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Geometrical and Electronic Structures of a Benzimidazobenzophenanthroline-Type Ladder Polymer (BBL)

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ABSTRACT: Variation of the geometrical and electronic structures of a benzimidazobenzophenanthroline-type ladder polymer (BBL) was theoretically investigated. The effect of charge transfer and protonation at the imine N sites revealed fundamental differences with respect to POL-type ladder polymers. Semiempirical (MNDO) solid-state theory was employed for geometry optimization, and the electronic structures were calculated from a modified extended Huckel energy band theory. Neutral BBL is predicted to have aromatic naphthalenic and benzenoid units and alternating bond lengths of imines in the ground state. This results in a band gap of 2 eV, in agreement with optical absorption experiments. The lowest empty band of the neutral form is flat. As charge transfer occurs, the naphthalenic unit becomes quinoid-like and the bond lengths around an imine N become almost equal to each other. The geometrical and electronic structures of neutral BBL are not much affected upon protonation, which induces creation of stable carbonium ions between two nitrogens along the *N*-imino amide units. Therefore, acid doping may increase the conductivity of BBL films not just through protonation but also through charge transfer. Asymmetry of the effect of donor and acceptor doping is interpreted in terms of molecular orbital theory. The absence of a red shift in the absorption spectrum upon doping in BBL is different from most conducting polymers, and is interpreted as being a consequence of the robustness of the geometry and the flatness of the conduction band.

BBL: A Conjugated Ladder Polymer

A large coplanar conjugated structure along the polymer backbone is responsible in part for the high electrical conductivity observed for most conducting polymers such as polyacetylene (PA), poly(*p*-phenylene) (PPP), and heterocyclic polymers, such as polythiophene (PT).[1] Thus, heteroaromatic ladder polymers appeared as attractive candidates for forming conducting complexes[1-8] and also for a new class of nonlinear optical materials.[9,10] Among this class of polymers, poly[7-oxo-7*H*, 10*H*-benz[*de*]-imidazo[4′,5′:5,6]benzimidazo[2,1-*a*]isoquinoline-3,4,10,-11-tetrayl)-10-carbonyl] (benzimidazobenzophenanthroline-type ladder polymer, BBL, see Figure 1) is soluble and forms tough and durable films with high tensile strengths (0.07 GPa)[3,11] and high thermal stability (≥500 °C).[3] The films have a mainly two-dimensionally oriented, fully conjugated, and layered structure with two main Bragg *d* spacings of 7.5 and 3.3 Å.[4] Pristine, undoped BBL, is an electrical insulator ($\sigma \approx 10^{-12}$ S/cm) with an optical λ_{max} at about 2-2.2 eV.[3,6,12] Thermal annealing of pristine samples was observed to dramatically increase the conductivity up to the semiconductor region ($\sim 10^{-6}$ S/cm).[3] This is suspected to be resulting from an increased structural perfection of the ladder or thermal activation to generate free radicals. BBL films can be doped with either electron donors or electron acceptors chemically,[3,5,6] electrochemically,[5] and by ion implantation.[4] Halogens such as iodine and bromine are found not to be effective as dopants.[3] The conductivity of BBL films has been reported to reach up to 1-2 S/cm with p-type (AsF_5 and H_2SO_4) doping[3,6] and up to 5-20 S/cm with the n-type electrochemical doping.[5]

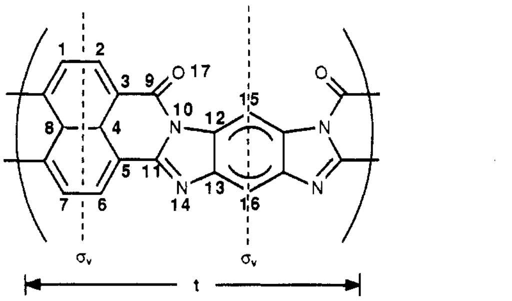

Figure 1. Geometry of a benzimidazobenzophenanthroline-type ladder polymer (BBL).

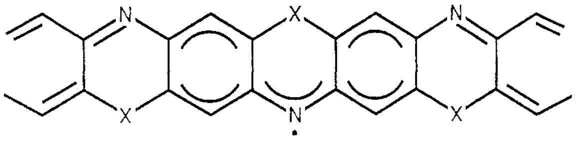

Figure 2. Soliton defect in PTL, separating the two degenerate regions.

