

# Strategies for Molecular Designing of Novel Low-Band-Gap Electrically Conducting Polymers

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## Abstract

Molecular designing of low-band-gap electrically conducting polymers continues to be a major challenge of the field of electrically conducting polymers. Such polymers are expected to show not only good intrinsic conductivity but also possibly a good transparency in the visible spectrum for their use as infrared sensors/detectors. Low-band-gap polymers can also be of great interest as new polymeric materials for nonlinear optics. Various routes presently followed to achieve this designing with special reference to the donor-acceptor polymers and important results obtained with this route are briefly reviewed.

**Index Entries:** Electronic structure; conduction properties; designing; band gap; copolymers; conducting polymers.

## Introduction

Electrically conducting polymers that combine the electrical, electronic, magnetic, and optical properties of the metals with the environmental stability, mechanical properties, and processibility of the conventional polymers are expected to be the key materials of the twenty-first century. Since their discovery in 1977 (1,2), these materials have been the focus of numerous theoretical and experimental studies (3–5). One of the goals of the field of electrically conducting polymers—the molecular designing of novel electrically conducting polymers with tailor-made conduction properties—however, continues to elude the scientists working in this field. The main reason is that there is an incomplete understanding of the relationship between the chemical structure of a polymer and its electronic properties such as ionization potential (*IP*), electron affinity (*EA*), and band gap (*E<sub>g</sub>*).

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Band gap of a polymer is a measure of its ability to show intrinsic conductivity, while *IP* and *EA* values of a polymer determine its ability to form conducting polymers through oxidative and reductive doping, respectively. Efforts are under way to gain insight into such a relationship because once such an understanding is achieved, it would facilitate the tailoring of conducting polymers with desired electronic properties and, hence, conductivity. On the basis of the existing knowledge of the structure-property relationship in the conducting polymers, five different routes are followed for designing novel conducting polymers: substitution/fusion, ladder polymerization, topologic methods, copolymerization (quasi-one-dimensional polymeric superlattices), and donor-acceptor polymerization.

## Routes for Designing Novel Conducting Polymers

### *Substitution/Fusion*

In the substitution/fusion method, one starts with very small band-gap polymers and then modifies their electronic properties by the action of substituents, provided their chemical nature allows substitution reactions. It is now well established that in the case of polymers with a degenerate ground state, such as *trans*-polyacetylene (band gap of 1.5 eV), the band gap decreases with decreasing bond length alternation (6). On the other hand, in the case of polymers with a nondegenerate ground state, such as polythiophene (band gap of 2.1 eV), the band gap decreases as a function of increasing quinoid (7) character of the polymer backbone. By using these two guiding principles, researchers have synthesized and studied many new systems and their derivatives (see, e.g., refs. 3, 4, 8, and 9).

### Ladder Polymerization

An exciting possibility in the search for novel conducting polymers is provided by the ladder structures. Among ladder polymers, hydrocarbon polymers with fused aromatic rings have been the focus of enormous interest. Unlike *trans*-polyacetylene, these polymers are expected to be more stable. This class of polymers, frequently referred to as the one-dimensional graphite family, includes polyacene, polyacenacene, polyphenanthrene, polyphenanthrophenanthrene, and polyperinaphthalene. The structures of these systems are shown in Fig. 1. There have been many theoretical investigations (10–15) of the electronic structure and conduction properties of the members of the one-dimensional graphite family. Polyacene is the most studied polymer of this family, followed by polyperinaphthalene, polyphenanthrene, and polyphenanthrophenanthrene.

