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Comparative Study of Electronic Properties of Some Donor-Acceptor Copolymers Using the Genetic Algorithm

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Abstract
An efficient designing route to novel low band gap copolymers is developed with the help of an artificial intelligence method-genetic algorithm. Using ab initio *Hartree-Fock crystal orbital results of four donor-acceptor polymers, the electronic structure and conduction properties of their novel binary copolymers have been investigated. One of the donor-acceptor polymers containing dicyanomethylene linkages, and based on silane moiety (SiH_2) is common in all the copolymers. The second donor-acceptor polymer is varied by replacing SiH_2 group with O, NH, and S, to obtain substituted furan, pyrrole, and thiophene, respectively. The introduction of electron accepting dicyanomethylene linkages between the aromatic rings of the unit cells induces major geometry changes within the rings, leading to combination of aromatic and quinonoid forms. The effect of substitution on the electronic properties of the copolymer is investigated. A decrease in band gap is expected to enhance the intrinsic conductivity of the resulting copolymer. Use of alternate donor-acceptor moieties within the repeat units is expected to maximize the extended ð-conjugation in the polymer backbone.*

Keywords: *Theoretical Chemistry, Genetic algorithm, Conducting polymers, Electronic structures, Copolymers, Donor-acceptor polymers, Band gap*

Introduction

The study of electrically conducting polymers (ECPs) has become one of the foremost areas of research and the vast applications of these materials have revolutionized the electronic industry. By bringing about subtle changes in the chemical structure of the molecules, we can modify and regulate the bulk properties of these polymeric materials. In order to successfully design and synthesize such novel materials it is necessary to have a fundamental *understanding of the relationship between the chemical structure of polymer and its electronic and conduction properties*. The magnitude of the band gap (E_g), IP (*ionization potential*, corresponding to the top of the VB), and EA (*electron affinity*, corresponding to the bottom of the CB) are the most important characteristics for determining the optical and electrical properties of a given polymer. Through numerous

manipulations and modifications of the chemical structures of conjugated polymers, band gaps as small as 0.5 eV to 2.0 eV have been achieved[1] and are being used for several customized applications such as electroluminescent diodes[2], solar cells[3], sensors[4,5], super-capacitors[6], thermoelectric devices[7-9], biorecognition and bioactive scaffolds[10], implantable bioelectronic devices[11], flexible and stretchable devices[12], OPVs (Organic Photo-Voltaics)[13-16], and many more.

Theoreticians have been successful in achieving very low band gap ECPs using efficient molecular modeling and simulation techniques such as, density functional approach[17-21], semi-empirical[22-24] and *ab initio* methods[25-28]. One widely accepted approach to design these polymers is the use of alternate electron donor and acceptor moieties in a polyconjugated backbone. A regular alternation of such repeat units in the ð conjugated chain significantly decreases the HOMO-LUMO separation. The band gap is expected to be the lowest for that particular combination in which the electro-negativity difference between the donor and acceptor (D-A) moieties is highest. Using this approach, several copolymers possessing small band gap have been successfully synthesized[29-31] as well as theoretically modeled[32-38].

A particular copolymer chain may be achieved through several permutations and combinations of homopolymer units, consequently, the task of obtaining a polymeric chain with desired properties is computationally expensive. An artificial optimization technique, the genetic algorithm (GA)[39], which is a powerful tool to solve high complexity computational problems, uses techniques inspired by evolutionary biology such as inheritance, mutation, selection, and crossover (or recombination). Following these ideas, this algorithm allows us to use the computer to evolve automatic solutions by rapidly converging through intelligent searches, with selective sampling of values in the entire configuration space.

In the present study we have proposed novel low band gap binary copolymers of D-A type polymers based on silane moiety and containing dicyanomethylene linkages. Silane containing units have been copolymerized with polyfuran, polypyrrole, and polythiophene. We have investigated three alternating D-A copolymers in the present study. Copolymer 1 consists of homopolymers PSICN ($[A]_x$) (Fig. 1) and PFUCN ($[B]_x$) (Fig. 2) as repeat units. Copolymer 2 consists of PSICN and PPYCN ($[C]_x$) as repeat units (Fig. 3) while copolymer 3 consists of PSICN and PTHCN ($[D]_x$) units (Fig. 4). The D-A polymers are designed in such a manner that the dicyanomethylene linkages are common to all the constituents (the PSICN component is common), while one of the hetero-atomic moieties is replaced in each copolymer. The electron rich heterocyclic rings have been used as donor moieties while dicyanomethylene groups complete alternation by acting as acceptor units.

