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Electronic Structures and Optical Absorption of N-type Conducting Polymers at Different Doping Levels

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Abstract

Theoretical understanding of the electronic structure and optical transitions in n-doped conducting polymers is still controversial for polaronic and bipolaronic states and is completely missing for the case of a high doping level. In the present paper, the electronic structure and optical properties of the archetypical n-doped conducting polymer, double-stranded benzimidazo-benzophenanthroline ladder (BBL) are studied using the density functional theory (DFT) and time-dependent (TD) DFT method. We find that a polaronic state in the BBL chain is a spin-resolved doublet where the spin-degeneracy is lifted. The ground state of two electrons corresponds to a triplet polaron pair, which is in stark contrast to a commonly accepted picture where two electrons are postulated to form a spinless bipolaron. The total spin gradually increases until the reduction level reaches $c_{red} = 100\%$ (i.e. one electron per monomer unit). With further increase of the reduction level, the total spin decreases until it becomes 0 for the reduction level $c_{red} = 200\%$. The calculated results reproduce the experimentally observed spin signal without any phenomenological parameters. A detailed analysis of the evolution of the electronic structure of BBL and its absorption spectra with increase in reduction level are presented. The calculated UV-vis-NIR spectra are compared

with the available experimental results. The electronic structure and optical absorption for different reduction levels presented here are generic to a wide class of conducting polymers, which is illustrated by the corresponding calculations for another archetypical conducting polymer, poly(3,4-ethylenedioxythiophene) (best known as PEDOT).

Introduction

Conducting polymers since their discovery¹ have been extensively studied in many optoelectronic applications including organic light-emitting diodes (OLEDs),² organic electrochemical transistors (OECTs),^{3,4} organic field effect transistors (OFETs),⁵ organic thin-film transistors (OTFTs),⁶ organic photovoltaics (OPVs),^{7,8} sensors⁹ and other energy¹⁰ and bio-applications.¹¹ Although the conductive nature of the polymers is related to the presence of the π -conjugation in their backbones and the π - π stacking between the chains enabling charge motion through the material, the majority of pristine (as-synthesized) π -conjugated polymers show either intrinsically insulating nature or very low conductivity. The conductivity of the conjugated polymers is drastically increased by means of doping¹² using the standard electrochemical cyclic voltammetry or by applying redox chemistry. In this way, it is pos-

sible to make a polymer as p-type (hole transport) and n-type (electron transport) material by respectively p- and n-doping. Because of a strong interaction between electronic and lattice degrees of freedom, charge carriers in conducting polymers are strongly localized over a distance of several monomer units thus forming quasiparticles termed as “polarons”. Two polarons can be further transformed into a single spinless quasiparticle, “bipolaron”, if the energy gain due to the lattice re-organization exceeds the Coulomb repulsion energy.¹³

The p-type polymers have been widely studied in the past due to their better stability compared to n-type polymers.¹⁴ Polythiophenes,¹⁵ poly(p-phenylene vinylene), polyfluorene¹⁶ and their derivatives are the commonly used p-type polymers. Among the p-type polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) have been extensively studied due to its high p-doped conductivity and high chemical stability^{17–20} (for recent reviews see e.g.,^{21–23}). Poly-benzimidazo-benzophenanthroline ladder type (BBL) and semiladder type (BBB), poly-bisindenofluorenedicyanovinylene (P-CN), poly-naphthalene diimide (PNDI) derivatives, poly-perylene diimide (PPDI) derivatives are the commonly used n-type polymers.^{24–26} Note that PEDOT is also possible to study as the n-type material^{20,27–30} with a remarkable stability. Unfortunately, most of the n-type polymers have the stability issue at ambient condition.³¹ The negative doping of the polymer to form an n-type material makes them very sensitive to ambient water and air which may result in unstable films.³² As a result, the performance of n-type polymer is typically not up to the mark as compared to their p-type counterparts. Hence, the need of the hour is to find an ideal n-type polymer with high electron mobility and good ambient stability to improve the performance of the organic electronic devices. In addition, the high electron affinity of n-type polymer could reduce the energy barrier of the interface between the polymer and the cathode to have a smooth electron transfer.³³

