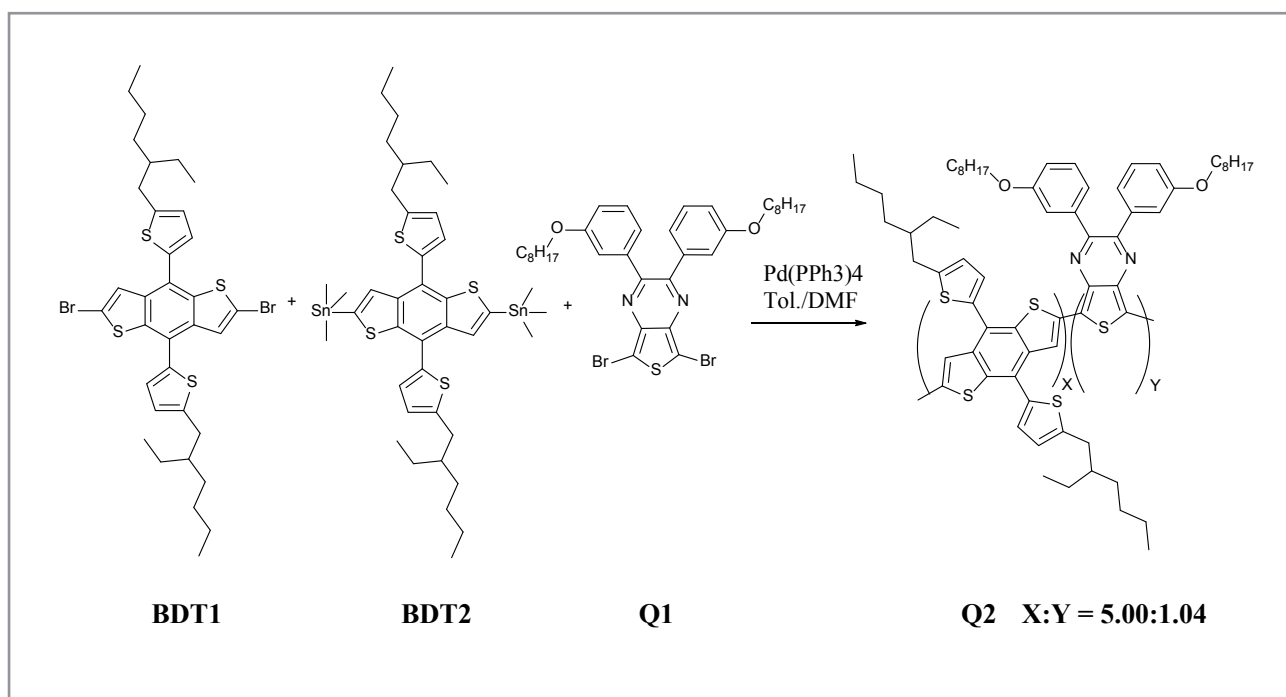


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In 2016, Bui and co-workers reported the highest PCE for a TP containing polymer Q1 (Scheme 1) in BHJs. The polymer was designed by coupling dibromo and bis (trimethyltin) -4,8-dialkylthienylbenzo [1,2-b:4,5-b'] dithiophene (BDT1 and BDT2 respectively) (Scheme 1) with TP units Q2 to form a semi-random polymer through the Stille coupling

polymerization. This polymer Q1 consisted of a higher ratio of donor units (BDT): that was achieved by reacting additional units of BDT1 monomer in the polymerization reaction. The photovoltaic devices were fabricated by using 105/PC71BM (1:2, w/w) and exhibited JSC of 8.88 mA cm⁻², VOC of 0.27V, FF of 59% and PCE of 3.85%.³⁷

