Computational atomistic blueprinting of novel conducting copolymers using particle swarm optimization

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Abstract A proficient metaheuristic approach viz., particle swarm optimization coupled with negative factor counting technique and inverse iteration method has been employed for designing novel binary and ternary copolymers based on thiophene, pyrrole and furan skeletons. A comparative study of the electronic structures and conduction properties of neutral heterocyclic copolymers and their benzene substituted analogues is inferred using the band structure results derived from *ab-initio* Hartree–Fock crystal orbital calculations. The band gap value decreases as a result of substitution on the polymer backbone due to increased quinoid contributions which is expected to enhance the intrinsic conductivity of the resulting copolymers. In general, it has been found that HOMO energies have a more decisive influence than LUMO energies on the relative fraction of constituents of the respective low band gap copolymers. The trends in the electronic properties of the respective copolymers are also verified and discussed with the help of density of states. These results can help streamline scrupulous synthetic efforts providing a potent route for molecular engineering of sustainable and efficient electronic materials.

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Introduction

The emergence of conduction in the otherwise insulating organic polymers has magnetized enormous enthusiasm amongst the scientific community witnessing comprehensive efforts in the past 36 years towards the proliferation of new technologies using these novel materials [1]. The self-merchandising attributes of electrically conducting polymers (ECPs) are low band gap, highly delocalized electronic structure, feasibility of high electrical conductivity, environmental stability, structural versatility and ease of processing. This active area of research has evolved with successful interdisciplinary convergence of various territories of science such as chemistry, condensed matter physics, materials science, and polymer science etc., for molecular designing and preparation of efficient, sustainable and non-toxic components for application in various devices such as solar cells, batteries, super-capacitors, organic light emitting diodes (OLEDs), sensors, smart windows, memory devices, drug delivery devices, analytical devices, nano-electronics etc. [2–5].

A plethora of organic conjugated polymers with custom tailored electronic properties has been theoretically designed as well as synthesized. However, the development of stable, process able polymeric systems with small or zero band gap is still a task to be accomplished, which is essentially consequential of substratal insight into the kinship between the chemical structure of the polymer and its electronic properties. Band gap is an important device parameter [6–8] which has been surveyed to be the most appropriate property to modulate in response to the structural variations in the polymer backbone [8–14]. Controlling the band gap is a prerequisite in optimizing the resulting devices as it dictates their electrochemical, optical and charge transport properties. The structural handles such
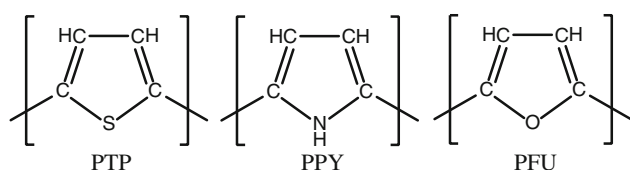
Fig. 1 Schematic structures of unit cell of polythiophene (PTP), polypyrrole (PPY) and polyfuran (PFU)

Fig. 2 Schematic structures of unit cell of polyisothianaphthene (PITN), polyisobenzopyrrole (PIBP) and polyisobenzofuran (PIBF)

as olefinic polymer backbone, the size and manner in which the repeat units propagates and appropriate side chains have provided lucrative opportunity for tuning and modification of the band gap of polymeric host materials.

One such structural paradigm that allows easy manipulation of the electronic structure and properties of the polymer backbone is that of copolymerization [15, 16]. Copolymerization aids opportune selection of homopolymers in the copolymer chain thereby favorably tuning the electronic properties of the resulting systems. The properties of copolymers can be varied over a wide range of conductivity, fusibility and stability depending on the type (and number) of co-monomers and their connectivity in the polymer chain. Generally, the designed copolymer has electronic properties tuned between those of its constituent components. A diverse class of copolymers has been investigated and synthesized with band gaps as low as 1 eV [17–19]. In this work, we investigated the electronic properties of binary and ternary copolymers based on five-member heteroaromatic polymers viz., polythiophene (PTP), polypyrrole (PPY) and polyfuran (PFU).

Polymers constructed of five-member heterocyclic aromatic rings such as thiophene, pyrrole and furan have commanded greater attention not only because of their small band gap, doping capability, ease of preparation and environmental stability but also because of their versatile technological applications [20]. The structural unit cells of these heterocyclic polymers are shown in Fig. 1, wherein each respective unit cell all the carbon atoms are sp^2 hybridized with the respective heteroatom contributing two electrons to the aromatic sextet, pushing electron density towards ring carbons. As a result, the carbon atoms in the ring acquire partial negative charge making PTP, PPY and PFU electron rich or π excessive systems. One important determinant of conduction and electrical properties of these poly(heteroaromatics) is the nature of the heteroatom (X = S, N, O) itself which brings a great deal of diversity owing to their different periodic positions. The copolymerization of PTP, PPY and PFU based heterocycles with each other and with other aromatics has afforded a profound array of systems whose architecture and properties are flexibly controlled by rational choice of co-monomers and synthetic conditions.

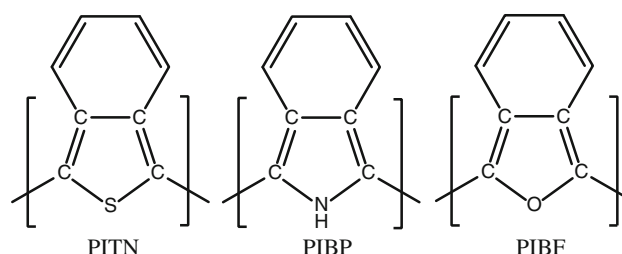Theoretical studies reveal that the band gap of such systems decreases as a function of the increasing quinoid