We have recently analyzed the geometrical and electronic structures of ladder polymers: polyphenothiazine, PTL, polyphenoxazine, POL, and polyphenoquinoxaline, PQL.[13] These polymers are in one important sense analogous to the prototypical conjugated polymer, polyacetylene, PA, in that for each of these polymers two alternative degenerate structures exist. Consequently[14] local defect states (solitons, see Figure 2) can be created in these polymers, which are at around the middle of the HOCO-LUCO gap.[14] (HOCO = highest occupied crystal orbital, LUCO = lowest unoccupied crystal orbital; it is more appropriate to talk about crystal orbitals rather than molecular ones in the case of extended systems, such as solids and polymers.) For a number of well-studied conjugated polymers such as poly(*p*-phenylene), PPP, polythiophene, PT, polypyrrole, PPy, etc., there are two competing states which are not degenerate, one being more stable by a few kilocalories per mole[15] than the other, as illustrated in Figure 3. Defect states in these polymers are bipolarons.[16] A common feature of these polymers is that charge transfer usually converts the order of the

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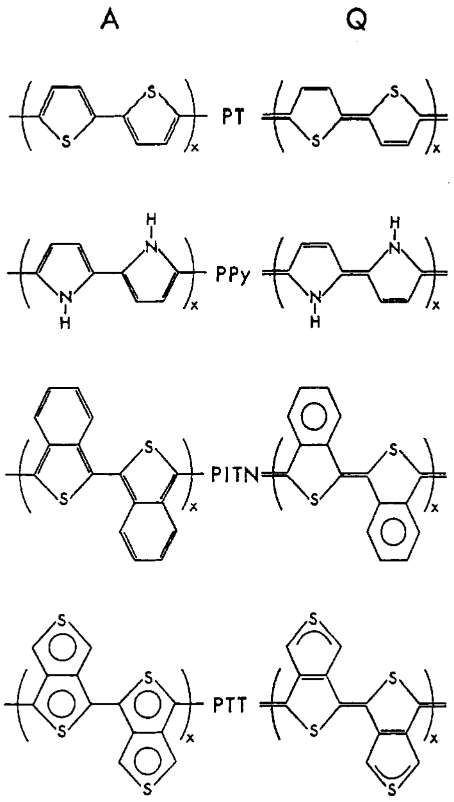

Figure 3. Conjugated polymers with two nondegenerate configurations: (A) aromatic and (Q) quinonoid.

stabilities of the two competing (aromatic and quinoid) structures. Bipolarons or polarons produce new absorption peaks, red shifted relative to the HOCO–LUCO gap of the undoped polymer. There is no such red-shifted peak in doped BBL.[2,3] Why is BBL so different from all other conjugated polymers?

The topology of BBL is very different from both groups (ladder or nonladder). It has essentially one stable geometry, which leads to a very *robust geometrical and electronic structure.*

It is desirable to understand how the geometrical and electronic structures of BBL vary upon doping and how they are affected by protonic acid doping. Doping with electron donors and acceptors strongly affects the electronic structures of quasi one-dimensional conjugated polymers, and by coupling to the bond distances through bonding and antibonding interactions doping affects their geometrical structures as well. It was predicted that Peierls distortion of *trans*-PA becomes depressed as charge transfer (CT) progresses and finally bond equalization is accompanied at CT of about 0.1e per CH unit.[17] We have recently shown[14] that PTL, POL, and PQL undergo a similar Peierls distortion in their undoped states and that the distortion disappears upon charge transfer of about ±0.8e per unit cell (amounts to ±0.05e per non-hydrogen atom). Conjugated polymers with nondegenerate ground states such as PPP, PPy, and PT were predicted to undergo geometrical modifications evolving from aromatic structures toward quinoid-like structures, as a result of CT with n-type dopants.[18] Protonic doping is well known in polyaniline (PANI) chemistry.[19] MacDiarmid et al.[20] have achieved metallic levels of conductivity ($\sigma \approx 5$ S/cm) for PANI by doping with dilute aqueous protonic acids. They have proposed that the conducting form of PANI corresponds to an iminium salt which does not involve formal oxidation unlike the case of usual p-doping of other conducting polymers. Kim[3] interpreted acid-doping in the BBL case as a Lewis acid-type charge-transfer complexation, not merely a protonation.