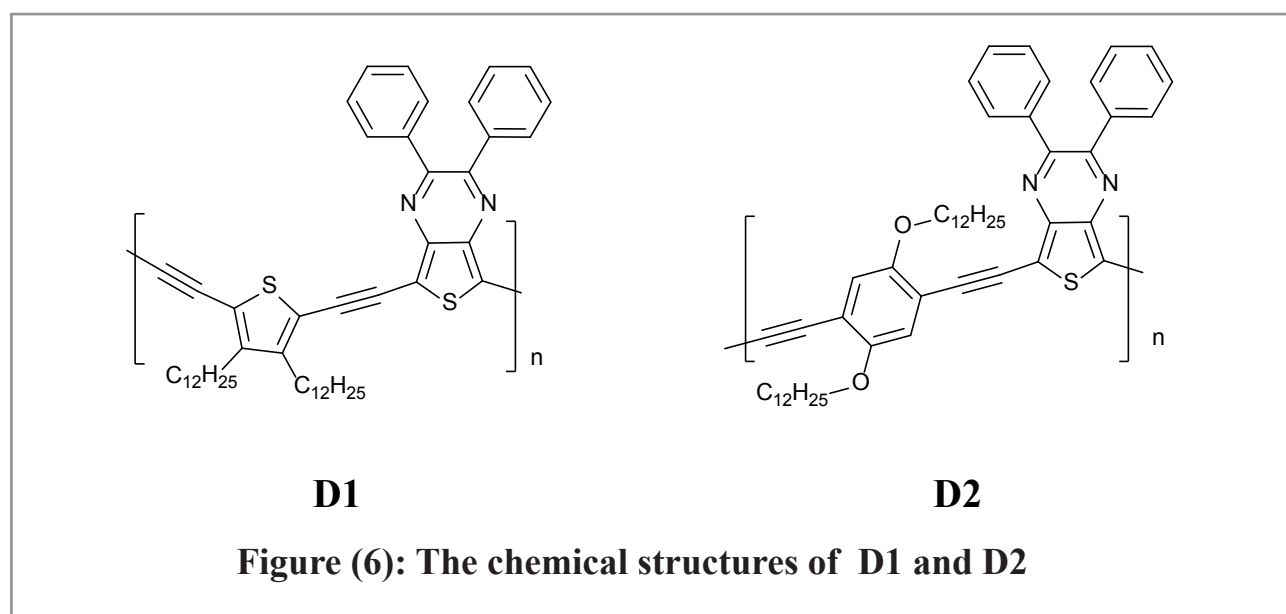


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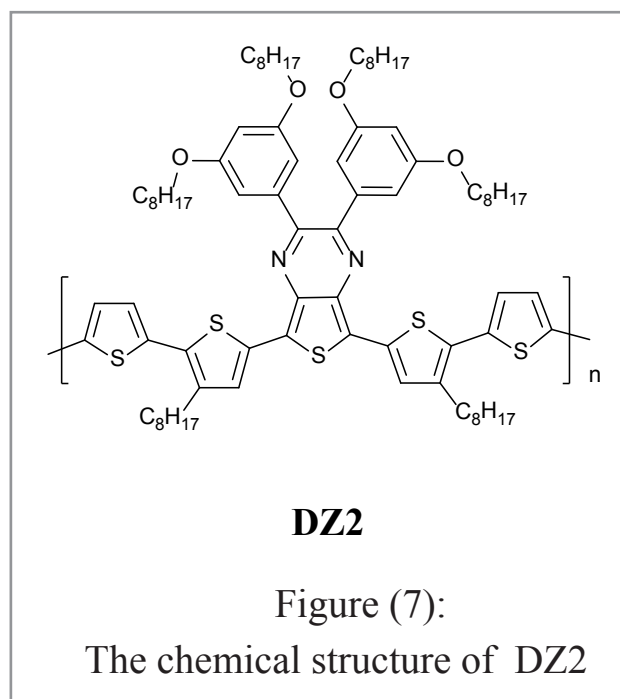
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In the same year, Ashraf and co-workers investigated two other TP copolymers with a wide absorption spectrum from 390 to 800 nm. Both polymers D1 and D2 (Figure 6) consisted of diphenylthieno [3,4-b] pyrazine as the electron deficient

group and alkyl thiophene diacetylene or alkoxy phenylene diacetylene as the electron rich group respectively. The two polymers D1 and D2 showed the same E_g 1.6 eV with different PCEs of 2.4% and 2.2% respectively under AM 1.5 illumination.³⁵



