Electronic Structure and Properties of Bunz' Polymers

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The Bunz polymers consist of *n*-membered rings of carbon atoms connected via *n* mono- or diethynyl units ($m = 1, 2$ respectively) to other such rings. Coordinated to the three-, four-, and five-membered rings are ML_n units (L = CO, Cp) which lead to 18-electron rule stability at each metal−organic center. The electronic band structures of the metal-free (often metallic) and metal-complexed (always insulating) materials are derived, and it is shown how the insulating polymer−$M(CO)_3$ systems may be converted to systems with small bandgaps by the loss of a CO group. Depending on the width of the conduction band, either small bandgap semiconductors, ferromagnetic metals or antiferromagnetic insulators are predicted. The properties of C_6ML_x polymers are also investigated (ML_x = NO, CO, $C_3H_3^+$). These consist of an ML_x unit attached to a graphite sheet. Bending the MNO group converts the linear three-electron donor "NO^+" unit into an "NO^-" moiety and generation of a metal. By construction of polymers with specific arrangements of $M(CO)_3$ and MCp groups, interesting patterns of metallic and insulating units may be envisaged at the atomic level.

Introduction

Recently Bunz and co-workers have synthesized and characterized pieces[1−4] of basically flat conjugated carbon fragments of different shapes (**1**−**3**, Chart 1), containing organometallic ML_x units, which are the building blocks of the two-dimensional polymers shown in **4**−**6**. The work builds on earlier studies[5] of perethynylated arenes of various types. The carbon skeletons of the polymers are variants of some of the many possible (on paper at least) elemental carbon structures which have attracted attention over the years.[6−10] In general the Bunz polymers consist of *n*-membered rings of carbon atoms connected via *n* mono- or di-ethynyl units ($m = 1, 2$, respectively) to other such rings. The infinite one-dimensional version of **4** with $m = 2$ and ML_x = CoCp (**7**, Chart 2) has actually been made,[11,12] along with well-characterized oligomers. $SiMe_3$ units are bound to the four-membered rings perpendicular to the polymer direction. (Related structural motifs are found in other parts of the periodic table. Those from tellurium chemistry have been studied[13] in electronic terms.) These two-dimensional polymers may be regarded, using the Schäfli notation, as P^n nets, specifically 6^3, 4^4, or 3^6 nets with respectively triangles, squares or hexagons at each node with spacers of varied complexity, polymer$_m$(P^n). Translational periodicity prohibits a similar polymer being built up from a five-membered ring unless it is a quasi-crystal, although nonplanar or distorted structures are possible. An interesting C_{180} fullerenyne has recently been proposed[1] based on this unit. As we have noted, these are but a few of the several different forms of carbon that may be envisaged. The Bunz molecules,[4] some of which are shown in **1**−**3**, are stabilized in practice, as are the polymers (**4**−**7**), by coordination of an ML_x unit at each three-, four-, or five-membered ring, its identity being such that an 18-electron count is satisfied at M. Thus for the four-membered ring ML_x = $Fe(CO)_3$, CoCp or in principle any isoelectronic analogue. We will show that interesting properties may be envisaged for the infinite two-dimensional polymers (yet to be made) by careful consideration of the ML_x substituent pattern. First we need to understand the electronic structure of these materials and their derivatives.

The 4^4 Polymer

Many of the basic electronic ideas are quite general to all of the polymers and will be illustrated by the results found for polymer$_m$(4^4). Figure 1 shows the electronic density of states computed using the extended Hückel implementation of tight-binding theory for the net of **8** which contains a diethynyl linkage, polymer$_2$-(4^4). (Geometrical details are given in the Appendix.) A projection of the pπ levels is shown. Alongside to scale are shown the energies of the pπ levels of the four-membered ring, of the ethynyl unit and from them the

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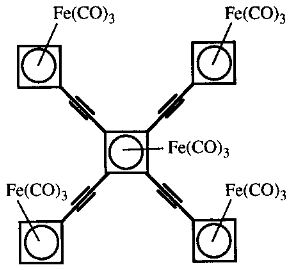
Chart 1



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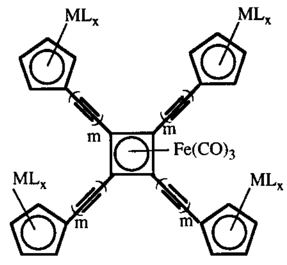

m = 1, 2; ML$_x$ = Mn(CO)$_3$
m = 1; ML$_x$ = Mn(CO)$_3$, FeCp

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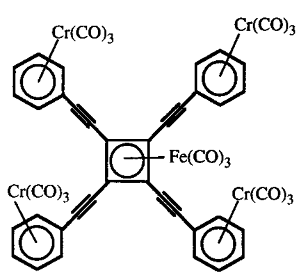

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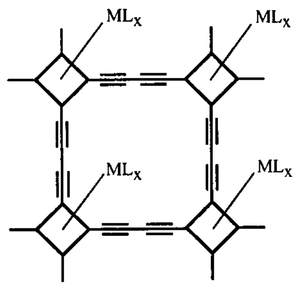

4^4

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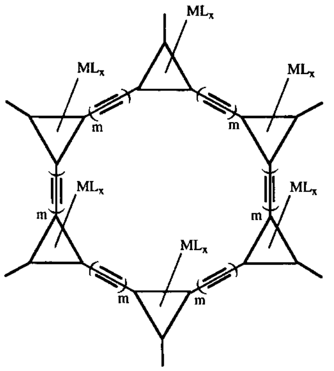

6^3

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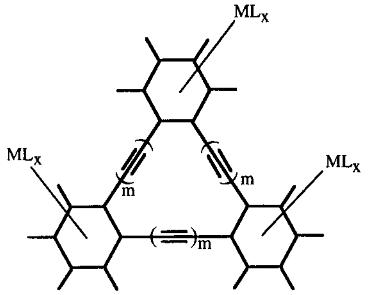

3^6

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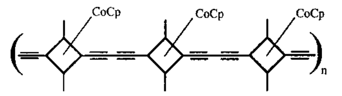
Chart 2



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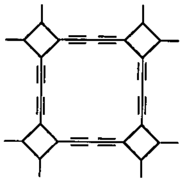

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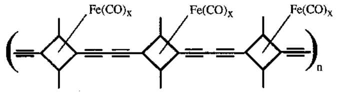

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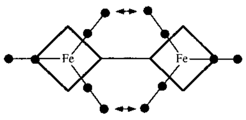

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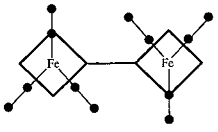

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assembly of the levels of the perethynylated square. The Fermi level of the polymer lies in the middle of a collection of energy levels associated with π-bonding as is to be expected given the electronic structure and electron count of the cyclobutadiene rings which dominate the structure. The Fermi level divides a band which is largely composed of the e_g set of the pπ orbitals of cyclobutadiene itself and in this way it carries an electronic memory of the square. From these results the all-carbon polymer with this structure will either be metallic or perhaps an insulator of some type if the band is narrow enough, a result perhaps predictable without a calculation. More sophisticated calculations of the spin-polarized FLAPW type (M. T. Green, unpublished) on this species show in fact that the paramagnetic metal is the lowest energy structure here.