Materials and Methods

Our purpose is to find the optimum relative concentrations of the constituent homopolymers in the binary copolymer formed, such that the copolymer has a minimum band gap value and maximum electronic delocalization, i.e., the copolymer with maximum conducting ability. We construct the Hückel determinant of a copolymer chain consisting of N units (taking N = 300). It is tridiagonal due to the fact that only first neighbour interactions are considered. á's and â's are the diagonal and off-diagonal elements respectively and ë's are the eigenvalues obtained[40]. The determinant is solved using simple NFC (negative factor counting) method to obtain the band gap value while the subsequent use of IIM (inverse iteration method)[41,42] provides the values of coefficients (c_{jr}) which when plugged into the formula,

$$I_j = \frac{\sum_{r=1}^{n} \left| C_{jr} \right|^4}{\left(\sum_{r=1}^{n} \left| C_{jr} \right|^2 \right)^2}$$

gives us the IPN, I_j (inverse participation number). IPN is a measure of the level of delocalization of a MO in the polymeric chain and can take up values between 0 (maximum delocalization) and 1 (localized over only one orbital). Thus, IIM proves to be very useful in obtaining the energy values of physical significance, viz., the energy levels in the upper regime of the occupied valence band (VB) and those in the lower regime of the unoccupied conduction band (CB). Hence the computational techniques of NFC and IIM have been used in combination with GA in order to "tailor-make" the desired copolymer.

A simple GA run starts with a randomly generated population of individuals (or chromosomes), each one being a sequence of bits (zeros and ones). We started with a population of 5 chromosomes. The sequence of steps followed by us is depicted in Fig. 5. The complete details of the methodology are mentioned in some of our earlier studies[43,44]. We evaluate each individual by defining a criterion of fitness (inspired by "survival of the fittest" rule of nature) known as the fitness function *f(x)* given by the relation,

$$f(x) = \frac{1}{(1/\rho)\ \text{gap} + \text{IPN}}$$

which calculates the fitness value of an individual using both gap value and IPN. We scale the two quantities using a constant '*ñ*' which is the difference between the highest occupied energy level (of VB) and the lowest unoccupied energy level (of CB) amongst the homopolymers of the copolymer being formed. We then allowed the population to evolve (over several iterative steps) until the convergence criteria is met with. Thus, GA technique is useful in finding the optimum solutions. A systematic analysis of each of the possible percentages would be computationally expensive.

To determine the electronic density of states (DOS), we have used an energy grid of 0.001 eV consistently in the calculations. It is known that the negative of HOMO correlates very well with the vertical ionization potential (Koopman's theorem). Based on this, the various á and â values of all four homopolymers, for both valence and conduction band, are listed in Table 1. These band structures used in our calculations have been obtained through ab initio Hartree-Fock CO method[28,45,46] using Clementi's minimal basis set. The results obtained are expected to provide able guidelines for synthesis of these copolymers with "tailor-made" electronic and conduction properties.

Results and Discussion

The values of all the electronic properties such as IP, EA and E_g of the copolymer chains investigated by us are listed in Table 2. Also tabulated are the optimized values of the relative amounts of the constituent homopolymers in the resulting copolymer, as obtained from GA. Molecular design and choice of specific substituents directly affect the properties of the polymer. The introduction of electron accepting dicyanomethylene linkages between the aromatic rings of the unit cells induces major geometry changes within the rings, leading to combination of aromatic and quinonoid forms.

The Band gap values are related to the conduction properties of the polymers in their pristine state whereas IP and EA values ascertain the ability of the copolymers to form conducting polymers through oxidative and reductive doping respectively. The results obtained from GA, for copolymer 1, suggest that the optimized solution would be the one which contains PSICN and PFUCN in the ratio 86:14 ($\mathbf{A_{86}B_{14}}$). From this we concluded that the homopolymer $[A]_x$ (or PSICN) should be present in maximum amount in the resulting copolymer so that the copolymer hence formed possesses maximum conducting ability and minimum band gap. The electronic DOS for the above copolymer mentioned corresponding to the optimized composition returned by GA is shown in Fig. 6a. Since there is random placement of units in the copolymer sequence, their respective environments keep

on changing and therefore, the DOS distribution consists of broad regions of allowed energy states.

