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A Review on the Thieno [2,3-c]pyrrole-4,6-dione-based small molecules for Organic Photovoltaic Cells

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***Abstract*— *Solution processed small molecules have drawn attention from the researcher and give competitive alternative to the polymer counterpart due to their advantages such as well define molecular structure and high purity without batch to batch variation. By incorporating D-A concept for structural framework, the photovoltaic performance of the small molecules had a great progress in recent years. The development of thieno[2,3-c]pyrrole-4,6-dione (TPD) as building block for small molecule Donor-Acceptor (D-A) structural framework had many potential advantages. This feature article reviews summarizes the progress of TPD based small molecules in organic photovoltaic cells.*

Keywords*— *Small molecules, Photovoltaic.

I. INTRODUCTION

Harvesting the solar energy was considered a solution for world increasing energy demand in the meantime can protect the environment. Inorganic silicon based devices were leading with high power conversion efficiency (PCE) over 20% [1]. However due to their high cost of fabrication and environmental issues [2], the search for better alternative were preferable.

In the meantime, solution processed organic photovoltaic cell (OPV) have received tremendous amount of consideration due to its advantages compares to inorganic silicon based such as low cost, lightweight, and flexible [3-5]. For the past few years, significance progress had been made with OPV based on conjugated polymer with power conversion efficiency of 9% [6] for single layer BHJ and 11% [7,8] for tandem junction OPV cells.

The good progress was mainly because of extensive development of perfect electron donating polymers and device optimization [9]. Meanwhile, conjugated small molecule have drawn an attention due to its well defined molecular structure, definite molecular weight, and high purity without batch to batch variation[10,11]. Currently, researchers are focusing on synthesis and processing of different small molecules based on D-A framework such as D-A-D [12] , D-A-A [13] and A-D-A [14-16] due to their excellence photovoltaic performance.

Thieno [2,3-c]pyrrole-4,6-dione (TPD) is known as acceptor unit and has a symmetric, coplanar structure and strong electron withdrawing properties due to imide group [17]. Besides that, TPD had good solubility and 3D arrangement in solid state [23]. It was used as building block in D-A structural framework polymers for OPV devices [18-23]. The highest PCE of 7.5% had been reported by Zhang *et al* (2015) for TPD based polymer [24]. Until recently, the review regarding TPD based polymer for organic photovoltaic devices were reported by Lerlerc (2013) and He (2016). There are rare reviews regarding TPD based small molecules. Here in this review, we will focus on small molecules based with TPD as acceptor unit for building block of solution processed OPV devices.

Tpd Based Small Molecules

The first example of TPD based small molecules was reported by Lin et al in 2011. The group synthesized a series of linear D-A-D small molecules with TPD as acceptor unit, while TPA as donor unit and thiophene as bridge[26] . According to author, all SM exhibit relatively low HOMO energy levels (-5.26 to -5.34 eV) because of electron withdrawing TPD unit. Fabricated BHJ OSC devices for SM **1a-c** exhibit a PCE between 2.7-2.9% without any post treatment. While 1b based devices with $PC_{71}BM$ (1:4, w/w) exhibit PCE of 3.31% with Voc of 0.91 V, Jsc of 7.7 $mAcm^{-2}$, FF of 0.473 after thermal annealing at 110°C for 10 min.

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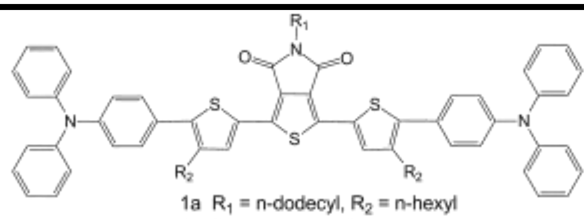


1a R_1 = n-dodecyl, R_2 = n-hexyl
1b R_1= n-dodecyl, R_2 = H
1c R_1 = 2-ethyhexyl, R_2 = H

Fig.1: Small molecule 1a-c.

