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Material design from first principles: the case of boron nitride polymers

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Received 31 May 2002

Published 11 October 2002

Online at stacks.iop.org/JPhysCM/14/9997

Abstract

In recent years, first-principles quantum-mechanical simulations have become established as a complementary tool to experiments in the design and characterization of new materials. Here we illustrate this in the case of boron nitride (BN) analogues of conjugated organic polymers which offer a cheap alternative to inorganic semiconductors in the manufacture of electronic devices. By analogy with heterostructures, such as quantum wells and superlattices, currently used by the conventional semiconductor industry, we show how copolymers consisting of sections of carbon and BN can be designed to tune the electronic properties of these new materials.

1. Introduction

Recent advances in synthesis and nanofabrication technologies have dramatically broadened the range of materials that can be designed with desired and controlled characteristics. In parallel with these developments, improvements in computer simulation algorithms and the availability of powerful computers offer a complementary way to probe the properties of potentially interesting materials, even before (or without) making them in the laboratory. In particular, first-principles methods (whose input parameters consist only of a list of the atoms in the system, and which then solve the Schrödinger equation for the interacting electrons in the potential of the nuclei) are a powerful and unbiased tool for predicting the behaviour of new materials at the atomistic level.

Among first-principles techniques, density-functional theory (DFT), which is a modern reformulation of quantum mechanics in terms of the electron density [1, 2], offers a favourable

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ratio between accuracy and computational cost, which makes it suitable for (relatively) large-scale calculations. Its success in describing structural and electronic properties of real materials has been recognized by the award of the 1998 Nobel Prize in Chemistry to its founder, Walter Kohn [3]. It has been combined with molecular dynamics, thus allowing the simulation of systems at finite temperature [4, 5]. Because of the absence of empirical parameters, DFT is suitable for applications in very diverse fields, from materials science to biochemistry [6, 7]. In particular, various properties of polymers have been studied with such a method (see e.g. [8–25]).

DFT accuracy has a price, which nowadays limits size and simulation time to a few hundred atoms and a few picoseconds. On the one hand, this is sufficient to study many properties successfully, as testified by the thousands of published papers on DFT applications [7]; on the other, it is spurring on the development of new methods for overcoming the scale and size limitations [26], as well as other pitfalls mainly due to the description of the troublesome electron exchange and correlation.

In this paper, we present an example of how state-of-the-art DFT calculations can be used to analyse the properties of a series of hypothetical systems, designed using BN polymers as building blocks [27]. For a preliminary screening, making these polymers in a ‘virtual matter laboratory’ [28] is easier, cleaner and less dangerous than trying to make them in a real laboratory.

2. Why boron nitride polymers?

Polymer semiconductors are becoming an increasingly attractive, versatile and cheap alternative to conventional solid-state semiconductors [29–31]. The key property of both conventional and polymer semiconductors is the energy band gap for electrons: combining materials with different band gaps lies at the heart of many modern electronic devices. The idea of this work came from the observation that the most popular conventional semiconductors (e.g. IV, III–V and II–VI semiconductors such as Si, GaAs and ZnSe, as well as ternary mixtures such as $\text{Al}_x\text{Ga}_{1-x}\text{As}$) are characterized by essentially the same crystalline structure, but made from different chemical elements. This results in different electronic properties, which can be further tuned by alternating thin layers of materials with different band gaps (e.g. GaAs and AlAs) in superlattices and quantum wells, where electrons and holes are confined within the narrow-gap material. This process of engineering the band gap by hand opens up a huge number of possible choices when building electronic devices.

In conjugated organic polymers (i.e. polymers with a delocalized π -electron system along the carbon backbone) the band gap usually depends on the structural details; hence it can be varied by modifying the structure, for example by adding side chains to the carbon backbone. However, the results can be complex with potential difficulties for processing. A different route, more akin to that of conventional semiconductors, might also be possible: can we tune the electronic properties by using and combining polymers with similar structures but made from atoms other than carbon? In other words, can we engineer the band gap in a manner similar to what is routinely done in conventional semiconductors?