The high electron mobilities³⁴ ($\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), low ionization potential³⁵ (4.0–4.4 eV), high structural and thermo-oxidative stabil-

ity make poly[(7-oxo-7,10H-benz[de]imidazo[4',5':5,6]benzimidazo [2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] polymer as an ideal n-doped polymer. This polymer, which is commonly known as ladder-type poly-benzimidazo-benzophenanthroline (BBL) was first discovered in 1966³⁶ in the laboratory of Van Deusen. BBL has an unique structural arrangement where naphthalenic and benzoid units are condensed with N-imino amide units. This two-dimensional polymer has an excellent thermal stability up to 600°C due to the unique ladder/sheet construction.^{36–38} However, the pristine (as-synthesized) BBL polymer is an insulator in nature with the conductivity $\sigma \sim 4 \times 10^{-4} \text{ S/cm}$.³⁹ Since 1960, a number of double-stranded ladder polymers were synthesized that exhibited excellent stability both in air and nitrogen.³⁶ The study of the electronic and optical properties of this stable polymer were reported in eighties when BBL films have been doped by chemical/electrochemical means as the n-type and p-type materials.^{39–45} The doped polymers exhibit high conductivities ($\sim 2 \text{ S/cm}$) based on electron donor strength (p-type)^{45,46} which is attributed to the backbone planarity of the polymer. It is noteworthy that the electron mobility of BBL matches the hole mobility of P3HT.⁴⁷ Hence, to enhance the performance of the all-polymer organic electronic devices, BBL can act as a good counterpart to the best p-type materials.⁴⁸ N-doping of BBL using the reducing agent, tetrakis(dimethylamino)ethylene (TDAE) gives the conductivity enhancement to $\sim 2.4 \text{ S/cm}$.⁴⁹ The ion-implanted doping of BBL film by B^+ , Ar^+ , Kr^+ ions gives the conductivity rise to $\sim 200 \text{ S/cm}$ without any significant alteration in the structure of the pristine polymers.⁵⁰

The property that differentiates the ladder (double-stranded) polymers from non-ladder (single-stranded) polymers is the retention of the mechanical and structural properties upon doping.⁵⁰ Two prominent peaks at 3.3 Å and 7.5 Å in the X-ray diffraction spectra reveal that the polymeric film made of BBL shows formation of crystalline structure.⁵⁰ Currently, there is a strong renewed interest to the n-doped polymers, and in particular, to BBL

which is motivated by e.g., their utilization in thermoelectric applications, where both n- and p- doped materials are required for the device operation.⁴⁹

Figure 1: Schematic electronic structure of polaron and bipolaron states in n-doped conducting polymers. a), b) traditional pre-DFT theories.¹³ c), d) existing DFT-based calculations.^{51–53}

Although electronic and optical properties of the n-doped BBL polymer have been extensively studied experimentally, the corresponding theoretical understanding is not satisfactory, with only a few theoretical studies of its electronic structure based on the pre-DFT semi-empirical approaches from early eighties treating BBL as an infinite periodic chain.^{54,55} It should be mentioned that current literature on conducting polymers (both p- and n-doped) is still strongly dominated by a traditional picture of the electronic structure based on the pre-DFT semi-empirical approaches developed in eighties and early eighties (for a review see e.g.,¹³). However, for p-doped polymers, there is now a growing consensus that the traditional pre-DFT approaches should be replaced by the modern DFT-based picture predicting qualitatively different electronic structure and optical transition in conducting polymer.^{51–53,56–59} Much less work has so far been done on n-doped polymers. The traditional picture predicts that upon doping with electrons, a pair of a spin-degenerate states appear in the gap, see Figure 1a,b.¹³ For the case of an electron-polaron (one extra electron in a chain), the states are filled as illustrated in Figure 1a. A combina-

tion of two polarons leads to a spinless state as shown in Figure 1b. However, the DFT theory predicts a qualitatively different electronic structure for n-doped polymers. Namely, a polaron state corresponds to the electron configuration where a spin degeneration is lifted and a single occupied molecular orbital appears in the gap between the valence and conduction bands as shown in Figure 1c.^{51–53} A bipolaron state corresponds to a spinless electron configuration as shown in Figure 1d.⁵²

