A SHORT REVIEW OF ISOINDIGO ACCEPTOR FOR CONJUGATED POLYMERIC PHOTOVOLTAICS

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ABSTRACT. *This paper focussed on the recent development of conjugated polymers that contains isoindigo as acceptor moiety in the application of copolymeric solar cell. In the past decade, various modifications have been done either on the isoindigo acceptor itself or incorporated the isoindigo with different donor moieties. Recently, the power conversion efficiency (PCE) of this isoindigo-based polymeric photovoltaics have achieved up to ~7%. Hence, it is a promising acceptor for the photovoltaics and is expected to break through the recent PCE achievement in the future. This review briefly summarized the structures and properties of the isoindigo-based polymers that have been investigated by the past researches.*

KEYWORD. Isoindigo; Conjugated copolymers; Polymeric solar cells; Small molecules.

INTRODUCTION

Nowadays, energy is highly demanded in both industrial and domestic usages. Energy depletion issues are highly concerned by most developing countries. The non-renewable energy sources, e.g. fossil fuels, natural gas, petroleum, and etc., will soon be completely ware out in the near future. Hence, lots of researches have been done to improve the efficiency of energy harvesting from various renewable resources, e.g. biofuels, geothermal heat, hydroelectricity, wind energy, and solar energy. Amongst these non-renewable energies, photovoltaic cells are one of the promising alternatives which attract the attention of researchers. The photovoltaic cells have been applied in various types of commercial devices, e.g. light emitting diodes (OLEDs), field-effect transistors photodiodes, photo detectors, and solar cells. (Herzog *et al*., 2001; Rand *et al*., 2007; Darling & You, 2013; Liu *et al*., 2014; Zhang *et al*., 2015). In the 1900s, photovoltaic technology was limited to the application of aerospace, before the first oil crisis eruption in the early 1970s (Braga *et al.*, 2008). Solar energy is one of the promising renewable resources. Various types of photovoltaic solar cells have been invented to harvest the energy from the solar power. Among the existing solar cells, organic conjugated polymeric solar cells have been intensively studied and modified to improve the power conversion efficiency (PCE) (Wang *et al.*, 2014).

LITERATURE REVIEW

First and foremost, polyacetylene (PA) was found to possess excellent electrical conductivity in 1977 (Hideki *et al.,* 1977; Morin *et al.,* 2005). This breakthrough urged the study of the PA and other polymers in the application of electrical conducting materials. Unfortunately, the PA was insoluble in many organic solvents and relatively unstable than other polymer in the ambient condition. Because of these limitations, scientists encountered various difficulties during the fabrication of PA-based conducting materials (Rehahn *et al.,* 1989; Morin *et al.,* 2005). Besides PA, lots of polymers have been discovered as conjugated polymers, for example, poly(phenylene) (Rehahn *et al.,* 1989; Morin *et al.,* 2005), poly(*p*-phenylenevinylene)s (Burroughes *et al.,* 1990; Morin *et al.,* 2005), polythophenes (Leclerc & Faid, 1997; Leclerc, 1999; Morin *et al.,* 2005), polypyroles (Watanabe *et al.,* 1989; Morin *et al.,* 2005), polyaniline (D 'aprano *et al.,* 1992; Morin *et al.,* 2005), polyfluorenes (Neher, 2001; Morin *et al.,* 2005), and etc.

The active layer present in the photovoltaic solar cells have evolved from the initial silicon p-n junctions (Chapin *et al.,* 1954; Goetzberger & Hebling, 2000; Scharber *et al.,* 2006), single-component (Wohrle & Meissner, 1991; Cheng *et al.,* 2009), bilayer heterojunction (Tang, 1986; Sathiyan *et al.,* 2016), until the recent bulk heterojunction (Yu *et al.,* 1995; Zhou *et al.,* 2012) configuration. The solar energy is converted into electrical energy through the organic photovoltaic solar cells. The efficiency of this conversion can be assessed through the PCE value, which is a dependent variable that consist of three parameters, i.e. open circuit voltage (V_{oc}), short –circuit current density (J_{sc}) and fill factor (FF). The relationship between these factors could be expressed via the following maths equation in (1) (Günes *et al.,* 2007; Zhou *et al.,* 2012; Sathiyan *et al.,* 2016).

$$\text{PCE } (\eta_e) = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \quad (1)$$

Over past decades, PCE of polymeric solar cells (PSCs) have been rapidly increased from 1% and eventually surpassed 10% (Cheng *et al.,* 2016). Various types of structural modifications have been done to improve the charge transport ability of the existing copolymers. A summary regarding the recent development of isoindigo-based copolymers with notable PCE value will be reported in the following section.