Many carbon structures can also be made from BN: from diamond, to graphite and even nanotubes [32, 33]. Replacing every pair of carbon atoms by one boron and one nitrogen atom results in stable structures, with generally larger band gaps. Would a similar substitution also hold for the organic polymer structures?

Benzene, which is an essential building block of conjugated organic polymers, does indeed have a BN analogue, borazine, which is easily synthesized. In terms of dimensionality, conjugated polymers can be ranked somewhere between benzene and graphite, both

characterized by π -bonding. Since these two extremes exist for BN compounds, we can argue that BN polymers could also be made. Indeed borazine-based polymers, with structures similar to the carbon polymer poly(*p*-phenylene) (PPP), have been recently synthesized [34, 35]. Experiments have been motivated so far by the search for good precursors to BN ceramics. However, we believe that BN polymers might be interesting in their own right because of their electronic properties.

Making a BN polymer out of a carbon one is equivalent to making a III–V compound out of a group-IV semiconductor: using adjacent elements in the periodic table results in an unchanged structure, accompanied by an increase in the ionicity of the bonds which, in turn, increases the band gap and modifies the electronic properties. This also allows us to investigate possible routes for extending (or breaking) the process of conjugation in polymers. Our goal is to see how we can tailor the electronic properties by combining BN polymers with their organic counterparts.

3. Method

We have performed DFT calculations, within a pseudopotential total-energy scheme for periodic systems [36]. We use the local-density approximation (LDA) [37, 38] for the exchange–correlation energy, Troullier–Martins pseudopotentials [39] for boron, carbon and nitrogen and a modified Kerker pseudopotential [40] for hydrogen, and a plane-wave basis set for the wavefunction expansion up to a kinetic energy cut-off of 60 Ryd. The polymers were modelled in a periodic cell with a large distance between neighbouring chains to minimize their interaction. The Brillouin zone was sampled using twenty *k*-points. Both the atomic coordinates and the cell degrees of freedom were fully relaxed.

4. Structures

The structures we chose are the analogues of PPP and poly(*p*-phenylenevinylene) (PPV), which are shown in figure 1. When made of BN, they become poly(*p*-borazylene) (PBZ) and poly(*p*-vinyleneborazylene) (PVB) respectively. As PPP is a sequence of concatenated benzene rings, PBZ is a sequence of concatenated borazine rings. An analogous substitutional process leads to the creation of PVB from PPV.

The charge densities in figure 1 clearly show the effects of the polar B–N bonds in comparison to the homonuclear C–C bonds. This is certainly related to the improved solubility of BN polymers compared to their organic counterparts: in fact, PBZ was found to be soluble in ethers [41] whereas PPP is insoluble. Side chains are usually attached to the backbones of insoluble polymers to make them soluble, leading to complex systems which are difficult to process. If BN polymers are soluble without the need to complicate their structures with side chains, they might be more easily processed to form films from solutions. Moreover, the absence of side chains would facilitate polymer alignment resulting in sharper features in the electronic spectra and enhanced mobility.

The calculated bond lengths and angles are reported in figure 2. An important difference between the geometries of the carbon and BN polymers is the twisting angle between monomers. The bonds linking the monomers together are not necessarily rigid and therefore the monomer planes need not align. The torsion angle between the monomers measures the deviation from the planar configuration. In carbon polymers, the twisting is induced by the significant charge transfer in C–H bonds. In fact, because of the different electronegativities of the two atoms (2.2 for hydrogen versus 2.55 for carbon on the Pauling scale), the carbon

