

A Quantum Chemical Study on Polythiophenes Derivatives as Donor Materials in Bulk-heterojunction Polymer Solar Cell

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Abstract: For the optimum design of the donor and acceptor materials in polymer solar cells, it is very important to do a theoretical calculation for the energy levels and energy gaps. In this work we used the semi-empirical method Austin Model1 (AM1) to investigate the Higher Occupied Molecular Orbital (HOMO) and Lower Unoccupied Molecular Orbital (LUMO) of polythiophenes derivatives/fullerenes combination (bulk heterojunction polymer solar cells). The overestimation on the HOMO and LUMO values was corrected by using experimental data from literature as criteria of correctness. Using our correction method, a reasonable linear relationship between the computed energy band gaps of polythiophenes derivatives and the experimental band gaps were found. The corrected HOMO and LUMO energies of polythiophenes derivatives match well with the experimental one. This method can serve as a road map in order to design and synthesis appropriate combination of polythiophenes derivatives/fullerenes for bulk heterojunction solar cells.

Keywords: Austin Model 1, Conjugated polymers, Polymer solar cells, Quantum chemical methods

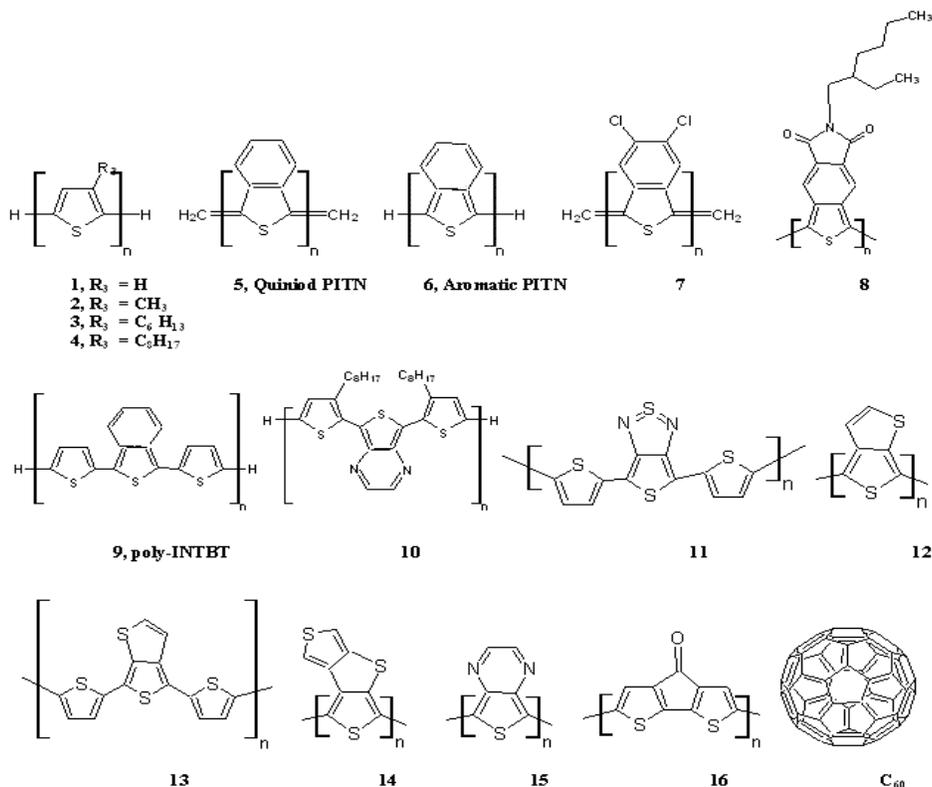
INTRODUCTION

Semiconducting polymers have received considerable attention in the last few years as donor materials used in Bulk Heterojunction (BHJ) photovoltaic cells. They combine the opto-electronic properties of conventional semiconductors with the excellent mechanical and processing properties of plastic materials (MacDiarmid, 2000). Additionally, they possess an unprecedented flexibility in the synthesis, allowing for alteration of a wide range of properties, such as band gap, molecular orbital energy level, structural properties, as well as doping (Roncali, 1997; Shirakawa *et al.*, 1977). This ability to design and synthesize polymers and molecules that can be casted from solution using wet-processing techniques such as spin-coating (Brabec *et al.*, 2001), screen printing (Shaheen *et al.*, 2001) and inkjet printing (Eom *et al.*, 2010), represents an enormous attractive route for cheap production of large-area photovoltaic cells that can be applied to systems that require flexible substrates. For a successful molecular design of conjugated polymers it is necessary to have a complete understanding of the relationship between the chemical structure of the polymer and its electronic properties such as ionization potential, electron affinity and band gap. Quantum chemical calculations have proven to be useful in gaining insight into the electronic properties of conjugated polymers (Bakhshi and Pooja, 1998; Davis *et*