character of the polymer backbone [21]. This quinoid structure of poly(heteroaromatics) can be further stabilized by appropriate fusion/substitution of the heterocyclic ring with other aromatic system, which results in extension of conjugation length, thereby narrowing the band gap. This procedure offers vast scope for structural alteration of the polymeric backbone at the atomistic level to fine tune the electronic properties of host materials [22–24]. Due consideration has been devoted to various structural aspects such as geometrical features, topology, steric influence, conformational arrangement, chemical make-up, supramolecular packaging, tractability and experimental conditions which make substitutions feasible and profitable, thereby improving solubilities, decreasing band gaps, extending electronic delocalization, increasing charge transport ability and intrinsic conductivity of the resulting substituted polymers. The electron rich heterocyclic systems are known to have larger π donating capacities at β carbon atoms in comparison to α carbon positions. Fusion of a benzene ring on the two β carbon atoms of the PTP, PPY and PFU unit cells respectively gives polyisothianaphthene (PITN), polyisobenzopyrrole (PIBP) and polyisobenzofuran (PIBF) as shown in Fig. 2. Such a structural modification of heteroaromatic backbone is evident of favorable modulation of the electronic properties of their corresponding polymers [25]. Wudl et al. [26] synthesized PITN which was reported to have a band gap of 1 eV lower than PTP itself with quinoidal ground state geometry and high optical contrast ratio on reversible doping and de-doping. It has been calculated that the quinoidal form of PITN is 2.4 kcal/mol lower in energy than the aromatic form, as a result of stronger aromatic stabilization energy of benzene versus thiophene [27]. Recently, a set of low band gap polymers based on isothianaphthene has been synthesized and characterized for application in high performance organic photovoltaic devices [28]. Lately, Borrelli et al. [29] has also reported oxidative chemical vapor deposition synthesis of PITN with further decreased band gap value of 1.05 eV. Though a great deal of research has been devoted towards evolution of PITN and its derivatives to extract narrow band gap materials,

however, not much application based research has been dedicated towards β,β'-substituted benzene analogues of PPY and PFU viz., PIBP and PIBF to best of our knowledge. In view of the desirability of low band gap materials, we attempt to design novel binary and ternary copolymers of PITN, PIBP and PIBF.

Since, various copolymer configurations are possible which differ in number and arrangements of repeat units (homopolymers) in the chain, there is a considerable challenge in finding how best to couple the statistical nature and the properties of the combining components. Experimental as well as theoretical analysis of various possible combinations of homopolymers for a given copolymer family is a time expensive hard task. To simplify this complication, adaptation of metaheuristic search techniques has provided an intelligent route minimizing extensive manual effort and guiding experimentalists towards optimized results. One such metaheuristic procedure that has been widely explored for various combinatorial optimization problems is the particle swarm optimization (PSO) algorithm [30]. Originally proposed by Kennedy and Eberhart in 1995, PSO is a population based search algorithm, motivated by social behavior of bird flocking and fish schooling in search for food [31–34]. The underlying principle of PSO is social adaptation of knowledge, where a swarm of particles (agents) with limited individual intellect interacts locally among themselves and with their environment (social interaction) without any central supervision leading to the emergence of intelligent global and self-organized behavior. PSO algorithm has been adapted for designing conducting polymers as it simplifies the compositional choice of building blocks of the respective copolymers enabling fine tuning of band gap values.

In this work, we have drawn a comparative study of the electronic properties between the binary and ternary heteroaromatic copolymers and their benzene substituted analogues respectively as obtained using binary particle swarm optimization (BPSO) algorithm [22].

Methodology

In this study, we attempt to analyze the effect of substitution on the polymer backbone and compare the electronic properties of heteroaromatic copolymers and their benzene counterparts using the PSO metaheuristic scheme to return intrinsically conducting polymeric compositions.

The operating variables of PSO algorithm are *position* and *velocity*. And the movement of the entire swarm is referred to as iteration in context of the algorithm. For any given problem, a swarm of particles is randomly initialized in the designed search space with a *position* value. Along with *position*, a *velocity* is assigned to each particle with which it's moving.

Velocity is nothing but a mode of communication amongst the particles in the swarm. It keeps track of movement of the particle in the space and is used to update the positions of the swarm. Or in other words, *velocity* is probabilistically decoded into a new *position* for each respective particle.

To design novel binary and ternary copolymers with optimal electronic properties, we fit in BPSO search technique [35] to unfold this puzzle. With an objective to determine relative percentage compositions $x\%$ and $y\%$ (or $x\%$, $y\%$ and $z\%$) of the constituent homopolymer units A and B (or A, B and C) in the binary (or ternary) copolymer $(A_xB_y)_l$ (and $(A_xB_yC_z)_l$) respectively where $l = chain\ length/(x + y)$ (or $l = chain\ length/(x + y + z)$), under the condition imposed that $x + y = 100$ (or $x + y + z = 100$), we incline towards those values of x and y (or x, y and z) that correspond to minimum band gap value and maximum conducting ability. To accomplish this task, we constitute BPSO with two numerical methods, namely, negative factor counting (NFC) technique [36] and inverse iteration method (IIM) [36, 37].

This computational optimization process is initiated with random generation of a swarm (population) of particles (individuals). Each particle is represented in a binary number form which on conversion to decimal number represents particle *position* and *velocity* where *position* is nothing but the percentage composition of the respective homopolymers corresponding to which a copolymer chain of 300 units is generated using a quasi-random function [38]. Assuming unit time step, i.e., considering every iteration taking place at unit time step, initially both *position* and *velocity* terms for each particle are randomly assigned the same value. For every copolymer chain, the Hückel determinant is build up taking nearest neighbor interactions (tight binding approximation) into account. A tridiagonal framework is obtained as shown below with α's and β's as the diagonal (coulomb integral) and off-diagonal (resonance integral) elements respectively and λ's as the eigenvalues.

$$H(\lambda) = \begin{vmatrix} \alpha_1 - \lambda & \beta_2 & 0 & \ldots & 0 \\ \beta_2 & \alpha_2 - \lambda & \beta_3 & \ldots & 0 \\ 0 & \beta_3 & \alpha_3 - \lambda & \beta_4 & 0 \\ 0 & 0 & \beta_4 & \ddots & \beta_N \\ 0 & 0 & 0 & \ldots & \alpha_N - \lambda \end{vmatrix} = 0$$

This determinant is solved using NFC technique, computing eigenvalues without direct diagonalization, to obtain ionization potential (IP), electron affinity (EA) and band gap (E_g) values. Once eigenvalues are obtained, eigenvectors (coefficients C_{iv}) of interest are obtained using IIM. The normalized coefficients returned by IIM are then used to compute the inverse participation number (IPN, I_i) [39] which is coded as

$$I_i = \frac{\sum_{v=1}^{n} |C_{iv}|^4}{\left(\sum_{v=1}^{n} |C_{iv}|^2\right)^2}$$

and is a measure of the extent of delocalization of a MO in the polymer chain. It assumes values between 0 (maximum delocalization) and 1 (complete localization over one orbital). Each particle (potential solution) is evaluated using a fitness function formulated as

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

which gives equal statistical weight to E_g and IPN values. This fitness function so incorporated in the algorithm is the only problem dependent component which has been appropriately adjusted by scaling E_g using a constant 'ρ' which is the difference between the highest occupied energy level of the valence band (VB) and lowest unoccupied energy level of the conduction band (CB) amongst the combining homopolymers for a given copolymer system.

