# Molecular designing of novel ternary copolymers of donor–acceptor polymers using genetic algorithm
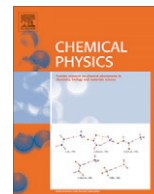
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# Molecular designing of novel ternary copolymers of donor–acceptor polymers using genetic algorithm

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## ARTICLE INFO

## ABSTRACT

An efficient designing route to novel ternary copolymers consisting of polypyrrole (PPy), polythiophene (PTh) and polyfuran (PFu) is developed with the help of genetic algorithm. Using the band structure results obtained from *ab initio* crystal orbital (CO) calculations, the electronic structures and conduction properties of real ternary copolymers based on donor acceptor type polymers are investigated. The electron rich heterocyclic rings in the backbone chain of the copolymer are joined together by electron withdrawing groups $Y$, carbonyl group ($>C=O$) and difluoromethylene group ($>C=CF_2$) in an attempt to design the conducting polymer with lowest band gap. A comparative study of various electronic properties is presented. The effects of substitution on the behaviour and properties of the copolymers as well as on the density of states (DOS) are discussed. Band gap decreases as a result of substitution on the polymer backbone chain due to decrease in ionization potential and increase in electron affinity values. This is expected to enhance the intrinsic conductivity of the resulting copolymer. Use of alternate donor acceptor moieties within the repeat units should maximize the extended $\pi$ conjugation.

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## 1. Introduction

Conducting polymers have attracted a great deal of attention ever since their discovery by Shirakawa et al. [1]. There have been enormous experimental and theoretical efforts in the area because of the versatile properties of these materials which combine the high conductivity of pure metals while being corrosion resistant, light in weight and easy to process. These features make them one of the most widely applicable classes of materials. Their applications include super capacitors, electronic devices, organic light emitting diodes (OLED), optical devices, electrochromic or smart windows, anti static coatings, sensors, batteries, solar cells, artificial muscles, memory devices, imaging materials, nano switches and transistors [2–6]. The chemical structures of these organic conjugated polymers can be manipulated in several ways to obtain properties as desired. But limited processibility remains a major drawback with conducting polymers.

In order to "tailor-make" these polymers and obtain desired properties out of them, it is very important to first understand the relationship between the chemical structure of the polymer and its properties. Efforts are thus being made to make these materials intrinsically conducting and more process able. There have been several advances in designing of polymers with small band gap so as to obtain conductivity in the metallic regime

[2,7,8]. One approach to design these polymers is the use of alternate donor (electron rich) and acceptor (electron deficient) moieties in a polyconjugated backbone. A regular arrangement of such repeat units in the $\pi$ conjugated chain significantly decreases the HOMO–LUMO separation. The band gap is expected to be the lowest for that particular combination in which the electronegativity difference between the donor and acceptor moieties is highest.

Using this approach, several copolymers have been successfully synthesized, possessing band gap around 1 eV [9]. Quantum mechanical calculations have also been performed by several theoreticians in this regard [10]. When it comes to synthesizing a polymer, there can be enormous number of ways in which the homopolymer units may be arranged to form a polymeric chain. As a result, the task of obtaining a polymeric chain with desired properties becomes very cumbersome and computationally expensive. To simplify this problem, recently many research groups have endeavored to the use of several optimization techniques to design these synthetic materials. One such technique which is gaining immense popularity is the genetic algorithm [11–13] (GA), which is a powerful tool to solve high complexity computational problems. GA, a class of evolutionary algorithms, 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 for diverse problems over time. The versatility of the technique lies in its attributes such as ease of use, flexibility and

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wide applicability. GA can be adapted to the given task and is thus, a problem specific algorithm.