Copolymer 2, a binary copolymer comprising of PSICN and PPYCN as repeat units, is on the contrary found to contain the maximum percentage of pyrrole-based units PPYCN ($\mathbf{A_{12}C_{88}}$). A comparison of the electronic properties of copolymer 2 with those of copolymer 1 clearly shows that the IP value of the former has decreased by almost 1 eV (refer to Table 2). As a result of this decrease of IP value, copolymer 2 is expected to be a better candidate for *p*-doping because the loss of electrons is now relatively easier. Hence appropriate copolymerization helps to achieve extrinsic conductivity in a polymer. Moreover, a decrease in the IP value also decreases the band gap of the copolymer 2 (E_g = 4.252 eV), due to which it becomes a better intrinsic conductor in comparison to copolymer 1. It can also be seen in the corresponding DOS (Fig. 6b) that the separation between the cluster of VB and CB peaks has decreased on replacement of furan units with pyrrole units.

In the third case, when thiophene units are present in the backbone chain, copolymer 3, the optimum solution is found to contain 99% of PTHCN ($\mathbf{A_1D_{99}}$). The EA values of copolymers 2 and 3 are almost equal. But if we compare the band gap value with any of the former copolymers it is highest in this case. Fig. 6c shows the DOS of copolymer 3.

Thus, we can finally conclude that the copolymer 2 is the best intrinsic conductor among the three since it has the minimum band gap value. Moreover, it also has the lowest IP value, so it is also the most suited candidate for *p*-doping. On the other hand, copolymer 1 has the highest EA value owing to the highest electronegativity of the O atoms present in the chain, which tend to pull the charge cloud, so, it is expected to be the best candidate for *n*-doping (or reductive doping).

In addition, higher the electronegativity of the hetero-atom, lesser is the aromaticity of the resulting compound. Oxygen atom being the most electronegative of all, pulls the electron cloud towards itself making furan moiety to be the least aromatic of all. It can be observed in the copolymer of PSICN-PFUCN (copolymer 1) that the percentage of furan units is in minority (optimized solution in the ratio 86:**14** as suggested by GA). Sulphur on the other hand, is less electronegative, making thiophene moiety to be the most aromatic of all. In addition to the electronegativity difference, the S atoms have 3s, 3p as the valence electrons (more delocalisation takes place) in contrast to the 2s, 2p valence electrons of O, N. This is reflected in the copolymer of PSICN-PTHCN (copolymer 3), where PTHCN units are in majority. Hence, the structure-property relationship is well established in the results reported by us in Table 2. The calculated gap values (from NFC) of such copolymers are in very good agreement with the expected values (if calculated from the band alignments directly).

Conclusions

We have described an efficient route for designing novel low band gap binary copolymers using alternate D-A strategy within the repeat units to maximize the ð-conjugation. Such a strategic arrangement of D-A moieties in a copolymer is capable of inducing charge transfer within the backbone chain. The band gaps of copolymers can also be tuned to almost any value between those of the constituent homopolymers by varying the nature of substituents.

In the present study, we have designed novel copolymers of D-A polymers which contain heterocyclic rings as the main framework of the polymer backbone. We investigated a system where the D-A polymer PSICN is common in all the copolymers, and we varied the other D-A polymer in each of the binary copolymers by replacing SiH_2 with groups such as O, NH and S. The bridging group >C=C$(CN)_2$ was kept common in all the copolymers. This facilitated in investigating the effect

of hetero atom substitution on the electronic properties of electrically conducting polymers. The trends in electronic properties, as obtained using genetic algorithm, have been discussed quantitatively as well as in a qualitative manner through the DOS plots.

Systematic search is an unwieldy assignment and involves lot of computational time. On the other hand, GA technique due to its adaptability, directly provides the optimized composition of the copolymer possessing minimum band gap along with maximum electronic delocalization. These theoretical calculations can prove supportive in the pursuit of novel polymers with high conducting capability as well as offer guidelines for their synthesis.