For every particle in the swarm, a fitness comparison is performed between its current and previous solutions, storing the best amongst the two as particle's *pbest* (personal best) *position*. Once the entire swarm has been evaluated and updated, another comparison between *pbest* positions of all the particles in the swarm is executed storing the best among the entire swarm as *gbest* (global best) *position*. The fitness function value is only used for making comparisons and its value is not used directly anywhere in the update equations. Once the entire swarm has been evaluated, the convergence/termination criterion is checked. For this problem, the algorithm is terminated if no variation in *gbest* value is found over last 20 iterations. If the termination criterion is not satisfied, a new swarm is generated using the update rules of BPSO algorithm as follows:

Step 1: Two *velocity* terms were introduced for each particle of the swarm, V_i^1 (probability that the bits change to 1) and V_i^0 (probability that the bits change to 0),

$$V_i^0 = \chi(V_i^0 + d_{i0}^1 + d_{i0}^2)$$
$$V_i^1 = \chi(V_i^1 + d_{i1}^1 + d_{i1}^2)$$

where d_{i0}^1, d_{i1}^2, d_{i1}^1, d_{i0}^2 are temporary values which are obtained using following equations:

If $pbest_i(bit\ value) = 1$ $d_{i1}^1 = C_1.r_1$ $d_{i0}^1 = -C_1.r_1$
If $pbest_i(bit\ value) = 0$ $d_{i1}^1 = -C_1.r$ $d_{i0}^1 = C_1.r_1$
If $gbest_i(bit\ value) = 1$ $d_{i1}^2 = C_2.r_2$ $d_{i0}^2 = -C_2.r_2$
if $gbest_i(bit\ value) = 0$ $d_{i1}^2 = -C_2.r_2$ $d_{i0}^2 = C_2.r_2$

C_1 and C_2 are the acceleration coefficients that maintain the stochastic influence of the cognitive and social components of the particle's velocity. And r_1 and r_2 are random

numbers [0, 1] generated for each move randomly. The factor χ constriction coefficient controls the exploration–exploitation tradeoff ensuring convergence [40].

Step 2: The *velocity* of change (probability of change) was defined for every bit of each particle taking into account their V_i^1 and V_i^0 values as,

$$V_i^c = \begin{cases} V_i^1, & if\ x_i = 0 \\ V_i^0, & if\ x_i = 1 \end{cases}$$

Step 3: All the real valued numbers of velocity were mapped to the range [0, 1] using the "Sigmoid function" which is given as,

$$S(V_i^c) = \frac{1}{1 + \exp(-V_i^c)}$$

Step 4: The new particle *position* was then computed using the following relation,

$$x_i(i+1) = \begin{cases} \overline{x_i(i)}, & if\ r_i < S(V_i^c) \\ x_i(i), & if\ r_i > S(V_i^c) \end{cases}$$

where, $\overline{x_i(i)}$ is the 2's complement of $x_i(i)$ and r_i is a uniform random number [0,1].

The new *positions* obtained were then evaluated with the constraint of not allowing the particles to revisit any *position* in its entire cycle. To further enhance the efficiency of the methodology, a boundary condition was specified which functioned to draw back the particles to their upper and lower limits, if they explored beyond the specified limits.
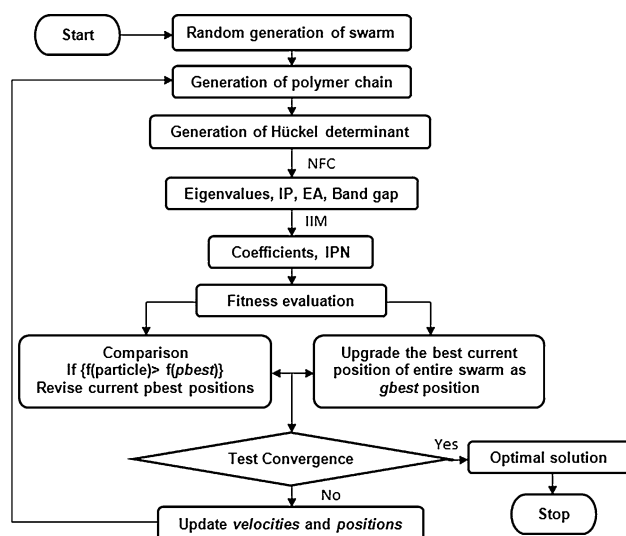
The set of algorithm parameters so used in this algorithm are given in Table 1. The detailed procedure and choice of various parameters used in this optimization process has been discussed in our earlier study [40]. The execution of this BPSO algorithm for efficient engineering of ECPs takes place in the manner depicted in Scheme 1.

To determine the electronic density of states (DOS), we have consistently used an energy grid of 0.001 eV in all the calculations. The relative band alignments of the homopolymers are shown in Fig. 3a, b which have been obtained assuming coplanar structures of the polymers with alternating co-oriented rings linked by α–α' bonds [41–43]. The band structures used in our calculations have been obtained from ab initio Hartree–Fock crystal orbital (CO) method using Clementi's 7s/3p minimal basis set. As a consequence, the electronic properties presented are slightly overestimated due to the neglect of electron correlation effects. However, such theoretical investigations can effectually streamline the meticulous experimental efforts on the choice and proportions of various constituents in a polymer with desired properties.
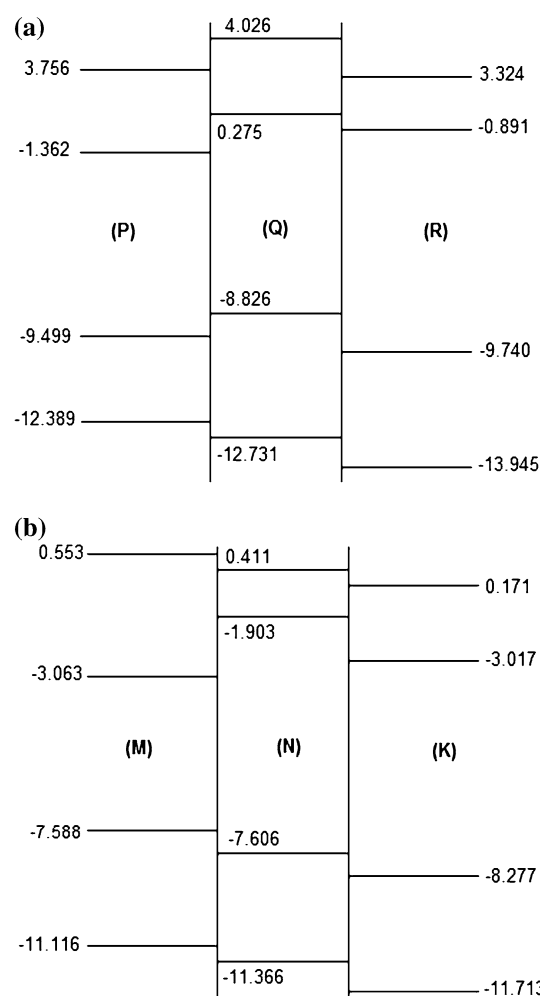
Scaling the band alignments of the combining constituents results in four classes of copolymers, viz. Type I (energy gap of one component lies within the band gap of