In the present study we attempt to design novel low band gap [14] ternary copolymers of donor acceptor type polymers based on polypyrrole or PPy (A), polythiophene or PTh (B) and polyfuran or PFu (C) as repeat units using the GA. We have investigated three copolymer systems in the present paper. System 1 (Fig. 1) consists of homopolymers PPy, PTh and PFu as repeat units, while in systems 2 and 3 there is an alternation of donor and acceptor moieties because of bridging groups Y (>C=O, >C=CF$_2$). Introduction of >C=O groups in homopolymers PPy, PTh and PFu leads to poly-4H-cyclopentadipyrrole-4-one (PCDP), poly-4H-cyclopentadithiophene-4-one (PCDT) and poly-4H-cyclopentadifuran-4-one (PCDF), respectively. While the introduction of >C=CF$_2$ groups gives us polydifluoromethylene cyclopentadipyrrole (PFPy), polydifluoromethylene cyclopentadithiophene (PFTh) and polydifluoromethylene cyclopentadifuran (PFFu), respectively. Their structures are shown in Fig. 2a–c. The electron rich heterocyclic rings have been used as donor moieties while the carbonyl and difluoromethylene groups complete alternation by acting as acceptor units. The genetic operators which need to be essentially defined for a representation are: initialization, mutation, crossover and comparison. The algorithm would rapidly converge to the optimum solution through intelligent searches, with selective sampling of values in the entire configuration space, i.e., return the optimum relative concentration of the copolymer possessing minimum band gap value and maximum electronic delocalization.

## 2. Methodology

Our purpose is to find the optimal relative concentrations of the three constituent homopolymers, A (=x%), B (=y%) and C (=z%) in the copolymer $A_xB_yC_z$ so formed, such that the copolymer has a minimum band gap value and maximum electronic delocalization, i.e., the copolymer with maximum conducting ability. Using the condition, x + y + z = 100, the values of 'x', 'y' and 'z' hence obtained in the converged solution would be the optimal percentages of homopolymers A, B and C, respectively in the random copolymer $A_xB_yC_z$.

We construct the Hückel determinant of a copolymer chain consisting of N units (taking N = 300).
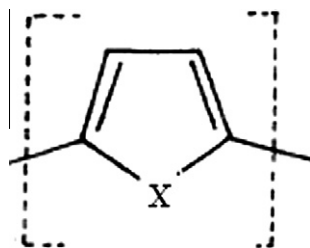




**Fig. 1.** Schematic structure of unit cells of homopolymers PPy, PTh and PFu, where X = NH, S and O, respectively.

It is tridiagonal due to the fact that only first neighbour interactions are considered. Here α's and β's are the diagonal and off-diagonal elements, respectively and λ's are the eigenvalues obtained. The determinant is solved using simple NFC (negative factor counting) method [15] to obtain the band gap value while the subsequent use of IIM (inverse iteration method) [15,16] provides the values of coefficients ($c_{jr}$) which when plugged into the formula,

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

gives us the IPN, $I_j$ (inverse participation number). IPN [17] 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 [18] population of individuals (or chromosomes), each one being a sequence of bits (zeros and ones). We start with a population of five chromosomes. The sequence of steps followed by us is depicted in Fig. 3. The complete details of the methodology have been mentioned in our earlier study [19]. 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 'ρ' 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 allow the population to evolve (over several iterative steps) until the convergence criteria is met with. Thus, GA technique is useful in finding the optimal solutions through intelligent searches with selective sampling of values in the entire configuration space. A systematic analysis of each of the possible percentages of A, B and C 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. The band alignments of homopolymers units in different systems are shown in Fig. 4a–c. The band structures used in our calculations have been obtained through *ab initio* Hartree Fock CO method [20] using Clementi's minimal basis set. Consequently, the electronic properties might be slightly over estimated due to neglect of correlation effects. However, the results obtained are expected to provide able guidelines for synthesis of these copolymers with "tailor-made" conduction properties.

## 3. Results and discussion

In our previous approach [19] we had used the GA technique for investigation of model binary polypeptide chains. The technique proved to be very effective and reliable as well. In the present study, we have extended the algorithm in order to investigate real ternary copolymer systems. We have focused on organic conjugated polymers which possess high conducting ability.

