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REGULAR ARTICLE

Heuristic approaches to the optimization of acceptor systems in bulk heterojunction cells: a computational study

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Abstract A computational protocol combining a heuristic search based on genetic algorithms (GAs) and quantum chemistry methods is implemented and applied to a family of acceptor compounds based on the 9,9′-bifluorenylidene backbone, to be coupled with the poly-3(hexylthiophene) polymer (donor) in a bulk heterojunction solar cell. Highly performing candidates are generated via GA from an initial generation, after a number of iterations (i.e., new generations), under the selective pressure of electronic constrains calculated at density functional theory level. The combination of heuristic search techniques and advanced electronic structure methodologies for characterization seems to be amenable to further applications in the field of molecular design.

Keywords Organic photovoltaics · Solar cells · Density functional theory · Genetic algorithms

1 Introduction

Computational chemistry can be a useful tool in helping to design a new molecular structure with defined electronic or structural properties. Usually, however, the search space is non-linearly dependent upon the problem dimensions. Standard optimization methods must make way to alternative approaches. For this reason there is a considerable interest in heuristic techniques that can usually find a near-optimal, or even just a reasonable solution in an acceptable computational time. A large class of techniques is based on genetic algorithms (GAs) [1], which are stochastic global optimization methods [2] inspired by the biological mechanisms of evolution and heredity, implementing processes such as mutation, selection, crossover, etc. The versatility of GAs lies in their flexibility and potential applicability to a wide range of problems [3, 4]. Recently, the application of GAs to computational chemistry and biology has spread considerably. Examples of computer-aided molecular design are reported by Clark [5] and Parrill [6]. Several GAs-based studies are related to the investigation of biomolecules [7–9]. Other examples are focused on the conformational analysis of small molecules [10], inclusion complexes [11], structure of interfaces [12], evolution of catalysts [13], and parameterization of NDDO wavefunctions [14].

We present here a computational study based on the combination of GA search and direct evaluation of molecular electronic properties via quantum mechanics (QM) methods. Previous combined applications of GAs and QM and/or molecular mechanics (MM) calculations are mostly concerned with the optimization of force field parameters [15–19] or energy minimization [20–23]. Arora [24] investigates via GA/QM methods novel ternary copolymers of donor–acceptor polymers [3] and polypeptide chains [24], and Cartensen [25] employs a GA approach to tune two excitation wavelengths of a molecular switch backbone.

In this work, we use a GA approach combined with QM calculations to optimize a family of acceptor compounds based on the 9,9′-bifluorenylidene backbone, to be coupled with the poly-3(hexylthiophene) (P3HT) polymer (donor) in a bulk heterojunction (BHJ) solar cell. We consider a

Dedicated to Professor Vincenzo Barone and published as part of the special collection of articles celebrating his 60th birthday.

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fixed backbone and explore the combinations of different substituents. Exploration of this "virtual chemistry space" of combination is rather large, over a million of possible molecules, and the problem can be suitably tackled with GAs methodologies. Interest in designing organic components of solar cells has spurred a considerable amount of theoretical and experimental studies in the last decade. Several strategies have been set up to improve the performance of these devices, but the screening of candidate molecular systems and of specific molecular properties can still be considered a bottleneck [26].

The paper is organized as follows: in Sect. 2 the molecular system is described; Sect. 3 summarizes the computational approach. In Sect. 4, results are presented and discussed.

2 Molecular system

We explore the design of acceptor compounds based on the 9,9′-bifluorenylidene (99′BF) backbone (Fig. 1a), which can be coupled with the P3HT polymer acting as donor in an ideal BHJ solar cell device. These systems have been proposed by Brunetti [27]. Since the idea of bulk heterojunction (BHJ) organic solar cell emerged over one decade ago [28], there has been an intense activity in this field [29]. Organic solar cells based on BHJ are particularly attractive due to their mechanical flexibility and potential low cost [30]. They are based on photoinduced charge transfer from an electron-donating material, such as a hole-conducting and light-absorbing polymer, to an electron-accepting component, typically fullerene (c60) [27]. The typical structure of these devices consists of an interpenetrating network of electron acceptor and donor material, sandwiched between two electrodes having different work functions [31].

