

Band Gap Engineering of Conjugated Polymers for Solar Cell Application using Donor-Acceptor Route

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Abstract—The paper focuses on the strategy to design low band gap polymers for organic solar cell application. The main objectives are to identify suitable organic molecules as donor and acceptor moieties, and to model alternate donor-acceptor (DA) monomeric systems based upon their polymers. Initial models are derived from low band gap conjugated systems like polythiophene and some commonly known acceptor and donor groups. A framework for electronic calculations based on *ab initio* and semi empirical methods is proposed. The structural changes needed for optimization of electronic and solubility properties of the potential DA systems are explored. Optimization is controlled by three design handles namely, electron withdrawing group (X), electron donating group (Z), and solubility-aid group (Φ).

1. INTRODUCTION

Solar cells bring tremendous hope when concerns about looming energy and environmental problems are raised [1-4]. Efforts are on for discovering high efficiency solar cells with low cost to performance ratios. Though silicon based solar cells still command commercial markets [1], organic solar cells hold distinct place and great potential when it comes to processibility and flexibility in use of materials and low cost [2-5]. Unfortunately, the organic solar cells show significantly low efficiency (1-5%) [2] compared to their silicon counterparts (10-24%) [1]. However, by using improved materials and design, organic solar cells can be made more efficient. The proposed study intends to contribute to this ongoing effort in improvising performance of organic solar cell by improving light absorbing organic materials employed.

An important part of the study is building a knowledge base of the DA model systems. These model systems will aid in designing potential low band gap polymers for solar cell use. The low band gap materials are needed for absorption of more prominent lower wavelength region in the solar spectrum². However, currently employed low band gap materials, generally a conjugated polymeric material, are not efficiently able to do the job, mainly because of mismatch of absorption spectrum and significantly low mobility [2]. Many of these polymers use donor acceptor route to suppress the band gap

[6]. Thus it is crucial to utilize the flexibility provided by this method to develop an efficient low band gap polymer. So far, this method has been used with no or little input from theoretical studies on these systems. Structure – Property relationship is most fundamental to material design. The central aspect of the study is inculcating this fundamental principle by doing a structure-property correlation, experimentally and theoretically. The study identifies the four basic components of the DA systems, viz. molecular unit (U), electron withdrawing group (X), electron donating group (Z), and solubility-aid group (Φ). Another, significance is the study of the morphology of the thin films of polymers/blend in order to optimize the charge separation and mobility. Most of the studies including by Colladet et⁷ al have overlooked this aspect [6,7]. Also, acceptor moieties based upon dye molecules are carefully examined for structural design of DA systems.

The operating principle of the solar cells is based upon creation of electron-hole pairs (excitons) upon absorption of light and separation of these charge carriers by existing internal field at the interface [2]. In organic cells light is absorbed by a low band gap organic molecule (donor), usually, a conjugated polymer and separation occurs at the bulk heterojunction with another organic molecule with (acceptor) a low lying LUMO, usually a fullerene derivative [2]. Fig. 1 illustrates the operating principle and scheme of a fabricated solar cell. For efficient harvesting of solar light reaching the earth surface, the absorbing material must be able to absorb the more prominent lower wavelength region of the solar spectrum strongly [2-4]. This requires materials of low band gap with wider absorption spectrum. In designing such a low band gap polymer incorporating alternate donor acceptor groups in the conjugated polymer framework has proved to be an effective route [6]. The interaction between the frontier molecular orbitals of the alternate donor acceptor groups significantly lowers down the band gap by suppressing the LUMO and elevating the HOMO. By employing a suitable donor with strong electron donating group like alkoxy and an

acceptor with a strong electron withdrawing group like nitro or cyano band gap can be made low enough (< 1.5 eV) [6, 8-11].

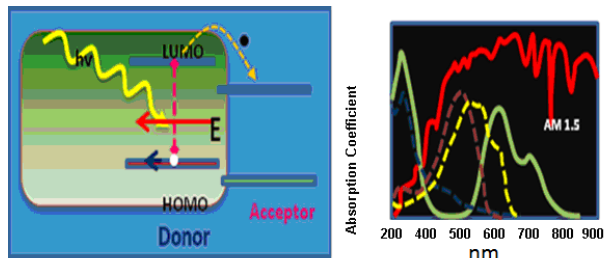


Fig. 1: Operating principle (Left), absorption spectrum of some of the low band gap organic materials along with AM 1.5 spectra (Right) [18].