A year later, Zoombelt and co-workers synthesised a new small bandgap copolymer BZ2 which was used in BHJs together with PC71BM reporting a PCE of 1.41% under AM 1.5. Copolymer BZ2 (Figure 7) is based on the alternation between a thienopyrazine unit and a quarter thiophene segment, leading to a E_g of 1.32 eV.³⁶



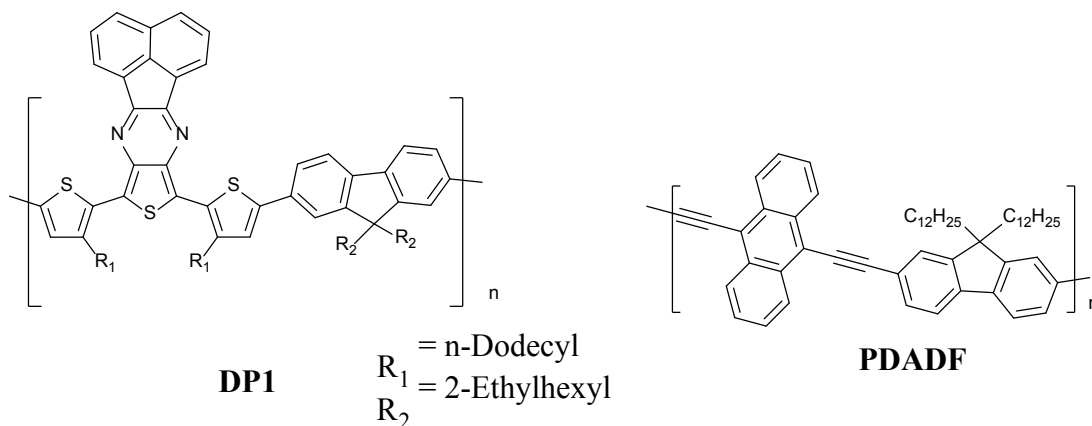
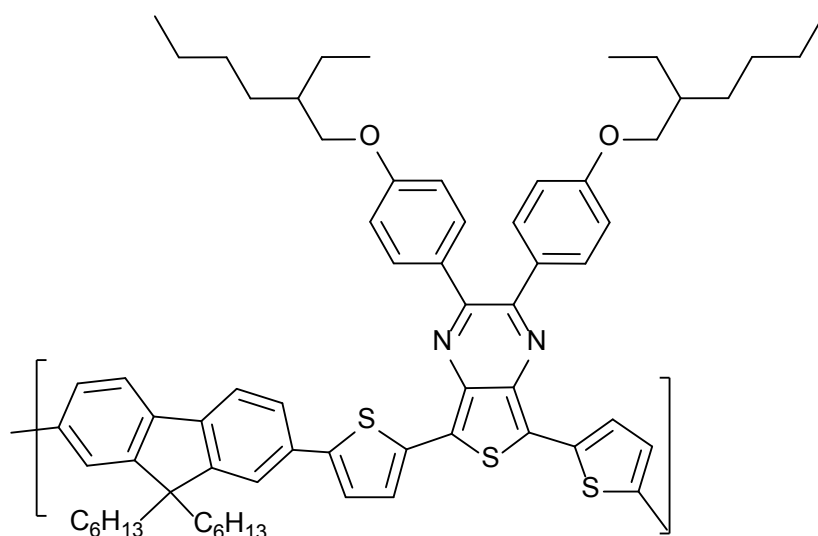


Figure (4): The chemical structures of DP1 and PDADF

Thieno [3,4-b] pyrazine containing polymer in BHJs.