Table 1
The ab-initio electronic properties (of both valence band and conduction band) of the four D-A homopolymers

D-A Polymer	Valence Band		Conduction Band	
	α (in eV)	β (in eV)	α (in eV)	β (in eV)
PSICN ($[A]_x$)	-10.655	0.829	-3.300	0.252
PFUCN ($[B]_x$)	-10.905	0.954	-3.749	0.212
PPYCN ($[C]_x$)	-9.917	0.931	-2.592	0.087
PTHCN ($[D]_x$)	-10.649	0.697	-3.055	0.142

Table 2
Calculated electronic properties-IP, EA and E_g of the random binary copolymers along with their optimum percentage compositions as obtained from GA. PSICN (denoted by $[A]_x$) is common in all copolymers

Copolymer	*IP (eV)*	*EA (eV)*	*E_g (eV)*	*Optimum composition*
PSICN-PFUCN	8.996	4.171	4.825	$A_{86}B_{14}$
PSICN-PPYCN	8.054	3.802	4.252	$A_{12}C_{88}$
PSICN-PTHCN	8.996	3.803	5.194	A_1D_{99}

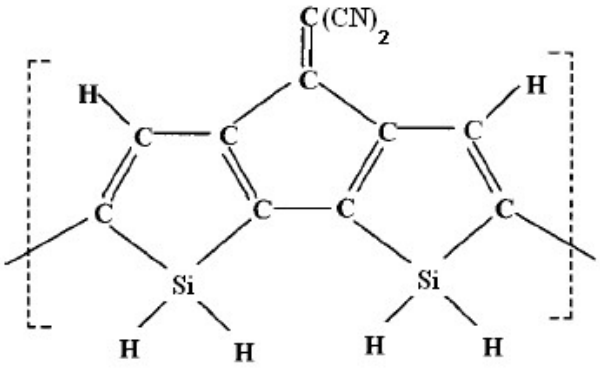

Fig. 1. Schematic structure of unit cell of homopolymer $[A]_x$, PSICN

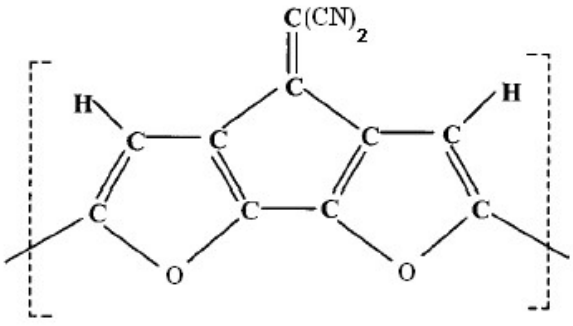

Fig. 2. Schematic structure of unit cell of homopolymer $[B]_x$, PFUCN.