Table 1 BPSO Algorithm parameters

	BPSO algorithm parameters
Meta-heuristic	Swarm intelligence
Population	Swarm
Candidate solution	Particle
Population size	20
Representation of candidate solutions	Binary
Initialization	Random
Update criteria	Velocity and position update
Parameters for algorithm	Bit size: 7
	C_1, C_2: 2.05
	χ: 0.729
	Star topology
Assumptions	Unit time step
	A particle is not allowed to revisit a position in the entire process
Convergence criteria	Unchanged *gbest* value over 20 iterations

Scheme 1 Flowchart of BPSO methodology

Fig. 3 a Band alignments of (polymer family P1) homopolymers PTP (*P*), PPY (*Q*) and PFU (*R*). **b** Band alignments of (polymer family P2) homopolymers PITN (*M*), PIBP (*N*) and PIBF (*K*)

possible binary combinations of the respective polymer families P1 and P2 and also their ternary derivatives.

the other component), Type II staggered (top of the VB of one component lies within the band gap of the other and the bottom of the CB of the second lies in the band gap of the first), Type II misaligned (the CB minimum of one is below the VB maximum of the second component) and Type III (one component is semi-metallic while the other is a normal semiconductor) [15]. Depending on this criterion, copolymers $P1_{b2}$ (P and R), $P1_{b3}$ (Q and R), $P2_{b1}$ (M and N) and $P2_{b2}$ (M and K) belong to the class type I whereas $P1_{b1}$ (P and Q) and $P2_{b3}$ (N and K) are type II staggered copolymers (Fig. 3). In order to bring out the best possible combination, we have thoroughly investigated all the

Results and discussion

In our earlier study, we investigated an elementary case of a model binary copolymer where systematic search is feasible, to verify the reliability and robustness of our BPSO methodology. We satisfactorily concluded this in-silico approach effectual for molecular engineering of ECPs.

Comparative study of electronic properties

In the present study, we have focused on designing novel thiophene, pyrrole and furan based copolymers with low band gap and high intrinsic conductivity. The electronic properties (obtained using Koopman's theorem) viz., IP, EA and E_g are given in Table 2.

Table 2 Optimum percentage compositions of respective homopolymer units in the binary copolymers ($b1$, $b2$ and $b3$) of polymer family P1 and P2 obtained from BPSO. The corresponding electronic properties viz., IP, EA and E_g and electronic delocalization (IPN) are also reported along with the fitness values of optimum solutions so returned from algorithm

Systems	Optimized composition	IP (eV)	EA (eV)	E_g (eV)	IPN	Fitness value f(x)
$P1_{b1}$	$P_{19}Q_{81}$	8.825	1.354	7.471	0.00913	0.98991
$P2_{b1}$	$M_{99}N_1$	7.588	3.062	4.526	0.00621	0.99370
$P1_{b2}$	$P_{99}R_1$	9.499	1.361	8.138	0.00739	0.99255
$P2_{b2}$	$M_{99}K_1$	7.588	3.062	4.526	0.00749	0.99249
$P1_{b3}$	$Q_{72}R_{28}$	8.826	0.888	7.938	0.01025	0.98952
$P2_{b3}$	$N_{85}K_{15}$	7.605	2.839	4.766	0.00870	0.95479

IPN values so reported for the respective copolymers indicate the extent of delocalization which influence charge carrier mobility. The fitness values depict the strength of the optimal solutions so found by BPSO procedure. The resulting percentage composition of the constituent homopolymers in the respective binary and ternary copolymers corresponds to a minimum band gap value and a highly delocalized polymer chain configuration.

Molecular modification has been an efficient tool for controlling the HOMO and LUMO energy levels and hence the electronic properties. IP value (corresponding to top of VB) is a measure of the polymer's ease towards acceptor doping while EA value (corresponding to bottom of CB) indicates the relative inertia of the polymer structure towards donor doping. While E_g determines the intrinsic conductivity of the polymer backbone.

The system $P1_{b1}$ is a binary type II staggered copolymer derived from PTP and PPY. The optimized composition ($P_{19}Q_{81}$) returned by BPSO indicates that a higher percentage of homopolymer Q (or PPY) results in a low band gap copolymer conferring high intrinsic conductivity. Moreover, it is important to point out that amongst the two homopolymers, PPY is the one with lower IP (8.826 eV) as is noticeable from their relative band alignments (Fig. 3a). Hence, we come to a conclusion that PTP–PPY copolymer with a higher percentage of pyrrole backbone is expectedly labile towards p-doping.

The optimized solution ($M_{99}N_1$) obtained from BPSO for the copolymer $P2_{b1}$ (benzene analogue of PTP–PPY) is found to contain a higher percentage of thiophene based units PITN, which has a lower IP value (7.588 eV) in comparison to PIBP. Such an observation is in contrast to the solution obtained for copolymer $P1_{b1}$ because of the fact that benzene substitution on the polymer backbone alters the electronic properties of the respective homopolymers as is evident from their band alignments (Fig. 3b)

transforming the PITN–PIBP system to type I copolymer. This benzene substitution lowers the IP of thiophene based moiety by 1.911 eV while that of pyrrole skeleton is reduced by 1.22 eV. It means that benzene substitution stabilizes the thiophene structure more than pyrrole. This must be because of the participation of $3d$ electrons of sulfur atom (absent in the case of nitrogen) resulting in effective coupling with neighboring π electrons, thereby enhancing electron delocalization in the polymer backbone. Further, on comparison of the electronic properties of copolymer $P2_{b1}$ with $P1_{b1}$, it is found that IP of this copolymer is decreased by 1.2 eV while EA has increased by more than twice the previous value. This implies that the PITN–PIBP copolymer is expected to be a better candidate for n-doping allowing relatively easier gain of electrons. This significant increase in EA value notably lowers the band gap of the resulting copolymer (by almost 2.9 eV).