Isoindigo has been widely applied as the acceptor moiety along the polymeric backbone. It was found to have excellent electron withdrawing ability as it comprises two lactam rings (Stalder *et al.,* 2010; 2011; 2013, Sonar *et al.,* 2013; Wang *et al.,* 2014). The chemical structure of the isoindigo is illustrated in **Figure 1** (Estrada *et al.,* 2013). Recently, researchers have modified the isoindigo structure in various ways. One of these is that the benzene rings were replaced by five-membered thiophene rings and it was found that the polymer with thiophene substituted isoindigo possesses deep LUMO level which resulted

excellent ambipolar charge transport (Ashraf *et al.,* 2012; Dutta *et al.,* 2013). Besides that, 7,7'-diazaisoindigo was introduced in 2016, which the carbon located on the 7th and 7-th positions of isoindigo were replaced with nitrogen atoms (de Miguel *et al.,* 2016). This novel 7,7'-diazaisoindigo was found to have longer fluorescence lifetime than its isoindigo counterpart.

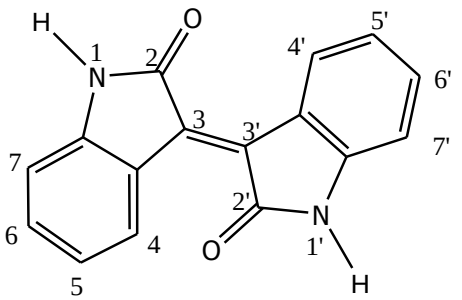


Figure 1 The isoindigo.

Isoindigo-Based Copolymers

The isoindigo monomer is normally synthesized with two bromine atoms located at its 6th and 6'th- positions. These bromine substituents are essential for the carbon-carbon coupling reaction with the chosen donor monomers to obtain the desire isoindigo-based polymers, as illustrated in **Figure 2**. Besides the Stille's protocol as shown in Figure 2 (Mei *et al.,* 2010), Suzuki's coupling reaction is also one of the pathways to polymerize the isoindigo with other monomers. However, the bromine substituents are required to convert to boron esters before carbon-carbon coupling reaction is carried out (Grenier *et al.,* 2012).

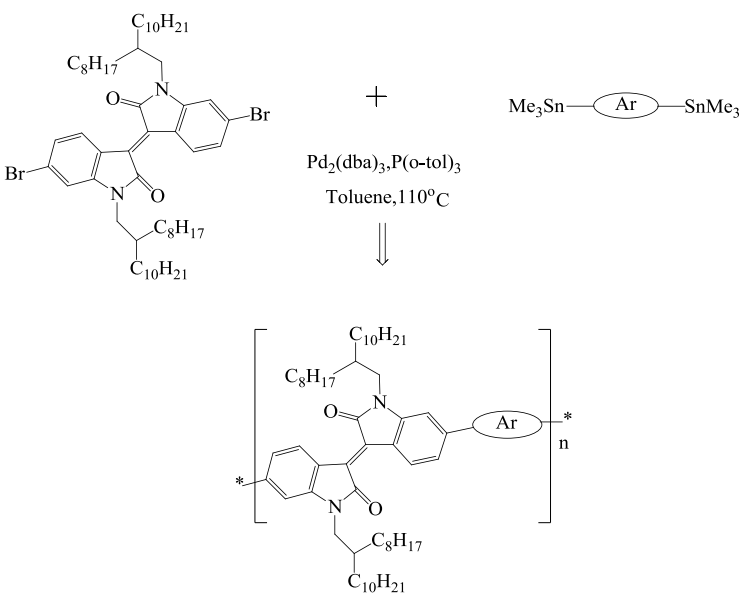
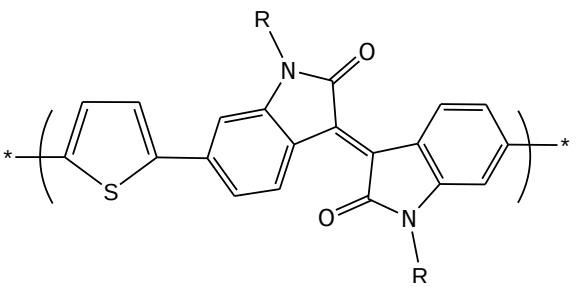