Half-filled bands are often subject to Peierls distortions. Indeed a distortion of the one-dimensional version of this polymer, locally geometrically analogous to the Jahn–Teller distortion of the free cyclobutadiene molecule (Figure 2) leads to the opening of a gap, an energetic stabilization of the system and the generation of a semiconductor. Peierls in his original formulation of the idea showed how the effect was restricted to one-dimensional systems since only here could it be guaranteed that the Fermi surface is always perfectly nested. Indeed, the two-dimensional analogue (polymer$_2$(4^4)), with a distortion of the same type at each center, leads to a very small computed energetic stabilization (0.01 eV/atom) but not to the opening of a gap. The calculated Fermi surface is shown in **9**. It is not perfectly nested but does suggest that an energy stabilization will be found for the pair of vectors **a***/2 and **b***/2. The

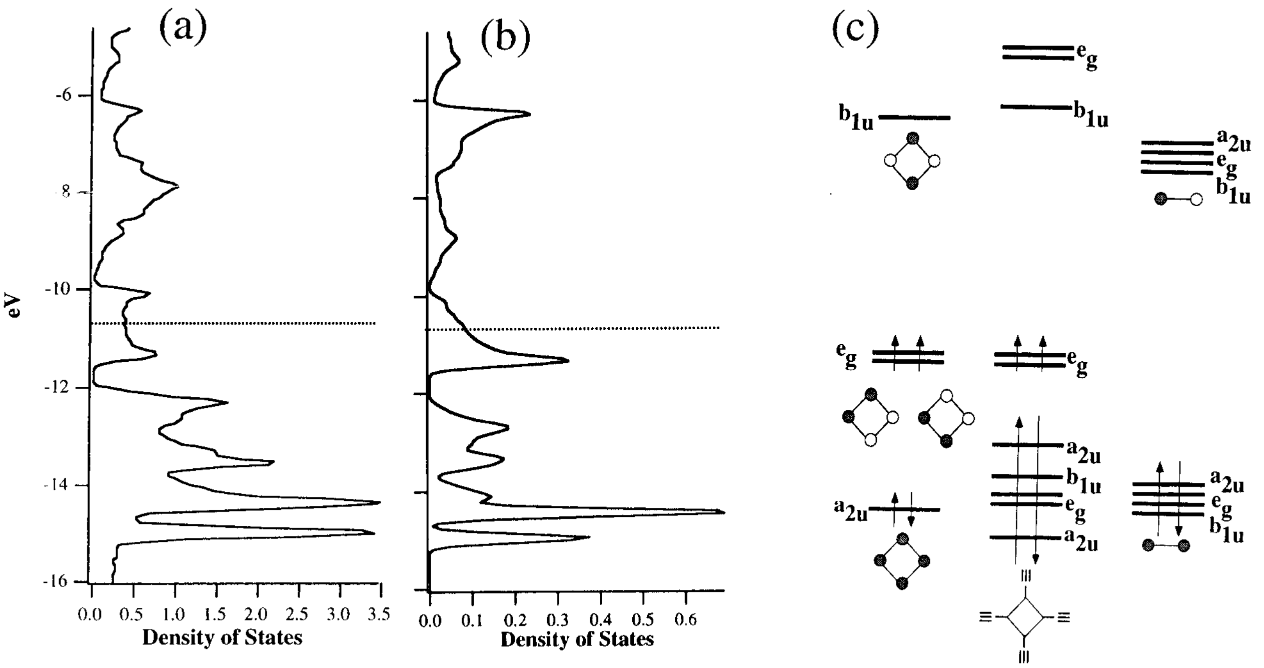


Figure 1. (a) Electronic density of states computed using the extended Hückel implementation of tight-binding theory for the net of **8**, polymer$_2$(4^4). (b) A projection of the pπ levels. (c) The energies of the pπ levels of the four-membered ring and of the ethynyl unit. The dotted line represents the Fermi level.

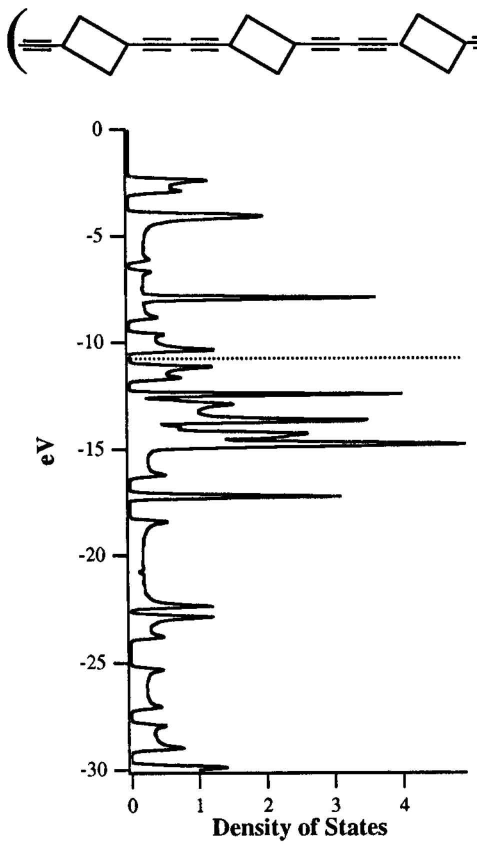
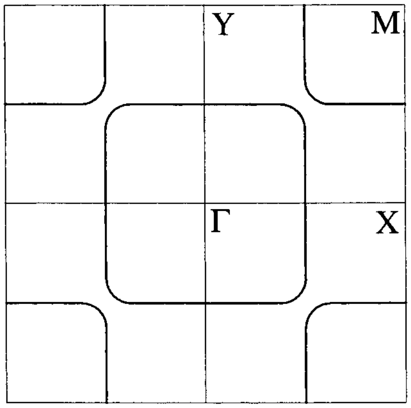


Figure 2. Density of states of a Peierls distorted one-dimensional version of polymer$_2$(4^4), geometrically analogous to the Jahn–Teller distortion of the free cyclobutadiene molecule. The dotted line represents the Fermi level.