The electronic structures of n-doped conducting polymers presented above have been calculated for polythiophenes (PTs)^{51,52} as well as poly(p-phenylene) (PPP).⁵³ So far, DFT-based calculations of the electronic structure of BBL is missing. (Note that a DFT study of the optical absorption and electronic structure in undoped BBL has been recently reported by Kim et al.⁶⁰ and optical absorption in BBL for the case of an electron-polaron have been recently reported by Wang et al.⁴⁹). It should also be mentioned that the above-cited studies of n-doped PTs and PPPs were limited to the case of the relatively low doping levels, with the charge on the monomer chain $Q = -1e$ (polaron)^{51,52,53} and $-2e$ (bipolaron).⁵² In this context, recently, absorption spectrometry study of multielectron reduction of some oligomers, e.g., polyfluorenes with hexyl (pF) and butyloctyl (pBuoF) groups, poly(phenylene-vinylene) (PPV), and ladder-type poly(para-phenylene) (LPPP) and 2,7-(9,9-dihexylfluorene) were studied by Miller and co-workers.^{61,62}

In the present study we calculate the electronic structure and the optical absorption spectra of the neutral and n-doped BBL oligomers using the DFT and time-dependent (TD)-DFT method. A special attention is given to the evolution of the electronic structure, spin signal and optical absorption with the variation of the doping level, when the charge on the chains varies from $Q = -1e$ to $-6e$, corresponding to the doping (reduction) level up to $c_{red} = 200\%$ (i.e. 2 charges per monomer unit). We also calculate the optical absorption at different doping levels, and relate the calculated absorption peaks in the spectrum to the

transition between different states. Based on the calculated absorption spectra we analyze the available experimental results. Finally, we stress that the calculated results concerning the character of the electronic band structure and optical transition at different doping levels presented in this paper are not only specific to BBL, but are also generic to a wide class of n-doped conducting polymers. We illustrate this by performing calculations for n-doped PEDOT, whose electronic structure and the absorption spectra qualitatively show the same features as those of BBL.

Model and Methods

BBL is an unique polymer where one imidazole ring is fused between one benzene ring and one naphthalenic ring to form one monomer unit of the polymer, as shown in Figure 2a. Here, in this paper, the unit containing the naphthalene ring with two adjacent fused pyridine rings is called as *A* and the benzene ring with two adjacent fused imidazole rings is called as *B*. We refer to BBL as an oligomer instead of polymer as we consider its chain length N to be three monomer units. In this context, we also calculated the properties of BBL oligomer with the longer chain length of $N = 6$ monomer units. We found that the electronic structure and the absorption spectra show the same features for $N = 3$ and $N = 6$, see Figure S1,S2 in the Supplementary Information. Therefore, in order to save computational efforts, all the results presented in this study are reported for BBL oligomers with $N = 3$.

All the geometry optimizations for this study were performed using Gaussian 09⁶³ package without imposing any constraints on initial structures. Neutral single polymer chain ($Q = 0$) and n-doped single polymer chain ($Q = -1, -2, -3, -4, -5, -6$) were optimized at ω B97XD⁶⁴/6-31+G(d)⁶⁵ level of DFT. ω B97XD is the range-separated hybrid functional that accounts for 22% Hartree-Fock (HF) exchange at a short range, and 100% HF exchange at a long range. This functional is shown to overcome the localization

problem inherent to many popular functionals such as B3LYP, and quantitatively reproduces electronic properties of conjugated polymeric systems (polyenes, thiophenes and other oligomers), including the electron affinities, ionization energies and the excitation energies.⁶⁶ (Note that the charge is given in units of $|e|$). Spin-restricted DFT calculations were carried out for the neutral chain ($Q = 0$) and for the case of the singlet states of the chains with even number of electrons ($Q = -2, -4$ and -6). Spin-unrestricted DFT calculations were carried out for the chains with odd number of electrons ($Q = -1, -3$ and -5) and for the case of the triplet states of the chains with even number of electrons in order to account the unpaired electrons. Vis/NIR absorption spectra were calculated by using TD-DFT at the same level of theory i.e., ω B97XD/6-31+G(d) and by applying the similar spin rule. A detailed discussion of the choice of the functional can be found in Ref.⁵⁶

When dealing with multiply charged anions, the question naturally arises if they are bound. Indeed, starting from $Q = -4$, (i.e. -1.333 charges per monomer) the calculated electron affinities turn out to be increasingly positive, as shown in Figure S3. The fact that the calculations result in well converged bound states is due to the limited basis set, which effectively creates a barrier for the extra electron; this is well understood in the literature.^{67,68} All the above mentioned studies refer to isolated anions in the gas phase. In condensed mphase, the situation changes drastically. For example, it is well known that $O(2^-)$ is unbound in the gas phase but becomes a stable moiety in solid or cluster cages.⁶⁹ In the case of BBL, the measurements attest that an attainable charge per monomer is at least -1,^{41,70} and according to Zheng et al.⁷¹ even -2. Therefore, the existence of multiply charged polymer chains is an established experimental fact. In our calculations, as it will be shown below, the higher occupied states of BBL anions do not qualitatively change with increasing charge. Thus, extra electrons do not tend to occupy the available diffuse orbitals predominantly. We consider, therefore, that by forcing the extra elec-

trons to stay within the molecule in our gas-phase counter-ion free calculations, we actually model solid-state confined BBL polyanions. As for the gas-phase electron affinity values, these are irrelevant for the condensed-state properties, and it is not our purpose to discuss them.

