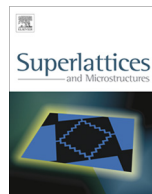




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# Designing novel copolymers of donor–acceptor polymers using an artificial intelligence method

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## ABSTRACT

Using the *ab initio* Hartree–Fock crystal orbital results of three donor–acceptor polymers, PFUCO ( $[A]_x$ ), PSIFCO ( $[B]_x$ ) and PSIFCH ( $[C]_x$ ), the electronic properties of their novel quasi-one-dimensional copolymers  $(A_mB_n)_x$  and  $(A_mC_n)_x$  were investigated using an artificial intelligence technique, the genetic algorithm, in combination with negative factor counting and inverse iteration method. The repeat units in PFUCO consist of bifuran bridged by electron accepting groups Y ( $>C=O$ ); while in PSIFCO and PSIFCH, the repeat units consist of bicyclopentadifluorosilole bridged by electron accepting groups Y (Y is  $>C=O$  in PSIFCO, and  $>C=CH_2$  in PSIFCH). The trends in the electronic properties of the copolymers  $(A_mB_n)_x$  and  $(A_mC_n)_x$  as a function of block sizes  $m$  and  $n$ , and arrangement of units (periodic and random) in the copolymer chain are also discussed. The results obtained are important guidelines for molecular designing of copolymers with tailor-made conduction properties.

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## 1. Introduction

Conducting polymers have attracted a great deal of attention ever since their discovery by Hellström et al. [1]. In recent years, there has been tremendous research interest in the synthesis [2] and theoretical designing [3] of low band gap organic conjugated polymers because of the versatile properties of these materials which combine the high conductivity of pure metals with properties like resistance to corrosion, lighter weight and easier process ability. These features make them one of

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the most widely applicable materials. Their applications include super capacitors, electronic devices, organic light emitting diodes (OLED), optical devices, electrochromic windows, anti-static coatings, sensors, batteries, solar cells, artificial muscles, memory devices, imaging materials, nano switches and transistors [4–8]. The chemical structures of these organic conjugated polymers can be manipulated in several ways to obtain desired properties though their limited process ability continues to remain a major drawback with conducting polymers.

One of the promising routes for designing [9] low band gap organic conjugated polymers is through donor–acceptor (D–A) polymerization. A donor–acceptor polymer consists of a regular alternation of donor (electron rich) and acceptor (electron deficient) moieties along a conjugated backbone. These moieties may be hetero atoms or some other groups. A regular arrangement of such repeat units in the  $\pi$ -conjugated chain significantly decreases the HOMO–LUMO separation. The band gap of a D–A polymer is expected to be the lowest for that particular combination in which the electronegativity difference between the donor and acceptor moieties is the highest. The stability of such polymers is also believed to be considerably higher because of  $\pi$ -conjugation in the chain. Moreover, substituents can be easily introduced in such systems via electrophilic substitution reactions. Nature of hetero atom also significantly changes the optical and electronic properties of the donor–acceptor polymer. With the result, there is vast scope of chemical engineering at the molecular level (of the polymer) in order to fine tune the properties of the D–A polymer.

Copolymerization is a very efficient strategy for designing of polymers having properties intermediate between those of the constituent homopolymers. In the present study, we have combined the strategy of copolymerization with that of D–A polymerization to investigate the conduction properties of copolymers of D–A polymers. D–A polymers offer several advantages as compared to their carbon-analogues. Using this approach, several copolymers have been successfully synthesized, possessing band gap around 1 eV [10]. Quantum mechanical calculations have also been performed by several theoreticians in this regard [11]. In the present study, we attempt to design novel binary copolymers of donor–acceptor polymers based on furan and silole moieties. Our target is to attain a copolymer which has a minimum band gap value and hence maximum intrinsic conductivity.

Much attention has been focussed on siloles as target molecules in the field of material science because of their unique electronic properties and potential applicability to organic electronic devices. Amongst various heteroles, siloles have exceptionally low-lying LUMO level arising from  $\sigma^*$ - $\pi^*$  conjugation [12]. The low lying LUMO levels of siloles confer upon their polymers characteristic low band gaps. The  $\sigma^*$ - $\pi^*$  conjugation gives siloles and their derivatives unique  $\pi$ -electron systems, especially in contrast to the  $\pi$ -electron excessive heteroaromatic systems like furan, thiophene and pyrrole. Thus, incorporation of silole based homopolymer units into a copolymer is expected to further lower the LUMO levels and hence impart quite different electronic structures and properties from those of the conventional heteroaromatic systems like polyfuran (PFu), polythiophene (PTh), etc. It has also been experimentally established using UV–visible absorption spectra studies that there is lowering of the LUMO level in  $\pi$ -conjugated copolymer systems due to increase in the silole content [13]. Several methodologies have been worked out by research groups across the world to synthesize polysilanes and their derivatives [14]. Many new silole derivatives are being structurally modified and especially fabricated [15] for making efficient OLEDs and optoelectronic devices.

Polyfuran, on the other hand, has attracted less attention as compared to its contemporary heterocyclic polymers because the former is synthesized with some difficulty. Due to high oxidation potential of furan, it is generally observed that cleavage of furan ring occurs during electro polymerization, hence breaking the expected  $\pi$ -conjugated structure [16]. The resulting polymer obtained is either dielectric or has very low electrical conductivity. Therefore, copolymerization is an important method to modify the properties of the individual homopolymers. Electrochemical copolymerization of furan and 3-methyl thiophene has been successfully performed with the resulting polymer having electrical conductivity  $0.36 \text{ S cm}^{-1}$  [17]. Recently, DFT has been used by Vivas-Reyes et al. [18] to study electrical conducting properties of substituted furan oligomers. They have established that furan-based substituted polymers can be obtained with less difficulty than the non-substituted polymer and present lesser  $E_g$  value.

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