The efficiency of a BHJ is controlled by several factors [32]. The donor must have a small band gap to efficiently absorb light in the visible region of the solar spectrum, i.e., an optimal $|E_{\mathrm{HOMO}-D} - E_{\mathrm{LUMO}-D}|$ separation is typically 2 eV. This value was estimated by Koster [30], Scharber [33], and Lenes [34]. Another factor is the necessity of improving the open-circuit voltage (V_{OC}), i.e., the electronic match between the donor and acceptor component must be optimized in order to minimize unnecessary internal loss of open-circuit voltage. Although the recent literature [35–38] suggests that there is no general consistent understanding of the origin of open-circuit voltage of the BHJ solar cells, experimental evidence reveals a linear relationship between the $E_{\mathrm{HOMO}-D}$ and $E_{\mathrm{LUMO}-A}$ energy difference and the V_{OC} of the bulk heterojunction device [31, 39]. Thus, a promising strategy to improve the BHJ cell efficiency is raising the $E_{\mathrm{LUMO}-A}$ [32]. However, one must take also into account that since after photoexcitation the electron is transferred from the LUMO of the donor to the LUMO of the acceptor, in the extreme case, if the two LUMO levels become too close in energy, the driving force would be lost [34]. An optimal condition turns out to be $\Delta E_{\mathrm{LUMO}} = E_{\mathrm{LUMO}-D} - E_{\mathrm{LUMO}-A}$ of 0.3 eV [33, 40].

On the basis of these considerations, different methods have been employed experimentally to improve the BHJ cell performance by acting on the molecular orbital energies (Fig. 1b): (1) lowering $E_{\mathrm{LUMO}-D}$ results in small-band gap donors that have the capability to absorb a larger part of the solar spectrum; (2) lowering both $E_{\mathrm{LUMO}-D}$ and $E_{\mathrm{HOMO}-D}$. In this case, the bandgap of the donor is constant and the device gains in efficiency due to an enhanced V_{OC}; (3) raising the $E_{\mathrm{LUMO}-A}$, also resulting in an increase of open-circuit voltage [32, 41]. Following these hints, several acceptor molecules have been synthesized and investigated by QM calculations [42].

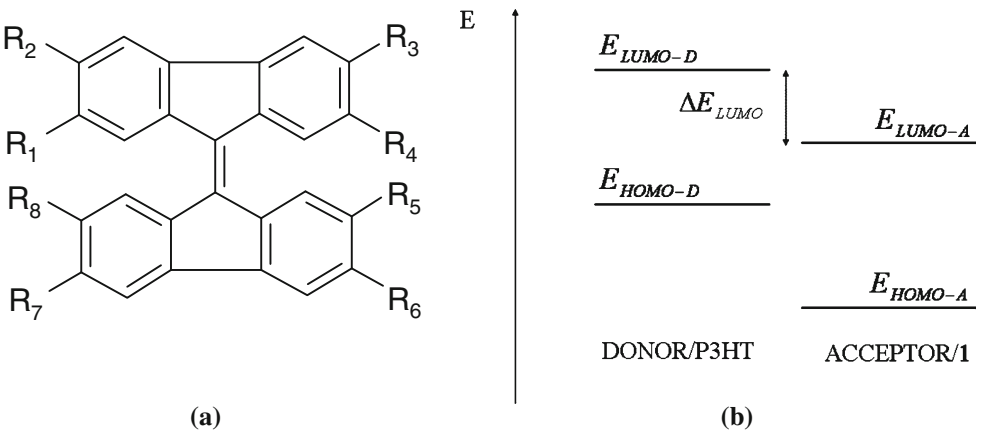

Fig. 1 **a** 9,9′-bifluorenylidene (99′BF) (**1**) and **b** energy level diagram for a donor–acceptor heterojunction