al., 1999; Hung *et al.*, 2009). However, it is well known that theories rely on a variant of full nonlocal exchange Hartree Fock (HF) theory systematically overestimate the energy gap of conjugated polymers (Kertesz *et al.*, 2005). These methods include widely used semi-empirical techniques, such as Austin Model 1 (AM1), Modified Neglect of Differential Overlap (MNDO), parameterization method 3 (PM3) and Zerner's version of the Intermediate Neglect of Differential Overlap (ZINDO). In this paper we used AM1 semi-empirical method with a proposed correction method to investigate the polythiophenes derivatives band gaps, the effective energy band gap (the difference between the HOMO of the donor and the LUMO of the acceptor) and the LUMO offset (the difference between the LUMO of the donor and the LUMO of the acceptor) of some polythiophenes derivatives/fullerenes combination used for bulk-heterojunction polymer solar cells. In order to check the accuracy of this method we compared our results with the available experimental values found in literature. The chemical structure of the polythiophenes derivatives studied in this study and C₆₀ are shown in Fig. 1.

MATERIALS AND METHODS

The concept of an organic bulk-heterojunction: Shining light on a polymer solar cell generates mobile excitons that have a binding energy of several tenths of

Fig. 1: Chemical structures of the investigated polymers and C_{60}

electron volts. On the other hand, the diffusion length of an exciton in most conjugated polymer films is quite low (less than 20 nm) (Haugeneder *et al.*, 1999). This makes a bottleneck to charge generation as it leads to enormous amount of recombination within the bulk of the active layer. To achieve substantial photovoltaic effect in polymer solar cells, excited charge pairs need to be dissociated into free charge carriers through the assistance of electric field, bulk trap sites or interface of materials with different electron affinities. A revolutionary development in organic photovoltaic's came in the mid 1990s with the introduction of the dispersive (or bulk) heterojunction, where the donor and acceptor material are blended together (Yu *et al.*, 1995). Power conversion efficiencies of greater than 4% have been achieved for polymer/fullerene bulk heterojunction solar cells based on poly(3-hexylthiophene) (P3HT) as absorbing and electron donating material (Kim *et al.*, 2006; Reyes *et al.*, 2005).

It should be noted that in BHJ based polymer solar cells, the effect of electrodes on the open circuit voltage (V_{oc}) is neglected only for ohmic contacts (Mihailetchi *et al.*, 2003). It is commonly accepted that open circuit voltage of bulk heterojunction polymer solar cells is proportional to the effective band gap defined by the energy difference between the HOMO of the electron donor materials and the LUMO of the electron acceptor

materials (Scharber *et al.*, 2006). Pursuing a higher open circuit voltage by using electron donor materials with a deeper HOMO level is an effective approach for achieving higher power conversion efficiency (Scharber *et al.*, 2006; Gadisa *et al.*, 2004). To achieve the maximum potential, an ideal conjugated polymer for polymer solar cells should have both low band gap and also a deeper HOMO level (Chen *et al.*, 2009).

Computational Details: Starting geometry of the oligomers was constructed using (Argus Lab 4.0.1, 1997-2004) program (Mark Thompson and Planaria Software LLC, 1997). Full geometry optimizations were carried out at the AM1 levels, utilizing the MOPAC quantum chemical program packages (MOPAC MANUAL, James Stewart). During the process of optimization 'precise' keyword was used and Herbert's test was used to justify the optimized geometries. Origin 6.0 program was used to sketch the graphs. All AM1 calculations were implemented in MOPAC program, running on Pentium (R) 4 CPU 2.4 GHZ. For all computations, the parameters and algorithms are those given by the original workers. Polymers electronic properties (band gaps, HOMOs and LUMOs) were evaluated by plotting results for oligomers with increasing chain length against $1/n$, (n is the number of repeated units). The data were extrapolated using linear fitting.