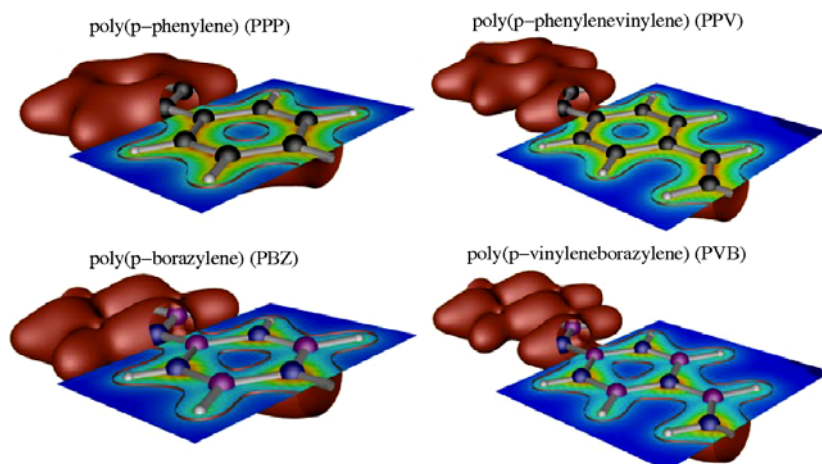


Figure 1. Structures and charge densities for the carbon polymers PPP (top left) and PPV (top right) and their BN analogues PBZ (bottom left) and PVB (bottom right).

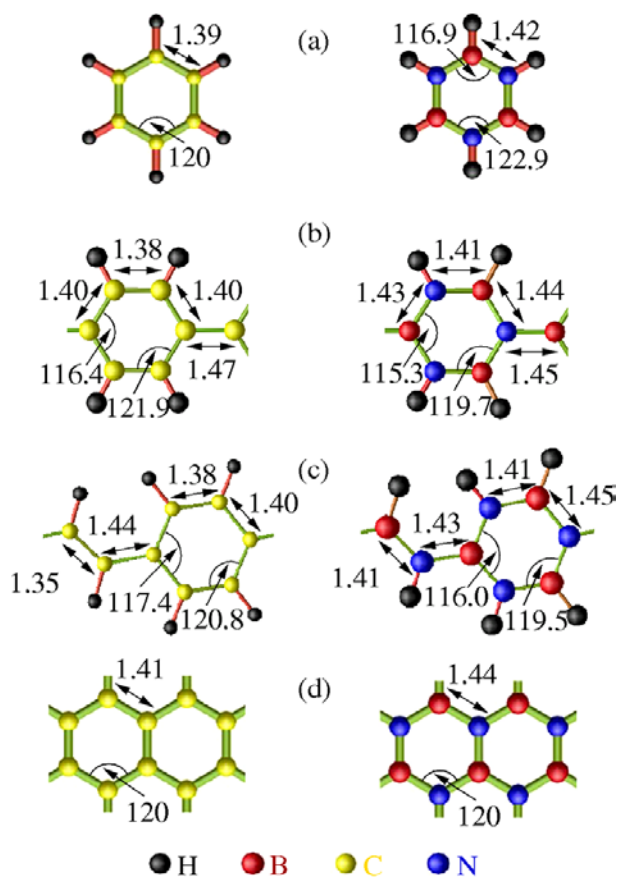


Figure 2. Comparison of the geometries of carbon and BN structures: (a) benzene and borazine; (b) PPP and PBZ; (c) PPV and PVB; (d) graphite and graphitic BN. All bond lengths are in Å and angles in degrees.

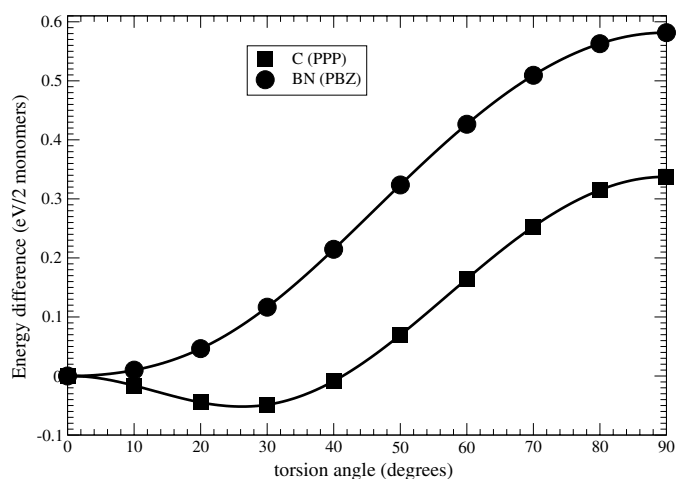


Figure 3. Energy differences versus twisting angle for PPP (squares) and PBZ (circles).