### Topologic Methods

In the case of fused-ring polymers, the electronic properties are found to depend strongly on the particular way the rings are fused, and recogni-

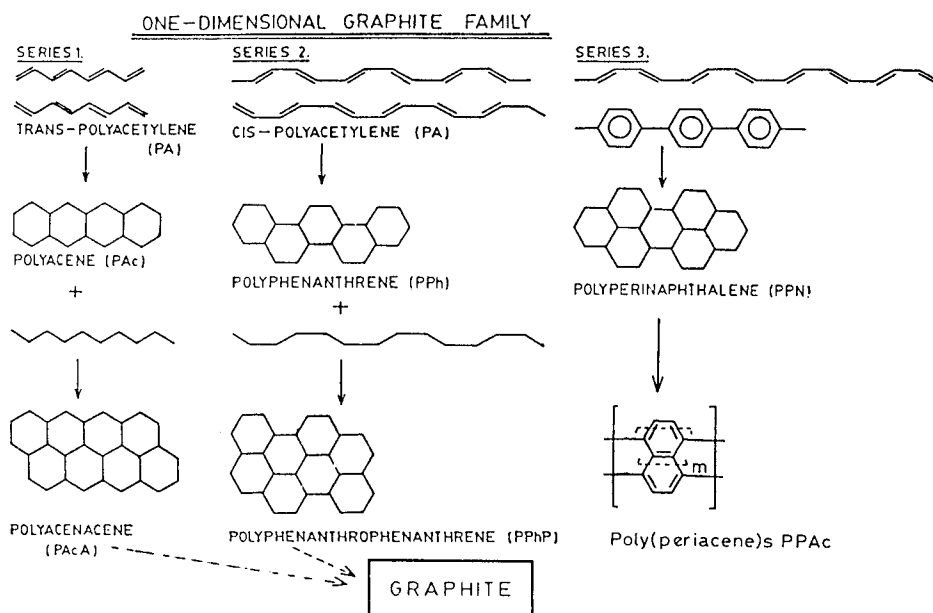


Fig. 1. Various members of the one-dimensional graphite family.

tion of this has led to the employment of topologic methods based on the concept of topomers for estimating band-gap relations among polymers and also for designing novel conducting polymers. For example, these topologic arguments have been recently used to rationalize the large differences in the electronic properties of the fused-ring polymers polyacene, polyphenanthrene, and polybenzanthracene (16) and in the search for novel low-band-gap conjugated polymer polyisophenanthrene, which has been predicted to have a band gap between polyacene and polybenzanthracene (17).

### Copolymerization (Polymeric Superlattices)

This route to obtaining novel conducting polymers is through the technique of growing quasi-one-dimensional superlattices (copolymers) of conducting polymers. The polymeric quasi-one-dimensional superlattices (or copolymers) can have tailor-made properties depending on the choice of two semiconducting components, their relative amounts, and their arrangement in the polymer chain. Depending on the band alignments of the two constituent polymers, polymeric superlattices such as the inorganic superlattices may be divided into four types (18): type I; type II staggered; type II misaligned; and type III (Fig. 2). The electronic density of states of the various periodic and random quasi-one-dimensional model superlattices (copolymers) of the type  $(A_m B_n)_x$  belonging to the class of type I and type II staggered superlattices have been calculated by Bakhshi (19).

The electronic structures and conduction properties of copolymers of donor-acceptor polymers (polydicyanomethylenecyclopentadithiophene [PCNTh]) and (polydicyanomethylenecyclopenta-dipyrrole [PCNPy])