Another binary copolymer investigated comprises of PTP and PFU, i.e., system $P1_{b2}$. The optimized solution ($P_{99}R_1$) returned by BPSO is found to contain the maximum amount of thiophene units, PTP which has lower IP value (9.499 eV) than PFU. Replacement of one component in the $P1_{b1}$ system PPY by PFU results in a copolymer $P1_{b2}$ having higher IP, higher EA and higher band gap in comparison to copolymer $P1_{b1}$. This is because the electronic structure so deduced for PFU is influenced by the chemical nature of the heteroatom (oxygen) giving a higher IP value and lower EA value than PTP (sulfur) as indicated by their respective band alignments (Fig. 3a). Hence forth, the electronic structure of the copolymer is strongly dominated with higher percentage of PTP. Therefore, we conclude PTP–PPY combination more conducting than PTP–PFU copolymer. However, the electronic properties of copolymer $P1_{b2}$ are better in comparison to their parent homopolymers.

The optimized result ($M_{99}K_1$) obtained from BPSO for benzene substituted PTP–PFU type I copolymer (system $P2_{b2}$) is yet again found to contain higher amount of thiophene based units, PITN, which have lower IP value (7.588 eV) than the other furan based units PIBF, as is the case of their un-substituted copolymer $P1_{b2}$. Hence from the results obtained for copolymer $P2_{b1}$ and $P2_{b2}$, we conclude PITN to have more intrinsically conducting and delocalized electronic structure in comparison to PIBP and PIBF. A more or less similar kind of pattern is observed in the electronic properties of copolymer $P2_{b2}$ in comparison to $P1_{b2}$, as is observed for $P2_{b1}$ relative to copolymer $P1_{b1}$. The IP value has decreased by 1.9 eV while the EA value has increased by 1.7 eV, thereby lowering the band gap by 3.6 eV. As a result, this benzene substituted copolymer $P2_{b2}$ has increased conductivity as well as p- and n-dopant philicity in comparison to its parent copolymer $P1_{b2}$.

The other binary combination possible is that of pyrrole and furan units. The optimized composition ($Q_{72}R_{28}$) returned by BPSO for type I copolymer (PPY–PFU) $P1_{b3}$ system containing a higher proportion of pyrrole moiety forms a lower band gap copolymer, with PPY having lower IP value (8.826 eV) in comparison to PFU. The IP value of the resulting copolymer is found comparable to that of system $P1_{b1}$, with pyrrole being the common and lowest IP component in both the cases whereas it is lower than that obtained for copolymer $P1_{b2}$, favorably making copolymer $P1_{b3}$ p-dopant philic. However, the EA value (0.888 eV) is found to be much lower than copolymers $P1_{b1}$ and $P1_{b2}$. In all, copolymer $P1_{b3}$ has electronic properties suitably tuned between those of its constituent homopolymers conferring high conductivity to the system.

The benzene substituted type II staggered copolymer $P2_{b3}$ of PPY and PFU so designed by BPSO returns a configuration ($N_{85}K_{15}$) containing higher volume of pyrrole based units PIBP, with PIBP having lower IP (7.606 eV) than PIBF. Hence, copolymer with a higher percentage of PIBP is expected to deliver a better conducting system with lower band gap. On comparing the electronic properties of copolymer $P2_{b3}$ with its parent copolymer $P1_{b3}$, it is found that IP value has decreased by 1.2 eV while EA value has increased by more than three times the parent copolymer value, increasing the n-dopant philic nature of this system. As a result of this substantial increase in EA value, the band gap of the system decreases by 3.1 eV. Although the IP, EA and E_g values of copolymer $P2_{b3}$ are suitably tuned in comparison to its parent homopolymers, however, this copolymer configuration is less conducting with higher IP, lower EA and higher E_g values in comparison to copolymers $P2_{b1}$ and $P2_{b2}$.

A comparative pictorial representation of electronic properties viz., HOMO levels, LUMO levels and band gap values of the above discussed binary heteroaromatic copolymers and their benzene analogues so obtained using BPSO algorithm is shown in Fig. 4. The band gap value of the un-substituted homopolymers increase in the order PTP < PFU < PPY (Fig. 3a) while that of the copolymers increase in the order $P1_{b1}$ < $P1_{b3}$ < $P1_{b2}$. With thiophene being the lowest band gap component amongst the homopolymers, copolymer containing maximum amount of pyrrole skeleton in the polymer chain is obtained with lower band gap. This is because the PPY has the lowest IP amongst the others. Now comparing the benzene analogues with their copolymers, it is found that the band gap increases in the order PITN < PIBF < PIBP and for their copolymers $P2_{b1}$ = $P2_{b2}$ < $P2_{b3}$. Over here, thiophene based units are found to be present in maximum amount in the resulting low band gap solutions, consistent with the trend observed in their parent structures with PITN being the lowest band gap and lowest IP component.
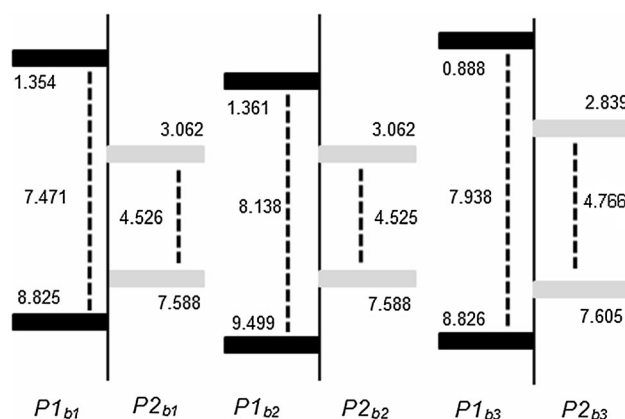

Fig. 4 Pictorial comparison of optimized electronic properties of binary heteroaromatic copolymers (P1) and their benzene analogues (P2) obtained from BPSO algorithm

The electronic DOS curves obtained for all the six binary copolymers corresponding to the optimized solutions are shown in Fig. 5 consisting of broad regions of allowed energy states as the units in the copolymer sequence are randomly arranged with the neighboring environment changing for each respective unit. The comparative picture drawn above between heteroaromatic copolymers and their benzene substituted analogues is also clear from the DOS curves. It can be seen that the energy separation between the array of VB and CB peaks of each respective heteroaromatic copolymer ($P1_{b1}$, $P1_{b2}$, $P1_{b3}$) has decreased after benzene substitution ($P2_{b1}$, $P2_{b2}$, $P2_{b3}$), suggestive of enhanced intrinsic conductivity in the respective benzene substituted copolymers.