Results and discussion

Electronic Structures

First, we performed the ground state DFT calculations of BBL oligomers by varying the reduction (doping) level c_{red} in terms of number of negative charges per chain, Q . Figure 2b shows the total energy of the systems calculated for the cases of different spin multiplicities, $M = 2S + 1$, (where S is the total spin) and different doping levels. Figure 2c shows the corresponding electron spin S as a function of charge Q per monomer unit. An addition of one electron to the BBL chain ($Q = -1$), gives rise to the doublet state ($M = 2$) with one unpaired electron of the spin $S = \frac{1}{2}$, see Figure 2c. This state with $Q = -1$ is commonly known as a polaronic state. An addition of second electron to the chain can result in the total spin, either $S = 0$ or $S = 1$, corresponding to the singlet ($M = 1$) or triplet ($M = 3$). The state with $Q = -2$ is commonly known as a bipolaronic state with $S=0$. Although the bipolaron states for n-doped polymers were generally postulated to be spinless ($S = 0, M = 1$) both in the semi-empirical pre-DFT approaches,^{13,72} and in the DFT approaches,⁵² our calculations show that two electrons in BBL form the triplet state rather than the singlet. This result is consistent with the corresponding finding of p-doped polymers,⁵⁶ where the removal of a second electron also leads to the triplet ground state. Such the state is called a “polaron pair” because it corresponds to two spatially separated polarons (see Figure 3 c), as opposed to the “bipolaron” corresponding to two electrons spatially localized at the same place and occupying the same spin-degenerate level (The question of polarons, bipolarons, polaron pairs has been extensively debated in the past, for references see.^{56,73} Fur-

ther, an addition of 3rd electron to the chain (i.e., $Q = -3$, which corresponds to one electron per monomer unit, $c_{red} = 100\%$) results in three unpaired electrons having the total electron spin $S = \frac{3}{2}$ corresponding to the quartet state ($M = 4$). The filling of orbitals of the BBL chain described above can be understood as a manifestation of the Hund’s rule prescribing a single filling of available degenerate orbitals to decrease the repulsion energy among the electrons.

Further addition of electrons to the chain results in the reduction of the total spin. That is, for the case of $Q = -4$ ($c_{red} = 133\%$) the ground state is the triplet ($S = 1, M = 3$), and for the case of $Q = -5$ ($c_{red} = 166\%$) the ground state is the doublet ($S = \frac{1}{2}, M = 2$). An increase of the reduction level of the BBL chain to $Q = -6$ ($c_{red} = 200\%$) results in the singlet state ($S = 0, M = 1$). Apparently, the decrease of the total spin of the ground state when the reduction level goes from $c_{red} = 100\%$ to $c_{red} = 200\%$ is also consistent with the Hund’s rule. It should be noted however that a deviation of the Hund’s rule was observed in calculations performed for longer BBL chains, where, for example, the ground state for $Q = -6$ ($c_{red} = 200\%$) can be a triplet. Also, it is noteworthy that the energy of the doublet and quartet states for $c_{red} = 100\%$ is almost degenerate.

Experimentally, the spin signal of n-doped BBL was studied by Zheng et al.⁷¹, where the reduction level was varied between $0 < c_{red} < 200\%$. The spin signal exhibits a pronounced Λ -shaped dependence peaked at $c_{red} = 100\%$ (i.e., one electron per monomer unit), see Figure 2c. It is noteworthy that this dependence is strikingly different from corresponding dependencies observed in p-doped polymers such as PEDOT, which typically exhibit a gradual increase of the spin signal followed by its saturation.⁵⁶ Our DFT calculations reproduce the evolution of the spin signal in BBL as a function of the reduction level without any fitting parameters. As discussed above, the pronounced Λ -shaped dependence of the spin signal can be understood as a manifestation of the Hund’s rule in the filling up the electronic states in the BBL oligomer.