To our knowledge, there has been no theoretical study about the geometrical and electronic structures of BBL. In this study, we calculate the geometrical and electronic structures of BBL as a function of CT in the range of $-4e \le q \le +4e$ per unit cell and with the protonic doping at all imine sites.

Method

Fully optimized geometrical structures were obtained by total energy calculations using the solid-state version of the modified neglect of diatomic overlap (MNDO) method.[21] The corresponding electronic structures are calculated with the modified extended Huckel (EH) band calculations,[22] which is designed to produce reliable π–π^* absorption peak values of conjugated polymers and has predicted those values quite well[22,23] for a number of conjugated heterocyclic polymers. Five representative wave vectors (**k**) were chosen from 0 to π/t (t is the unit cell length) with regular intervals. The neighboring unit cells as far as the second nearest ones were involved in the lattice sum. CT values were limited to $q = -4, -2, 2$, and 4 per unit cell of BBL, by taking out electrons ($q < 0$) from the highest occupied bands or by putting electrons ($q > 0$) into the lowest unoccupied bands. (q is measured in e units.)

Recently, the EH method has been reparametrized with the aim to predict more accurate band gap values of conjugated polymers,[22] which the standard EH method[26] is known to underestimate. At the same time, self-consistent-field Hartree–Fock methods such as ab initio and MNDO greatly overestimate band gaps of polymers.[27] The modified EH method has predicted band gaps of various conjugated polymers usually within 0.3 eV of the experimental values of the π–π^* λ_{max} of optical spectra and also produces bandwidths consistent with the electron energy loss spectroscopy observations.[22,23] We used that set of EHT parameters which were optimized to be used in conjunction with MNDO geometries.[22] The valence orbital exponents (ζ) and the valence-state ionization potentials (VSIP) used for O 2p orbitals are 2.275 and −14.8 eV, respectively. The atomic parameters used for N 2p orbitals are 1.950 eV for ζ and −13.4 eV for VSIP.

Geometry of BBL as a Function of Doping

BBL consists of naphthalenic and benzenoid units condensed with *N*-imino amide units. Thus, complicated stereochemistry is expected during the condensation reaction.[24] We considered in this study only the cis–cis form among the possible isomers of BBL. For geometrical optimizations, we employed a unit cell of BBL as shown in Figure 1 and imposed two mirror planes perpendicular to the polymer plane. This makes BBL isomorphous with the C_{2v} point group, according to the line group theory[25] which takes into account one-dimensional translation symmetry. Two base sites are possible to be protonated: the amide carbonyl and the imine sites. Electrochemical studies[24] revealed that a preferred protonation site strongly depends on the solution pH and that at low pH (pH < 2) imine protonation is predominant over amide carbonyl and is responsible for the high electrical conductivity of BBL. Therefore, we placed H$^+$s at all imine sites for modeling protonic doping in this study.

The optimized geometrical parameters for BBL in the ground state and in selected doped states are given in Table I. According to the calculations, in the neutral state the naphthalenic and benzenoid rings are aromatic with bond length variations of about 0.05 Å. The C=N bond length (1.327 Å) of the imine is 0.075 Å smaller than the corresponding C—N bond length. The three C—N bond lengths of the tertiary amide are all close to 1.43 Å. At the lower donor doping level ($q = 2$), the naphthalenic unit becomes quinoid-like with bond variations of ca. 0.08 Å and bonds between the naphthalenic and the N-imino

Table I
Selected Bond Distances (Å) from MNDO-Optimized Geometry of the Infinite Ladder Polymer BBL, as a Function of Charge Transfer (q) (Notation According to Figure 1)[a]

		acceptor		proton	neutral	donor	
i	j	$q = -4$	$q = -2$	$2H^+$	$q = 0$	$q = 2$	$q = 4$
1	2	1.409	1.437	1.446	1.431	1.368	1.369
2	3	1.447	1.397	1.393	1.392	1.452	1.458
3	4	1.439	1.450	1.453	1.447	1.428	1.485
4	5	1.451	1.452	1.442	1.446	1.425	1.486
5	6	1.466	1.414	1.399	1.392	1.447	1.454
6	7	1.391	1.419	1.421	1.424	1.368	1.371
4	8	1.466	1.433	1.434	1.430	1.480	1.397
3	9	1.509	1.493	1.499	1.504	1.462	1.427
9	10	1.511	1.488	1.493	1.432	1.445	1.459
10	11	1.405	1.416	1.387	1.429	1.428	1.441
5	11	1.468	1.447	1.466	1.462	1.441	1.406
10	12	1.406	1.406	1.440	1.425	1.432	1.445
12	13	1.458	1.487	1.448	1.450	1.452	1.455
13	14	1.361	1.359	1.405	1.402	1.394	1.383
11	14	1.383	1.375	1.366	1.327	1.351	1.393
12	15	1.456	1.423	1.420	1.410	1.414	1.421
13	16	1.468	1.431	1.402	1.403	1.406	1.420
9	17	1.202	1.209	1.208	1.223	1.240	1.266