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calculated density of states for such a distortion (Figure 3c) is shown in Figure 3b and shows how a gap indeed opens at the Fermi level of the undistorted parent (Figure 3a). Energetically however, the distortion is not a favorable one with an energy penalty of 0.11 eV/atom from calculation. This may readily be traced to the energetic preferences of the lower energy filled σ manifold of orbitals. As with many potential molecular Jahn–Teller distortions or CDWs in the solid state, the magnitude of the distortion is a balance between the electronic driving force at the Fermi level (or HOMO in molecules) and the generally conservative forces associated with the lower energy orbitals which tend to favor the undistorted structure.

Figure 4a shows the computed electronic density of states for this polymer with an Fe(CO)$_3$ unit coordinated to each square, polymer$_2$(4^4)Fe(CO)$_3$. Note that since the Fermi level lies in a gap for this material (Figure 4), unlike its metal-free parent, polymer$_2$(4^4), the system is an insulator with a calculated bandgap of around 1.7 eV. The electronic reasoning behind this is quite straightforward. The generation of the 18-electron count at the (4^4)ML$_x$ node is analogous topologically to the generation of an insulating tetrahedral carbon center with an eight-electron count, as in diamond for example. An orbital picture of the assembly of the bands of the polymer$_2$(4^4)Fe(CO)$_3$ species is shown in Figure 4b. It shows a scheme very similar to that for the assembly from the relevant fragments for cyclo-

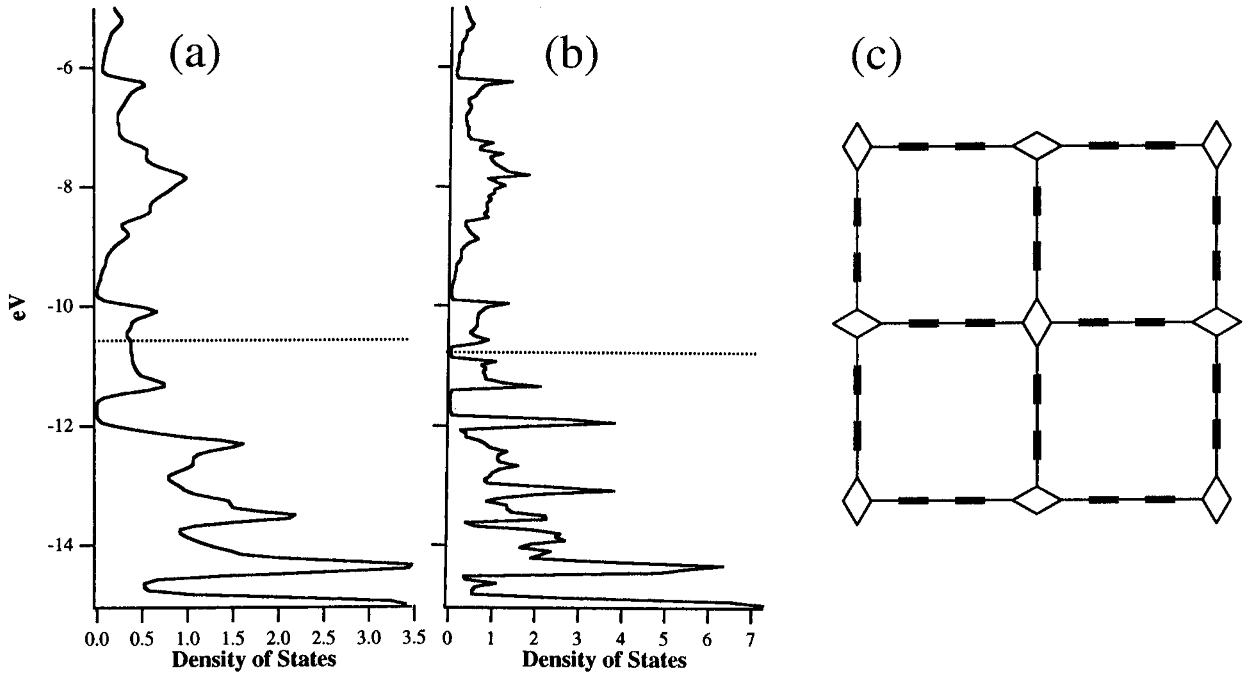

Figure 3. (a) Calculated electronic density of states for the net of **8**, polymer$_2$(4^4). (b) The opening of a gap as a result of the distortion (c). The dotted line represents the Fermi level.

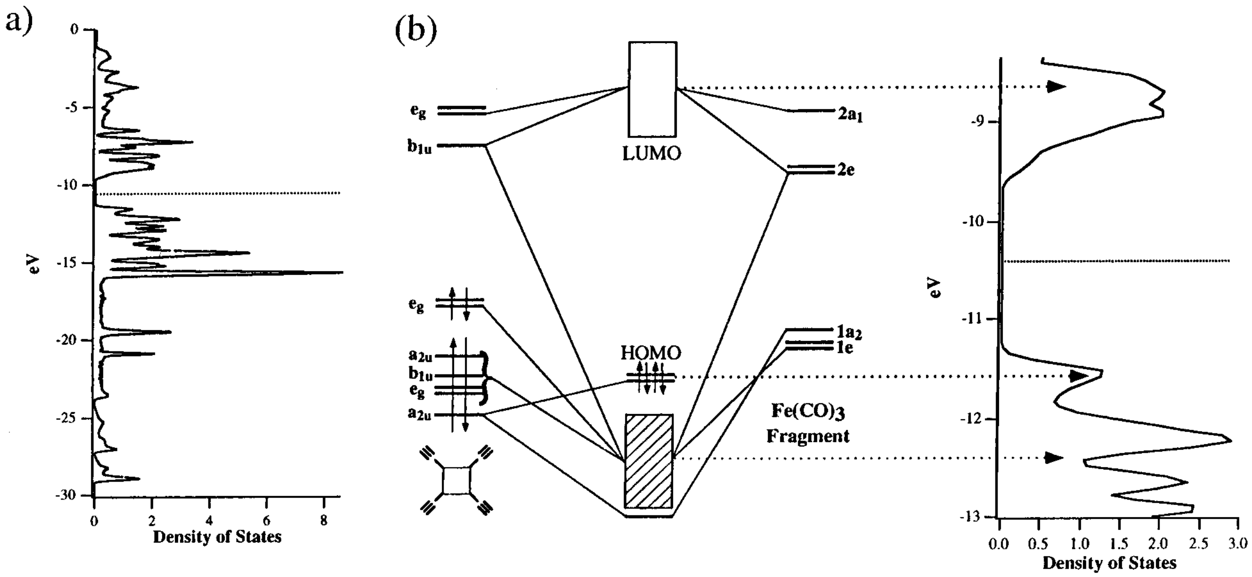

Figure 4. (a) Calculated electronic density of states for polymer$_2$(4^4)Fe(CO)$_3$. (b) Electronic origin of the bandgap. The dotted line represents the Fermi level.