atoms are negatively charged, whereas the hydrogen atoms are positively charged. Using Mulliken population analysis, we estimate the positive charge on the hydrogen to be around 0.3 electron charges. Taking PPP as an example, the close positively charged hydrogens attached to adjacent monomers will repel one another. To minimize the repulsion, they will try to maximize their distance by inducing a torsion between the monomers, with 90° as the most effective value. On the other hand, the overlap of the π -orbitals on neighbouring carbons belonging to adjacent monomers will be maximal when the polymer configuration is perfectly planar: there would be no overlap for 90° torsion. The energy gain arising from the π -electron delocalization depends on this overlap: it is at its maximum in the planar configuration. Hence there are two competing contributions to the total energy, resulting in an equilibrium angle between 0 and 90° . For the isolated PPP chain, we obtained a torsion angle of about 26° , which compares well with a previously reported value [19].

In BN polymers, the situation is different. The electronegativities on the Pauling scale are 2.04 for boron and 3.04 for nitrogen. Since the hydrogen electronegativity lies in between these values, in the N–H bond the nitrogen will be negatively charged and the hydrogen positively charged, while the opposite will hold in the B–H bond. In PBZ for example, the hydrogen atoms facing each other on adjacent monomers have opposite charge and therefore tend to attract each other: this has the effect of reinforcing the planar structure. The variations of the total energies of PPP and PBZ as a function of the twisting angle between monomers is shown in figure 3.

This difference, induced by polarity, between the carbon and BN polymers, will certainly manifest itself in the excited state behaviour. By comparing the absorption and emission spectra of carbon polymers such as PPP, a strong Stokes shift is observed, which is a signature of the different atomic arrangements in the ground and excited states. A relevant component of the excited state geometry relaxation is related to the change of the torsion angle towards a more planar configuration. Since the BN polymers are already planar in the ground state, the torsion angle should not change upon excitation.

For simplicity, especially in the case of copolymers and crystals, we have enforced the planar configuration in the calculations that will be presented in the rest of the paper.

Table 1. Average binding energy per electron for carbon and BN systems. The energies of the graphitic phases are for isolated sheets.

Binding energy/electron (eV)			
C systems		BN systems	
Benzene	2.24	1.99	Borazine
PPV	2.22	1.98	PVB
PPP	2.22	1.98	PBZ
Graphite	2.20	1.96	Graphitic BN

5. Energetics

To investigate the energetics of these different structures, we have calculated their total binding energies with respect to their constituent atoms. Trends in the energetics can be observed in both the average bond energies (i.e. the total binding energy divided by the number of bonds in the structure) [27] and the binding energy per electron (i.e. the total binding energy divided by the number of valence electrons), which we report in table 1.

We compare the energies of the (one-dimensional) polymers to the (zero-dimensional) molecules (benzene and borazine) used to build them, and to the corresponding (two-dimensional) graphitic forms. As expected, the polymers fall energetically in between these two extremes, with the same trend for the BN and the carbon compounds, and small energy variations within compounds of the same family. This suggests that the chemistry of the BN polymers should be similar to that of the carbon polymers.

6. Band structures and wavefunctions

The electronic properties of these polymers are important for potential technological applications. In general, BN compounds tend to have larger energy gaps than their carbon analogues due to the polarity of the chemical bonds. This effect, which is observed when the band gaps of group-IV semiconductors are compared to those of III-V and II-VI semiconductors, also occurs for first-row elements: e.g. cubic BN has a larger band gap than diamond, and graphitic BN is a wide-gap insulator whereas graphite is a semi-metal. We therefore expect similar behaviour in the polymers. In figures 4 and 5 the band structures for PPP and PBZ from the Kohn-Sham eigenvalues obtained in our DFT calculations are shown, along with some of the wavefunctions for states close to the band gap. In particular, the lowest unoccupied (LUMO) state represents the wavefunction for electrons in the first excited state, while the highest occupied (HOMO) state represents the holes. It is known that DFT band calculations underestimate the band gap; for example for PPV we obtain a gap of 1.2 eV [27], whereas the known optical gap is 2.5 eV [30]. However, the error does not scale with the magnitude of the gap and it is usually less severe for large-band-gap compounds. Moreover, to quantitatively describe the absorption spectra of polymers, the electron-hole interaction, accounting for exciton formation, needs to be included [42–50]; this would lead to much more complicated and computationally demanding calculations. However, the comparison of these band structures should still capture the crucial qualitative features of the BN systems, as previously confirmed in the case of BN nanotubes [51].