Figure 2: a) Schematic representation BBL polymer chain where carbon, oxygen, nitrogen atoms are represented as grey, red, and blue sphere, respectively. Hydrogen atoms are not shown for clarity. One A unit of BBL are marked by red circle and one B unit is marked by blue circle. b) Total energy of a BBL chain of different spin states for different charged states from -1 to -6. (For convenience all ground state energies are shifted to zero). c) Spin of the electrons (S) plotted as a function of the reduction level c_{red} , i.e. number of charges Q per monomer (the line is to guide the eye). The experimental data are adapted from the work of Zheng et al.⁷¹

Figure 3e-k shows the electronic structure of the ground state of a neutral/undoped ($Q = 0$) and reduced/doped ($Q = -1$ to -6) BBL chains. The levels in the valence band (i.e., the occupied electronic levels) are depicted as blue lines, and the levels in the conduction band (i.e., unoccupied electronic levels) are depicted as red lines. The spin-up ($\uparrow$) and spin-down ($\downarrow$) orbitals are labelled by up- and down-arrows. The ground state of the neutral chain is singlet and thus all levels are spin degenerated. For the polaronic state $Q = -1$, the spin degeneracy is lifted and a new level occupied by an electron (say, in the spin-up state), appears in between the valence and conduction band thus decreasing the gap between them, as shown in Figure 3e. (Here and hereafter all the newly formed occupied levels in the gap are marked in Figure 3e-k by blue dashed line to distinguish them from the occupied levels in the valence band). The electronic structure of the polaronic state is qualitatively different from the

pre-DFT predictions,¹³ but is consistent with the corresponding predictions for other n-doped conducting polymers,^{51–53} c.f. Figure 1. Addition of one electron ($Q = -1$) to the chain leads to a formation of single polaron and the corresponding electron density distribution is plotted in Figure 3b. It is mainly localized in one of the naphthalenic units (A_1) of the BBL chain. We also calculated the total spins for all naphthalene ring, and, as expected, the spin of the first naphthalene ring, where the polaron is localized, $S_1 \sim 0.58$ is close to $\frac{1}{2}$, whereas the spins of the remaining rings are 0.

To outline the structural changes in the chain, the bond-length alternations of the two carbon rings of the naphthalenic unit were calculated, see Figure 3b,c,d. One naphthalenic unit has two benzene rings with eleven C-C bonds, as shown in Figure 3a. Figure 3b shows the bond-length alternation of six carbon rings of three A units of $Q = -1$. Due to formation of the polaron on the first naphthalenic unit, the bond

Figure 3: a) BBL chain where all the fused pairs of the benzene rings of the naphthalenic ring (A) with the C-C bond number are marked. b) c) d) l) m) n) Bond length alternation of doped BBL of the naphthalene rings which are fused pairs of the benzene rings from M_1 repeating unit with the corresponding electron densities of polaron/bipolaron states are shown for all the charged states ($Q = -1, -2, -3, -4, -5, -6$). S_1, S_2, S_3 give the integrated spin for 1st, 2nd and 3rd naphthalene rings. e) Band diagrams of undoped ($Q = 0$) and f) g) h) i) j) k) doped BBL ($Q = -1$ to -6). Empty electronic states in the conduction band are plotted as red lines, occupied electronic states in the valence band are plotted as blue lines and the occupied polaron/bipolaron states are marked as dotted lines. Spin up and spin down electron levels are shown as up- and down-arrows, respectively. S indicates the total spin of the ground state; P and BP refer to polarons and bipolarons respectively.

length alternation in the first A_1 unit is changed from the benzoid-type for the neutral case to the quinoid-type for the doped case. Rest of the A units is not structurally altered.

Let us now consider the cases of two or more electrons in the chain. The ground state of BBL chain with two electrons ($Q = -2$, $c_{red} = 66\%$) is triplet with the energy levels as shown in Figure 3g. The “polaron pair” nature of this state is clearly manifested in the distribution of the electron density of the occupied levels as shown in Figure 3c, with two states being localized at different naphthalenic (A_1, A_3) units. An alternation of the corresponding bond length distribution as well as the spin distribution are apparently correlated with the position of the localized orbitals as illustrated in Figure 3c. It is noteworthy that the calculated electronic structure is different not only from the pre-DFT predictions,¹³ but also from the corresponding predictions for n-doped conducting polymers⁵² where a possibility of a triplet state as the ground state has not been accounted for, c.f. Figure 1.