In general, the IPN values prognostic of electronic delocalization in the copolymer backbone obtained for benzene substituted heteroaromatic copolymers are found to be better than their un-substituted counterparts. These values of the order of 10^{-3} reveal the maximum level of electronic delocalization over the entire polymer backbone imparting high charge carrier mobility.

With this broad overview on all possible binary combinations in each respective polymer family, we attempted to tailor ternary copolymers using the same BPSO algorithm with the same set of parameters for which the results are reported in Table 3. The optimized solution ($P_{16}Q_{83}R_1$) obtained for PTP–PPY–PFU copolymer $P1_t$ yet again reveals that the presence of maximum proportion of pyrrole moieties in the resulting copolymer forms a low band gap and highly delocalized structure, enhancing intrinsic conducting power of the system. As observed in the case of binary copolymers, homopolymer Q (or PPY) has lowest IP value (8.826 eV) amongst the three homopolymers and is present in major amount in the optimized composition. While component R (or PFU) having highest IP value (9.740 eV) is present in least amount. The same ternary

Fig. 5 DOS distribution in the valence band and conduction band regions of the binary copolymers $P1_{b1}$ and $P2_{b1}$, $P1_{b2}$ and $P2_{b2}$, $P1_{b3}$ and $P2_{b3}$ for the corresponding optimal solutions obtained from BPSO
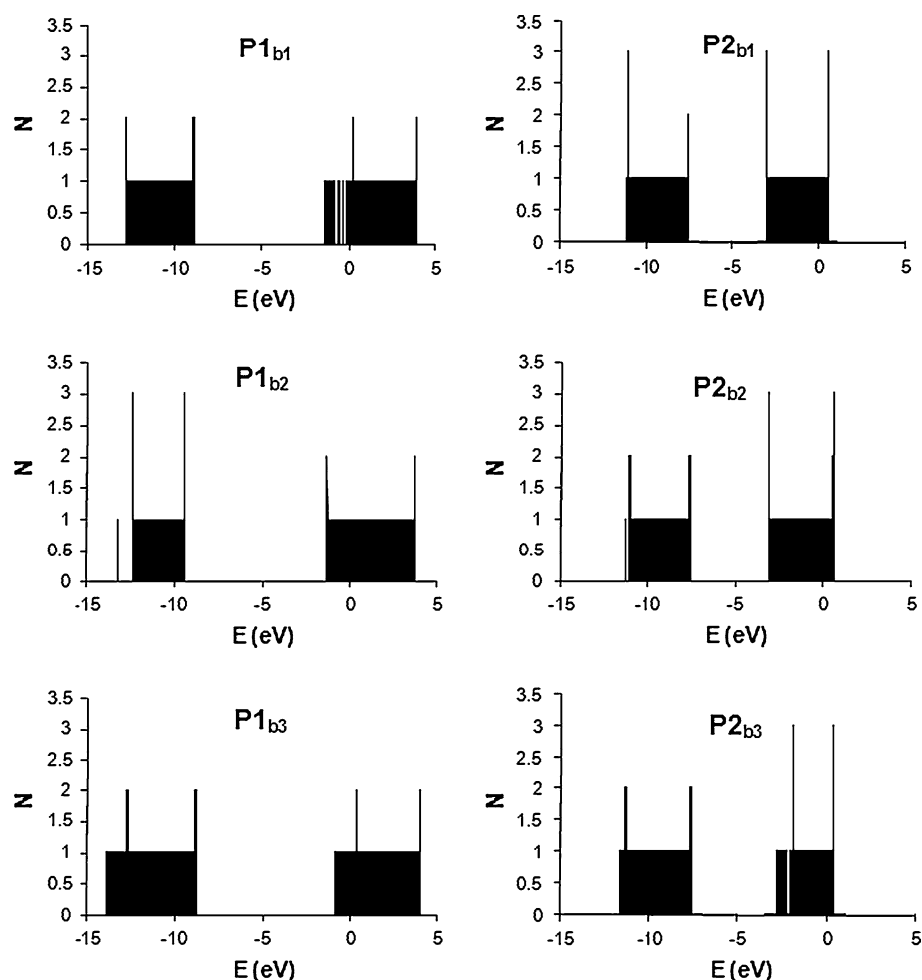
copolymer has been investigated using genetic algorithm (GA) for which the best solution reported gives more or less a similar kind of trend in terms of relative compositions and electronic properties [44]. However, the optimized copolymer compositions derived by BPSO and GA are different as each correspond to a different molecular arrangement of the constituents in the copolymer chain. Importantly, this BPSO and GA comparison acknowledges the fact that these copolymer compositions corresponding to optimal electronic properties are worth experimental attention as both the meta-heuristics working in their own fashion converge accordingly to a similar kind of solution.

Comparing the optimized results of copolymer $P2_t$ with that of $P1_t$, it is found that the resulting composition ($M_{98}N_1K_1$) so returned by BPSO contains maximum volume of PITN, component with lowest IP value in its array of combining homopolymers PIBP and PIBF. Hence, we come to the same conclusion that benzene substitution on thiophene moiety in comparison to pyrrole and furan leads to greater electron delocalization due to the participation of $3d$ electrons on sulfur (which are absent in the case of nitrogen and oxygen). The IP value of copolymer $P2_t$ has

Table 3 Optimum percentage compositions of respective homopolymer units in the ternary copolymers $P1_t$ and $P2_t$ and their corresponding electronic properties viz., IP, EA and E_g, electronic delocalization (IPN) and fitness values obtained from BPSO

Systems	Optimized composition	IP (eV)	EA (eV)	E_g (eV)	IPN	Fitness value f(x)
$P1_t$	$P_{16}Q_{83}R_1$	8.826	1.350	7.476	0.00891	0.98963
$P2_t$	$M_{98}N_1K_1$	7.587	3.062	4.525	0.00752	0.99246

decreased by 1.2 eV relative to un-substituted copolymer while EA value has increased by 1.7 eV. This decrease in IP and increase in EA leads to a decrease in band gap value by 2.9 eV. The trends in the DOS of copolymer $P1_t$ and $P2_t$ are shown in Fig. 6. Further, IPN values indicate better electronic delocalization in copolymer $P2_t$ in comparison to $P1_t$ as has been the case for binary copolymers, reason being the benzene substitution on the polymer backbone which leads to a higher degree of quinoidal character due to various possible resonance structures as shown in Fig. 7.