It is known that the negative of HOMO correlates very well with the vertical ionization potential (Koopman's theorem). Table 1 shows the calculated electronic properties such as IP (ionization
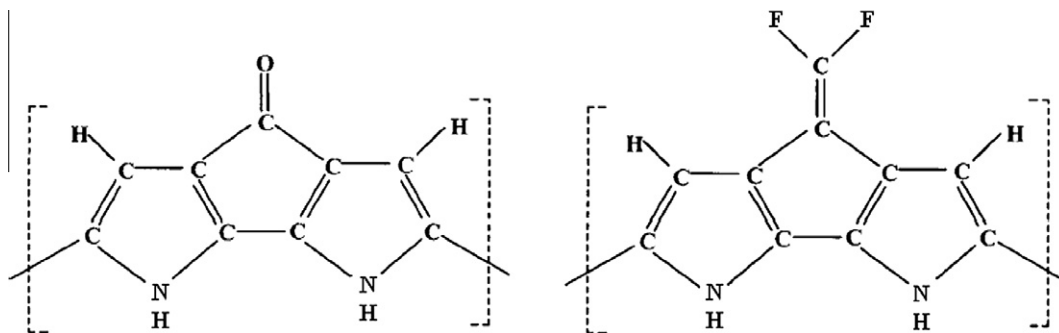
**Fig. 2a.** Schematic structures of unit cells of poly-4H-cyclopentadipyrrole-4-one (PCDP) and polydifluoromethylene cyclopentadipyrrole (PFPy).
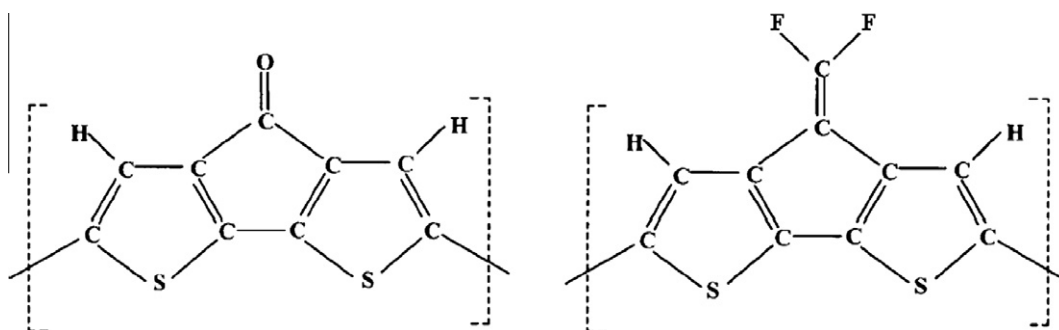


**Fig. 2b.** Schematic structures of unit cells of poly-4H-cyclopentadithiophene-4-one (PCDT) and polydifluoromethylene cyclopentadithiophene (PFTh).
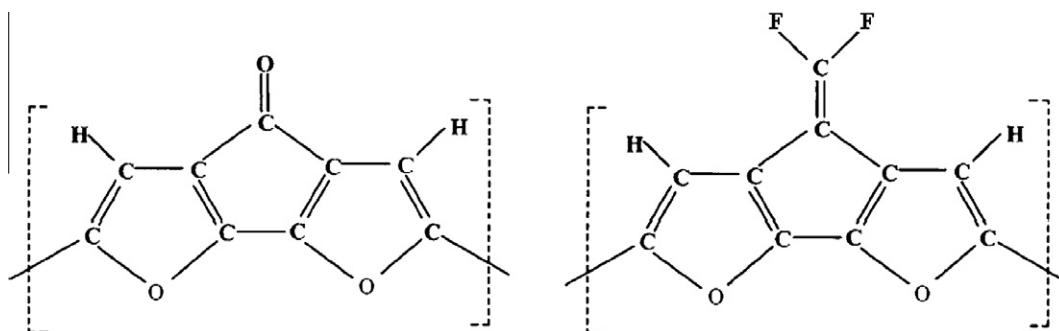


**Fig. 2c.** Schematic structures of unit cells of poly-4H-cyclopentadifuran-4-one (PCDF) and polydifluoromethylene cyclopentadifuran (PFFu).

potential corresponding to the top of the VB), EA (electron affinity corresponding to the bottom of the CB), $E_g$ (band gap) of the random copolymer chains (of $A_xB_yC_z$ type) and the optimized percentage compositions (or optimized solutions) obtained from GA. These are the optimized values of the relative concentrations of the three constituent homopolymers in the resulting copolymer, which possesses minimum gap value and maximum level of delocalization in the chain. Molecular design and choice of specific substituents directly affect the properties of the polymer. 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 systems to form conducting polymers through oxidative and reductive doping, respectively.