[a] $2H^+$ indicates protonic doping at all N14 sites.

Table II
Comparison of Electronic Properties of Undoped Ladder Polymers

	E_g (eV)			
polymer[a]	EH method[b]	exptl[c]	E_f (eV)[d]	highest valence bandwidths (eV)
BBL	1.99 (0.94)	2–2.2	−11.75	0.61
PTL	0.78 (0.32)		−10.68	1.18
PQL	0.62 (0.41)		−10.13	1.52
POL	0.76 (0.46)		−10.41	1.52

[a] BBL = benzimidazobenzophenanthroline; PTL = polyphenothiazine; PQL = polyphenoquinoxaline; POL = polyphenoxazine. [b] Values in parentheses are obtained from unmodified EH band calculations. [c] Experimental values correspond to absorption peaks of optical spectra.[3,12] [d] Highest occupied level.

amide units become shorter. The C═N bond of the imine becomes longer, resulting in a reduction of the imine bond alternation to 0.04 Å, and the C═O bond of the amide becomes longer by 0.02 Å. Further doping ($q = 4$) follows the same trends, a more quinoid-like naphthalenic unit and more or less complete depression of the bond alternation of imine C—N bonds. The behavior of geometrical variations at the lower acceptor doping level ($q = -2$) is different from that found in the case of donor doping. Bond alternations of C—N bonds of the imine and of C—C bonds in the lower part of the naphthalenic unit almost vanish, whereas the upper part of the naphthalenic unit changes little. The C—N bond of the amide becomes longer, and the C═O bond gets slightly shorter. The *N*-imino amide unit becomes more strongly bonded to the benzenoid unit at this doping level. Further doping up to $q = -4$ induces the naphthalenic unit to relax weakly toward a quinoid-like form with bond alternations of 0.04–0.07 Å, and the bond length variation of the benzenoid unit nearly vanishes.

The geometrical structure of protonated BBL is very similar to that of unprotonated BBL in the neutral state. Only slight geometrical changes can be found along the *N*-imino amide unit. Most of the positive charge resides on C11 of the imine rather than N14. Therefore, geometrical relaxation occurs in order to form the stable carbonium ion, and bond lengths along the *N*-imino amide unit vary accordingly; i.e., the C11═N14 and C9—N10 bond lengths slightly increase while the C11—N10 and C9═O17 bond lengths decrease. Shortening of the C═O bond is consistent with the spectroscopic observation[3] which indicates the shift of the IR C═O stretching band to a higher frequency upon acceptor and protonic acid doping. However, the increase of C═N bonds, irrespective of doping directions, is in contrast to the experimentally observed up shift of the IR peak position, which has been preliminarily assigned to a C═N vibration mode.[3]

In summary, as CT occurs in either direction, the naphthalenic unit becomes quinoid-like, and bond alternations of the benzenoid unit and the imine vanish. However, the variation is asymmetrical with respect to the direction of CT. Protonic doping only affects the *N*-imino amide unit. Upon protonation, the C11═N14 bond of the imine becomes slightly longer while the C11—N10 bond gets shorter, creating a stable carbonium ion in each repeat unit. As experimentally observed, the C═O bond is predicted to become shorter upon acceptor and protonic doping, while it elongates upon donor doping.

Electronic Structure of BBL

The calculated electronic properties of the neutral BBL and other ladder polymers, PTL, POL, and PQL, are presented in Table II. The band gap of the neutral BBL is calculated to be 1.99 eV comparable with the corresponding optical λ_{max} values of 2–2.2 eV.[3,6,12] The calculated π bandwidth of the highest valence band (VB) is quite narrow, 0.61 eV, indicating poor hole delocalization along the polymer backbone. The low Fermi level is consistent with the experimental observations[3] that halogens such as iodine and bromine are not effective acceptors for BBL. The π-band structure of neutral BBL is shown in Figure 4. For simplicity, only the lowest 20 of the total 26 π bands are shown. As indicated by the Fermi level (E_f), 14 of them are filled, since the amino N contributes two π electrons. The band symmetries are assigned according to the line group theory.[25] The bands are separated with relatively small gaps at the center and the edge of the Brillouin zone, resulting in narrow bands. The lowest conduction band (CB) is flat and is located at 2.21 eV below the higher CB.