Nevertheless, most of the organic solar cells including those employing low band gap DA type polymers show extremely low efficiency ($< 1\%$). The main reason for this is low mobility of charge carriers (holes) in organic polymers. Absorption of lower wavelengths is still an important criterion, not completely fulfilled by present low band gap polymers.

There have been several attempts to obtain low band gap polymers by DA route. The commonly employed molecular units are thiophenes and pyrroles with strong electron withdrawing groups like cyano and nitro [6]. Zotti et al experimentally verified the effectiveness of the cyano group on polypyrrolevinylene [8]. The cyano on vinylic linker acted as acceptor moiety reducing band gap from 2.6 eV to 2.2 eV. When an electron withdrawing group methyl was used in place of cyano, band gap in fact increased. It proved that acceptor moieties are necessary for band suppression. Lin et al in an important study showed that these moieties must be linked in certain favorable positions [9]. Cyanovinylene linkers (acceptor) when in para position on the phenylene ring show lower band gap (1.77 eV) than when in meta (2.82 eV). In addition to greater electronic effect, para configuration will have better pi-pi stacking and chain packing. Thus, it proves that not all configurations are effective and structure must be carefully designed. Zhang et al obtained polythioles with amino and nitro groups showing much lower band gap (1.1 eV) [10], which greatly decreased (0.36 eV) when pyrazines and ethylenedioxy was used by in a milestone discovery by Akoudad et al [11]. Thus, it demonstrates the ability of DA route in engineering band gap by using very simple architectures and appropriate functional groups.

Motivated by the flexibility and power of DA method, several theoretical studies have been done too [15]. They have also been encouraged by success of first principle (ab initio) and density functional theory (DFT) [12] based calculations in predicting conformations and electronic structure of simple conjugated systems like polythiophene [13] and polyparaphenylene [14]. However, the studies on the DA systems have mainly engaged themselves in band gap

calculations on known systems with little effort into structure tailoring for modulating electronic properties and solubility as well [15].

2. STRATEGY

The idea of having alternate donor and acceptor moieties to lower the band gap of a conjugated polymer system is well conceived [6]. In principle, the basic architecture for a DA polymeric system may be based upon any conjugated system framework with electron donating and electron withdrawing groups at alternate positions constituting donor and acceptor moieties. Strong electron donating and withdrawing groups are desired for this purpose. However, the low band gap is not the only criteria required for solar cell application, as there are other factors equally important to be discussed later.

The present study builds upon this idea by separating the DA systems into four different components viz. molecular unit (U), electron withdrawing group (X), electron donating group (Z), and solubility-aid group (Φ). Each must be studied separately. Also, the effort in choosing the right model systems for further consideration for experimental work can be greatly reduced by first doing a theoretical study. The other parameters for efficient cell performance are primarily based upon fabrication techniques and cell design itself, which are outside the scope of the present proposal. Some of the critical areas of improvement and related constrains/parameters are listed in Fig. 2. The ones highlighted in red relate to structural design of the polymer, while the dark brown ones relate only partially. These are considered toward final structure design. It may also be seen that all these requirements translate into LUMO – HOMO fine tuning at molecular level.