The system 1 under consideration is a ternary copolymer based on heterocyclic homopolymers PPy, PTh and PFu. An analysis of the optimized solution obtained from GA ($A_{87}B_{12}C_1$) reveals that the homopolymer $A$ (or PPy) should be present in maximum amount in the resulting copolymer so that the copolymer hence formed possesses maximum conducting ability and minimum band gap.

Here it would be worth mentioning that out of the three homopolymers, $A$ (or PPy) is the one with lowest value of IP (8.826 eV) as is evident from the band alignments (Fig. 4a). While the component present in least amount, $C$ (or PFu) has the highest IP value (9.740 eV). We therefore conclude that the resulting ternary copolymer with highest percentage of pyrrole skeleton is expectedly a suitable candidate for $p$ doping.

The electronic DOS for the above system corresponding to the optimized composition returned by GA are shown in Fig. 5a. 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. Such broadening in aperiodic systems is consistent with our earlier observations on aperiodic model polypeptide chains [19].

In the other two systems which we have studied, the electron rich heterocycles act as donor units while the bridging groups act as acceptor moieties. System 2, a ternary copolymer of donor acceptor type polymers based on carbonyl substitution, comprises
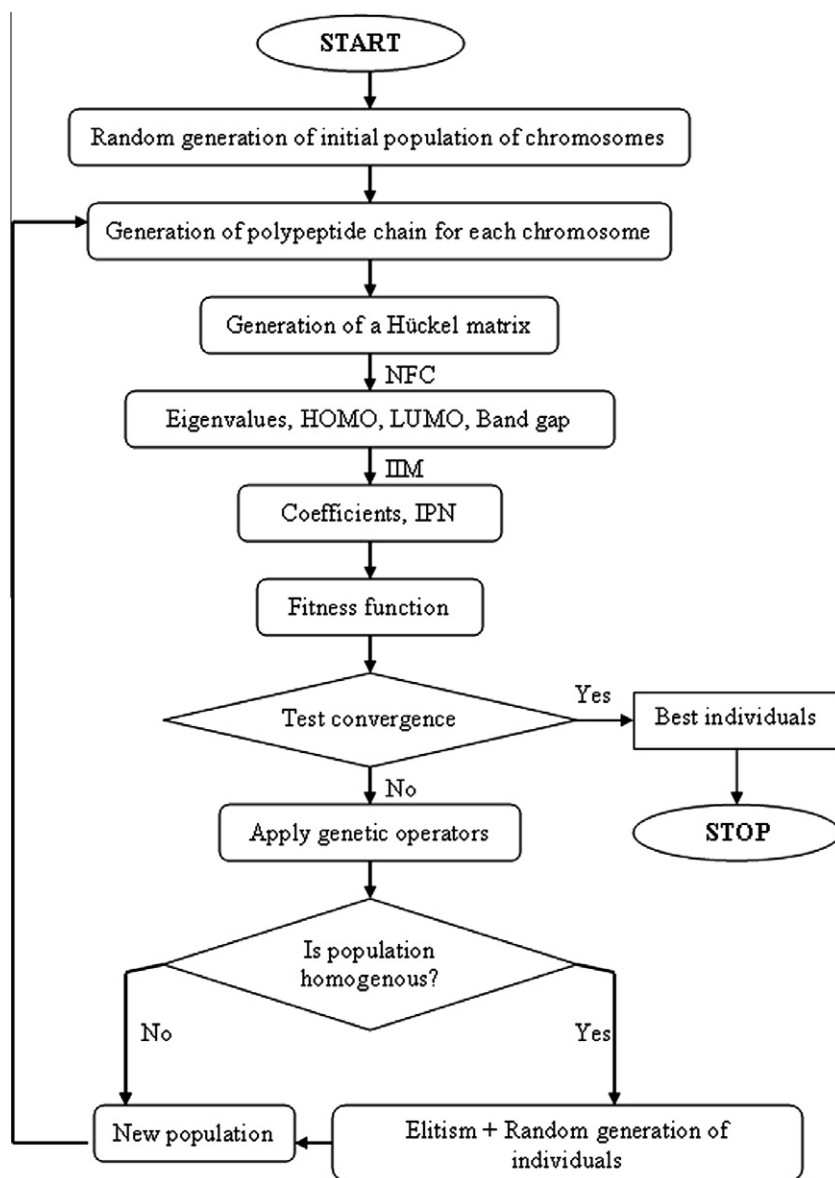
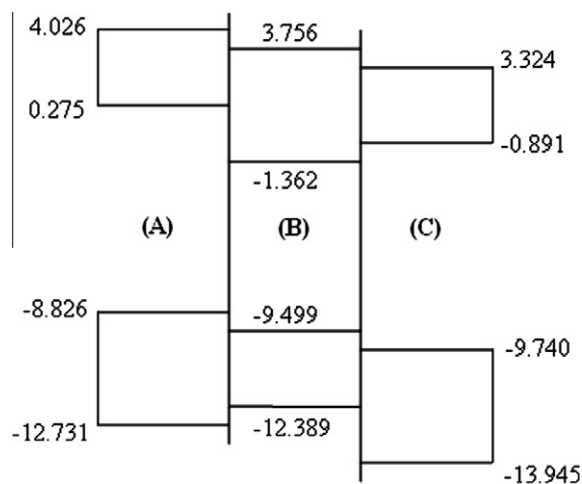Fig. 3. Steps involved in the optimization process using genetic algorithm.