Indeed, the band gaps of the BN polymers are much larger than those of the equivalent carbon systems; accounting for the correction in the gap underestimation and for the electron-hole interaction, this will result in band gaps in the UV. Wide-gap materials are

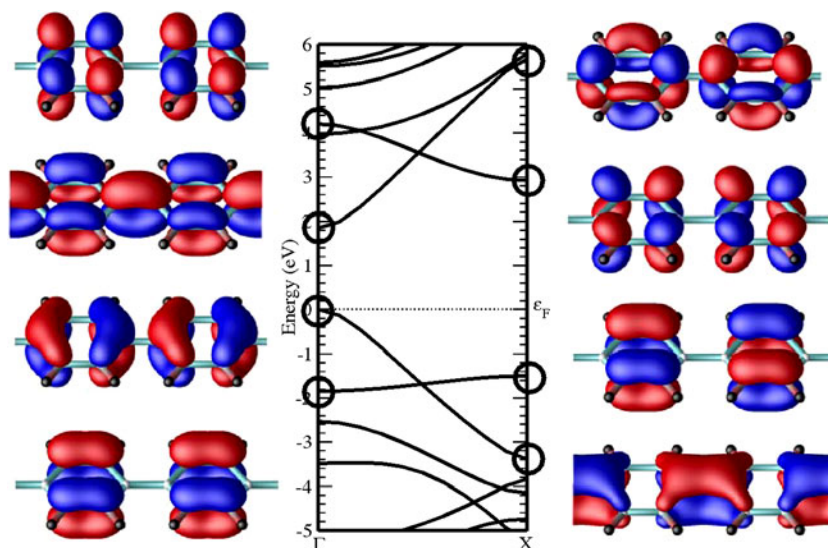


Figure 4. PPP band structure with selected wavefunctions close to the band gap. Red and blue indicate positive and negative sign respectively.

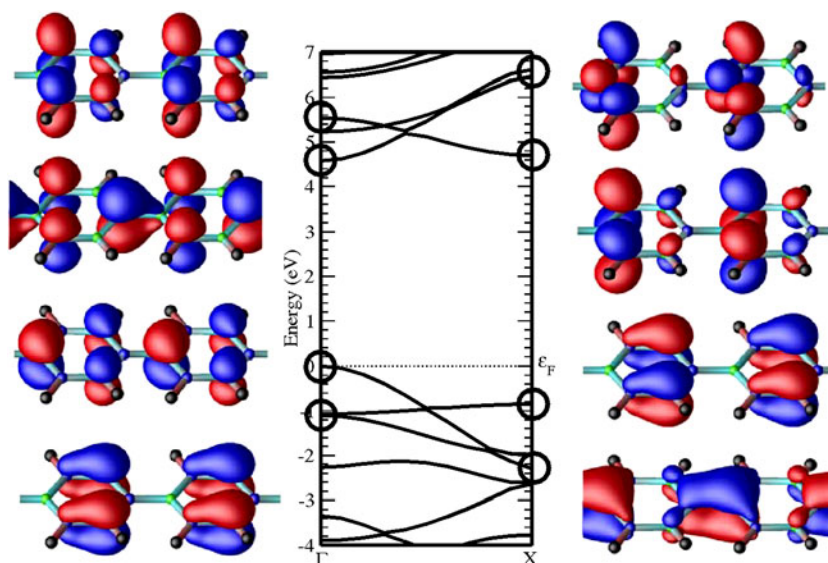


Figure 5. PBZ band structure with selected wavefunctions close to the band gap.

interesting *per se*, as attested to for example by the rapidly developing research on GaN. Pure BN polymers, which are likely to have band gaps even larger than GaN, could be suitable candidate materials for ultraviolet detectors and emitters. Shorter wavelengths could be important for nanotechnology applications, where the effort is to build devices on increasingly smaller scales.