For the case of three electrons in the chain ($Q = -3$, $c_{red} = 100\%$), the ground state is quartet, which corresponds to three polarons of the same spin localized at different naphthalenic units, see Figure 3d,h. When one more electron is added to the chain ($Q = -4$, $c_{red} = 133\%$), the electronic structure of BBL exhibits a new feature, namely, a co-existence of polaronic and bipolaronic states at the same chain. Indeed, there are one spin-up and one spin-down states in the gap that are in fact spin degenerate, i.e. they have the same energy and the same wave functions, see Figure 3l, (states marked as “BP”). This means that these states correspond to a bipolaron, where two electrons are localized in the same place in the chain. To our knowledge, the co-existence of polarons and bipolarons on the same chain has never been reported before in any theoretical study in conducting polymers. It is also interesting to note that one of the polaronic states (localized at unit A_3) is moved into the valence band. Inset to Figure 3l shows the distribution of spins in the chain, and this distribution reflects the spatial positions of the polaronic states local-

ized on units A_2 and A_3 . Finally, the change in the bond length alternation as compared to the neutral case is larger at unit A_1 as compared to A_2 and A_3 . This is due to the fact that two charges (i.e. the bipolaron) are localized at A_1 , whereas units A_2 and A_3 are occupied by single charge, which apparently leads to smaller changes in the bond alternations.

The chain with 5 added electrons ($Q = -5$, $c_{red} = 166\%$) has the ground state with two bipolarons and one polaron, see Figure 3j,m, whereas the ground state of the chain with 6 added electrons ($Q = -6$, $c_{red} = 200\%$) corresponds to three bipolarons, see Figure 3k,n. As for the previous cases, the spin distribution over the monomer units as well as the magnitude of the changes in the bond length distribution reflect the localization of polarons/bipolarons in the chain. Finally we note that for all considered cases, as expected, a number of occupied polaronic/bipolaronic levels in the gap (accounting for spin degeneracy) is equal to the number of the added charges. It should be noted that the occupied orbitals in the gap are localized mostly on naphthalenic units A . However, as the reduction level is increased, the spatial extend of the polaronic states is also increased and they become extended into neighbouring benzene and imine rings, see Figure S4 and Figure S5 in Supplementary Information. The corresponding charge density of all the charged states are also plotted in Figure S6.

It is noteworthy that the evolution of the electronic structure of n-doped polymers as the reduction level increases (exhibiting the electron-polaron (or bipolarons) formation in the gap) follows a pattern that is rather similar to one of the p-doped polymers as the oxidation level increases (exhibiting the hole-polaron (or bipolarons) formation in the gap), c.f. Figure 3 and Figure 3 in Ref.⁵⁶

It is interesting to note that the conduction band of a neutral BBL chain shows a miniband formation where a band of low-lying states at the bottom of the conduction band is separated by a minigap from the higher-lying states, see Figure 4a. In order to outline the origin of the miniband formation, the electron densities of LUMO through LUMO+4 are plotted

Figure 4: Band diagrams of a) undoped ($Q=0$) and b) doped BBL ($Q=-2$) are plotted and their empty electronic states in the conduction band are visualized.

in Figure 4. Note that corresponding HOMO states are plotted in Figure S7. Apparently, the miniband corresponds to the orbitals localized at the naphthalenic units (A), whereas higher-lying states correspond to the orbitals extended into B units. The miniband structure is also preserved in the reduced states as illustrated in Figure 4b where LUMO through LUMO+4 for spin-up and spin-down states are plotted.

Optical Properties

The optical absorption spectra of the neutral and doped BBL are calculated using the TD-DFT approach and are plotted in Figure 5a-d. Figure 5a shows the absorption spectra of a neutral BBL where the dominant transitions between the energy levels corresponding to the largest configuration interaction coefficients are indicated. Unlike other linear polymers such as PEDOT,⁵⁶ showing a single absorption peak due to the HOMO-LUMO transition, the neutral BBL exhibits two distinct peaks. This is related to the formation of the miniband structure as discussed in the previous section. The first peak at ~ 280 nm corresponds to the tran-

sitions from the valence band to the miniband in the conduction band as shown in Figure 5a. Transitions from the valence band to higher energy states of the conduction band contribute to the formation of the second peak at ~ 437 nm.