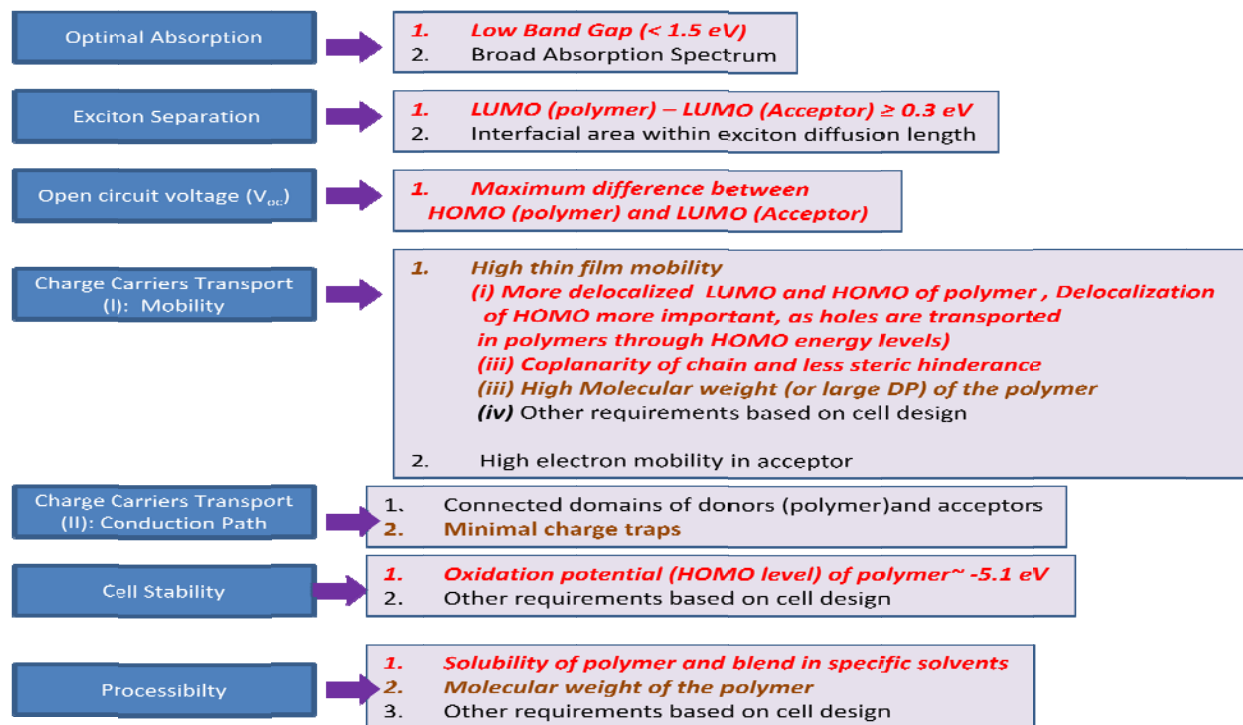


Fig. 2: Performance parameters for DA polymers and corresponding requirements.

Note: The requirements in red primarily relate to structure of the polymer and constitute design constrains, those in black relate to cell design and fabrication and those in brown relate partially to both.

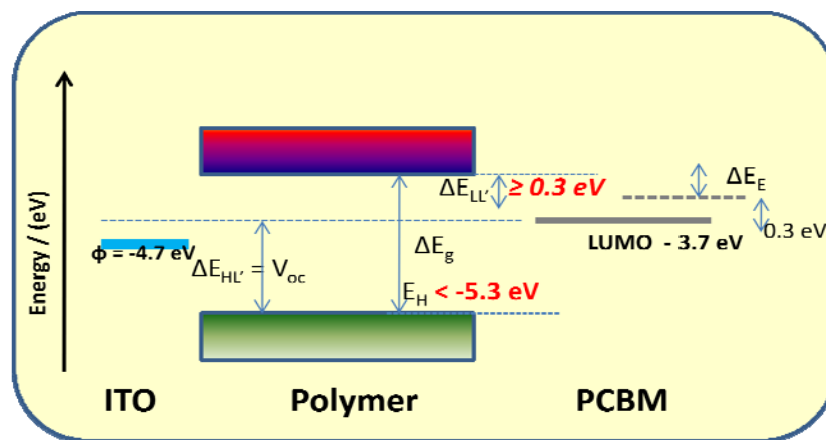


Fig. 3: Energy constrains for the low band gap polymers with reference to PCBM as acceptor

$E_{LUMO(Poly)} - E_{HOMO(Poly)}$ (ΔE_g): Minimization of the band gap along with a broad absorption spectrum, as discussed in the previous sections is the main goal. This is an important requirement for efficient absorption of solar spectrum. One approach could be HOMO-LUMO gap and other being the band diagram itself. The HOMO-LUMO gap would give a reasonable estimate of the band gap. If a band gap diagram is obtained it would give an idea of the broadness of the absorption spectrum along with band gap.