butadieneFe(CO)$_3$ itself,[14] a result in accord with our comments above concerning the nature of the highest occupied band. A trio of largely iron-centered frontier orbitals in Fe(CO)$_3$ are destabilized on interaction with the organic unit.[15] The two electrons from the filled frontier orbital pair of Fe(CO)$_3$ and the two electrons from the "e" set of the polymer lead to a filled band, a mixture of the two. This viewpoint suggests that removal of a CO ligand from polymer$_2$(4^4)Fe(CO)$_3$ should lead to the regeneration of a metal since the 18-electron count is now lost. Electronically, one of the frontier orbitals in Fe(CO)$_3$ should drop in energy or alternatively should remain at low energy when assembling the band structure from polymer + Fe(CO)$_2$. This state of affairs turns out not to be the case. From calculation the orbital concerned does not drop far enough in energy for the material to become a metal. The results of a calculation are shown in Figure 5. The material is predicted to have a very small bandgap separating valence and conduction bands. This comes about in part because the conduction band is quite narrow. This is largely because of its predominantly metal-located character. If it were broadened by interatomic interactions along either of the polymer directions, we could envisage true band overlap and the generation of a metal. Since the conduction band is largely Fe(CO)$_2$-located and whereas the valence band is largely organic polymer located, an interesting possibility for this material is as a ferromagnetic metal where there is promotion of elec-

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(14) *Orbital Interactions in Chemistry*; Albright, T. A.; Burdett, J. K.; Whangbo, M.-H.; Wiley: New York, 1985.

(15) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

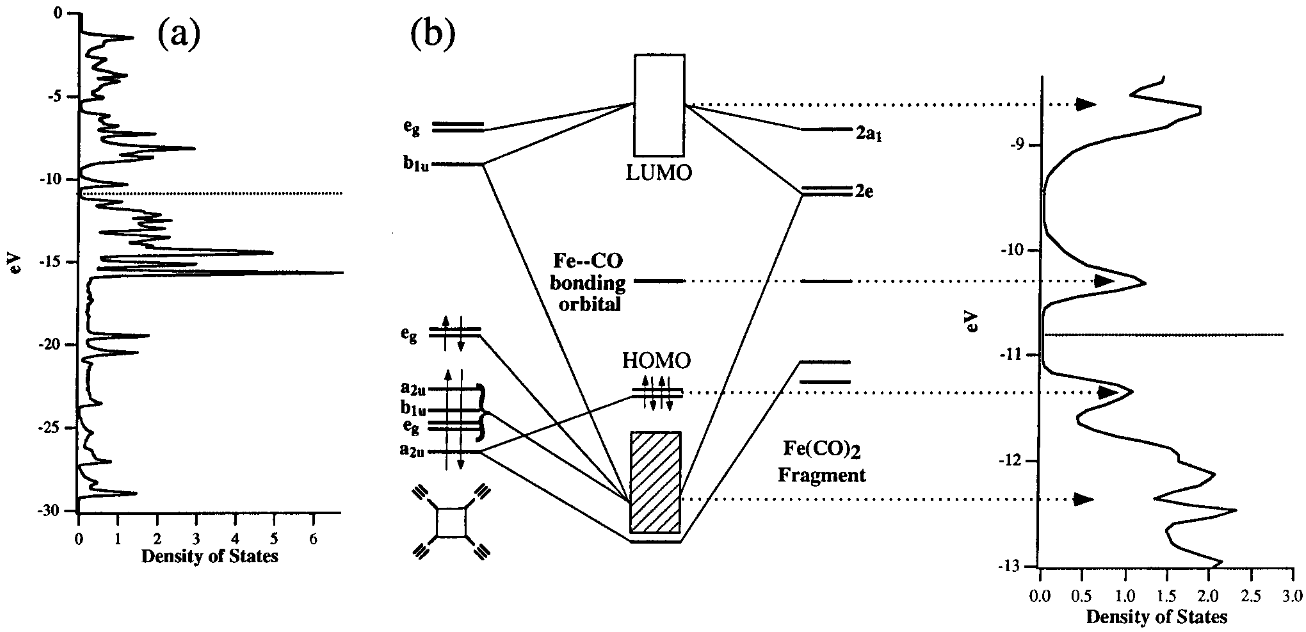

Figure 5. (a) Calculated electronic density of states for polymer$_2$(4^4)Fe(CO)$_2$. (b) Electronic origin of the bandgap. The dotted line represents the Fermi level.

trons into the conduction band. This recognizes one of the criteria (orbitals spatially separated) for the formation of ferromagnetic systems.[16]

The results just described are not very sensitive to the nature of the ligands attached to the iron atom. Calculations using Ru(CO)$_2$ and Fe(PH$_3$)$_2$ or Fe(PH$_3$)(CO) as ligands coordinated at the cyclobutadiene site showed rather small changes in the calculated gap. In terms of the chemistry of these systems, replacement of CO by phosphine is a facile process,[17] and so synthetic realization of such materials containing derivatives of this type should not be difficult. Perhaps a diphosphinoethane ligand of the correct size could be used to link two adjacent metal atoms. It might be sufficient to broaden the conduction band and lead to a metal.