While PPP clearly has a direct gap, the similar energies of the conduction states at Γ and X of PBZ cannot rule out an indirect gap. For light polarized along the polymer chain,

the direct HOMO–LUMO transitions at Γ and at X are optically allowed in both PPP and PBZ, as demonstrated by the symmetry of the valence and conduction states at Γ and X (see figures 4 and 5). Both PBZ and PVB show less dispersion in the states close the Fermi level as compared to PPP and PPV respectively. These features, together with the large gaps, will affect the electron–hole interaction, leading to differences in the absorption spectra of the BN and carbon polymers.

7. Copolymers as one-dimensional superlattices

Current research focuses mainly on polymers with band gaps smaller than our forecasts for BN polymers. However, it is desirable to have polymers with band gaps spanning the whole spectral range, from infrared to ultraviolet, thus expanding the possibilities for nanotechnology applications.

By combining carbon and BN monomers in the same chain, one-dimensional superlattices or copolymers can be created. By analogy with conventional semiconductor superlattices and quantum wells, we expect to be able to tune the gap by varying the lengths of the BN and carbon segments. Copolymers derived from borazine and silazane have been successfully synthesized [52] as precursors to SiNCB ceramics. Our study focuses on the electronic properties of carbon and BN copolymers, and allows us to investigate the performance of polymers made up of a mixture of organic and inorganic monomers. Indeed, it is also possible to tune the band gaps using conjugated oligomers of different lengths [53] or polymers where the conjugation is broken by adding different components. The systems we propose here are characterized by essentially the same polymer structure over their entire length. Given the difference in band gap between the carbon and BN systems, the range of band-gap tuning will be fairly large, thus covering a large region of the spectrum and being of interest for a wide range of applications.

The variation of the band gap is shown in figure 6, where the calculated energy gaps for copolymers of PPP and PBZ are shown as a function of the number of PPP monomers. There are three sets of data differing in the number of BN monomers in between the carbon regions, and one set of data for the carbon oligomers. As expected, all the energy gaps of these copolymers lie in between the pure PPP and PBZ values (1.81 and 4.66 eV respectively, if calculated within DFT-LDA). Although these results suffer from the DFT-LDA underestimation of the band gap and the neglect of the electron–hole interaction, they clearly show a tuning trend.

Figure 7 shows the HOMO and LUMO states for the 3–1 copolymer, i.e. made of three monomers of carbon separated by one monomer of BN. Figure 8 shows the same states but for the case of the 3–2 copolymer. Because of the large difference in the BN and C gaps, we expect that the HOMO and LUMO states should be confined mainly within the carbon segment. Of course, the larger the BN segments are, the more definite the confinement is and the less tunnelling which occurs. This is evident for the structures shown: in the case of the 3–1 copolymer, there is significant spilling of the otherwise confined wavefunctions into the BN segment, resulting in a continuous wavefunction along the entire copolymer. When the length of the BN segment becomes significant, the band gap essentially depends on the length of the carbon segments. The characters of the HOMO and LUMO states in these copolymers, except for the confinement, are essentially the same as the ones shown for the PPP polymer in figure 4.

The energy cost for the formation of the copolymers was calculated to be about 1 eV per unit cell, independent of the carbon polymer length. This suggests that the dominant cost is related to the formation of the C–B and C–N bonds at the interfaces between segments of the different copolymers.

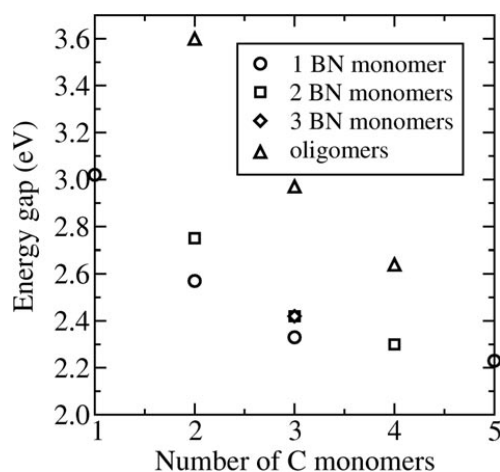


Figure 6. Band gaps for copolymers with different numbers of BN monomers between the carbon regions and for carbon oligomers.