As CT occurs in either direction, the $6a_2$ to $9b_2$ gap near the Fermi level becomes smaller, but does not disappear even at high doping levels ($q = \pm 4$). Doping of course moves the Fermi level, as the bands become populated or depopulated upon doping. (Each band can hold two electrons per repeat unit.) The electronic π-band structures of doped BBL with CT of ±2e per unit cell are shown

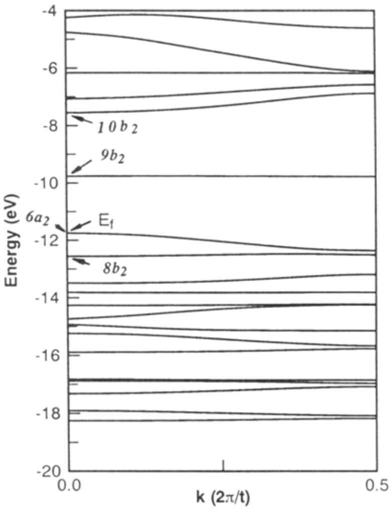

Figure 4. Modified extended Huckel π-band structure of neutral BBL (the lowest 20 or 26 π bands are shown for simplicity).

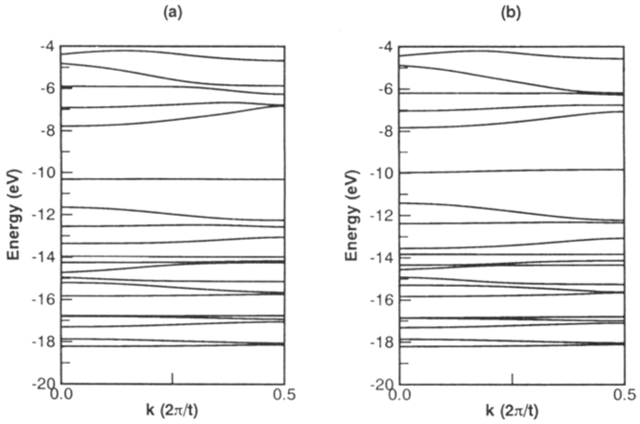

Figure 5. Modified extended Huckel π-band structures of doped BBL with charge transfer of ±2e per unit cell: (a) donor doping and (b) acceptor doping.

in Figure 5. Overall, no significant change of the π-band structures of BBL is found with CT, except the decrease of the $6a_2$ to $9b_2$ gap. At low doping levels, this gap decreases to 1.33 eV for the donor doping ($q = 2$) and to 1.43 eV for the acceptor doping ($q = -2$). Further donor doping ($q = 4$) decreases the $6a_2$ to $9b_2$ gap to 0.91 eV. However, further acceptor doping ($q = -4$) does not induce further significant reduction of this band gap (1.28 eV). The absorption peak of BBL films doped with AsF_5 was observed at ca. 1.5 eV.[6] The π-band structure of the protonated BBL, $(H_2BBL)^{2+}$, is quite similar to that of the unprotonated BBL in the neutral state as expected from the similarity of two corresponding geometries and the fact that the number of electrons does not change upon protonation. The highest occupied band of $(H_2BBL)^{2+}$ is also $6a_2$. The band gaps between the bands $6a_2$ and $9b_2$ and between the bands $9b_2$ and $10b_2$ of $(H_2BBL)^{2+}$ are predicted to be 1.96 and 2.16 eV, respectively.