Ha *et al* (2014) synthesized two TPD based small molecule with BT-TPD (**2a**) as simpler D-A framework and TBDT-TTPD (**2b**) bearing A-D-A structure with BDT as core and thiophene bridged TPD as arm [27]. Both of it exhibit low HOMO level energy of (-5.36eV). 2b blend with $PC_{61}BM$ (1:1,w/w) based devices shows PCE of 4.62% after annealed at 120°C compared to PCE of 3.90% without annealing. The author suggested that the change in PCE was mainly due to the improved short circuit current density (Jsc) from 7.9 to 9.1 mWcm-2 and affected by nanoscale morphology after treatment.

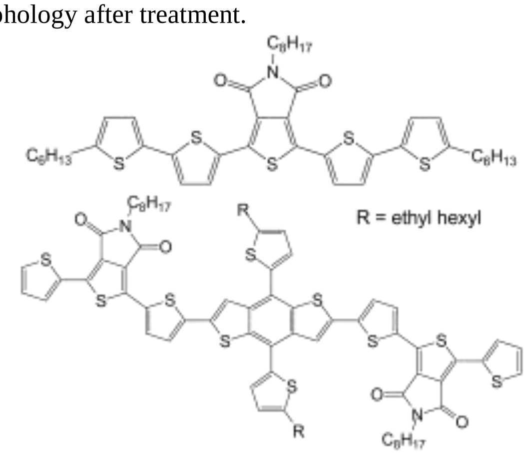
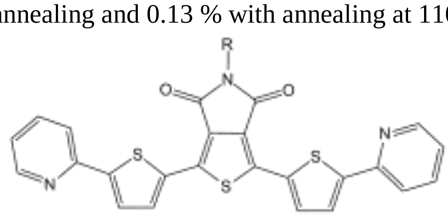


Fig.2: Small molecule 2a-b

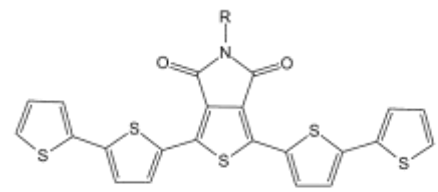
Kim *et al* (2015), synthesized **3** which contain TPD based SM and pyridine as end groups which basically on A_2-D-A_1-D-A_2 framework[28]. Pyridine act as relatively weaker electron withdrawing at end group with strong electron withdrawing TPD as the core unit. The HOMO and LUMO energy level was -5.39 and -3.17 eV respectively. The blend of SM **3** with $PC_{71}BM$ (2:1,w/w) yield the PCE of 0.16 % without annealing and 0.13 % with annealing at 110°C.



R = 2ethylhexyl

Fig.3: Small molecule 3

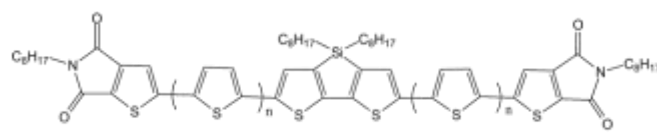
Recently, Lim had reported small molecule **4** with D-A-D framework with bithiophene as donor groups [29]. The HOMO and LUMO energy level were -5.4 and -3.2 eV respectively. Blend of 4 with $PC_{71}BM$ (2:1,w/w) shows only PCE of 0.14 % and 0.15 % after thermal annealing. According to author, the low PCE were due to low Jsc of 0.68 mA cm^{-2} and FF of 22% which in general attributed to poor form film quality and inferior charge transport to electrode.



R = 2ethylhexyl

Fig.4: Small molecule 4

Fu *et al* (2012) synthesized dithienosilole (DTS) and TPD unit bridged with thienylene and bithienylene [30]. The structure was based on A-π-D-π-A framework**. 5a-b** had a HOMO energy level of (-5.52 and -5.55 eV) and LUMO energy level (-3.57 and -3.44 eV) respectively. The author indicated that the different π-bridge units of neutral electron withdrawing ability of thiophene and bithiophene were not strong enough to influence the bond length alteration (BLA). 5a blend with $PC_{61}BM$ (2:3, w/w) and MoO_3 as electron blocking layer shows a PCE of 1.2% and Voc of 0.97 V after thermal annealing at 110°C for 3 min.