LUMO-LUMO offset ($\Delta E_{LL'}$): When the excitons are created upon absorption of the photons they must be separated into electron hole pairs free to move to the respective electrodes. For this, binding energy holding the electron and hole pairs in the excitons must be overcome. In organic solar cells this is compensated by an energy offset mismatch between LUMO of donor (polymer) and LUMO of acceptor (usually a C60 derivative). The binding energy has its origin in electrostatic interaction between electron and hole pairs. In such polymers

which are usually low dielectric materials the binding energy is relatively high and can vary (0.3 eV- 0.5eV) depending upon the polymer. The more widely reported value is about 0.3 eV [37], which is also considered here. However, if the energy mismatch between LUMO levels widens up beyond the energy required for exciton separation (binding energy), the extra energy would be simply wasted and decrease the overall efficiency. So, this mismatch should be kept greater than but as close as possible to binding energy.

$E_{\text{LUMO(Acceptor)}} - E_{\text{HOMO (Poly)}} (\Delta E_{\text{L-H}})$: The difference between the LUMO level of acceptor and HOMO level of polymer is directly related to the open circuit voltage of the cell (nearly equal) and hence overall efficiency. The greater this difference, greater would be V_{oc} and hence the cell efficiency.

$E_{\text{HOMO(Poly)}} (E_{\text{H}})$: Some studies have shown that for stable operation of the cell (to avoid oxidation) in atmosphere the oxidation potential (HOMO) should be at least -5.1 eV. Then, it will also be less than the work function of commonly employed ITO electrode.

The strategy is outlined below.

1. From the above logic it may be concluded that we should first find an electron rich conjugated backbone (containing donor sites). The donors can be selectively chosen to have a HOMO level near around -5.3 eV and better delocalized orbitals.
2. The attention to the LUMO will be given in the next stage. This is also the most crucial stage. An acceptor with appropriate electron withdrawing strength will be put at the right places (keeping in mind regioregularity, symmetry that in turn would also decide delocalization in LUMO, as discussed above). The aim would be to lower down the LUMO to around -3.8 eV. P3HT which is also one of the widely explored DA polymers has it at -2.7 eV. The offset of about 1eV is responsible for energy losses in P3HT-PCBM cell, which is one of the main causes of lower efficiency (other important cause is low mobility, a common problem).

The first step in this screening process for acceptor would be to quantify the electronic effect by some known well performing acceptor groups along with other commonly known electron withdrawing groups, with respect to dimers based on phenylene vinylene, thiophene and pyrrole. α and β are the two new parameters introduced in order to quantify electron effects on HOMO and LUMO respectively. It's clear now that we should look for groups with small α value and just appropriate β values.

3. The charge density isosurface as part of the theoretical calculation should then be obtained to ascertain delocalization in HOMO and LUMO. Acceptor group will have more influence on the resultant LUMO and delocalization affected by their positioning.

Hence, a regioregular and symmetric position will be preferred.

4. Shape-Orbital-Energy have close relations and coplanarity and charge density isosurface is a part of it. Steps 1-3 may be revisited for an optimization
5. Effect of alkyl groups (C6-C12) both branched and non-branched and alkoxy (-OR) will be ascertained by doing calculation on the simple polymer systems like polyacetylene. See solubility section for other details. Usually, solubility aid groups (with very less electronic effect on the system) would not change charge density isosurface. However, it may change coplanarity of the chain, which may in turn have effect on charge density isosurface. So, repositioning or reselection might be required.

The best model systems (lowest band gaps) hence selected, may then be studied for their thin film (polymer and blend) properties. Mobility which is an equally important factor (in fact more responsible for poor performance of organic cells) depends not just upon the molecular structure but also the morphology of the thin film. The better the packing of the polymer chains better is the charge conduction and losses due to recombination. Also, architecture of the bulk heterojunction where, excitons separate into charge carriers is directly related to morphology [3].