3 Methods

3.1 The genetic algorithm

GAs are global search heuristic techniques, employed currently in optimization problems of large dimensions [24]. The principle of evolution "Survival of the fittest" first described by Charles Darwin is exploited by mimicking the evolutionary principles and chromosomal processing in natural genetics [43], in which the basic idea is to maintain a population candidate solution, which evolves under selective pressure. A fitness value is assigned to every solution (i.e., individual of a given population), which is directly related to the objective of the optimization problem. Each individual (*chromosome*) represents a possible solution to the optimization problem. Chromosomes are commonly encoded as string of integer or binary numbers. An initial population (first generation) is created and the fitness of each individual is evaluated. The next generation is built by selecting individuals from the previous generation, based on their fitness values, and by forming new individuals via suitable *crossover* and *mutation* operators. New generations are created until a stop criterion (e.g., a certain number of generations reached) is fulfilled. In practice, the steps are (1) encoding a representation of the individuals and (2) defining a fitness function to evaluate the individuals. A number of control parameters need to be specified and optimized for each GA implementation; the most relevant are population size, mutation probability (p_m), crossover probability (p_c), the maximum number of generations, the type of selection. In our case, a chromosome corresponds to a combination of substituents and is represented by a string of integer numbers (see below). The roulette wheel parent selection [44] is chosen as a selection operation. Finally, the best performing individuals of the previous generation are always retained (*elitism*) [43]. The GA procedure was implemented in the form of a home-made code (Fortran90). The program works iteratively by (1) generating the input files and submitting them automatically to the Gaussian09 package, (2) analyzing the output Gaussian09 files, and (3) creating a new population (set of chromosomes) and starting again from 1.

3.2 Quantum–mechanical calculations

Molecular systems are characterized in silico as follows, using the Gaussian 09 package [45]. First the geometry of **1** is optimized by an hybrid DFT approach with Becke's three-parameter exchange energy density functional combined with the Lee–Yang–Parr correlation energy density functional, B3LYP and the Pople's 6-31G basis set [46, 47]. In this first accurate optimization process, the eight sites are linked to hydrogen atoms. During the GA search, the optimized geometry is taken as input, with random substituents in the eight available sites. Each individual is optimized by the semi-empirical method Austin Model (AM1). Tests performed randomly of different individuals show that AM1 geometries compare satisfactorily to full B3LYP/6-31G outcomes, but have a considerably smaller computational cost (cfr. Table 1). The energy $E_{\mathrm{LUMO}-A}$ and the total electric dipole moment of each individual are next estimated for the optimized geometry at B3LYP/3-21G level [29].

To examine the impact of the basis set on the accuracy of LUMO energy levels, we tested different basis sets, including the minimum basis sets STO-3G, 3-21G, 6-31G, 6-311G(d,p), 6-311++G(d,p), and a different level of theory, i.e., HF/6-31G. For each model, the optimized geometry is the same. As shown in Table 1, all methods fail to predict $E_{\mathrm{LUMO}-A}$, for the three test molecules T1 (fully hydrogenated parent compound), T2 with sites 1,4,5,8 = OCH_3, and T3 with 2,3,6,7 = OCH_3 (cfr. Fig. 1). $E_{\mathrm{LUMO}-A}$ is overestimated, as expected [48], but the differences between calculated and measured values [27] are roughly constant, within the same basis set. Therefore, we assume as a compromise required by the need of keeping the overall computational time per individual as low as possible that a constant systematic error affects $E_{\mathrm{LUMO}-A}$, as evaluated at B3LYP/3-21G level.