As mentioned above, TP derivatives have attracted attention as low-bandgap organic conjugated polymers.^{29- 32} Recently, polymers based on TP have been widely used as electron donor materials in BHJs.^{17,18,33} For instance, in 2006, Zhang and co-workers reported the synthesis of a new polythienopyrazine

with donor-acceptor structure which was used as a donor material blended with PC61BM in BHJs, with PCE 2.2%. This copolymer was derived from 9,9-dioctyl-9H-fluorene (donor) and 5,7-bis (thien-2-yl) thieno [3,4-b] pyrazine (acceptor) AD1 (Figure 5) and gave an band gap of 1.6 eV.³⁴



**Figure (5):
The chemical
structure of
DP1**

Thieno [3,4-b] pyrazine, history and properties.

Thieno [3,4-b] pyrazine (TP) (Figure 2) is an organic heterocyclic compound, usually employed as a building block for many organic conjugated polymers.^(15- 18) TP is easy to synthesise by condensation of thiophene-3,4-diamine with α -diones. In 1957, Imoto and co-workers first reported the synthesis of a TP derivative (2,3- diphenylthieno [3,4-b] pyrazine).⁽¹⁹⁾ Following this, Binder and co-workers reported modifications in the synthesis of a new TP derivative, by reaction of thiophene- 3,4- diamine with 2,3-butanedione to prepare a 2,3-dimethylthieno [3,4-b] pyrazine with 85% yield.⁽²⁰⁾ In 1995, Kastner and co-workers synthesised a series of 2,3-disubstituted TP derivatives, where the substituents were methyl, hexyl, undecyl and 2- thienyl.⁽²¹⁾

TP is a common building block for the preparation of a wide range of materials with low

energy gap.⁽²²⁾ This characteristic behaviour is due to the quinoidal character (Figure 3), as well as its high ambipolar character, which leads to an internal intramolecular charge transfer (ICT) between the HOMO (localised on the thiophene unit) and the LUMO (localised on the pyrazine unit).^(22- 24) The planarity of TP is shown to improve the charge mobility, by promoting the π - π stacking among the polymeric chains.^(25- 26) This is seen, for instance, in thienopyrazine-based polymer (DP1) which achieved a charge mobility as high as 0.2 cm²/Vs,²⁶⁹ if compared with another conjugated polymer such as PDADF which achieved the mobility 6.0×10^{-4} cm²/Vs (Figure 4).^(27 - 28)

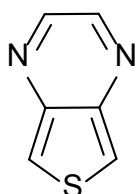


Figure (2): the chemical structure of Thieno[3,4-b]pyrazine (TP)