Table 1: Electronic properties of polythiophenes derivatives and fullerenes calculated using AM1 semi-empirical method, (The numbers in the first column is referring to chemical structure in Fig. 1).

Polymer	HOMO (eV)	LUMO (eV)	E_g (eV)	Corrected E_g (eV)	Experimental E_g (eV)
PT	-7.71	-1.59	6.12	2.10	2.10 (Kertesz <i>et al.</i> , 2005)
P3MT	-7.52	-1.45	6.08	2.06	2.00 (Patil <i>et al.</i> , 1988)
P3HT	-7.50	-1.42	6.08	2.06	2.00 (Patil <i>et al.</i> , 1988)
P3OT	-7.52	-1.41	6.11	2.09	2.00 (Valaski <i>et al.</i> , 2003)
Quinoid PITN	-6.81	-1.88	4.93	0.91	1.00 (Kertesz <i>et al.</i> , 2005)
Aromatic PITN	-6.78	-2.22	4.56	0.54	0.54 (Huang, 1998)
7	-7.29	-2.48	4.81	0.79	0.80 (Huang, 1998)
Poly(EHI-ITN)	-8.02	-2.96	5.06	1.04	1.30 (Winder, 2001)
Poly-INTBT	-7.36	-1.86	5.50	1.48	1.7±0.1 (Roncali, 1999)
10	-7.32	-1.80	5.52	1.50	1.45 (Campos <i>et al.</i> , 2005)
11	-7.31	-2.32	4.99	0.97	0.90 (Roncali, 2007)
12	-6.94	-2.04	4.90	0.88	0.90 (Roncali, 2007)
13	-7.39	-1.75	5.64	1.62	1.60 (Bundgaard and Fredrik, 2007)
14	-7.18	-1.78	5.40	1.38	1.15 (Roncali, 1997)
15	-7.09	-2.25	4.84	0.82	0.95 (Roncali, 2007)
16	-7.87	-2.23	5.65	1.63	1.20 (Roncali, 1999)
C ₆₀	-9.64	-2.95	6.69	2.30	2.27 (Gopal, 2007)
PCBM	-9.29	-2.82	6.47	2.08	2.40 (Kim <i>et al.</i> , 2005)

RESULTS AND DISCUSSION

We have calculated the HOMO, LUMO energies and energy band gap (E_g) of a series of polythiophenes derivatives as donor materials and C₆₀ as acceptor by using quantum chemical Austin Model 1 (AM1) semi-empirical method (Table 1) and correlated the calculated values with the experimental values found in the literature. Figure 2 shows the plot of the AM1 calculated E_g versus the experimental E_g . The plot shows a good linear correlation with a slope of ~1 and correlation coefficient ($R = 0.952$). The AM1 calculated values are about 4.02 eV higher than the corresponding experimental values, the overestimation is systematic. The good correlation between theoretical energy band gap and the experimental one from the literature made it possible to suggest a correction relation.

Description of the correction method: In a bulk-heterojunction polymer solar cell when the exciton diffuses toward the donor/acceptor interface, it is energetically favorable if the electron is transferred to the acceptor molecule. From classical Marcus electron transfer theory (Marcus, 1997), the electron transfer rate constants can be defined as:

$$K_{ET} = A \exp [-(\lambda_c + \delta E)^2 / 4 \lambda_c K_B T] \quad (1)$$

where λ_c is the reorganization energy which contains contributions from molecular motions, vibrations, solvent effects and can be estimated from molecular vibrational spectroscopy or from excitation-emission spectroscopy. K_B is the Boltzman constant and T is the temperature. δE is the LUMO offset between donor and acceptor, providing the driving force for charge separation. As the value of the open circuit voltage is governed by the effective band gap, [$E_g(Donor-Acceptor)$] a higher open circuit voltage can be achieved by fine tuning the energy levels,

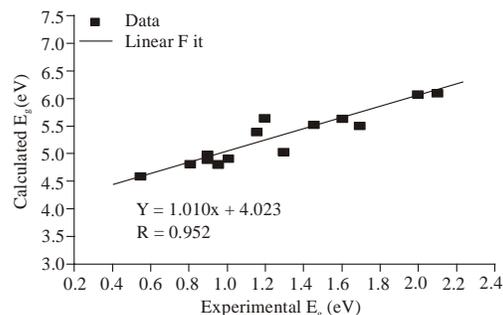


Fig. 2: Correlation of AM1 calculated energy band gaps and experimental band gaps