Discussion: Correlation of Geometry and Electronic Structure

Variation of the geometrical and electronic structures of BBL with CT can be understood from the properties of the π-crystal orbitals near the Fermi level, as shown in Figure 6. The diameter of a circle represents the square of the coefficient of the corresponding π-type atomic orbitals. Orbitals with weights smaller than 0.004 are not shown. The highest VB orbitals, $6a_2$ and $8b_2$, largely consist of contributions from the benzenoid and the *N*-imino amide units. In the orbital $6a_2$, there are some contributions from the lower part of the naphthalenic unit with (anti)bonding character of C4—C5 and C5—C6 (C4—C8 and C6—C7) bonds. The interactions of N14 with neighboring C atoms are bonding for C11=N14 and antibonding for C13—N14 in this orbital. In the lower band orbital $8b_2$, the contribution of the naphthalenic unit is small. N14 interacts with C11 in a nonbonding and with C13 in an antibonding manner. The lowest CB orbital $9b_2$ comes mainly from the naphthalenic and the *N*-imino amide units, while $10b_2$ is completely delocalized. In the orbital $9b_2$, interactions of C1—C2 and C6—C7 (C2—C3 and C5—C6) bonds in the naphthalenic unit are (anti)bonding. The interaction of N14 is antiboding with C11 and bonding with C13 in this orbital. Orbital $10b_2$, in addition to bonding features similar to those of $9b_2$, also has significant contributions from the benzenoid unit.

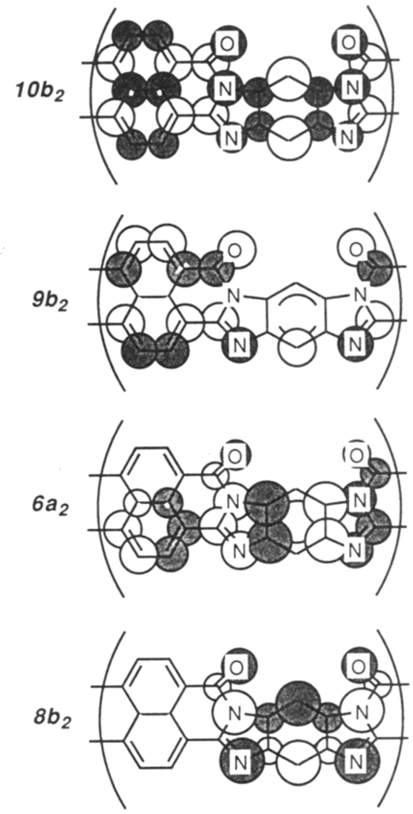

Figure 6. π-type crystal orbitals of the neutral BBL around the Fermi level, at $k = 0$.

Withdrawal of electrons from the band $6a_2$ decreases the (anti)bonding interactions of C4–C5 and C5–C6 and C4–C8 and C6–C7) bonds of the naphthalenic unit and the short (long) imine C–N bond. This induces geometrical relaxations of these bonds to raise the $6a_2$ level and to lower the $9b_2$ level at the center of the Brillouin zone ($k = 0$), resulting in the reduction of the corresponding gap, as has been discussed in connection with Figure 5. Further withdrawal of electrons from the band $8b_2$ mainly relaxes the benzenoid unit and does not reduce the band gap significantly as predicted at the high doping level of $q = -4$. Similarly, putting electrons into the $9b_2$ band relaxes the naphthalenic unit and the C–N bonds at the imine site so as to increase (decrease) the anti(bonding) interactions. Therefore, the naphthalenic unit relaxes toward a quinoid-like form, and the C–N bonds at the imine site move toward a smaller bond alternation of 0.04 Å. This stabilizes the $9b_2$ band and destabilizes the $6a_2$ band at $k = 0$, resulting in the small band gap as predicted at the donor doping of $q = 2$. Because of similarities of orbitals

$10b_2$ and $9b_2$, further donor doping ($q = 4$) consistently follows the trend at the lower doping level ($q = 2$). That is, the naphthalenic unit becomes more quinoid-like, and the bond alternation of the imine C–N bonds almost disappears, leading to a further decrease of the band gap. The gap between the bands $9b_2$ and $10b_2$ does not change with CT in either direction because of the similar neighboring interactions of those band orbitals.

The calculated band gaps for neutral and doped BBL are in excellent agreement with the experimental values, which are 2.0–2.2 eV for the neutral and 1.5 eV for the AsF_5-doped BBL. The next peak at about 3.5 eV is probably due to a $6a_2$ to $10b_2$ transition.[3,12]

The interaction between C and O atoms in the amide carbonyls is antibonding near the Fermi level. Therefore, acceptor doping reduces the antibonding character of the C=O bond, resulting in a decrease of the bond and the shift of the C=O stretching frequency to a higher position as observed from the FTIR spectrum,[3] whereas donor doping increases the C=O antibonding interaction.