Absorption spectra of doped BBL chain at different oxidation levels are plotted in Figure 5c. An analysis of the configuration interaction coefficients shows that there are three types of peaks that can be distinguished according to the types of the transitions between the level. This is illustrated in Figure 5b for representative cases of $Q = -3$ and $Q = -1$. Peak T_P corresponds to the transitions from the polaronic/bipolaronic levels to the conduction band. Peak T_V is due to the transitions from the valence band to the conduction band and the peak T_{P+V} is a mix of both transitions. For an each doping level the spectrum typically includes all three peaks in the region 400-600 nm. The positions or intensities of the peaks do not show any systematic trends as the reduction level varies. Note that BBL absorption spectra for the case $Q = 0, -1$ was calculated by Wang et al.⁴⁹, and our calculation are in good agreement with their calculated spectra.

Figure 5: a) UV vis/NIR absorption spectra of a neutral BBL chain where the transition from valence band to conduction band corresponding to the absorbance peaks are also shown in the band structure, b) The absorption peaks due to the transition from polaronic/bipolaronic states to conduction band are named as T_P , transition from valence band to conduction band are named as T_V , from both the polaronic/bipolaronic and the other states of valence band to the conduction band are named as T_{P+V} , c) UV vis/NIR absorption spectra of a BBL chain for several doped states from $Q = -1$ to -6 .

Optical properties of BBL films are probed using UV-vis-NIR spectrometry when the oxidation level can be varied by means of the electrochemical doping. In what follows, we compare the theoretically calculated absorption spectra of BBL chains with the experimentally measured spectra of BBL films reported in the literature. Our calculations

show two prominent absorption peaks of undoped BBL; the first being in the range of 200-300 nm (at ~ 281 nm) and the second one in the range of 400-500 nm (at ~ 437 nm), as shown in Figure 5a. Experimentally, Jenekhe and Johnson⁷⁴ and Quinto et al.⁷⁵ found the first absorption peak in the range of 300-400 nm and the second peak in the

range of 500-650 nm in AlCl_3 /nitromethane and tetra-n-butylammonium hexafluorophosphate (TBAPF_6) acetonitrile solution, respectively. Hirvonen and Tenhu⁷⁶ measured the UV-vis spectra of the BBL polymer in water and found two prominent peaks at 354 nm and 580 nm. The spectra they measured for BBL film in water were quite different from those measured in MeSO_3H solvent. Wang et al.⁴⁹ also found two peaks of undoped BBL almost at the same wavelengths as in the previous study. All the experimental studies mentioned above agree with our calculated absorption spectrum that also shows two absorption peaks for the undoped BBL, but where, however, the peak positions are shifted ~ 100 nm to the lower wavelengths.

Upon doping the absorption intensity in the range of 200-300 nm decreases, but a strong peak between 400 to 500 nm is always present, see Figure 5c. Also, as doping level increases, a weaker and a wider peaks develops in the region 600-800 nm. These results are also in line with the experimental findings of the Wilbourn and Murray⁴² where they found the intense absorption in the region of 400-550 nm and a weak absorption in the range of 600-800 nm. Wang et al.⁴⁹ also mentioned that the strength of the peak at ~ 580 nm decreases and the strength of the peak at ~ 900 nm increases upon doping which is inline with the measurement of Yohannes et al.⁷⁰. The difference in the calculated and the measured spectra can be attributed to a number of factors. In experiment to calculate the spectra, the films made of BBL polymers are considered whereas in our calculation we considered only single BBL oligomer. At least three different factors can contribute to this discrepancy. First, we calculated the absorption spectra for a single oligomer. At the same time, BBL films show $\pi - \pi$ stacking between the chains,⁷⁷ such that the inter-chain coupling might affect the optical absorption. Second, the calculated electronic and optical properties do not account for the effect of solvent, which might be important in experimental samples. Third, at high doping levels, the counterions are expected to strongly affect

the electronic structure, which in turn would affect the absorption, especially at higher wavelengths (for a detailed discussion of the effect of counterions and disorder see Ref.^{56,78}). Despite of these discrepancies we can conclude that the calculated spectra are in a reasonable agreement with the experiments.