Fig. 6 DOS distribution curves for the ternary copolymers P1$_t$ and P2$_t$ for the corresponding optimal solutions obtained from BPSO
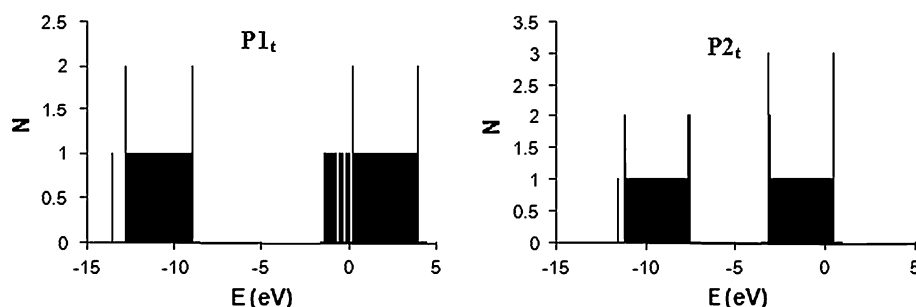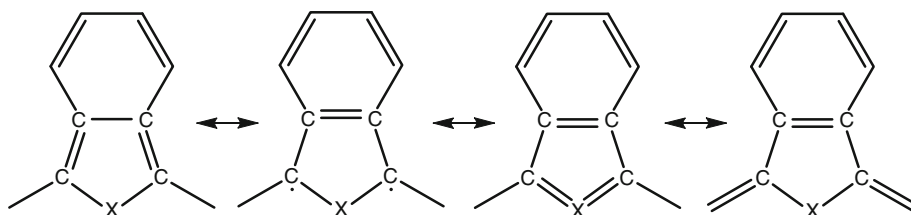

Fig. 7 Various resonance structures of benzene substituted heteroaromatic unit cell (X = S, NH, O)

In both these ternary copolymers, the compositions so returned contain the least amount of furan based units which although has a lower band gap relative to its nitrogen counterparts. This is because the band gap value of the homopolymers is not the ultimate criterion for determining the best composition of the copolymer. The band alignments, bandwidths and band gaps of the respective homopolymers, all influence the electronic properties of the copolymers. The α and the β values of the homopolymers so used in our work take into account band alignments, band gaps and bandwidths of the combining homopolymers for a given copolymer system which has been derived taking due account of the chemical nature of the heteroatom in the respective polymer system.

On the whole, we can say that, the nature of the heteroatom as well as the substitution on the polymer backbone more significantly alters the LUMO energies (EA values) than HOMO energies (IP values). Also, the low band gap copolymer composition so obtained in each respective case accommodates highest proportion of the lowest IP value component. This means HOMO energies have a more decisive influence than LUMO energies on the relative fraction of the constituents that make up the respective low band gap copolymer. The benzene substituted copolymers so designed have lower IP values, higher EA values, lower band gap values and more delocalized structures than their un-substituted counterparts because of extended π-conjugation in the chain, which in turn leads to better charge transfer within the backbone.

Analysis of BPSO algorithm

With the goal to blueprint molecular code of low band gap copolymers, BPSO methodology so integrated with a reasonable choice of parameters is potent to return good solutions in reasonable times with an effective exploration of the search space and efficient exploitation of the best solutions. Figure 8 shows the exploration skills of the algorithm for the copolymer P2$_{b1}$, where the entire range of solutions explored for the copolymer is displayed in reference to the number of fitness evaluations, sketching the movements of the entire swarm over the available search space. The swarm so well distributed over the search space is indicative of good exploration skills of the algorithm making it less probable to get stuck into local optimal solutions giving the opportunity to cover a range of good solutions in the given area. A similar kind of trend is observed in all the cases so investigated. The complexity of this problem increases on moving from binary to ternary system, where the number of possible outcomes increases demanding more careful and intelligent examination. With a population size of 20 and a converging limit of 20 movements, the algorithm returned best solution for ternary copolymer P2$_t$ after 23 iterations, i.e., after 460 fitness evaluations. Figure 9 displays the swarm fitness profile for copolymer P2$_t$ where *pbest* positions in one dimension are plotted against number of iterations. It is observed that at each successive movement all the respective particles evolve towards better solutions (or positions), thereby promising to return a global best solution. Moreover, the algorithm at the end results in a swarm of good solutions, giving a choice to select from for respective use or application.

Program efficiency in terms of runtime is an objective matter. Analysis of a program can be done on the basis of computer configuration (single/multiprocessor, read/write speed of the memory etc.) or the nature and size of the input data. With the evolution of 5th generation computing systems, computer configuration has not much to affect the
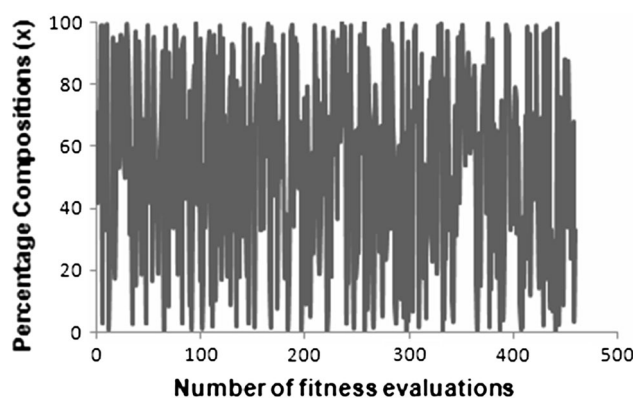
Fig. 8 Exploration of solution search space by the swarm with respect to fitness evaluations (copolymer P2$_{b1}$)
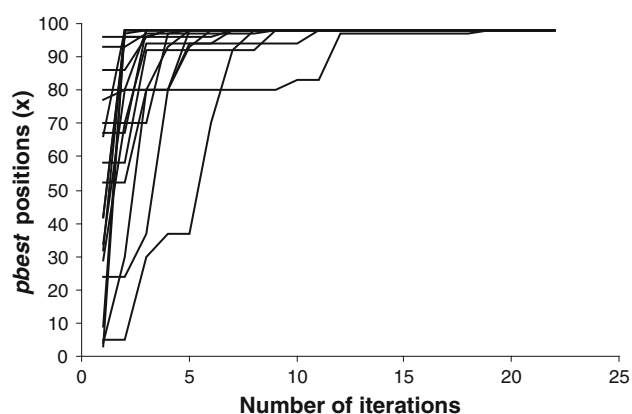

Fig. 9 Plot of the *pbest* solutions exploited by the swarm with increasing iterations (copolymer P2$_t$)

runtime of an algorithm. And therefore, the algorithm runtime complexity is concerned with how fast or slow the *in-silico* operation performs for a given set of inputs.