MNDO calculations show that a simple protonation at the imine N affects the geometry of BBL locally along the *N*-imino amide units and most of the positive charge resides on C11 rather than on N14 of the imine. As protons interact with unshared lone pair electrons of nitrogens at the imine sites, charge redistribution occurs along the *N*-imino amide units because of the O and N atoms with one or more lone pairs of electrons. This charge redistribution induces the formation of a polarized carbonium-type ion between the two nitrogens. Therefore, the mechanism of the C=O frequency shift toward a higher position upon the light doping with sulfuric acid is different from that observed in the case of CT. Extensive electrochemical studies of BBL in acidic solutions have been done by Wilbourn and Murray.[8,24] A BBL film in equilibrium with a low-pH electrolyte ($\mathrm{pH} \ll \mathrm{p}K_a \approx 2.2$) is mainly in the $HBBL^+$ form, exhibiting a single reduction peak for the $HBBL^+$ couple.[8] λ_{max} of the unprotonated BBL is at 534 nm (2.3 eV) in acidic solutions and shifts to 466 nm (2.7 eV) upon more or less complete protonation in pH 0.45 solution.[24] The peak shows no shift during reduction in this solution. If the redox couple H_2BBL^+/H_2BBL is assumed in pH 0.45 solution, their observations qualitatively agree with our calculated electronic structures. The H_2BBL^+ species has the band $9b_2$ half-filled. Therefore, the absorption in H_2BBL^+ occurs from the band $9b_2$ to the band $10b_2$, leading to a larger value than the transition of neutral BBL from the band $6a_2$ to the band $9b_2$. The flatness of the bands $9b_2$ and $10b_2$ in the $0 \le -k \le -\pi/t$ range can explain the absence of any significant shift of the absorption peak during the reduction of protonated BBL.

Since most of the geometry of BBL and its π-electronic structure remain unchanged with protonation, the increase of conductivity of BBL films upon acid doping seems unlikely to be a direct consequence of protonation. Wilbourn and Murray[24] suggested that the electrical conductivity along BBL chains results from the current of a positively charged imine site to a different imine nitrogen within the context of structurally equivalent resonance forms as proposed by MacDiarmid et al.[20] in the case of polyaniline. However, the formation of a stable carbonium ion between two nitrogens along the *N*-imino amide unit indicates that such a charge flow is likely to occur along the *N*-imino amide unit, not producing any net current along the BBL chain.

Conclusion

BBL is a semiconductor with a flat empty band approximately halfway between the second conduction band and the valence band. The band gap between the valence and empty conduction band is 2 eV, and the gap between the empty conduction band and the second conduction band is calculated to be 2.2 eV. The band gap at the Fermi level mainly arises from the aromatic form of the naphthalenic unit and the bond alternation of C–N bonds at the imine site.

As charge transfer occurs in either direction, the naphthalenic unit relaxes toward a quinoid-like form and the bond alteration of C–N bonds at the imine site vanishes, resulting in the decrease of the band gap. However, the $6a_2$ to $9b_2$ band gap remains open even at high doping levels ($q = \pm 4$) since the conduction band near the Fermi level has orbital contributions different from those of the valence band. Donor doping decreases this gap more effectively since the conduction bands near the Fermi level have more naphthalenic contribution than the valence bands. The gap between the empty conduction band and the second conduction band changes little with charge transfer because of the similar bonding features of the corresponding orbitals.

A protonation at the imine N induces charge redistribution along the *N*-imino amide because of electron-rich O and N atoms. As a result, geometrical relaxation occurs only along the *N*-imino amides, changing the bond lengths alternatively and creating the stable carbonium ion. Therefore, most of the BBL geometry varies little, leading to no perceptible change of the π-electronic structure. Consequently, it is expected that a high level of protonic acid doping induces the formation of mobile positive charge carriers through protonations at the imine nitrogens and the relaxation of the whole BBL geometry through Lewis acid-type charge-transfer complexation, resulting in the increase of BBL conductivity.

The absence of a red shift upon doping in the absorption spectrum of BBL has been attributed to the fact that BBL has no alternative structure and therefore no polarons or bipolarons are formed upon light doping. This distinguishes BBL and its whole family of ladder polymers from other conjugated single chain polymers, such as polythiophene, and ladder polymers such as PTL and others.[28]

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