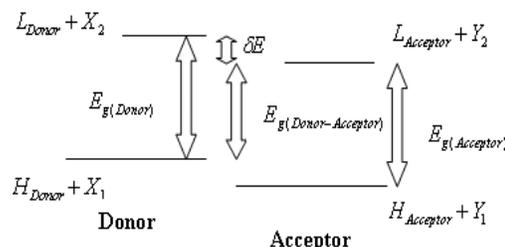


Fig. 3: Simplified schematic showing the HOMO and LUMO energies for a donor and acceptor materials calculated using AM1 semi-empirical method. For ohmic contact the V_{oc} is mainly determined by $E_g(Donor-Acceptor)$ and the LUMO offset by δE

such as increasing the LUMO of the acceptor or decreasing the HOMO of the donor. However, increasing the acceptor LUMO will reduce K_{ET} and decreasing the donor HOMO will increase the band gap of the donor material and consequently reduce the light absorption. Hence, a tradeoff between a sufficient electron transfer driving force and a large open circuit voltage origin should be carefully controlled for obtaining an efficient

solar cell. Figure 3 shows the HOMO and LUMO energies for a donor and acceptor materials calculated using AM1 semi-empirical method in a bulk-heterojunction polymer solar cell. To correct the overestimation on the AM1 calculated energy gaps; we assumed that the HOMO and LUMO energies of the donor are overestimated by X_1 and X_2 respectively and for the acceptor are overestimated by Y_1 and Y_2 , respectively.

The basic equations used in our correction method were used to determine the values of the donor band gap [$E_{g(Donor)}$], acceptor band gap [$E_{g(Acceptor)}$], the effective band gap [$E_{g(Donor-Acceptor)}$] and the LUMO offset [δE]. The correct energy band gap for the donor is given by:

$$L_{Donor} - H_{Donor} = E_{g(Donor)}(correct) \quad (2)$$

and the calculated energy band gap is given by:

$$(L_{Donor} + X_2) - (H_{Donor} + X_1) = E_{g(Donor)}(cal) \quad (3)$$

From which:

$$L_{Donor} - H_{Donor} = E_{g(Donor)}(cal) - (X_2 - X_1) \quad (4)$$

Substitute (2) into (4), we obtain:

$$\begin{aligned} E_{g(Donor)}(correct) &= E_{g(Donor)}(cal) - (X_2 - X_1) \\ &= E_{g(Donor)}(cal) - (\delta X) \end{aligned} \quad (5)$$

where, δX is the total overestimation in the calculated donor bandgap. In previous work we found that AM1 semi-empirical method overestimate the energy band gap for polythiophene by about 4.02 eV (Omer and Ahmed, 2005).

The same analysis can be performed to the correct acceptor band gap:

$$\begin{aligned} E_{g(Acceptor)}(correct) &= E_{g(Acceptor)}(cal) - (Y_2 - Y_1) \\ &= E_{g(Acceptor)}(cal) - (\delta Y) \end{aligned} \quad (6)$$

The correct energy band gap between the donor and the acceptor is given by:

$$L_{Acceptor} - H_{Donor} = E_{g(Donor-Acceptor)}(correct) \quad (7)$$

The calculated energy band gap between the donor and the acceptor is:

$$(L_{Acceptor} + Y_2) - (H_{Donor} + X_1) = E_{g(Donor-Acceptor)}(cal) \quad (8)$$

From which:

$$\begin{aligned} L_{Acceptor} - H_{Donor} &= E_{g(Donor-Acceptor)}(cal) \\ &- (Y_2 - X_1) \end{aligned} \quad (9)$$

Insert (7) into (9), we obtain:

$$\begin{aligned} E_{g(Donor-Acceptor)}(correct) &= E_{g(Donor-Acceptor)}(cal) \\ &- (Y_2 - X_1) \end{aligned} \quad (10)$$