Figure 2: The Stille's protocol of the carbon-carbon coupling reaction.

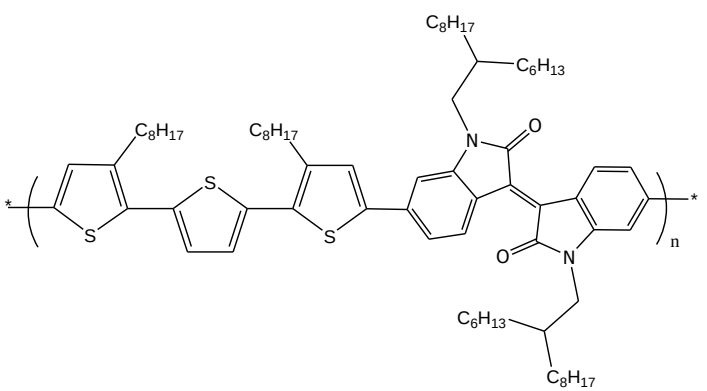
Initially, the researchers incorporated the isoindigo acceptors with thiophene rings, i.e. **P1**-**P3**. Meanwhile, the influence of the N-alkyl chains which were located in the isoindigo was intensively studied. It was found that 2-hexyldecyl alkylated isoindigo-based copolymer **(P1)** shown best performance among the 2-ethylhexylated **(P2)** and 2-octyldodecylated **(P3)** isoindigo-based copolymer. **P1** possesses excellent thermal stability, while **P2** was found to be insoluble in common organic solvents. The PCE value obtained from P1-based copolymeric solar cell (PSC) is 3.0 %. For the **P3**, the PV performance is very low, c.a. 0.92 % PCE value. This is because the low hole mobility of the **P3**-based copolymer (Wang *et al.*, 2011a; Zhang *et al.*, 2011). Hence, the isoindigo monomers synthesized in the most of the later researches have applied the 2-hexyldecyl N-alkyl chains.