3. IMPLEMENTATION

The conjugated framework is modeled with the units drawn from familiar low band gap conjugated systems like polythiophene, polyphenylenevinylene (PPV) and polyfluorene. Specific electron donating and electron withdrawing groups also drawn from experimentally studied DA systems will be used as donor and acceptor groups. Some of the choices for a preliminary study is summarized in Fig. 4. Branched alkyl chains (C4-C7) will be tried along with aryls like phenyls for modulating solubility. Phenyls and thiols when present as side groups may significantly modulate electronic properties too. Squaric acid derivatives will be used as acceptor moieties with the different donor moieties like pyrrole. Groups like ethylene dioxy, thienothiadiazole, pyrazine and thienothiadiazole-pyrazine are of special interest considering better pi-pi stacking and chain packing. Rationale for this specific approach is discussed in the previous section. Some of the low band gap DA systems hence modeled are listed in Fig. 7.

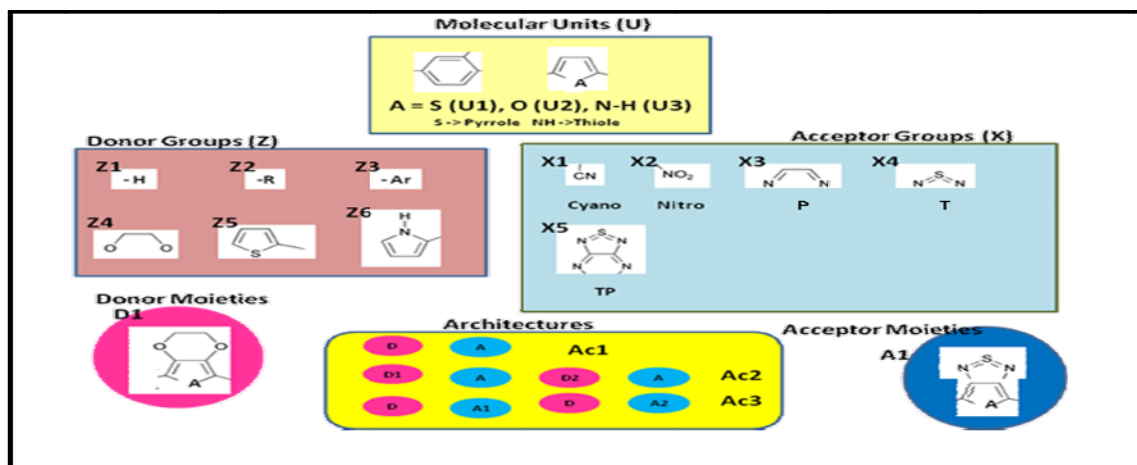


Fig. 4: Proposed structural components and architectures of DA systems for preliminary studies

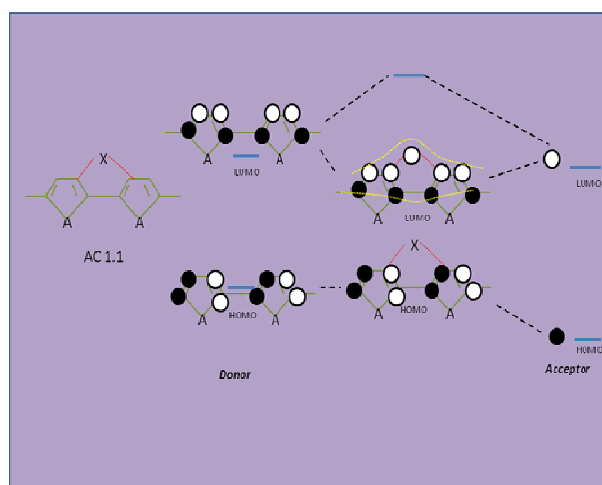


Fig. 5: Formation of LUMO and HOMO on coupling of AC1.1 polymer framework with an acceptor group (X) at a regiosymmetric position and corresponding effect on charge density [33, 36].