5a n= 1
5b n= 2

Fig.5: Small molecule 5a-b

Later Choi *et al* (2014) reported two TPD based small molecule with D_1-A-D_2-A-D_1 framework. D_2 was DTS and D_1 was end capping bithiophene (2T) [31]. The author was focusing on the effect of different position of alkyl substitution for molecular packing and photovoltaic performance. **6a** had n-alkyl group substituted at central of TPD while **6b** had n-alkyl group substituted at the chain end. Both 6a-b exhibited low lying HOMO (-5.50eV) and LUMO (-3.83 eV) energy level. The 6a blend with $PC_{71}BM$ show promising PCE of 6.0% with high Voc of 0.94V, Jsc of 11.8 mA cm^{-2} and FF of 0.54. While 6b shown moderate PCE of 3.1% with high Voc of 0.93V, Jsc of 6.4 mA cm-2 and FF of 0.52. The author suggested that, the higher Jsc

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value of 6a compared to 6b were due to face on orientation of crystallite leading to high SCLC hole mobility that affect the PCE.

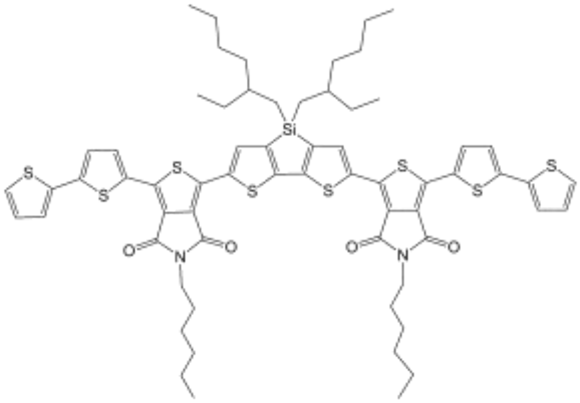

Fig.6: Small molecule 6a

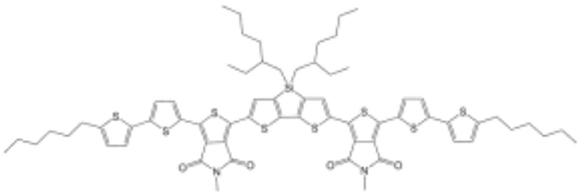

Fig.7: Small molecule 6b

Mercier *et al* (2014) later reported of two new TPD based small molecule with A-D-A framework containing dithieno[3,2-b:2′,3′-d]pyrrole (DTP) as central and TPD as end capping unit[32]. **7a** and **7b** blend with $PC_{71}BM$ (2:3, w/w) DIO as additive shows PCE of 1.2 % and 2.6 % respectively compared to 0.4 % and 2.2 % respectively without DIO additives. According to author, 7b exhibited better PCE compared to 7a due to higher Jsc and FF mainly attributed from strong absorption and better charge transport.

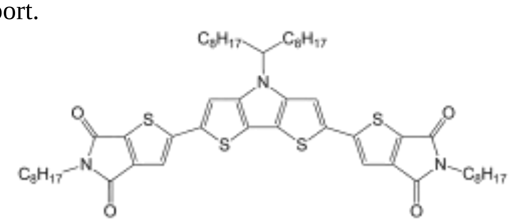

Fig.8: Small molecule 7a

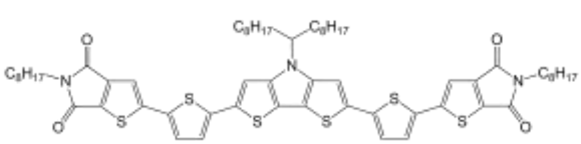

Fig.9: Small molecule 7b

Cheon *et al* (2014) reported **8** with A-D-A framework incorporating dithienobenzodithiophene (DTBDT) as core and thiophene-TPD as arm unit[33]. 8 exhibited HOMO and LUMO energy level of -5.61 and -3.55eV respectively. SM 8 blends with $PC_{71}BM$ thermally annealed at 175°C shows PCE of 4.98% with Voc of 0.85 while while without annealing only shows PCE of 3.95%. The author suggested that thermal annealing resulted in favorable highly ordered π-stacked structure compared to untreated film.