A calculation on polymer$_2$(4^4)Fe(CO) however, does show (Figure 6) a metal but with a very low density of states at the Fermi level. The loss of the large bandgap found for the polymer$_2$(4^4)Fe(CO)$_3$ parent for both polymer$_2$(4^4)Fe(CO)$_2$ and polymer$_2$(4^4)Fe(CO) are in accord with the expectations of the 18-electron rule. Similar results are found for the one-dimensional variant of these polymers **10**. The tight-binding method invariably gives bandgaps which are too large, and thus these systems may in fact be true metals as a result of band overlap. The lowest unoccupied band is quite narrow for both systems, polymer$_2$(4^4)Fe(CO)$_{1,2}$. In both cases the lowest unoccupied band is largely metal in character, and thus its dispersion is expected to be rather small since through-bond coupling between the centers is of long range (seven linkages). Because of such narrow bands electron doping of these systems, if possible, may lead to a localized state with the unpaired electrons residing on the metal.

The results of calculations for the analogous polymer but with a single bridging acetylene unit, polymer$_1$(4^4)-ML$_x$, are more complex. The parent material, polymer$_1$(4^4), is metallic as found before for the case of $m = 2$. However, adjacent iron atoms in polymer$_1$(4^4)Fe(CO)$_3$ are 6.07 Å apart, to be compared with 8.67 Å for $m = 2$. This means that the CO units attached to them can become even closer. These relatively close interactions between the O atoms of the CO units range from collision (**11**) to 3.11 Å (**12**). From the calculations we find that the properties of the polymer depend dramatically on the orientation of the Fe(CO)$_3$ units. Figure 7 shows the results of a band structure calculation for the chemically realistic structure where the carbonyl oxygen atoms are kept as far apart as possible (3.11 Å). The material is found to be an insulator for ML$_x$ = Fe(CO)$_3$. The very close interactions between the O atoms of the

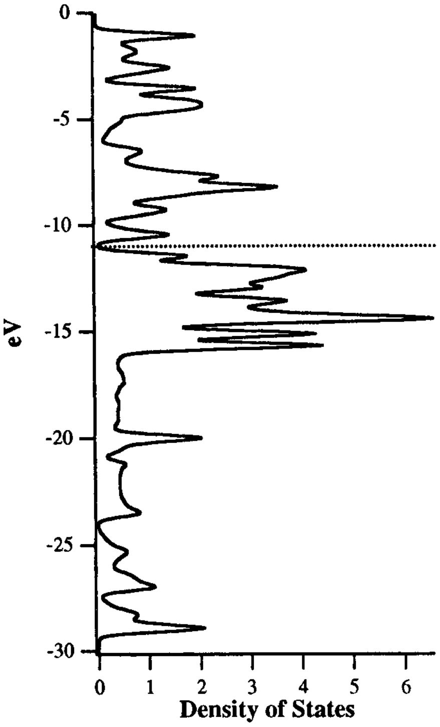

Figure 6. Calculated electronic density of states for polymer$_2$(4^4)Fe(CO). The dotted line represents the Fermi level.

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(16) See, for example: *Molecular Magnetism*; Kahn, O.; VCH: New York, 1993.

(17) Jänicke, O.; Kerber, R. C.; Kirsch, P.; Koerner von Gustorf, E. A. *J. Organomet. Chem.* **1980**, *187*, 361.

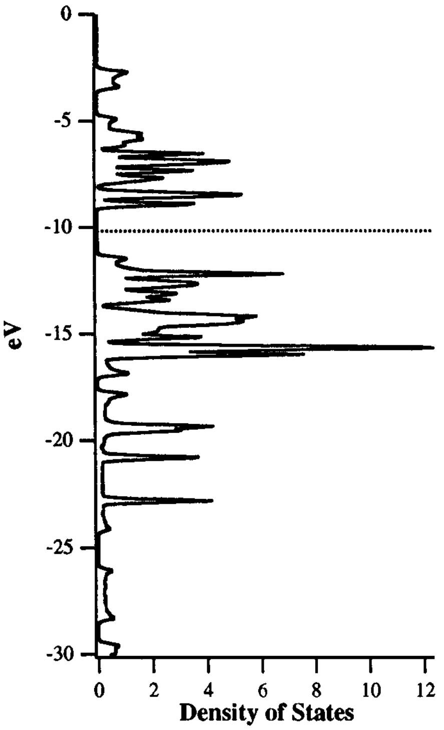


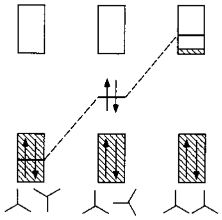
Figure 7. Calculated electronic density of states for polymer$_1$-(4^4)Fe(CO)$_3$ where the O atoms of the Fe(CO)$_3$ units are 3.11 Å apart. The dotted line represents the Fermi level.

CO units in orientation **11** lead to several two orbital-four electron repulsions which lead to movement of filled orbitals into the "18-electron rule gap". One of these orbitals is a formally Fe−CO nonbonding orbital (one of the filled, nonbonding (9 − *n*) orbitals of the (4^4)Fe(CO)$_3$ unit).[14] A band calculation gives a gap for ML$_x$ = Cr(CO)$_3$. **13** (Chart 3) shows the results of a molecular orbital calculation on a dimer (**14**). Notice how the nonbonding, filled orbital moves up into the gap as the steric interaction increases. Thus for the dimer of this particular (4^4)ML$_x$ system, a gap is found for M = Mn. From such a result for the polymer the appropriate metal would be M = Cr, as indeed found from the band calculation. Such a system would be strongly destabilized by these nonbonded repulsions. In the molecule **1** with $m = 1$, which has already been characterized by Bunz and co-workers,[4] a calculation using the geometry from the crystal structure (O···O ≈ 2.8 Å) shows that the CO group orientation is such that a good HOMO−LUMO gap is found for M = Fe. Polymers with coordinated MCp units with $m = 1$ will experience even more severe problems of this type.

The 6^3 and 3^6 Polymers

Figures 8 and 9 show the computed electronic densities of states for these polymers with and without coordinated M(CO)$_3$ units. The behavior of polymer(6^3) (**15**) is similar to that described above for polymer(4^4) (**8**). The bare polymer is metallic, but the system polymer$_2$(6^3)Co(CO)$_3$ (**5**) is an insulator. Recall that neither cyclic building block as neutral units satisfy Hückel's rule, and so by analogy with Figure 1, the highest occupied band should be only partially full and lead to metallic behavior. Notice that the band containing the "metallic electrons" in Figure 8 for the bare polymer$_2$(6^3) derives from the e″ levels of the triangle and that the band is both extremely narrow and half-filled. Such a situation suggests that this metallic state of affairs will not exist. A Peierls distortion is one possibility, a feature shared by the polymer$_m$(4^4) as well of course. With these very narrow bands an antiferromagnetic insulator is perhaps more likely here. An important question is the origin of such distinctive features in the electronic density of states. Hughbanks and co-workers have explored[18−20] the electronic−topological requirements for such a high density of states at certain values of the energy. The requirements for such orbital "superdegeneracies" in the density of states, which will lead to this state of affairs are building blocks with a local C_3 axis or higher, bridging groups and no trans substitutions. Polymer$_m$(6^3) satisfies these criteria perfectly, but polymer$_m$(4^4) and polymer$_m$(3^6) have trans groups and thus do not. Of the computed densities of states for the three polymer$_m$(P^n) systems "spikes" are found only for the density of states of polymer$_m$(6^3) in accord with these broad ideas. Superdegeneracies are found for both σ and π manifolds, but the important one here is with the half-filled band and is associated with the π system (Figure 8c).