N-doped PEDOT

The features of the electronic spectra and optical properties of n-doped BBL are not specific to this polymer, but are generic to a wide class of conjugated n-doped polymers. We illustrate this by calculating the electronic structure and optical absorption of the archetype polymer PEDOT at different reduction levels. The results of the calculations are shown in Figures S8-S10 in Supplementary Information. Figure S8 shows the total energies of the ground states corresponding to different spin multiplicities. The trends are similar as those for BBL depicted in Figure 2b. In particular, it is noteworthy that the $Q = -2$ state is also a triplet polaron pair rather than the bipolaron. The evolution of the electronic structure with the increase of the reduction level of n-doped PEDOT, shows the same trends as BBL, see Figure S9. The absorption spectra (see Figure S10) exhibits peaks that, as in the case of BBL, can be attributed to the transitions from the polaronic levels to the conduction band (peak T_P), transitions from the valence band to the conduction band (T_V), and to a mix of both transitions (peak T_{P+V}).

Conclusions

For many years, the theoretical understanding of the electronic structure and optical properties of the conducting polymers have been based on “pre-DFT” semi-empirical theories.¹³ For p-doped polymers, there is now a growing consensus that the traditional pre-DFT approaches should be replaced by the modern DFT-based picture predicting qualitatively different electronic structure and optical transition in conducting polymers. Much

less work has so far been done on n-doped polymers, where the theoretical understanding is still controversial for polaronic and bipolaronic states (i.e. charge $Q = -1$ and -2 correspondingly), and is completely missing for the case of high doping levels. In the present work, the electronic structure and optical properties of the archetypical n-doped conducting polymer, double-stranded benzimidazobenzophenanthroline ladder (BBL) were studied using the density functional theory (DFT) and time-dependent (TD) DFT method.

We find that the electronic structure of the n-doped polymers is qualitative different from the traditional predictions.¹³ For the case of the polaron state the electronic structure of BBL is qualitative similar to those of n-doped PTs⁵⁷ and PPPs⁵³ calculated using the DFT approach. The ground state of two electrons in a chain corresponds to a triplet polaron pair, which is in a stark contrast to a commonly accepted picture where two electrons form the bipolarons, which is postulated to be a spinless quasiparticle (both in pre-DFT and DFT theories). This finding is however consistent with the corresponding case of p-doped polymers, where the triplet state is formed as well when two electrons are removed.⁵⁶ The total spin gradually increases until the reduction level reaches $c_{red} = 100\%$ (i.e., one electron per monomer unit). With further increase of the reduction level the total spin decreases until it becomes 0 for the reduction level $c_{red} = 200\%$. The filling of orbitals of the BBL chain can be understood as a manifestation of the Hund's rule prescribing a single filling of available degenerate orbitals to decrease the repulsion energy among the electrons. The calculated spin signal exhibits a pronounced Λ -shaped dependence peaked at $c_{red} = 100\%$, which reproduces the evolution of the experimentally observed spin signal in BBL as a function of the reduction level without any fitting parameters.

A detailed analysis of the evolution of the electronic structure of BBL as the reduction level varies is provided (see Figure 3), which represents one of the main results of the present work. It is noteworthy that for higher reduc-

tion levels we find the co-existence of polarons and bipolarons on the same chain that, to our knowledge, has never been reported before in conducting polymers.

Using the TD-DFT we also calculate the absorption spectra of BBL at different reduction levels and identify three types of transitions responsible for the absorption peaks in the spectra. Namely, peak T_P corresponds to transitions from the polaronic levels to the conduction band; peak T_V is due to transitions from the valence band to the conduction band and the peak T_{P+V} is a mix of both transitions. For each doping level, the spectrum typically includes all three peaks in the region 400-600 nm, see Figure 5. The calculated UV-vis-NIR spectra is compared with the available experimental results.

Finally we stress that the electronic structure and optical absorption for different reduction levels presented here are generic to a wide class of conducting polymers, which we illustrate by performing the corresponding calculations for another archetypical conducting polymer, poly(3,4-ethylenedioxythiophene) (best known as PEDOT).

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Associated Content

Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX. Content:

- Figure S1, S2: Comparison of the electronic structure and the absorption spec-

tra for BBL chains of length $N = 3$ and $N = 6$.

- Figures S3. Electron affinity of a BBL chain for different charged states from -1 to -6.
- Figures S4, S5. Bond length alternation in the benzene and imidazole rings of the BBL chain.
- Figures S6. Charge distribution in the undoped and doped BBL chain.
- Figures S7. Occupied Electronic states of doped and undoped BBL chain.
- Figures S8-S10 Electronic structure and UV vis/NIR absorption spectra in PEDOT at different doping levels.

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