4 Results and discussion

Generations of $M = 24$ chromosomes each are employed. In this preliminary study, runs of $N = 100$ generations are investigated, with no other stop criteria than the completion

Table 1 Calculated and experimental LUMO energy values for the three test molecules T1 (fully hydrogenate parent compound), T2 with sites 1,4,5,8 = OCH_3, and T3 with sites 2,3,6,7 = OCH_3

Level of theory	T1	T2	T3
HF/6-31G[a]	0.77	0.96	0.68
B3LYP/STO-3G[a]	−0.34	0.29	−0.01
B3LYP/3-21G[a]	−2.46	−2.02	−2.31
B3LYP/6-31G[a]	−2.36	−2.02	−2.29
B3LYP/6-311G(d,p)	−2.65	−2.23	−2.54
B3LYP/6-311++G(d,p)	−2.75	−2.34	−2.64
B3LYP/6-31G[b]	−2.36	−2.02	−2.27
Experimental [19]	*−3.37*	*−3.11*	*−3.39*

All the energy values are expressed in eV

[a] Geometry optimized at AM1 level

[b] Geometry optimized at B3LYP/6-31G level

of the allowed number of generations. A chromosome is represented as an array of $m = 8$ possible replaceable positions. Each of the chosen $n = 7$ possible substituent is labeled by an integer number between 1 and n. The chosen substituents are H, Br, Cl, OCH_3, $C(CO)OCH_3$, $N(CH_3)_2$, and NO_2. Identical individuals, with all hydrogens (11111111), made up the first generation. New generations are obtained via a combination of crossover and mutation operations. In particular, the crossover-1-point operator is employed which selects a random cut point [49] and combines the first portion of one parent with the second portion of the other parent to produce two children. Genetic diversity is introduced by random variations or mutations [50]. Different fitness functions are investigated. The total fitness function for the generic α individual ($1 \leq \alpha \leq M$) is defined as the sum of partial fitness functions: $f^{(\alpha)} = \sum_i c_i f_i\left[x_i^{(\alpha)}\right]$ where $f_i\left[x_i^{(\alpha)}\right]$ is the i-th partial fitness (normalized for simplicity in the range $[0, 1]$) defined with respect to the calculated property $x_i^{(\alpha)}$, c_i is the weight for the i-th fitness. The condition $\sum_i c_i = 1$ is imposed, which implies $0 \leq f^{(\alpha)} \leq 1$.

Different selection criteria based are tested, some of them chosen to clarify methodological aspects. The first main criterion is related to ΔE_{LUMO} and it has a direct bearing on the specific problematic of BHJ systems. Next, we consider an additional physical molecular property to be optimized together with ΔE_{LUMO}: for sake of simplicity, we choose the permanent overall electric dipole moment (see below). Finally, we consider a relevant requirement for real-life molecular design, i.e., possible synthetic difficulties. Therefore, we consider an additional constraint which imposes that the substituents must be placed symmetrically with respect to the in-plane molecular axes, which makes the resulting structure considerably easier to synthesize. All together, three cases are considered in this preliminary study:

4.1 Case I

The fitness function depends only on the ΔE_{LUMO} energy gap; the empirical fitness is defined as $f(\Delta E_{\mathrm{LUMO}}) = (1.225 - 0.75\Delta E_{\mathrm{LUMO}})/\mathrm{eV}$ for $0.3 \leq \Delta E_{\mathrm{LUMO}}/\mathrm{eV} \leq 1.63$ and $f(\Delta E_{\mathrm{LUMO}}) = 0$ otherwise. This choice is suggested by experimental data [29]. Below 0.3 eV the transfer from donor to acceptor is no more competitive with respect to other possible processes. The energy of $E_{\mathrm{LUMO}-D}$ for the P3HT polymer is set to -2.7 eV [29]. We have tested four different couples of crossover/mutation probability p_c, p_m equal to (0.8, 0.05) [44], (0.95, 0.01), (0.95, 0.05), and (0.95, 0.025), with and without the presence of elitism.

4.2 Case II

Same as Case I, with symmetry conditions imposed, $R_1 = R_8$, $R_2 = R_7$, $R_3 = R_6$, and $R_4 = R_5$ that are addressed to counter possible actual problems in the synthesis of non-symmetric compounds.