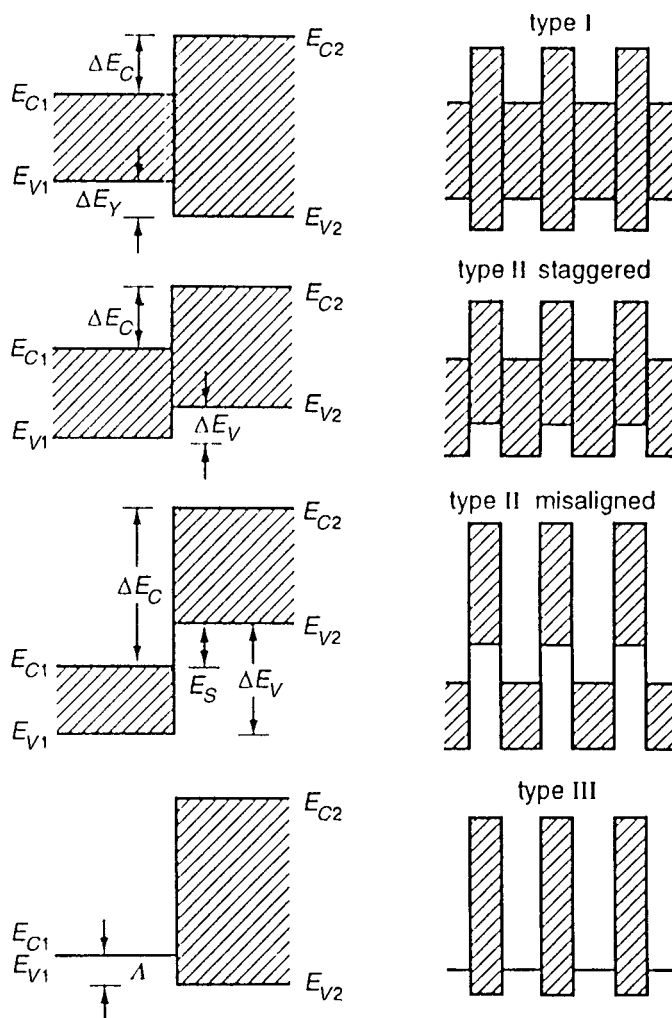


Fig. 2. Various types of superlattices.

using their semiempirical band structure results have also been studied (20). The results show that increasing the percentage of either of the two components improves the intrinsic conductivity with the corresponding higher n-dopantphilicity in the case of smaller band-gap component (PCNTh) and higher p-dopantphilicity for larger band-gap component (PCNPy). The electronic spectra of various quasi-one-dimensional compositional superlattices of polypyrrole (PPy) and polyisnaphthopyrrole (PINPy) belonging to the class type I superlattices (21) and those of silole and pyrrole belonging to the class of type II staggered superlattices (22) have also been the subject of study in the tight binding approximation using a direct numerical approach. The results obtained here provide researchers with important guidelines for designing novel copolymers.

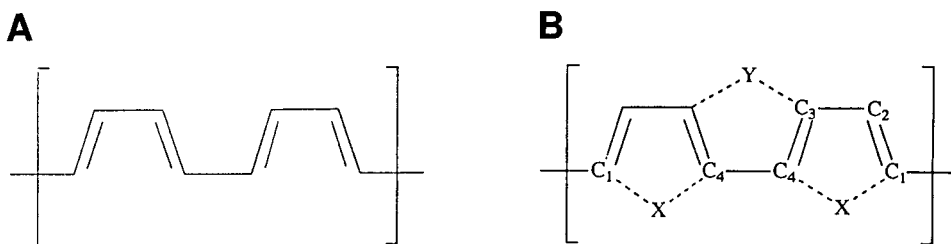


Fig. 3. Schematic structures of (A) *trans*-cisoid polyacetylene and (B) donor-acceptor polymers in which X is the electron-donating and Y an electron-accepting group.