The correct energy difference between the LUMO of the acceptor and the LUMO of the donor is:

$$\delta E(correct) = L_{Donor} - L_{Acceptor} \quad (11)$$

The calculated energy difference between the LUMO of the acceptor and the LUMO of the donor is given by:

$$\delta E(cal) = (L_{Donor} + X_2) - (L_{Acceptor} + Y_2) \quad (12)$$

$$L_{Donor} - L_{Acceptor} = \delta E_{cal} - (X_2 - Y_2)$$

$$\delta E(correct) = \delta E_{cal} - (X_2 - Y_2) \quad (13)$$

In this section, the correction method is put to the test. The electrochemical characteristics of polythiophene studied by cyclic voltammetry were found from the literature as follows $E_{onst,ox}$ is 0.5 V vs.SCE and $E_{onset,red}$ is -1.6 V vs.SCE (Huang, 1998). The HOMO and LUMO energies are calculated according to the relations (Li *et al.*, 1999):

$$E(HOMO) = - (E_{onset,ox} + 4.39)(eV)$$

$$E(LUMO) = -(E_{onset,red} + 4.39)(eV) \quad (14)$$

where, $E_{onst,ox}$ is the onset oxidation potential vs.SCE, $E_{onset,red}$ is the onset reduction potential vs.SCE.

From equations (14), the HOMO and LUMO values of polythiophene were found to be - 4.89 eV and - 2.79 eV, respectively. Using AM1 semi-empirical method we calculated the HOMO and LUMO energies and they were found to be - 7.71 eV and - 1.59 eV, respectively (Omer and Ahmed, 2005). From the experimental and calculated values of polythiophene energy levels, we found that $X_1 = - 2.82 eV$, $X_2 = 1.20 eV$ and using equation (4) we obtain $\delta X = 4.02 eV$. The experimental HOMO and LUMO energies of C₆₀ were - 6.1 eV and - 3.83 eV respectively (Gopal, 2007) and our calculated HOMO and LUMO energies using AM1 semi-empirical method were found to be - 9.64 eV and - 2.95 eV. That means $Y_1 = - 3.54 eV$, $Y_2 = 0.88 eV$ and $\delta Y = 4.42 eV$.

To show the reliability of our method; the polymers calculated energy band gaps were corrected by using Eq. (5) and compared with the experimental values found in the literature. The correlation between the corrected band gaps and the experimental one are shown in Fig. 4, the relation is reasonably linear (correlation coefficient = 0.952). Subsequently, the method is applied to P3HT/PCBM devices, which have been studied extensively, making them ideal for modeling purposes.

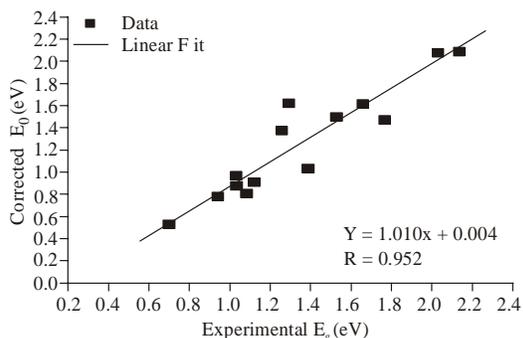


Fig. 4: Plot of the polymers corrected band gaps vs. the experimental band gaps

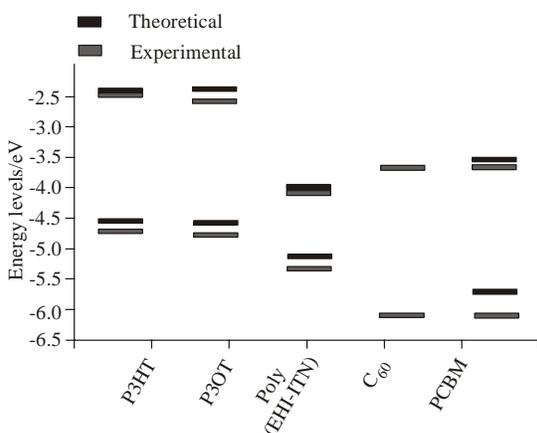


Fig. 5: Simplified schematic showing the HOMO and LUMO energies for P3HT, P3OT, Poly(EHI-ITN), C_{60} and PCBM bulk heterojunction solar cell, calculated using our method and experimental from the literature (Koster *et al.*, 2006; Gopal, 2007; Winder, 2001)

