3] S. Botti, A. Schindlmayr, R. Del Sole, and L. Reining, Rep. Prog. Phys. 70, 357 (2007).
[4] A. Gulans et al., J. Phys. Condens. Matter. 26, 363202 (2014).
[5] S. Sagmeister and C. Ambrosch-Draxl, Phys. Chem. Chem. Phys. 11, 4451 (2009).
[6] A. Zangwill and P. Soven, Phys. Rev. A 21, 1561 (1980).
[7] P. Ghosez, X. Gonze, and R. W. Godby, Phys. Rev. B 56, 12811 (1997).
[8] M. Rohlfing and S. G. Louie, Phys. Rev. B 62, 4927 (2000).
[9] P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. B 66, 165105 (2002).
[10] S. Abrahams and W. Lipscomb, Acta Crystallogr. 5, 93 (1952).