### Donor-Acceptor Polymerization

Recently, Havinga et al. (23) proposed a new route to design and synthesize small band-gap polymers. The principal idea behind this route is that the conjugated polymers with alternate donor and acceptor moieties in the main chain are expected to have a small band gap (Fig. 3). The band gap is expected to be the lowest for a combination in which the electronegativity difference between donor and acceptor moieties is highest. Experimental verification of this idea is reported in new classes of polysquaraines and polycroconaines (24,25). These new materials show band gaps down to 0.5 eV, conductivities about  $10^{-5} (\Omega \text{ cm})^{-1}$  and are stable in air up to 250°C or higher. Using the same route, Lambert and Ferraris (26,27) have synthesized poly-4H-cyclopentadithiophene-4-one (PCDT) and PCNTh, the two polymers with experimental band-gap values of 1.2 and 0.8 eV, respectively. The electronic and geometric structures of PCNTh and its nitrogen analog PCNPY and also of polydicyanomethylenecyclopentadicyclopentadiene have been the focus of study by Toussaint and Bredas (28,29). Recently, using a similar strategy some novel donor-acceptor polymers differing in their electron-donating and electron-accepting moieties have been theoretically designed and investigated (30,31) on the basis of one-dimensional (SCF-CO) method at the (MNDO-AM1) level of approximation. The band-gap values are found to be especially very low in the case of donor-acceptor polymers whose electron-donating moieties are derived from the bridging group containing group IV elements C, Si, and Ge. Polyaminosquaraine has also been studied (32), which consists of a squaraine ring connected by simple amine units. Prediction of a small band-gap of ~0.5 eV is based on calculations of geometric and electronic structure using the Car-Parrinello technique of simultaneous optimization. Quantum chemical results of the electronic structures of PCDT and PCNTh obtained with the aid of the *ab initio* Hartree-Fock crystal orbital method have been studied recently (33). Both polymers on the basis of their geometries as well as their bond orders are found to have benzenoid-like structures.

Table 1  
Calculated Electronic Properties (eV)  
of Donor-Acceptor Polymers (X=CH<sub>2</sub>) (Fig. 3B)

Y	>C=CH <sub>2</sub>	>C=O	>C=CF <sub>2</sub>	>C=C(CN) <sub>2</sub>
IP	7.364	8.081	7.580	8.478
EA	1.958	2.547	2.199	3.520
E <sub>g</sub>	5.406	5.534	5.381	4.958

## Donor-Acceptor Polymers Based on Polycyclopentadienylene

Table 1 reviews the ab initio electronic structure results of some novel donor-acceptor polymers based on poly(cyclopentadienylene) (34,35). All of these can be viewed as consisting of a backbone of sp<sup>2</sup> hybridized carbon atoms analogous to that of *trans*-cisoid polyacetylene stabilized by different bridging groups X (X = >CH<sub>2</sub>) and Y (Y = >C = O, >C = CH<sub>2</sub>, >C = CF<sub>2</sub>, or >C = C[CN]<sub>2</sub>) that are covalently bonded to neighboring carbon atoms to form heterocycle as shown in Fig. 3.

The band structure calculations of these donor-acceptor polymers were performed using their energetically optimized geometry in the framework of the ab initio Hartree Fock crystal orbital method. In this method, one solves the pseudoeigenvalue equation:

$$\underline{E}(k)C_n(k) = \epsilon_n(k)\underline{S}(k)C_n(k) \quad (1)$$

for different  $k$  values in the Brillouin zone.  $\underline{E}(k)$  and  $\underline{S}(k)$  are the Fock and Overlap matrices in the  $k$  representation. The index  $n$  denotes the band, and  $N$  is the number of neighboring cells explicitly taken into account. The Fock and Overlap matrix elements are given by

$$F_{ab}(k) = \sum_j \exp(ikR_j) f_{ab}^{oj} \quad (2)$$

$$S_{ab}(k) = \sum_j \exp(ikR_j) S_{ab}^{oj} \quad (3)$$

in which

$$S_{ab}^{oj} = \langle x_a^o(r) | x_b^j(r) \rangle \quad (4)$$

$$f_{ab}^{oj} = h_{ab}^{oj} + g_{ab}^{oj} \quad (5)$$

In Eq. 5, the one-electron term ( $h_{ab}^{oj}$ ) and the two-electron term ( $g_{ab}^{oj}$ ) are given by

$$h_{ab}^{oj} = -1/2 \langle x_a^o(r) | \nabla^2 | x_b^j(r) \rangle + \sum_h \sum_A \langle x_a^o(r) | Z_A/r - R_h - R_A | x_b^j(r) \rangle \quad (6)$$