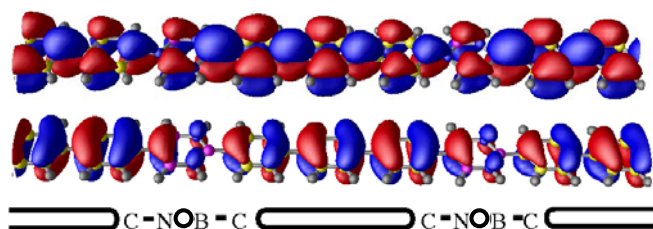


Figure 7. LUMO (top) and HOMO (bottom) wavefunctions for the 3-1 copolymer.

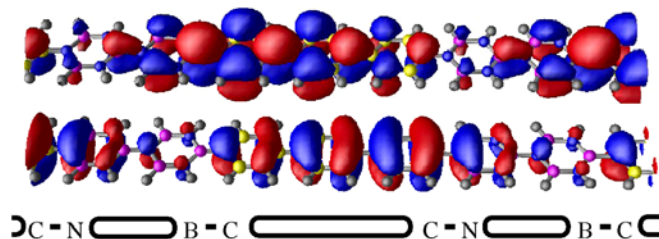


Figure 8. LUMO (top) and HOMO (bottom) wavefunctions for the 3-2 copolymer.

Since the BN monomer lacks inversion symmetry, the two interfaces that each BN region makes in a copolymer are different, being either a C–N or a B–C bond. This results in a different charge distribution at the two interfaces. In figure 8, the HOMO state resides mostly in the carbon region, but is weighted towards the end bonded to the nitrogen atom with significant weight on the nitrogen itself. On the other hand, the LUMO state is weighted towards the opposite end of the region close to the boron atom.

By alternating the orientation of consecutive BN regions, thus doubling the unit cell, it is possible to create inequivalent carbon regions, one terminated by a boron atom at each end and the other by nitrogen atoms. Figure 9 shows such model for the 2-1 copolymer. For this arrangement, all wavefunctions are completely symmetric with respect to the centre of

the carbon region as expected. The last two occupied states (HOMO and HOMO – 1) have wavefunctions with essentially the same character, similar to the HOMO of PPP, but localized in the two inequivalent carbon regions. The HOMO – 1 (with energy –1.2 eV) is localized in the carbon region interfaced by the boron atoms, whereas the HOMO (0 eV) is localized in the carbon region interfaced by nitrogen atoms. An interesting fact is that the HOMO and LUMO states are confined within different carbon regions as shown in figure 9. This will certainly affect the excited state behaviour, since there is practically no overlap between the electrons and the holes which make the exciton state. The energy gap of 2.0 eV for this 2–1 copolymer is significantly smaller than band gap (2.6 eV) for the 2–1 copolymer with BN region oriented in the same direction, which we report in figure 6.

Following a similar idea, DFT calculations have recently been performed to investigate the properties of BN/C nanotube superlattices, which could be used for band-offset nanodevice engineering, polarization-based devices and robust field emitters [54].

8. Mixed crystals

It is also interesting to mix carbon and BN polymers in the solid state, to explore properties with potential technological applications. The interactions between graphitic sheets are known to be comparable for both carbon and BN, giving rise to similar interlayer spacings in graphite, graphitic BN and their mixtures. This has been observed in nanoparticles and nanotubes made out of carbon and BN sheets [55]. There are indications [56] that similar interactions are also present in the solid phase of PBZ, consisting of a layered structure with spacings between 3.4–3.7 Å.

We have calculated the structural and electronic properties of the crystal phases of a mixture of carbon and BN polymers, assuming that, since the carbon and BN monomers are very similar in length and the polymers probably have similar interchain interactions, they could be combined in the same crystal. The starting crystal structures, then relaxed, were those of the carbon phases. One of two polymer chains in the orthorhombic (space group *Pbam*) crystal cell of PPP was replaced by its BN equivalent, thus creating a mixed crystal. A similar procedure was also applied to PPV, using the monoclinic structure with $P2_1/n$ symmetry. Upon relaxation of the lattice parameters and atomic coordinates, using a $4 \times 4 \times 4$ *k*-point grid, we found no significant deviation from the initial configurations: the chains remained separated with small variations in the cell volume.