The amount of data given as input to the program in terms of polymer problem include chain length, band structure parameters, type of copolymer chain etc. and PSO algorithm includes population size, termination criteria, fitness function etc. The most important algorithm parameter is the termination criterion which is taken as "Unchanged *gbest* value over 20 iterations". With all the other algorithm parameters being constant, the termination criterion is the only algorithmic parameter that may vary for every independent run of the program for a given set of band structure parameters. With increasing solution space complexity or in simple words, for a large number of combinations of constituents possible in a multi-component system, the best solution may not be returned by the program in first 20 iterations. With the lower limit as 20 and upper limit as 10,000, the runtime of program $T(n)$ has been estimated taking n as the number of iterations required for termination as

$$T(20) \leq T(n) \leq T(10000)$$

This means, in every iteration a swarm is generated and the desired operations are performed and the results are evaluated. The present *gbest* value is compared to last *gbest* value with a counter maintaining the record. If the counter strikes 20, program is terminated implying attainability of desired convergence criterion else positions are updated and another iteration is initiated. The upper bound for number of iterations has been set to 10,000 to avoid termination over local best solution of the search process. However in this study, the values of n obtained for copolymers P1$_{b1}$, P1$_{b2}$, P1$_{b3}$, P2$_{b1}$, P2$_{b1}$, P2$_{b2}$, P2$_{b3}$, P1$_t$ and P2$_t$ are 22, 23, 24, 23, 23, 30, 22 and 22, respectively. The runtime analysis for each independent run shows that on termination criterion not been satisfied the program reruns the entire set of operations again implying linear variation of $T(n)$ with n. With this we conclude the runtime of this methodology to be factor of n.

$$T(n) \propto n$$

The average runtime of this algorithm for designing binary and ternary copolymers comes out to be approximately 2 and 4 h respectively, with the difference being very much significant if compared to the synthesis and analysis of each possible combination which may take days or months. Also, it is worth mentioning that the time taken for exhaustive approach viz., systematic search of all possible combinations to find the best solution takes approximately 4 h for binary combinations and approximately 8 h for ternary combinations. Therefore, PSO with reasonable average runtime of 2–4 h not only help analyze good results but also provide a simplified route towards e-architecturing of various other materials anticipating the properties of interest. Hence, we can say that this versatile and computationally efficient nature inspired simulation approach viz., PSO algorithm is time and effort-saving without compromise on accuracy.

Conclusions

In this study we have designed novel binary and ternary low band gap copolymers based on thiophene, pyrrole and furan frameworks using the particle swarm optimization methodology. A comparative examination of electronic properties of neutral heterocyclic copolymers and their benzene substituted analogues is inferred. The optimized relative percentage composition of constituent homopolymers so returned by BPSO algorithm fit the criterion so defined assimilating low band gap value and extended π-delocalization in the copolymer backbone.

The fusion of benzene ring onto the heterocyclic skeleton has effectively increased quinoid contributions to the electronic structures thereby decreasing the IP value and increasing the EA value of the respective systems which inherently is seen in the electronic properties of the benzene derived copolymers having lower band gap value and hence more conductivity than their un-substituted counterparts. The enhanced π distribution in benzene substituted polymer backbone also precipitates enhanced electronic delocalization in the polymer chain which leads to better charge transport properties. In general, such a substitution and copolymerization scheme is not only worthy of stabilizing the energy levels but can also help improvise chemical and physical properties of the polymer backbone giving good opportunity for easy synthesis.

An examination of the evolution of the electronic properties of the copolymers shows that both the heteroatom substitution as well as substitution on carbon skeleton significantly alters the EA values, however, IP values are more strongly influenced by backbone substitution. Furthermore, it is found that the relative proportion of components that make up the respective low band gap copolymer is dependent on the IP values of the combining homopolymers. It is, therefore important to acknowledge that IP values of combining constituents are fateful in deciding the relative compositions of the respective copolymers. A comparative study reveals copolymer family P2 more conducting than copolymer family P1. Conjointly, the DOS distributions of the investigated copolymer systems give a similar qualitative picture of the trends in the electronic properties.

It is observed that pyrrole in copolymer family P1 is the lowest IP value component and is present in maximum percentage while in copolymer family P2, thiophene derived component PITN has the lowest IP value and largest proportion in optimized compositions so reported. This thiophene moiety becomes more stabilized on benzene substitution because of greater electron delocalization due to the participation of 3d electrons on sulfur (which are absent in the case of nitrogen and oxygen). Also, furan and its benzene derived unit have the highest IP value in each respective case and are found present in the least amount in the resulting systems. Oxygen being more electronegative than sulfur and nitrogen strongly drags the electrons towards itself thereby diminishing the π- electron delocalization in the polymer. En masse, we can say that both the choice of the heteroatom and the nature of the substituent attached to the polymer backbone have a multiform influence on the electronic properties of the copolymers.

Investigations are being carried out with some other appropriate substitutions on the polymer backbone to make them intrinsically more conducting and also to make them better candidates for p- and n-doping. From these systems, it is found that PITN is the sturdiest candidate for p-doping and n-doping. Therefore, a higher percentage of PITN backbone is obtained as the best solution.

This theoretical blueprinting of copolymer compositions corresponding to optimal electronic properties using BPSO algorithm is not only computational cost effective but also labor and time saving without costing precision. The effectiveness of BPSO algorithm is itself illustrated by the texture of the results reported where the numerical outcome of the process is evaluated and upgraded by the algorithm considering values up to three to five decimal places. Another factor that adds to the efficiency of the process is the fitness based evaluation which drives the swarm towards quality improvements. Such a skilful harmony set up between the PSO algorithm and polymer problem can help streamline scrupulous synthetic efforts providing an economical and potent route for molecular engineering of sustainable and efficient electronic materials. In all, this nature inspired particle swarm optimization so employed strengthens the numerical techniques viz., NFC and IIM for designing conducting copolymers simplifying the task in comparison to systematic search which involves rigorous examination of all the possible outcomes. An aptitude towards such an intelligent artificial intelligence technique in undeniable for the fact that such a methodology not only serves as an important aid for experimentalists but also help deduce finer details of structural influence on electronic properties.

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