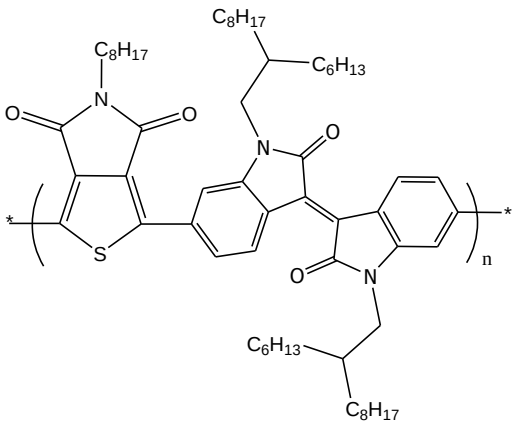
P1: R= 2-hexyldecyl

P2: R= 2-ethylhexyl

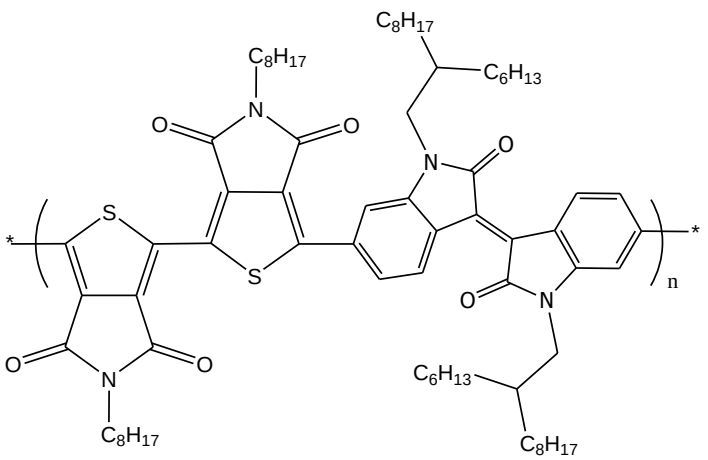
P3: R= 2-octyldodecyl



P4



P5



P6

In 2011, Wang and co-workers modified the donor moiety of P1-P3, by increasing the number of thiophene rings incorporated in between the isoindigo, i.e. **P4**. This has increased the conjugation length of the donor moieties. The PCE value has been improved up to 6.3% (Wang *et al.,* 2011b). During the past few years, various donors have been incorporated with isoindigo acceptors. One of the promising donor which has been used to polymerize with isoindigo is thieno [3,4-c]pyrrole-4,6-dione (BTD), for example the **P5** and **P6**. P5 consists of one BTD, while P6 comprises of two BTD for each donor-acceptor monomer. The results had shown that both P5 and P6 possess excellent electron mobility, i.e. 3.0 x 10^{-4} and 3.5 x 10^{-3} cm^2 s^{-1} V^{-1}, respectively (Grenier *et al.,* 2012). The details of P1-P6 have been summarized in **Table 1**. Furthermore, isoindigo have been intensively studied and incorporated with various types of donors to obtain PSC with excellent photovoltaic performance.

Table 1

Characteristics / Polymer	Copolymers						BHJ PSC								Ref.
	M_n [a] (kDa)	M_w [a] (kDa)	T_d [b] (^oC)	HOMO [c](eV)	LUMO [c] (eV)	PDI	E_g^{elec} [d](eV)	E_g^{opt} film [e](eV)	V_{OC} (V)	J_{SC} (mA/ cm^2)	FF	μ_h (cm^2/ Vs)	μ_e (cm^2/ Vs)	PCE (%)	
P1	n.a.	n.a.	400	-5.85	-3.88	2.2	1.97	1.60	0.89	5.4	0.63	n.a.	n.a.	3.0	(Wang *et al.*, 2011)
P2	Insoluble [No result]														(Zhang *et al.*, 2011)
P3	17.2	36.1	397	-5.49	-3.91	2.1	1.58	1.58	0.87	1.76	0.60	1.30×10^{-8}	n.a.	0.92	(Zhang *et al.*, 2011)
P4	n.a.	n.a.	380	-5.82	-3.83	n.a.	1.99	1.50	0.7	13.1	0.69	n.a.	n.a.	6.3	(Wang *et al.*, 2011)
P5	24	53	n.a.	-6.0	-4.2	2.2	1.8	1.72	n.a.	n.a.	n.a.	n.a.	3.0×10^{-4}	n.a.	(Grenier *et al.*, 2012)
P6	20	43	n.a.	-6.1	-4.2	2.2	1.9	1.75	n.a.	n.a.	n.a.	n.a.	3.5×10^{-3}	n.a.	(Grenier *et al.*, 2012)

[a] Measurement conducted by differential refractive index(DRI) detection. [b] Onset of degradation temperature obtained from TGA with 5% of weight loss. [c] HOMO and LUMO energy level determined from the onset of oxidation and reduction, respectively. [d] Electrochemical energy gap=| LUMO-HOMO | (eV). [e] Optical energy gap of the copolymeric thin film, E_g^{opt}. [f] μ_h represent hole mobility while μ_e represent electron mobility (cm^2/Vs).

CONCLUSION

Since isoindigo possesses excellent electron-withdrawing ability, it is a promising acceptor for the conjugated polymers in the application of organic photovoltaics. Various modifications on the chemical structure of the isoindigo still can be done in the future, to seek for a better isoindigo-based acceptor with promising properties.

LIST OF ABBREVATIONS

PCE = power conversion efficiency
PA = polyacetylene
V_{oc} = open circuit voltage
J_{sc} = short –circuit current density
FF = fill factor
HOMO = Higher Occupied Molecular Orbital
LUMO = Lower Unoccupied Molecular Orbital
BTD = thieno [3,4-c]pyrrole-4,6-dione

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