Chart 3



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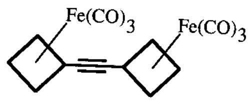

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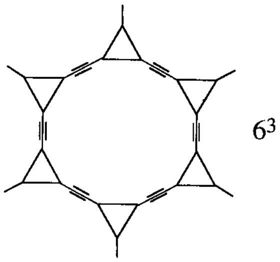

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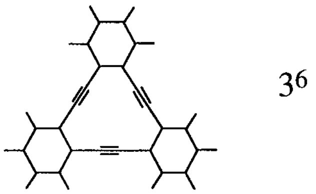

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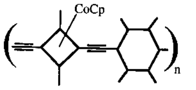

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The origin of the four e superdegenerate bands is relatively easy to see. There are two triangles and three spacers per unit cell. The spacers lead to two e sets, one bonding between the spacer atoms and one antibonding. The two triangles contribute two e sets. The result is a set of four pπ superdegenerate levels as shown in Figure 8.

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(18) Hughbanks, T. In *NATO Advanced Research Workshop on Magnetic Molecular Materials*; Gatteschi, D., et al., Eds.; Kluwer: Dordrecht, 1991; Series E, Vol. 198.

(19) Hughbanks, T. *J. Am. Chem. Soc.* **1985**, *107*, 6851.

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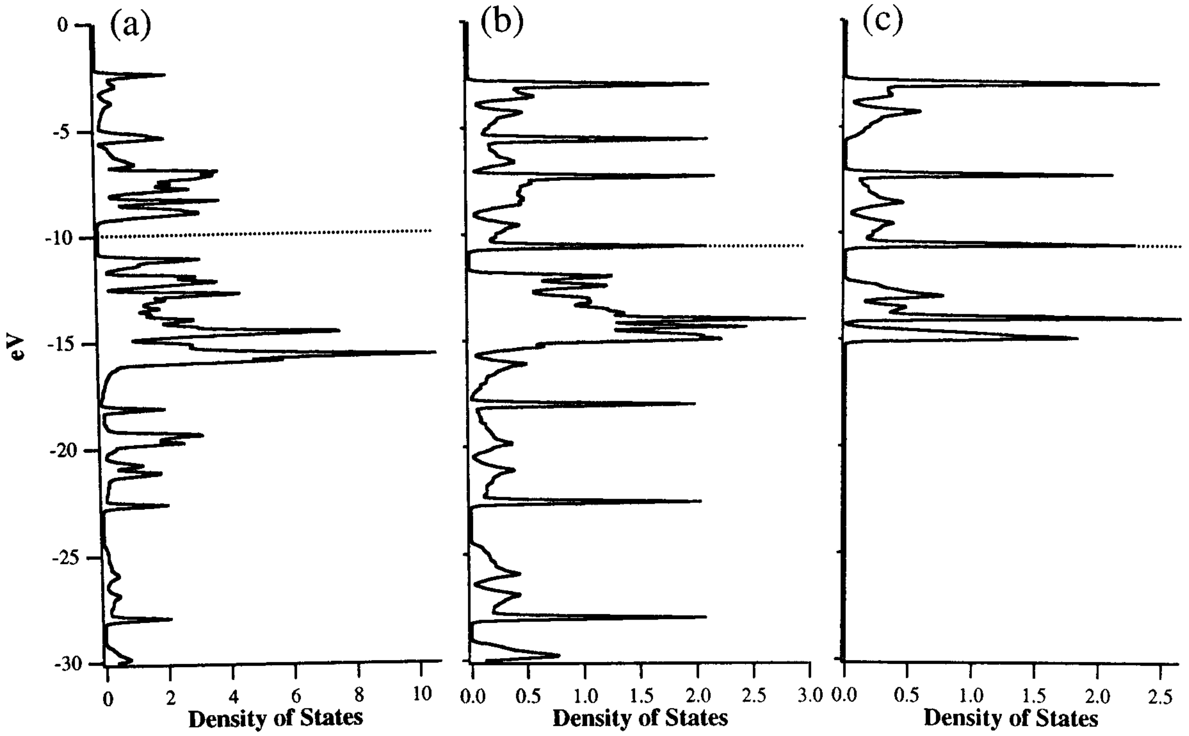

Figure 8. Calculated electronic density of states for (a) polymer$_2$(6^3)Co(CO)$_3$ and (b) polymer$_2$(6^3). (c) pπ projection of polymer$_2$-(6^3) which highlights the superdegeneracies. The dotted line represents the Fermi level.

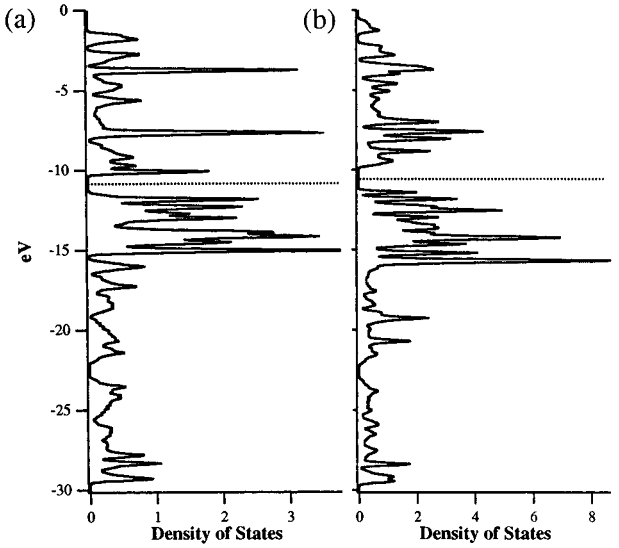

Figure 9. Calculated electronic density of states for (a) polymer$_2$(3^6) and (b) polymer$_2$(3^6)Cr(CO)$_3$. The dotted line represents the Fermi level.