The HOMO and LUMO energetic difference for P3HT has been estimated, using equation (5), to be about 2.06 eV, which is in a very good agreement with experimental values 2.1 eV (Koster *et al.*, 2006) and 2.0 eV (Patil *et al.*, 1988). The effective band gap $Eg_{(Donor-Acceptor)}$ and the LUMO offset δE were calculated using equations (10) and (13) and they were found to be 0.98 eV and 1.08 eV respectively, these values are agree well with the experimental values in the literature (Koster *et al.*, 2006) with a percentage error of 2% and 1.82%, respectively. The corrected HOMO and LUMO energy levels for P3HT were found to be (-4.68 eV) and (-2.62 eV) while for PCBM they were found to be (-5.75) and (-3.70 eV). From the literature (Koster *et al.*, 2006) the experimental values of the HOMO and LUMO energy levels for P3HT were (-4.80 eV) and (-2.70 eV) while for PCBM they were (-6.10 eV) and (-3.80eV). Comparisons of the corrected energy levels with the experimental one from the literature are shown in Fig. 5. Our method shows that the HOMO of P3HT is distinctively higher in energy

than that of PCBM which agree with experiment. As shown in Fig. 5, the difference between the LUMO of P3OT and the LUMO of C_{60} was found to be 1.22 eV which differ by about 0.22 eV from the experimental value (Gopal, 2007). The effective energy band gap $Eg_{(Donor-Acceptor)}$ for P3OT/ C_{60} was found to be 0.87 eV compared to the experimental value of 1.1 eV (Gopal, 2007), an error of ~ 0.2 eV seems to be large. However, the electrochemical data (HOMO, LUMO energy levels) normally measured experimentally using cyclic voltametry. It seems that there is a large uncertainty in the cyclic voltametry measurement because of external effects and inaccuracies of the measurement. Regarding electrochemical referencing in non-aqueous solvents (which are normally the media for conjugated polymer electrochemistry), wide range of reference electrodes is used in the literature but there seems to be a lack of consensus on how they relate to each other and to the vacuum scale (Johansson *et al.*, 2003). This makes it sometimes very difficult to compare data in the literature, especially when different solvents have been used.

From the literature (Winder, 2001) the experimental values of the HOMO and LUMO energy levels for Poly (EHI-ITN) were found to be (-5.40 eV) and (-4.10 eV) while for PCBM they were (-6.10 eV) and (-3.70eV), respectively. The corrected HOMO and LUMO energy levels for Poly (EHI-ITN) were found to be (-5.20 eV) and (-4.16 eV). Figure 5 shows that the position of the LUMO of poly (EHI-ITN) is lower than the LUMO of PCBM, consequently a selective charge transfer becomes uncertain or impossible which agree very well with the experimental data (Winder, 2001). The effective energy band gap $Eg_{(Donor-Acceptor)}$ for poly (EHI-ITN) / PCBM was calculated to be 1.50 eV and δE was calculated to be -0.46 eV compared to the experimental values of 1.6 eV and -0.3 eV, respectively (Winder, 2001).

From the above results it was clear that the accuracy of the energy gap and energy levels calculations using AM1 semi-empirical method has been improved using our proposed correction. Comparing the calculated HOMO and LUMO energies to the experimental one in Fig. 5, it is clear that they match each other well, so the method derived in this study can be used as a guideline for the material selection and material development for bulk heterojunction solar cells. However, it is important to note that, this kind of correction method may be used only to a chemically relevant set of polymers; otherwise the correction parameters may change.

CONCLUSION

In summary, by applying AM1 semi-empirical method and carrying out the proposed correction, we were able to bring theoretically calculated values to the experimentally observed band gap of each polythiophene derivative. The calculated energy band gaps of all investigated polythiophenes is clearly in a good

agreement with experimental values, they are clearly linearly correlated to the experimental values with a correlation coefficient $R = 0.952$. The HOMO and LUMO data obtained from our method match the experimental one, so they should be suitable to compare materials in different polythiophenes derivatives/fullerene pairs for bulk heterojunction solar cells. True success of this method in calculating the HOMOs and LUMOs of a donor/acceptor combination of a bulk heterojunction polymer solar cell can be determined after testing the method described here with many other polythiophenes derivatives for which experimental data of the HOMO and LUMO energies is available. This method can serve as a road map in order to design and synthesis appropriate combination of polythiophenes derivatives/fullerenes for bulk heterojunction solar cells.

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