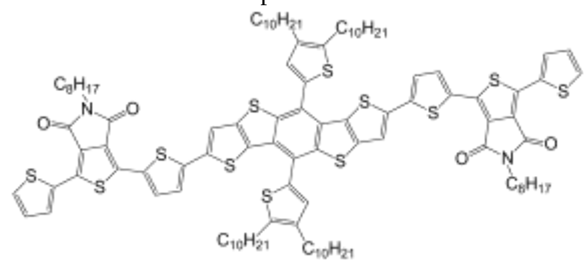

Fig.10: Small molecule 8

Two TPD based small molecule of **9a** and **9b** with A-D-A framework with benzodithiophene (BDT) as core unit were reported by Kim *et al* (2014). 9a contains a branched 2-ethylhexyl (2EH) side chain while 9b contains a linear n-octyl side chain on the BDT unit [34]. 9a blends with $PC_{71}BM$ (1:4, w/w) shows PCE of 2.40% compared to the 9a with $PC_{61}BM$ at the same ratio with PCE only 1.71%. While 9b PCE only 1.33% with $PC_{71}BM$ (1:4, w/w). The author concluded that, 9a exhibited higher light absorption, smaller band gap and more planar structure than 9b which affect the PCE.

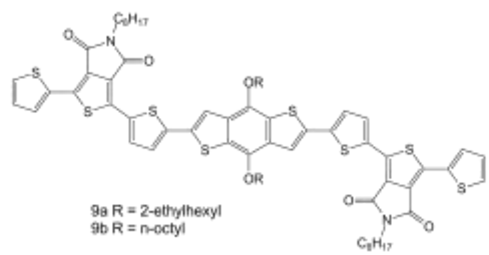

Fig.11: Small molecule 9a-b

Later on, Bagde *et al* (2016), reported two SM composed of naphthodithiophene (NDT) as core unit; **10a** had TPD acceptor unit end capped without alky-bithiophene and **10b** had TPD acceptor unit end capped with alkyl-bithiophene [35]. Different ratio of blend for 10a and 10b have PCE below 1 %. The author concludes that the lower PCE were due to large band gap, poor FF and unbalanced charge mobility. Only 10b blends with $PC_{71}BM$ (1:3,w/w) treated with 1.0 % DIO only manage to yield PCE of 1.31%.

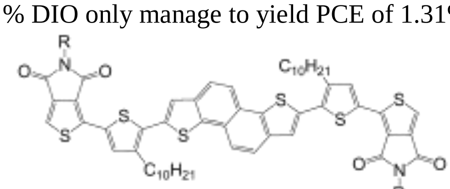

Fig.12: Small molecule 10a

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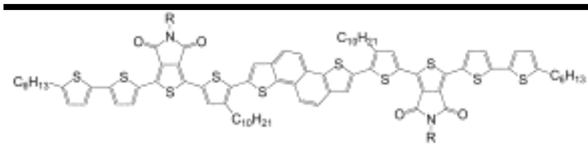

Fig.13: Small molecule 10b

In 2016, Tao *et al* developed small molecule of **11a** and **11b** which had structural framework of D(A-A')$_2$. Benzodithiophene (BDT) and thiophenyl-substituted benzodithiophene (BDTT) were used as central donor, diketopyrrolopyrole (DPP) and TPD acts as dual acceptor (A and A' unit) respectively[35]. 10a blends with $PC_{61}BM$ (1:3,w/w) produce PCE of 2.41% with Voc of 0.78 V while 11b blends with $PC_{61}BM$ (1:5:1,w/w) produce moderate PCE of 4.25 % and Voc of 0.77 V after annealing at 110°C. The morphology study of the blends film shows that 11a and 11b have finer features after treatment.