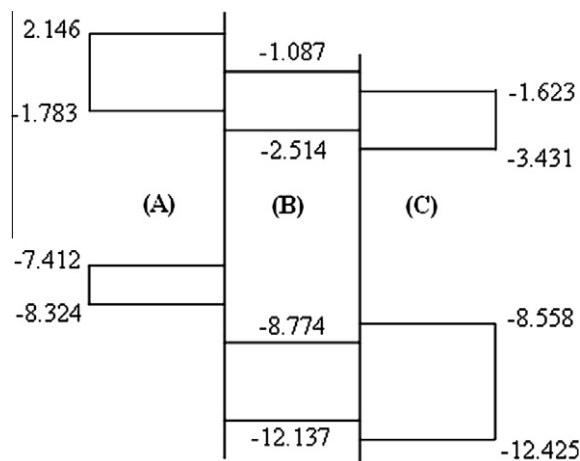Fig. 4a. Band alignments (system 1) of homopolymers PPy, PTh and PFu.



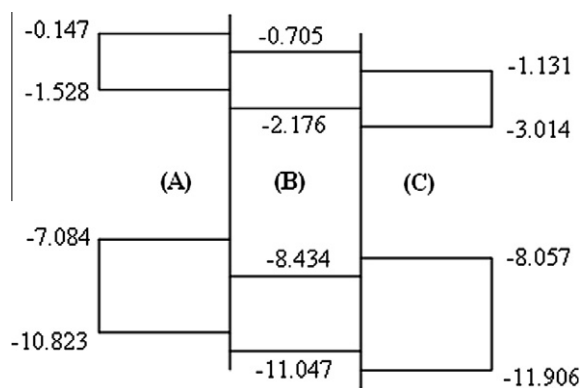Fig. 4b. Band alignments (system 2) of homopolymers PCDP, PCDT and PCDF.

**Fig. 4c.** Band alignments (system 3) of homopolymers PFPy, PFTh and PFFu.

**Table 1**
Calculated electronic properties-IP, EA and $E_g$ of the random ternary copolymer chains (of $A_xB_yC_z$ type) and the optimized percentage compositions obtained from GA. $Y$ denotes the bridging groups introduced in the carbon backbone chain of the ternary copolymer.