The 3-fold axis at each node and at each Co(CO)$_3$ unit leads to a perfect two-dimensional interlocking of the CO groups on adjacent units in polymer$_2$(6^3)Co(CO)$_3$. The material is predicted to be an insulator. Just as in polymer$_2$(4^4)Fe(CO)$_3$ loss of one CO group leads to a small bandgap, but loss of two CO groups to a true metal. In these materials the sharp features in the electronic densities of states are sometimes due to spatial localization of the wave function as described above for polymer$_2$(4^4)Fe(CO)$_2$ and sometimes to localization via the superdegeneracy mechanism, determined by the network topology.

The results for polymer$_2$(3^6), **16**, are a little different in that an insulator is predicted for both polymer$_2$(3^6) and polymer$_2$(3^6)Cr(CO)$_3$. The insulating characteristics of polymer$_2$(3^6) come directly from the presence of a HOMO–LUMO gap for the neutral six-membered ring, a result to be contrasted with those for the metallic all-carbon polymers based on three- and four-membered rings. Polymer$_2$(3^6)Cr(CO)$_3$ (**6**) leads (Figure 9) to a formal 18-electron rule count at the metal center. In a similar fashion to the other polymers, our calculations show that polymer$_2$(3^6)Cr(CO)$_2$ leads to a small-gap semiconductor and polymer$_2$(3^6)Cr(CO) gives a metal.

Related Polymers

Bunz and co-workers have also made[21] the polymer shown in **17**. It consists of alternating four- and six-membered rings coupled by acetylene units. From the experience above with four- and six-membered rings we should expect both the material free from coordinated Fe(CO)$_3$ and the material where Fe(CO)$_3$ is coordinated to the four-membered ring to be insulators. Importantly this is the first example of a thermotropic liquid-crystalline organometallic polymer.[21]

Graphite is a well-known semimetal with an extended two-dimensional 6^3 net. Extending the ideas developed above, examination of the electronic densities of states of C_6X or C_8X systems, the stoichiometries of two common types of graphite intercalate,[22] might be interesting. However, the material of stoichiometry C_6Cr(CO)$_3$ suffers from the same steric problem encountered above for polymer$_1$(4^4)ML$_x$, except that here there are close nonbonded O···O distances in any orientation. However, coordination of a linear metal nitrosyl unit, just as in the molecule CpNiNO does not suffer from this problem. Figure 10a shows a computed density of

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[21] Altmann, M.; Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 569.

[22] E.g.: Bartlett, N.; McQuillan, B. W. In *Intercalation Chemistry*; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982.

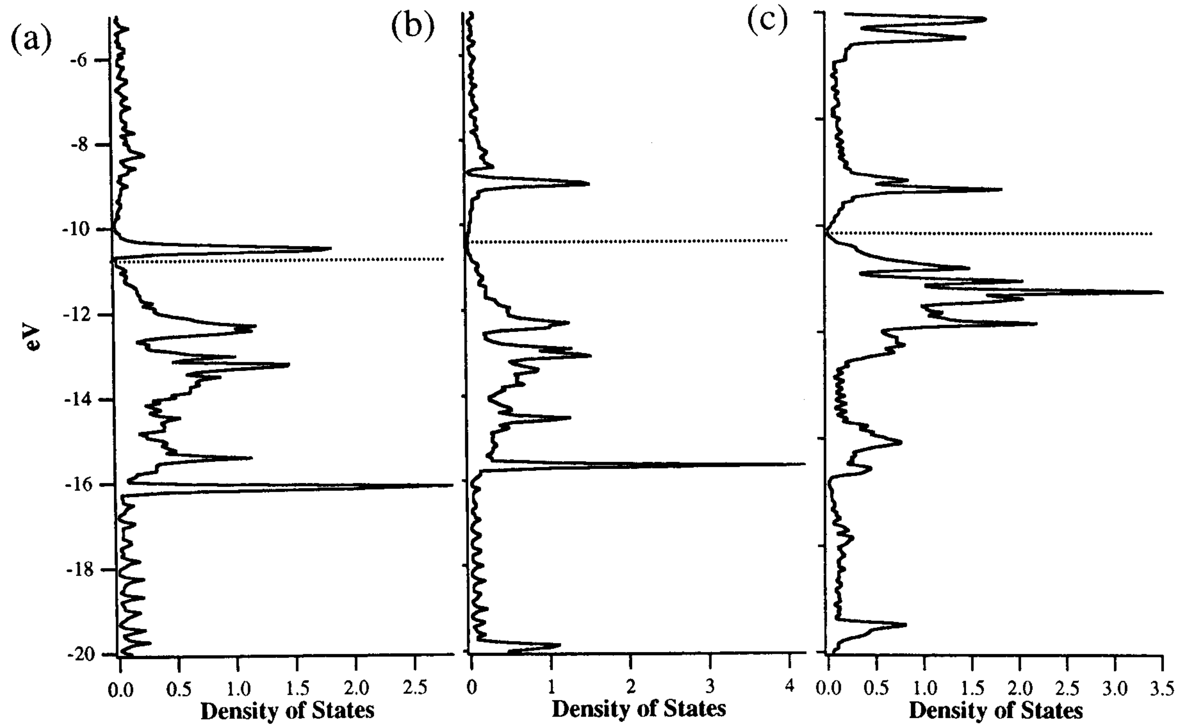
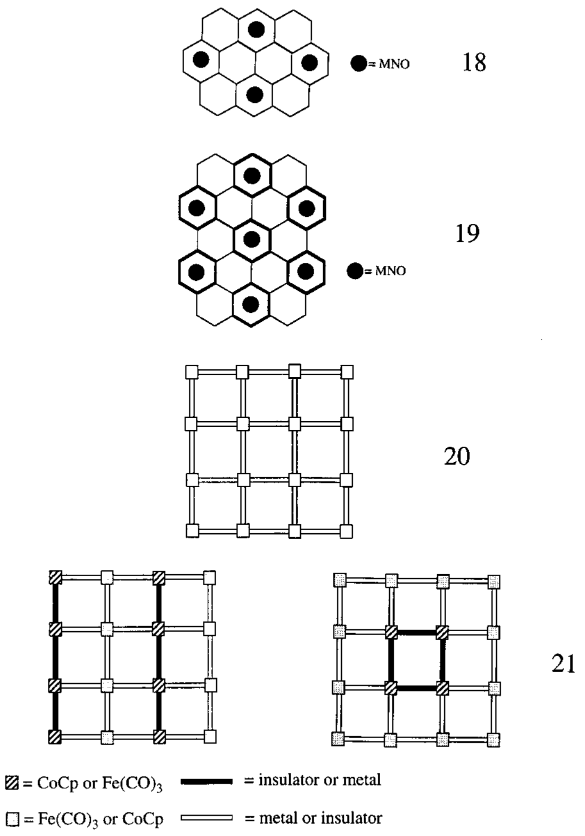


Figure 10. Calculated electronic density of states for C_6MX_n. The computed density of states (a) for the C_6MNO case (**17**), (b) for MX_n = CO, and (c) for MX_n = $C_3H_3^+$. The dotted line represents the Fermi level.