and

$$g_{ab}^{oj} = \sum_h \sum_l \sum_c \sum_d p_{cd}^{hl} \times 2 \left[ \left( \begin{smallmatrix} oj \\ ab \end{smallmatrix} \middle| \begin{smallmatrix} hl \\ cd \end{smallmatrix} \right) - \left( \begin{smallmatrix} oh \\ ac \end{smallmatrix} \middle| \begin{smallmatrix} jl \\ bd \end{smallmatrix} \right) \right] \quad (7)$$

respectively, with

$$p_{cd}^{hl} = \sum_k^{BZ} \sum_m^{OCC} \exp[-ik(R_h - R_l)] C_{c,m}^* C_{d,m} \quad (8)$$

and the two-electron integral is given by

$$\left( \begin{smallmatrix} o & j \\ a & b \end{smallmatrix} \middle| \begin{smallmatrix} h & l \\ c & d \end{smallmatrix} \right) = \int dr_1 \int dr_2 \cdot x_a^o(r_1) x_b^j(r_1) \frac{1}{|r_1 - r_2|} x_c^h(r_2) x_d^l(r_2) \quad (9)$$

in which  $x_b^j$  is the  $b$ th atomic basis function in the unit cell denoted by the upper index  $j$ ,  $Z$  and  $R$  are the charge and position of the 0th nucleus, and  $C_{d,m}(k)$  are the components of the  $m$ th eigenvector of Eq. 1. The first summation in Eq. 8 runs over all doubly filled bands and the second runs over the Brillouin zone. The eigenvalues  $\varepsilon_n(k)$  give the band structure of the polymer. All the computations were performed using Clementi's minimal set. All the multicenter two-electron integrals larger than the threshold value of  $10^{-8}$  a.u. were calculated, and the interactions up to second neighbors were taken into account.

The main important electronic properties such as the ionization potential (corresponding to the top of the valence band if one uses Koopman's theorem), the  $EA$  (corresponding to the bottom of the conduction band), and band gap of the various donor-acceptor polymers are given in Table 1. Among the polymers studied, the one with  $Y = >C=C(CN)_2$  has the smallest band gap (4.958 eV), whereas the one with  $Y = >C=O$  has the largest band gap (5.534 eV), implying that in these donor-acceptor polymers,  $>C=C(CN)_2$  is the strongest electron-withdrawing group and  $>C=O$  the weakest. The calculated band-gap values of the corresponding two sulfur analogs (33) (PCNTh and PCDT) are 5.917 and 6.260 eV, respectively, showing that the weaker electronic group  $CH_2$  lowers the band gap. Since the ab initio Hartree Fock crystal orbital method employed here is known to overestimate the band-gap value by a factor of 3 to 4, the actual band-gap values of these polymers are expected to lie between 1 and 2 eV. Further, one notices that the polymer with  $Y = >C=C(CN)_2$  also has the highest  $EA$  (3.5 eV), implying that this polymer has a very large capacity for undergoing reductive (n-) doping. On the other hand, polymer ( $Y = >C=CH_2$ ) with the lowest  $IP$  (7.364 eV) has the maximum capacity for oxidative (p-) doping.

An examination of the calculated  $\pi$ -bond orders of the polymers studied shows that all the polymers have the benzenoid-like electronic structures. The orbital patterns of highest occupied crystal orbit (HOCO) and lowest unoccupied crystal orbit (LUCO) for the four polymers are found to be similar. The electron-accepting group  $Y$  makes a negligible contribution to the HOCO but a significant contribution to the LUCO of these polymers. In light of these results, one can rationalize the small band-gap values calculated for these polymers by visualizing their formation through the interaction of a bicyclopentadienylene skeleton with an electron-accepting group  $Y$  terminated by H atoms (i.e.,  $Y = CH_2=O$ ,  $CH_2=C(CN)_2$ ,  $CH_2=CH_2$ ,  $CH_2=CF_2$ ) (Fig. 4). It has been shown that the band gaps of these polymers