| System | $Y$ | IP (eV) | EA (eV) | $E_g$ (eV) | Optimized composition |
|--------|-----|---------|---------|-----------|----------------------|
| 1 | – | 8.828 | 1.353 | 7.475 | $A_{87}B_{12}C_1$ |
| 2 | >C=O | 7.412 | 3.425 | 3.987 | $A_{86}B_1C_{13}$ |
| 3 | >C=CF$_2$ | 7.084 | 3.010 | 4.074 | $A_{84}B_1C_{15}$ |

of PCDP, PCDT and PCDF as repeat units. The GA optimized solution is again found to contain the maximum percentage of pyrrole based units PCDP, which have the lowest IP value 7.412 eV (Fig. 4b). On comparison of the electronic properties of this system with those of system 1, it is clear that the IP of the resulting ternary copolymer has decreased by ≈1.4 eV, while the EA has become more than double the previous value. As a result of this increase in EA value, the copolymer is expected to become a better candidate for $n$ doping (or reductive doping) because gain of electrons is now relatively easier. Moreover, an increase in the EA value decreases the band gap drastically (by almost 3.5 eV). This implies that the introduction of electron withdrawing carbonyl group in the backbone chain of the copolymer increases its intrinsic conductivity as well as dopant philicity because of extended π conjugation in the chain, which in turn, is due to charge transfer within the backbone. The effect of substitution is also very clear from the DOS of the optimized solution (Fig. 5b). It can be seen that the separation between the cluster of VB and CB peaks has decreased
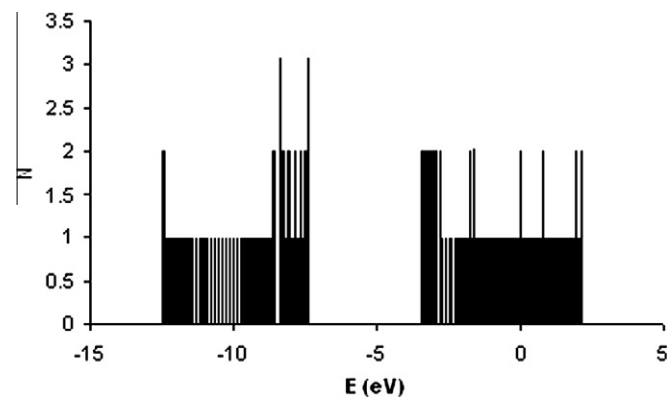


**Fig. 5b.** DOS distribution (system 2) of the copolymer of PCDP, PCDT and PCDF corresponding to the optimized solution.

significantly after substitution, thus enhancing the intrinsic conductivity of the copolymer.

When the difluoromethylene linkages are introduced into the polymer backbone chain, the ternary copolymer comprising of PFPy, PFTh and PFFu (system 3) is yet again found to contain maximum percentage of pyrrole based units, PFPy which have the lowest IP value (7.084 eV) amongst all three homopolymers (Fig. 4c). The trends in electronic properties are found to be more or less similar to those of the carbonyl based ternary copolymer. The IP value has decreased by ≈1.7 eV, while the EA value has increased by ≈1.7 eV. As a result of this decrease of IP value, the copolymer is expected to become a better candidate for $p$ doping because the loss of electron is now relatively easier. The resulting copolymer has high intrinsic conductivity, again because of extended π conjugation in the chain. The trends in the DOS are shown in Fig. 5c. Another important aspect related to this particular system is that, introduction of F atoms in organic molecules can profoundly influence their chemical and physical properties, leading to a range of compounds with highly desirable properties and remarkable physiological activity. These features are attributed to some unique properties of fluorine atom. Like, the largest electronegativity among all atoms and smallest Van der Waal radius (apart from H), because of which fluorine is not sterically demanding. Apart from these features, the C–F bond is also quite stable. These aspects can prove to be very useful during the synthesis of fluorine containing organic polymers.

In general, we can say that, the electron acceptor substituents on heterocyclic rings in the copolymer backbone chain influence the LUMO energies (EA values) much more as compared to the
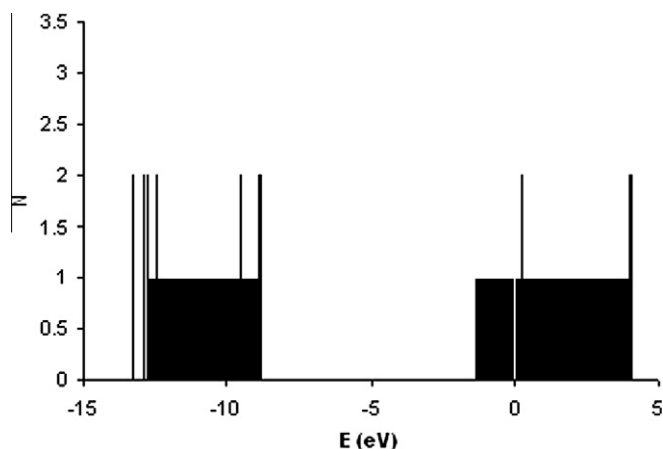