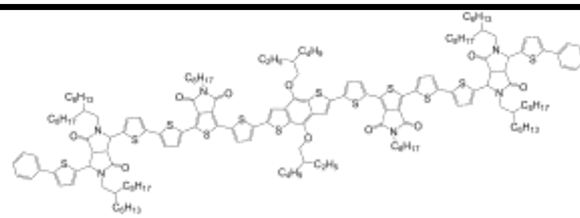
Fig.14: Small molecule 11a

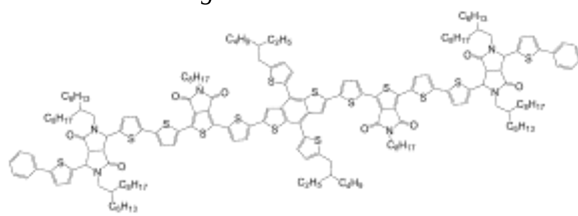
Fig.15: Small molecule 11b

Table.1: A summary of experimental and characterization data for Small molecule 1a to 11b

Characteristic / Small molecule	Td[a] (°C)	HOMO[b] (eV)	LUMO[b] (eV)	Voc (V)	Jsc (mA/cm^{-2})	FF	PCE (%)	**Ref**
1a	437	-5.34	-2.61	0.94	6.94	0.439	2.87	
1b	434	-5.32	-2.67	0.91	7.70	0.473	3.31	**[26]**
1c	424	-5.26	-2.96	0.91	6.39	0.464	2.70	
2a	442	-5.36	-3.17	0.84	6.2	23.1	1.43	**[27]**
2b	457	-5.36	-3.39	0.97	9.1	52.0	4.62	
3	n.a	-5.39	-3.17	0.83	0.73	26	0.16	**[28]**
4	n.a	-5.40	-3.20	1.04	0.68	22	0.15	**[29]**
5a	315	-5.55	-3.44	0.97	2.60	47.58	1.20	**[30]**
5b	258	-5.52	-3.57	0.88	2.59	32.90	0.75	
6a	n.a	-5.50	-3.78	0.94	11.8	0.54	6.00	**[31]**
6b	n.a	-5.50	-3.83	0.93	6.4	0.52	3.10	
7a	n.a	-5.60	-3.47	1.10	3.2	0.35	1.20	**[32]**
7b	n.a	-5.33	-3.45	0.95	5.8	0.47	2.60	
8	463	-5.61	-3.55	0.85	10.6	56.0	4.98	**[33]**
9a	390	-5.27	-3.34	0.92	4.7	54.4	2.40	**[34]**
9b	372	-5.33	-3.37	0.89	2.7	55.2	1.33	
10a	420	-5.38	-3.46	0.79	1.21	27.31	0.26	**[35]**
10b	352	-5.26	-3.55	0.75	3.32	52.44	1.31	
11a	371	-5.67	-3.63	0.78	5.69	54.5	2.41	**[36]**
11b	n.a	-5.68	-3.64	0.77	10.83	50.9	4.25	

[a]Onset of degradation temperature obtained from TGA with 5% of weight loss. [b]HOMO and LUMO energy level determined from onset of oxidation and reduction respectively.

II. CONCLUSION

In this review, we had summarized the TPD based small molecules for OPV devices. Until now only a few research were made for TPD based small molecules. The analysis of of the structural framework revealed that most of TPD based small molecules were based on D-A concept. Although the photovoltaic performance of small molecules based TPD compiled here was average and the higher PCE was only 6%, the versatility of TPD as the building block for small molecules could not be neglected. Thus it can be further improved through implementation of different donor (D) material, bridges and different structural of framework. In addition, further optimization of the device structure should be focused in order to improve the photovoltaic performance of TPD based small molecule. We look upon in the future the researcher will focusing more on the TPD based small molecule for application in OPV devices.

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