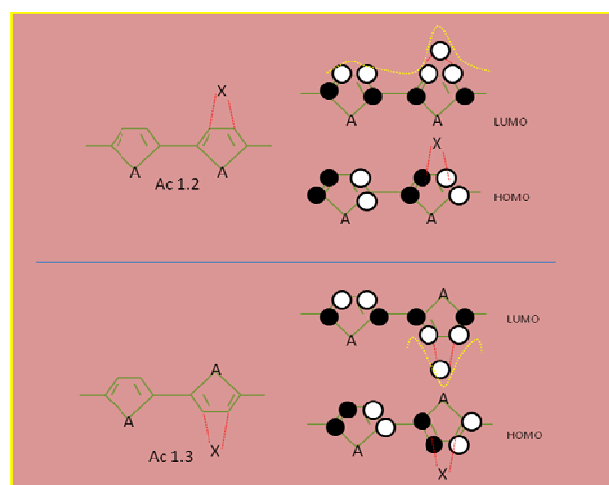


Fig. 6: LUMO and HOMO of AC1.2 and AC1.3 on coupling with an acceptor (X)

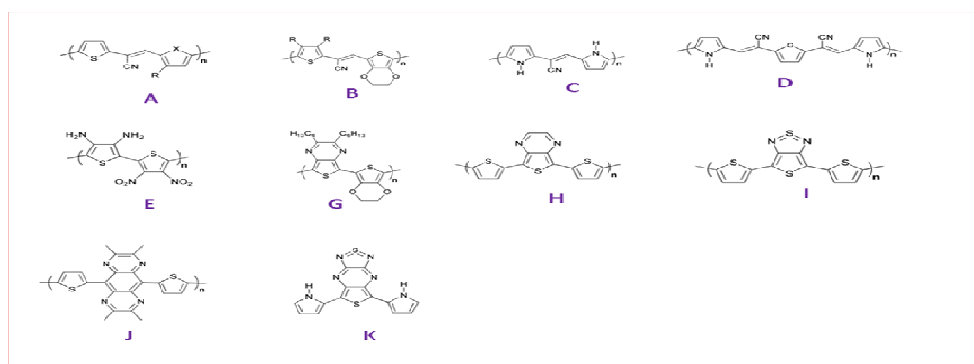


Fig. 7: Some well studied DA polymer systems for a comparative study with results from proposed theoretical study

Among various theoretical methods available to calculate electronic structure of a many body molecular system [12], the specific choice depends primarily upon the kind of information we would like to extract from the calculated electronic structure or the specific properties we are interested in, the type of molecular system, the level of accuracy desired and finally the computational resources available.

Band Gap: The basic approach in calculating the band gap of an extended system is based upon either a molecular [19-21] or solid state quantum mechanical treatment¹⁴. The later is more complex and is especially useful when a detailed band structure is sought. For the proposed study, molecular quantum mechanical treatment should be sufficient. In this approach, the HOMO-LUMO energy gaps (E_g) are calculated for a series of oligomers, starting from the monomer and E_g is plotted against $1/N_c$, where, N_c is the number of carbons along the conjugated chain in the oligomers. The E_g would decrease with decrease in $1/N_c$ (larger systems) and band gap of the polymer may be obtained by extrapolation of the curve.

The different methods employing E_g by extrapolation approach mainly differ in the type/level of quantum mechanical theory used. At the most basic level, Huckel type methods (HTM) give reasonable E_g values for many of the conjugated systems [22]. Hybrid DFT methods like B3LYP and ab initio methods like MP2 have been used with great success [21-24]. B3LYP and MP2 treat electron correlation and exchange more effectively.

π - π interactions: π - π interactions are the most important non covalent interactions in conjugated systems esp. aromatic molecules and play significant role in molecular packing and charge conduction [25]. Their strong dependence on dispersion forces and hence very weak strength (2-3 Kcal mol⁻¹) and association with multiple points in a molecule makes modeling difficult and requires sophisticated theoretical tools employing wavefunctions with effective inclusion of electron correlations. The theories based on electrostatics and electron densities are hence ruled out. The hybrid DFT based method; B3LYP which too essentially depends upon local density approximation has also been not so useful for the same reasons. The all electron ab initio method, MP2 has been most extensively (in fact solely) used for studying π - π interactions [25-29]. Further, it requires a large basis set to approximate a complete basis set with different polarization functions. However, associated huge computational cost severely limits our choices. No wonder, simplest systems like benzene [25-27] and pyridine [28] are still been explored and have been the subjects of some very recent studies. Finally, one must correct for basis set superposition errors (BSSE). The weak pi-pi interactions should be very sensitive to such errors.

4. ACKNOWLEDGEMENT

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