4.3 Case III

The fitness function is taken as $f = [f_1(\Delta E_{\mathrm{LUMO}}) + f_2(\mu)]/2$ where $f_1(\Delta E_{\mathrm{LUMO}})$ is the same as in Case I, and $f_2(\mu) = 0.1\mu/\mathrm{D}$ for $0 \leq \mu/\mathrm{D} \leq 10$ and 0 otherwise, where μ is the total electric dipole moment. Symmetry is imposed. In practice, we look in this case for symmetric molecules with

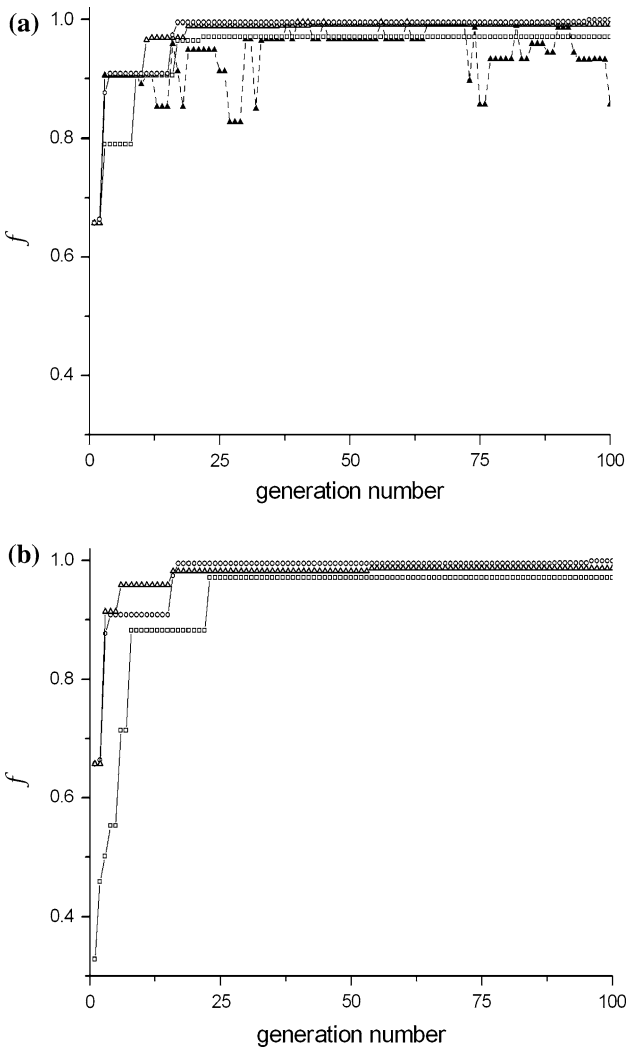

Fig. 2 **a** Evolution of maximum fitness (see text) in Case I for different choices of crossover and mutation probabilities: with elitism and p_c, p_m equal to 0.95, 0.025 (*triangles*), 0.95, 0.01 (*squares*), 0.95, 0.05 (*circles*); without elitism and p_c, p_m equal to 0.95, 0.025 (*filled triangles*) and **b** evolution of maximum fitness with optimized p_c, p_m equal to 0.95, 0.05, with elitism, for Cases I (*circles*), II (*triangles*), and III (*squares*)

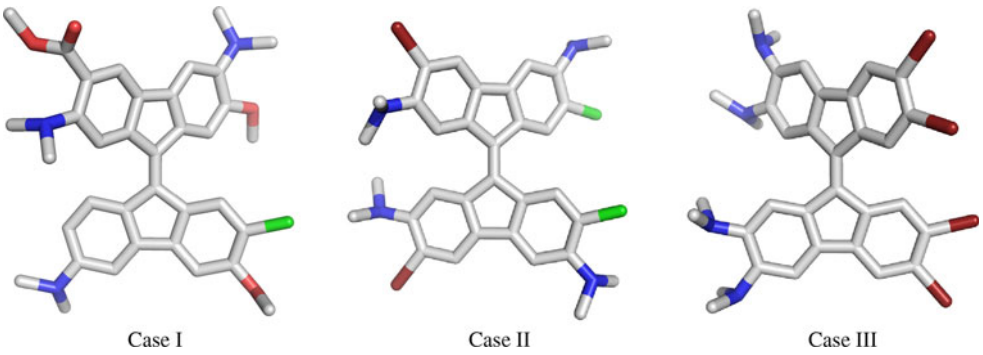

Fig. 3 Best performing selected molecular structures for the studied cases. (*Color code*: *gray* = C, *light red* = O, *dark red* = Br, *green* = Cl, and *blue* = N). H atoms are omitted for clarity