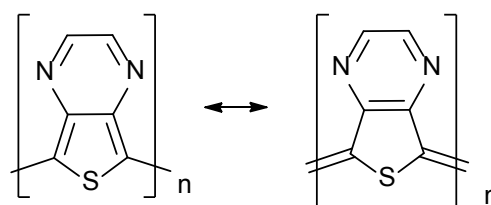
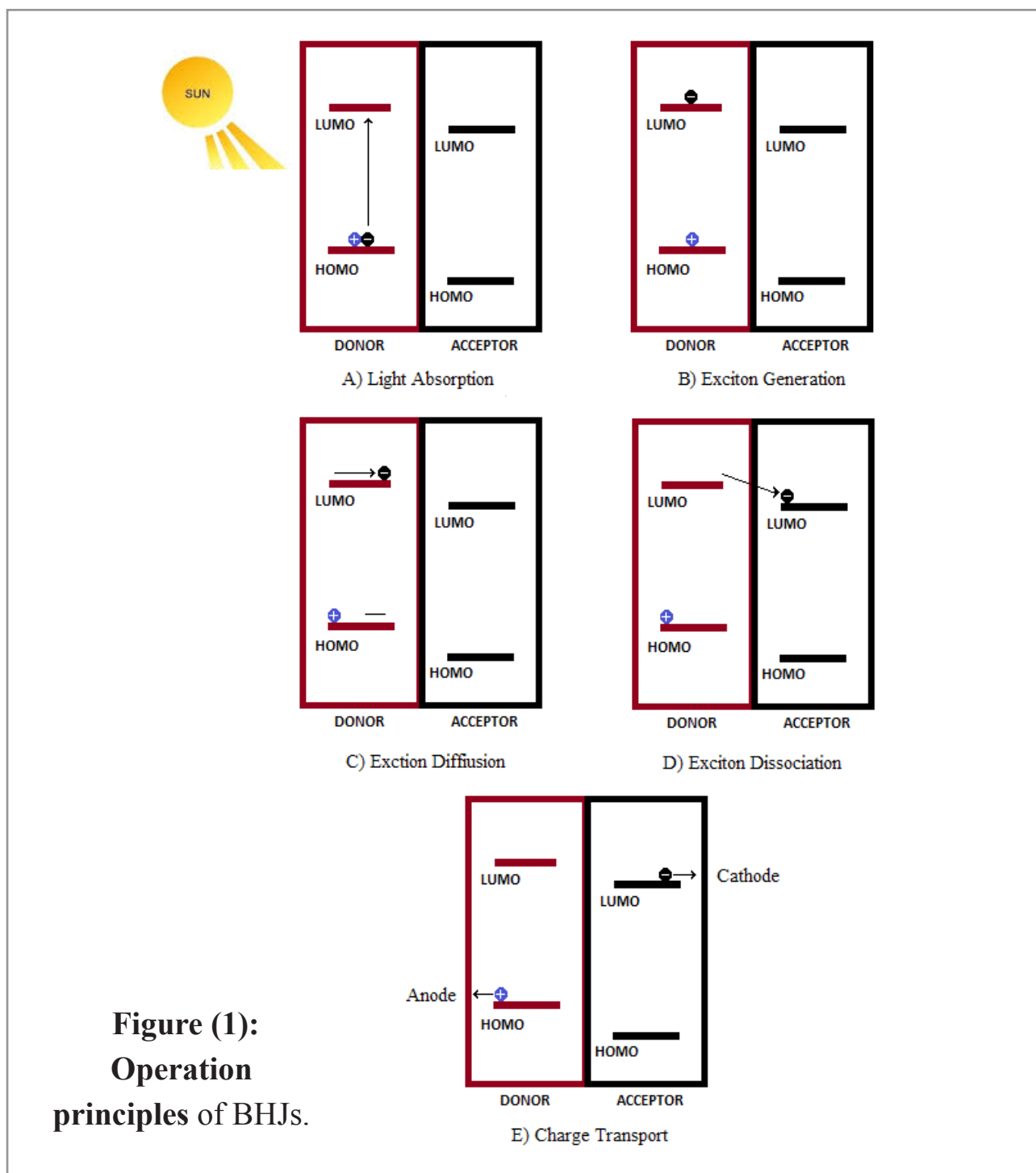


Figure (3): The quinoidal character for TP compound.

4- Charge transport: After the free charges have been produced, they move through specific materials and are collected by the electrodes. From this point, they are connected

to the external circuit. Charge transport efficiency is determined by the electrical conductivity, and the impedance of the organic materials.⁽¹⁰⁾



efficient exciton dissociation. The donor and the acceptor materials are then combined to produce the polymer blend on a scale of about 10 nm. The efficiency of BHJs depends on many parameters such as the materials composition, the chemical structure of the solvent used for film deposition, the ratio between the donor and acceptor, film morphology as well as the induced crystallization ⁽⁷⁻⁹⁾.

Operation principles of BHJs

The operation principles of BHJs are represented by four fundamental processes as shown in figure (1):

- 1- Absorption of light and exciton generation: The existence of a conjugated π electron system within organic compounds leads to interesting electrical and optical properties. The bandgap, in organic semiconductors, can be tuned to align with the solar spectrum energy, thus leading to the absorption of photons. This process leads to the formation of an electrostatically-coupled electron-hole pair, known as exciton.⁽¹⁰⁾
2. Exciton diffusion: Photo generated excitons have a very small lifetime of just a few picoseconds before recombining. This restricts the

mobility of excitons to only a few monomer units or molecules. The exciton can move within the chain, leading to local chain deformation, called polaron, or jump between two adjacent molecules, leading to an inter-molecular process called hopping. In total, the overall mobility of excitons is limited to a 1- 20 nm range, known as the 'exciton diffusion length'. Due to the fact that the excitons must dissociate within this range, the exciton diffusion length has an important influence on the design and performance of organic solar cells.^(11,12)