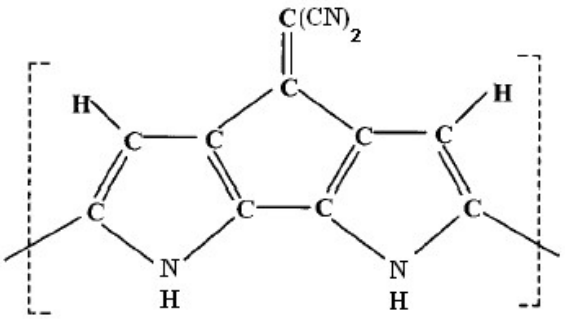

Fig. 3. Schematic structure of unit cell of homopolymer $[C]_x$, PPYCN

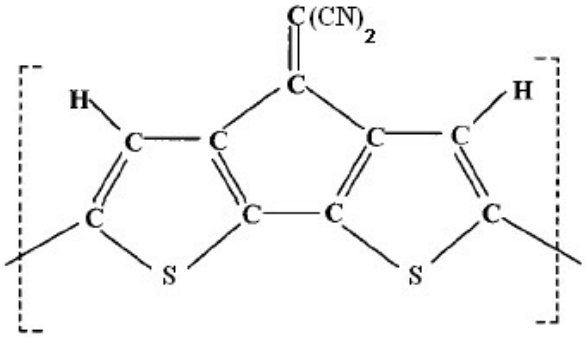

Fig. 4. Schematic structure of unit cell of homopolymer $[D]_x$, PTHCN

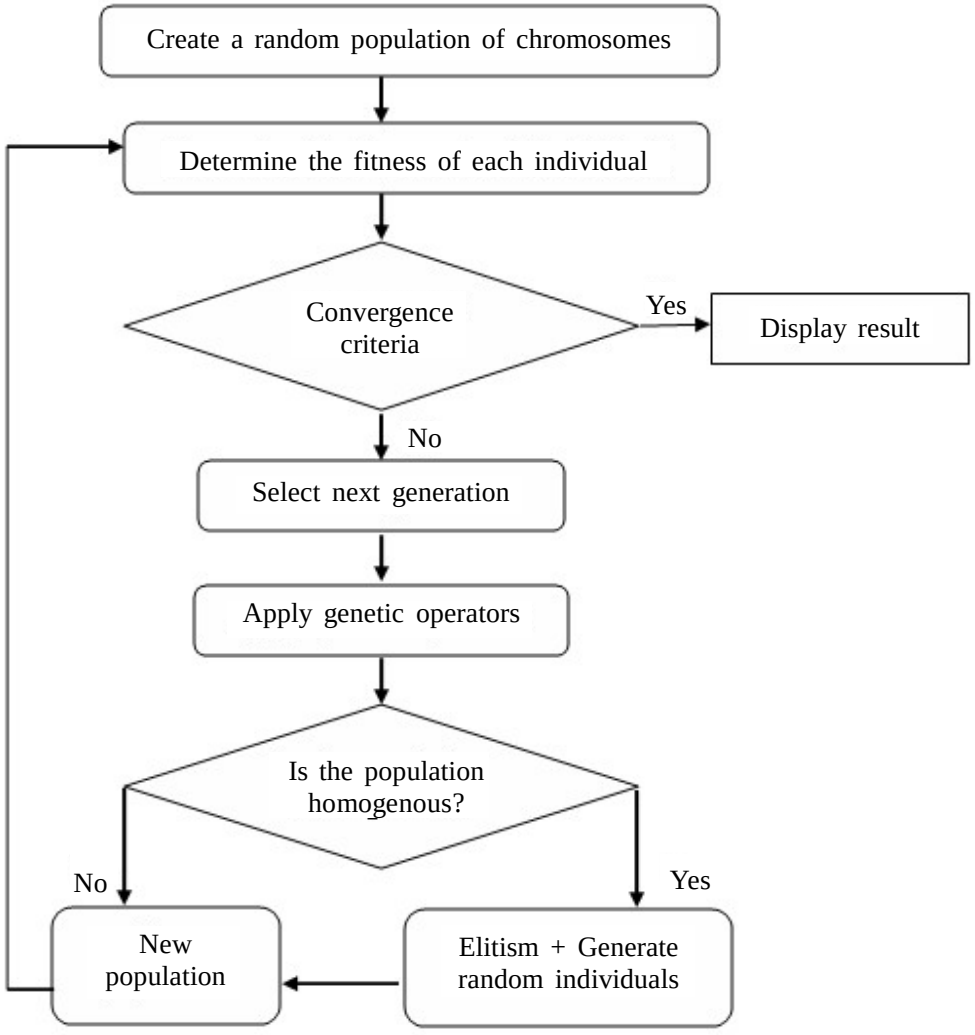

Fig. 5. Steps involved in the optimization process using genetic algorithm