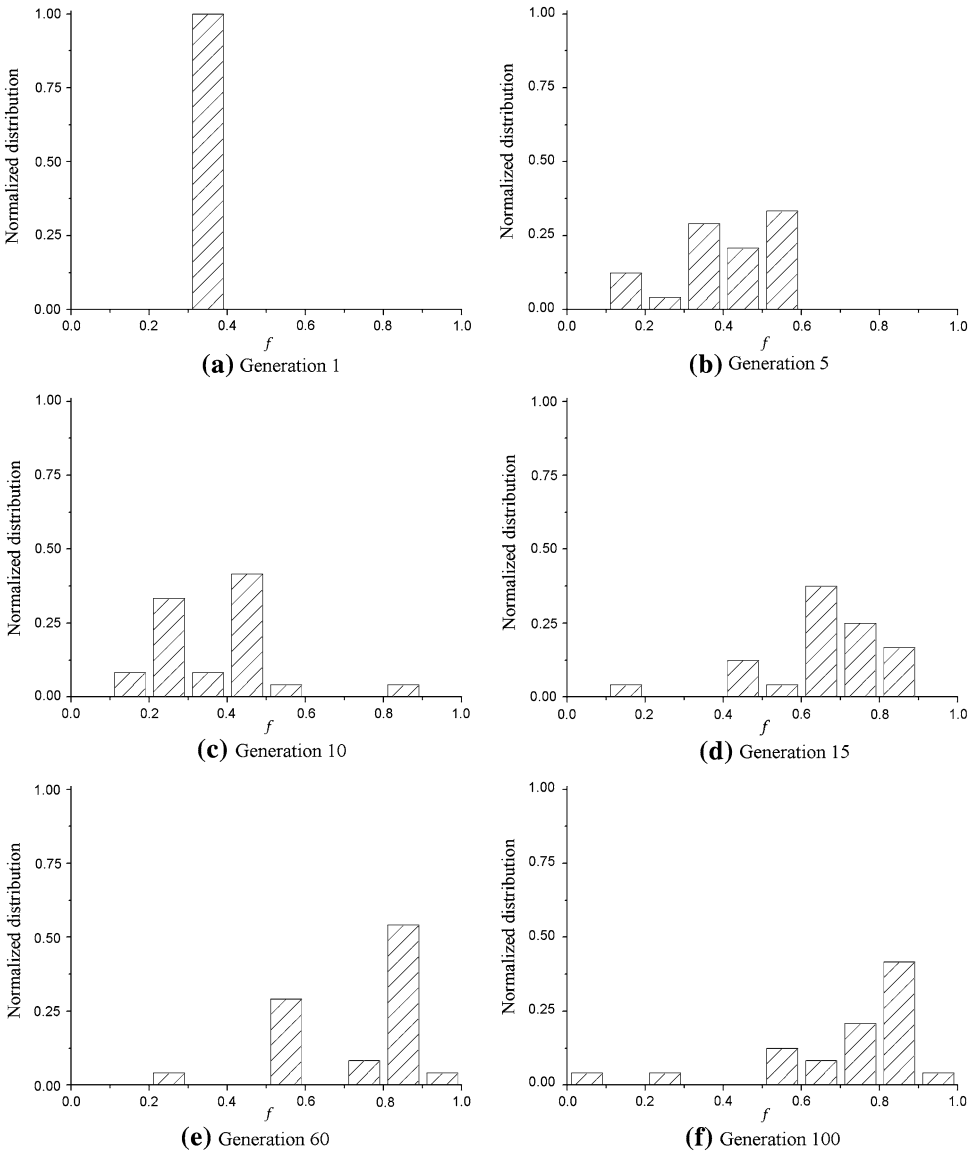

Fig. 4 Normalized distribution of the individuals at different generations for Case III with elitism and p_c, p_m equal to 0.95, 0.05, respectively. **a** Generation 1. **b** Generation 5. **c** Generation 10. **d** Generation 15. **e** Generation 60. **f** Generation 100