In figure 10 the electronic densities, projected onto the carbon (bottom panels) and BN (top panels) chains, are shown for both crystals. As for the isolated polymer chains, the energy gap between occupied and unoccupied states is larger for the BN chain than for the carbon one. On both the occupied and unoccupied sides of the gap, the carbon states are closer to the Fermi level than the BN ones, suggesting that electrons and holes will reside predominantly on the carbon polymers in the mixed crystals. This would result in larger ionization energies and lower electron affinities for the BN chains than for the carbon ones. In a hypothetical mixed device of carbon and BN polymers, holes could be injected into the BN system and would then be transferred to the carbon system.

9. Conclusions

First-principles methods are a powerful tool for investigating the structural and electronic properties of existing and potentially interesting new materials in a controlled way. Relying on their predicting power, we have used them to design a series of polymer structures, using

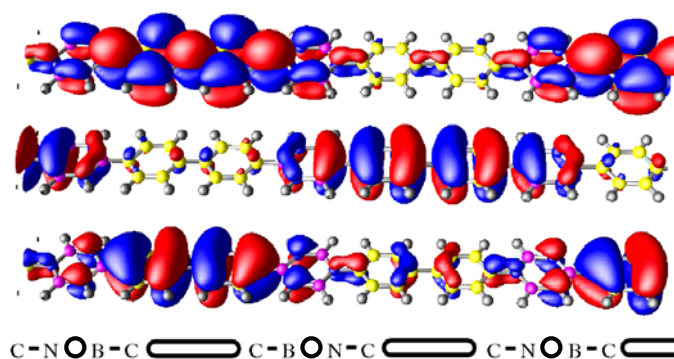


Figure 9. LUMO (top), HOMO (centre) and HOMO – 1 (bottom) wavefunctions for the 2–1 copolymer with opposite orientation of the BN monomers.

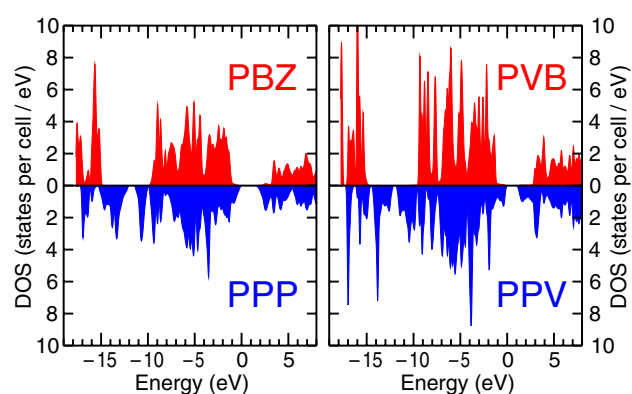


Figure 10. Electronic densities of states (DOS) for the mixed solids of PPP/PBZ (left) and PPV/PVB (right). The zero of the energy corresponds to the Fermi level.

BN and carbon monomers as building blocks. The energy gaps of BN polymers are larger than those of their carbon counterparts, making them active in a different spectral range. Band-gap engineering, with a wide tuning range, can be achieved by combining BN and carbon monomers in one-dimensional heterostructures, similar in spirit to conventional semiconductor heterostructures. While BN polymers are currently synthesized for other purposes, e.g. as precursors to ceramics, our calculations suggest that they may also be useful for making versatile materials which can be adopted in a wide range of applications in electronic devices.

Acknowledgments

We are grateful to F Cacialli, E Marseglia, R H Friend, R J Needs and E Tedesco (Cavendish Laboratory, Cambridge) for many inspiring discussions. The calculations have been obtained with the PARATEC [57] and ABINIT [58] codes. The computational resources were provided by the University of Cambridge High Performance Computing Facility. We acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (MC), Magdalene College, Cambridge (PDH), and of the UK Engineering and Physical Sciences Research Council (CM).

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