Chart 4



states for the C_6MNO case (**18**, Chart 4). The prediction is an insulator for the 18-electron count with M = Co. One way to see this is shown in **19**. It shows a view of the structure highlighting individual C_6MNO units each linked to six other similar units. The conduction band or LUMO in this material is largely NO π^* in character and thus is very similar to molecular nitrosyls. Thus we should expect an increase in bandgap for coordination of $C_3H_3^+$ or CO in place of NO. This is seen to be the case by calculation in Figure 10b,c. The conduction band is largely CO π^* or e″ $C_3H_3^+$ π^*. Bending the MNO group converts the linear three-electron donor "NO^+" unit into a bent one-electron donor "NO^-" unit, the 18-electron count at the metal disappears, and a metal should be found. Figure 11 shows the result. The NO π^* has split into two, and one component has dropped in energy. The overall result is in principle a metal, but the occupied NO π^* levels are quite localized.

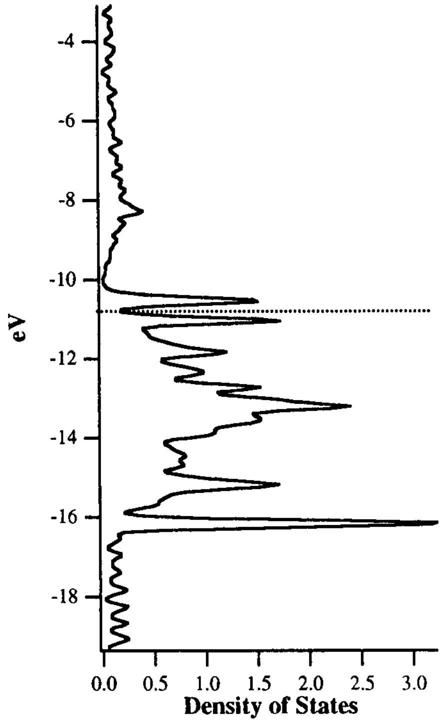


Figure 11. Computed change in the electronic density of states of C_6MNO (**17**) on bending the nitrosyl group. The dotted line represents the Fermi level.

Some of the other possibilities described above may result.

Some Properties of the Polymers

The results described above suggest some intriguing possibilities in terms of the design of materials with specific properties at the atomic level. As a general result, for $n = 3, 4, 6$, polymer$_m$(P^n)M(CO)$_3$ or polymer$_m$-(P^n)M′Cp systems are insulators as long as M and M′ are selected to locally satisfy the 18-electron rule. By way of contrast polymer$_m$(P^n)M(CO)$_2$ and polymer$_m$-(P^n)M(CO) systems are either ferromagnetic metals, small-gap semiconductors, or paramagnetic metals. (A recent study of some ferromagnetic systems based on other carbon skeletons is in ref 23.) It is then easy to imagine parts of a polymer coordinated by M(CO)$_3$ and parts by M′Cp, M and M′ being chosen to satisfy the 18-electron rule at each P^n center. Recalling the photochemical behavior of coordinated CO (labile) and Cp (inert) in molecules, on photolysis of the polymer, CO is released from those centers where it is coordinated to M in the parent, converting those regions of the polymer either into a metal or into one of the other electronic situations we have noted. Recoordination of CO regenerates the insulator. However, use of polymer$_m$-(P^n)M(PR$_3$)$_2$(CO)$_2$ where PR$_3$ is a bulky phosphine may inhibit the recoordination of CO. These regions of metallic or small bandgap material may be one atom wide as in the schematic of the 4^4 net in **20**, regions of the solid which are of the order of the dimensions of the hexagons, squares, or triangles at each node or to much larger units. Two simple patterns are shown in **21**. A major challenge for the experimentalist is to devise ways to synthetically build in such units, although we do note that one-dimensional polymers of this type have been made. A challenge for the theorist is to calculated which of the several electronic possibilities are stable.

The ML$_x$ unit in (P^n)ML$_x$ is chosen by the synthetic chemist to satisfy the 18-electron count at M. When ML$_x$ = Fe(CO)$_3$ for **1** then, as noted, a photolabile system is created. The resulting ML$_{x-1}$ = Fe(CO)$_2$ system, a 16-electron compound, is expected to be unstable and to readily recombine with CO. The quantum dot or wire is then a time-dependent phenomenon. By comparison with molecular photochemistry the photoproduct from ML$_x$ = Fe(PR$_3$)$_2$(CO) will be Fe(PR$_3$)$_2$. If R is a large group, then the unsaturated product may have a much longer lifetime due to steric inhibition of CO recombination. Other approaches can be imagined which would be just as satisfactory. Such polymers with different metal atoms may be useful too in studies of photochemically induced electron transfer processes of the type studied by Balzani.[24]

The graphite nitrosyl polymer is interesting in the same way. The situation where the MNO group is linear corresponds to an insulator, but on photolysis a bent geometry is expected[25,26] which from our calculations leads to either a metal or an interesting and very different electronic situation of the ferromagnetic or antiferromagnetic type.

Appendix

The calculations were performed using the extended Hückel[27] implementation of tight binding theory.[28] The orbital parameters were standard ones. Interatomic distances were taken from the crystal structures[1–4] of the molecular building blocks (**1**−**3**) and were as follows: C−C “single” bond 1.42 Å, C−C square net 1.45 Å, C−C “triple” bond 1.18 Å, C−Fe 2.039 Å, Fe−CO 1.77 Å, C−O 1.16 Å, C−C triangle 1.38 Å, C−Co/Ni/Cr-(graphite sheet) 2.133 Å.

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