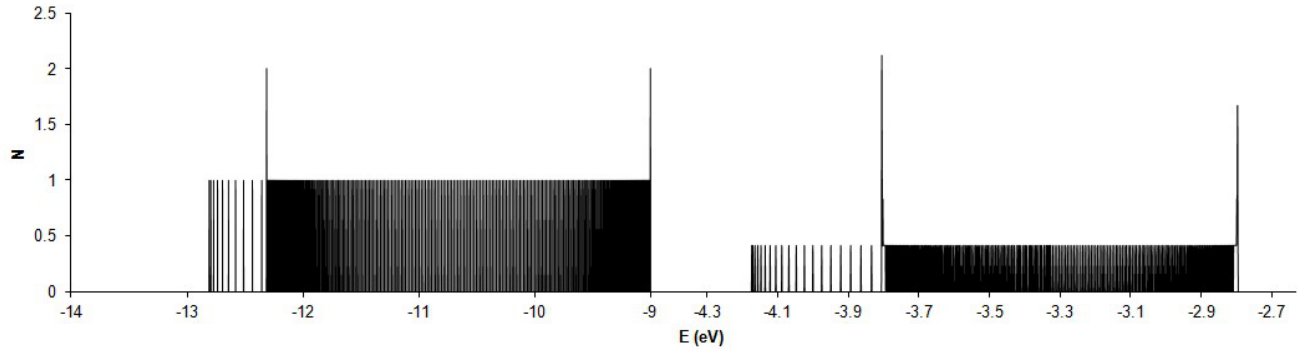

Fig. 6a. DOS distribution of copolymer 1.

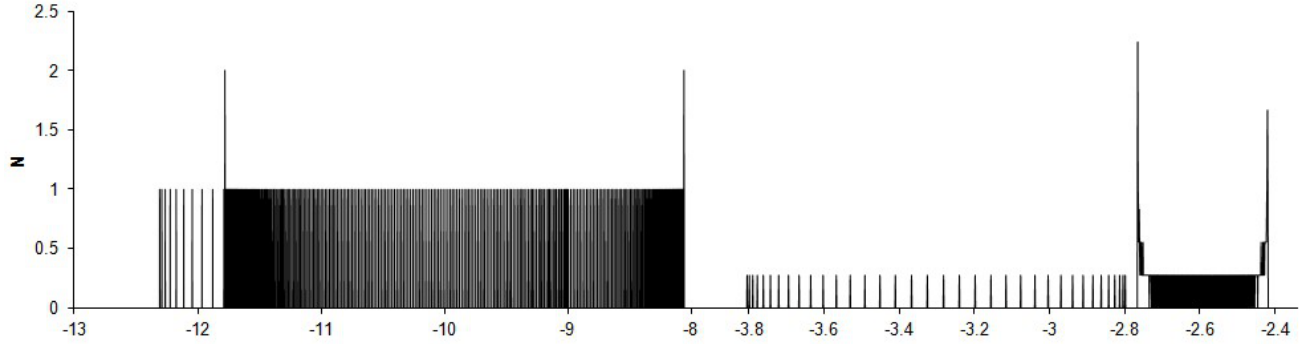

Fig. 6b. DOS distribution of copolymer 2

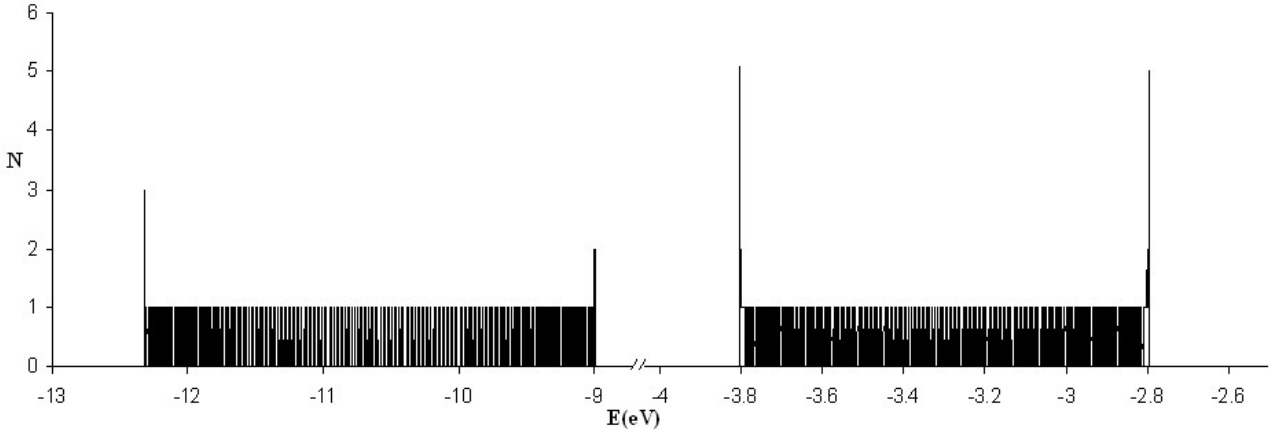

Fig. 6c. DOS distribution of copolymer 3

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