a dipole moment close to 10 D (an arbitrarily chosen value) and ΔE_{LUMO} close to 0.3 eV. In contrast with the constrain adopted in Case II, the choice of the electric dipole moment does not play a specific role in BHJ solar cells, but it is illustrative to show the capability and the versatility of the GA procedure.

Adjustment of search parameters is often tricky in GAs searches. Unsatisfactory searches' results are observed for low crossover probability ($p_c = 0.8$) and/or low mutation probability ($p_c = 0.95$ and $p_m = 0.01$). In addition, a high crossover probability ($p_c = 0.95$) is favored. The best results are obtained for $p_c = 0.95$ and $p_m = 0.05$, leading to a fitness function value of 0.9994. Elitism is shown to improve significantly the performance.

The "best" molecular structure in Case I is given by $R_{1,3,7} = N(CH_3)_2$, $R_2 = C(CO)OCH_3$, $R_{4,6} = OCH_3$, $R_5 = Cl$, and $R_8 = H$ with ΔE_{LUMO} equal to 0.3 eV. The GA optimization performance is illustrated in Fig. 2a showing the largest fitness f per generation, $f = \max\left[f^{(1)}, f^{(2)}, \ldots f^{(M)}\right]$, against the generation number for different combinations of crossover/mutation probabilities.

Next, Case II and Case III are explored, and results are summarized in Fig. 2b. Elitism is always included and the set of probabilities $p_c = 0.95$ and $p_m = 0.05$ is used. The "best" individual selected in Case II is characterized by $R_{1,3} = N(CH_3)_2$, $R_2 = Br$, and $R_4 = Cl$. The optimized ΔE_{LUMO} energy gap is 0.32 eV. Case III converges to a molecular structure with substituents $R_{1,2} = Br$ and $R_{3,4} = N(CH_3)_2$. In this case, the ΔE_{LUMO} energy gap increases to 0.38 eV, and the optimized dipole moment is 9.2 D. It is worth to notice that the selected molecular structures have electron donor substituents rather than acceptor group. The "best" individuals for Cases I, II, and III are shown in Fig. 3.

A specific case (Case III, elitism, $p_c = 0.95$, $p_m = 0.05$) has been selected to better highlight the evolution of acceptable solutions throughout generations. Figure 4 has been added showing distributions of fitness values at selected generations (1, 5, 10, 15, 60, and 100). In the x-axis, we reported the discrete step of the fitness function.

We choose a specific case (Case III, elitism, $p_c = 0.95$, $p_m = 0.05$) to illustrate the evolution of the solutions set. In Fig. 4 we show the normalized distribution values of the fitness function at selected generations (generation 1, 5, 10, 15, 60, and 100). The initial generation made of identical individual is naturally peaked around the single fitness value of 0.33. At increasing generation numbers, there is a gradual enhancement of the number of molecules with high fitness function values, although with a significant spread.

In conclusion, the present preliminary study confirms that the combination of heuristic search and in silico characterization may prove of help in selecting classes of molecules with desired structural electronic features, possibly contributing useful suggestions to synthetic efforts, at a minimal computational cost. Notice that in our case the full characterization of a single generation takes one CPU hour on a dedicated cluster; $M = 24$ nodes (four CPU per node) are employed, since the whole procedure is embarrassingly parallelized (one node per individual). The protocol is flexible and easily extendable to diverse molecular systems with specific requirements.

Further explorations are certainly required. The synthesis of the best performing individual obtained in Case II (cfr. Fig. 2a) has already been completed. Inclusion of the selected optimized acceptor molecule in BHJ devices is planned and will be thoroughly tested.

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