**Fig. 5a.** DOS distribution (system 1) of the copolymer of PPy, PTh and PFu corresponding to the optimized solution.
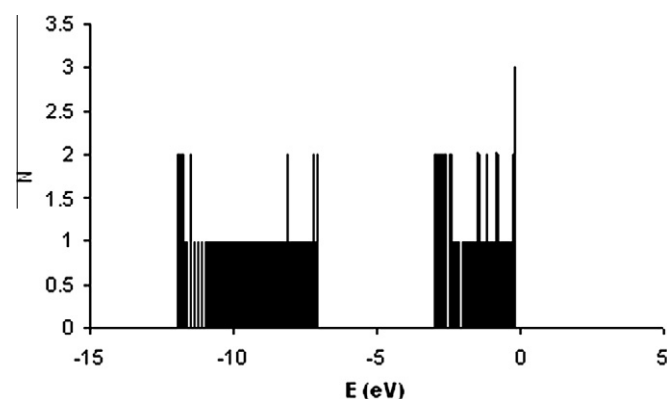


**Fig. 5c.** DOS distribution (system 3) of the copolymer of PFPy, PFTh and PFFu corresponding to the optimized solution.

HOMO energies (IP values) and thereby significantly lower the band gap of the copolymer. 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). Thus, the trends in homopolymer units reflect the polymer properties.

## 4. Conclusions

In conclusion, we have designed low band gap copolymers based on PPy, PTh and PFu skeletons, using alternate donor acceptor moieties within the repeat units to maximize the extended π conjugation. This arrangement may be capable of inducing charge transfer within the backbone chain. The presence of delocalization between the heterocyclic rings and substituents is expected to get enhanced by the electron withdrawing character of the substituents, which in turn enhances the delocalization of the conjugated system in the copolymer chain. The π effects are significant for electrically conducting polymers because the π electron donating and accepting nature of the groups directly affects the electronic properties like $E_g$, IP and EA. The values of these parameters have been calculated using genetic algorithm technique along with simple NFC and IIM.

An analysis of the trends in the electronic properties shows that the EA values depend more on the heterocyclic substitution, while the substitution on the backbone C atoms has more influence on the IP values. In addition, the DOS distributions of the copolymer systems also give a qualitative picture of the trends in electronic properties.

Systematic search involving ternary copolymer systems is a very cumbersome task and requires lot of computational time. The GA technique proves its versatility yet again and gives directly the optimized composition of the copolymer which possesses minimum band gap along with maximum electronic delocalization. These theoretical calculations can be helpful in the search of novel polymers with high conducting ability as well as provide able guidelines for synthesis of these compounds. Another bio-inspired evolutionary algorithm which is being widely applied is the Ant Algorithm (AA) technique [21]. It demonstrates the collective or swarm behaviour of social insects like ants. Both GA and AA are specialized in their own ways for solving discrete combinatorial optimization problems. The choice of algorithm for any problem is primarily application dependent while its success rate depends on the optimal solution returned at the end of a run as well as the time taken for computation. An interesting advantage of GA is that, once convergence is achieved, the algorithm not only produces an optimal individual, but a population of good individuals, thus enabling the user to choose from a collection of possible solutions.

We are exploring the possibility of other heteroatom substitutions in order to make the polymers intrinsically more conducting. Investigations are also being made for suitable bridging substitutions that may be carried out on the backbone to make the polymers better candidates for $p$ doping and $n$ doping. From these results, >C=O as bridging group seems to be desirable if $n$ doping is wanted. For $p$ doping, a higher percentage of pyrrole skeleton is the best solution.

## Acknowledgement

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