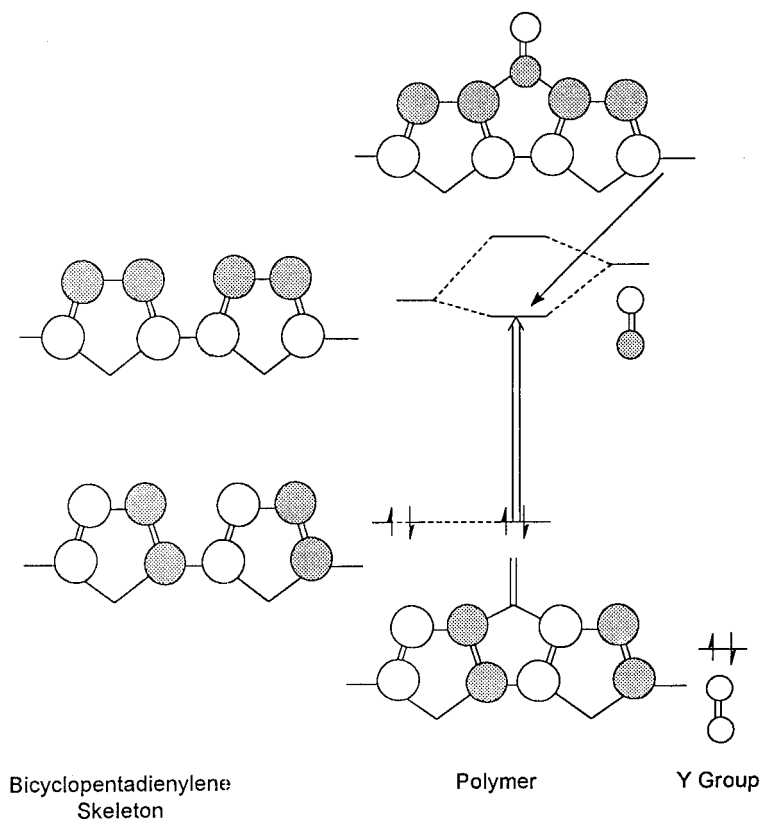


Fig. 4. Schematic energy levels depicting the formation of polymers from the interactions of the bicyclopentadienylene skeleton and the electron-accepting group Y terminated by H atoms. The pseudo-orbitals of  $\text{CH}_2$  are omitted.

are primarily determined by the strength of the bonding interactions between the LUCO of the bicyclopentadienylene skeleton and the lowest unoccupied molecular orbit (LUMO) of the electron-accepting group Y. The more lower lying the LUMO of the group Y is, the smaller will be the band gap of the resulting donor-acceptor polymer.

## Conclusion

We have given an overview of the various strategies presently pursued for designing novel electrically conducting polymers. Among these strategies, donor-acceptor polymerization seems to be the most promising one because polymers with very low band gap have been synthesized using this strategy. Donor-acceptor polymers can be viewed as consisting of a backbone of  $\text{sp}^2$  hybridized carbon atoms analogous to that of *trans*-cisoid polyacetylene but stabilized by different bridging groups X and Y that are covalently bonded to neighboring carbon atoms to form the heterocycles. These polymers have a regular alternation of donor and acceptor moieties

provided by the bridging groups X and Y, respectively. The recently obtained low-band-gap results of the donor-acceptor polymers based on polycyclopentadienylene are reviewed and rationalized. The band-gap values of these polymers are shown to be primarily determined by the strength of the bonding interactions between the LUCO of the bicyclopentadienylene skeleton and the LUMO of the electron-accepting group Y. The more stable the LUMO of the group Y is, the smaller the band gap of the resulting donor-acceptor polymer is expected to be.

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