- 3- Exciton dissociation: This process takes place at the donor-acceptor interface, or junction. Both the donor and acceptor materials are designed in such a way that there is a difference in the HOMO and LUMO levels of the two materials causing the exciton dissociation. For dissociation to be most efficient, this difference should be greater than that of the exciton binding energy. Usually, this difference is in the range of 0.2- 0.3 eV.⁽¹³⁾ In addition, generally, to achieve efficient charge separation: $\Delta (LUMOD - LUMOA) > \text{Exciton energy}$.⁽¹⁴⁾

Introduction

The Photovoltaic (PV) cells are one of the most promising method for a clean energy source production. The main component of PV cells is a semiconductor metal or an organic molecular dye, which generates electricity when exposed to sunlight. Essentially, the absorbed photons excite the electrons of the semiconductor, causing the electrons to become mobile within the cell and generating electric current in the process.^(1,2) Organic solar cells (OSCs) are promising renewable energy sources because of flexibility, low cost production, light weight and a vast synthetic way to different molecular structures.⁽³⁾ Organic photovoltaic (OPVs) cells can be divided into the three types of junction. Single junction devices cells have a simple structure compared to other organic photovoltaic cell types. In these cells, a thin film of organic semiconductor is sandwiched between two electrodes. Usually, these electrodes are a layer of indium tin oxide (ITO) which serves as a high work function and a layer of low work function metal, such as Al (4.06 eV) or Ag (4.26 eV).⁽³⁾ In such devices the variation in the work function of the

two electrodes creates an electric field within the organic layer. This serves to divide the excitation pairs by pulling the electrons towards the positive electrode and the holes towards the negative electrode. However, in practice, these devices did not perform well, and are very inefficient. The reported power conversion efficiencies are poor overall (ranging from 0.001 to 0.01%), although earlier models reached a notable 0.7% using merocyanine dyes.^(4,5)

The double-layer or bi-layer cells is formed from two active organic materials. One acts as a donor, which has a higher ionisation potential and usually used polymer or small molecule in this layer. The second type of active materials, acts as an acceptor with high electron affinity, such as C60-fullerene molecule. These layers are sandwiched between two electrodes. Such devices are more efficient than single-layer devices, as at the interface between the two materials an induced electric field facilitates the charge separation of excitons.^(3,5,6) the last type is BHJ solar cell, whereby a high interface area of three-dimensional networks of donors and acceptors is made, have emerged as a particularly promising method for

Review of thieno [3,4-b] pyrazine based conjugated polymer for bulk heterojunction solar cells: Operation principle and materials.

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Abstract

Bulk heterojunction solar cells (BHJs) have become one of the most solar cells technology in the last two decades because of their available materials and easy to fabrication process. The main idea of this review is to explain the operation principle of BHJs and review about historical background and different types of derivatives based on conjugated polymer

خلاصة :

مراجعة في استخدام مشتقات thieno [3,4-b] pyrazine للبولمرات المتعاقبة في الخلايا الشمسية الغير المتجانسة : مبداء عمل الخلايا و المواد المستخدمة .

اصبحت الخلايا الشمسية غير المتجانسة واحدة من اهم انواع الخلايا الشمسية في العقدين الاخيرين و يعود سبب ذلك الى توفر موادها و سهولة تصنيعها. تتمثل الفكرة الرئيسية لهذه المراجعة في شرح مبداء تشغيل الخلايا الشمسية الغير متجانسة و كذلك التركيز على استخدام مشتقات thieno [3,4-b] pyrazine للبولمرات المتعاقبة في هذا النوع من الخلايا .