Synthesis of pyridine-capped diketopyrrolopyrrole and its use as a building block of low band-gap polymer for efficient polymer solar cells

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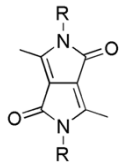
Introduction

❖Diketypyrrolopyrrole (DPP) as a building block of conjugated polymer

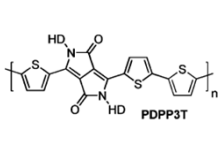


general structure of DPP molecule

Features of DPP derivatives as a building block of conjugated polymer

→ Easy to synthesis, high molar absorptivity and stability
→ Highly conjugated structure, which leads to strong π–π interaction
→ Strong electron deficiency for potential electron accepting moiety in low band-gap conjugated polymers

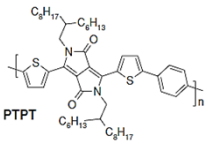
❖Low HOMO level of conjugated polymer based on thiophene-capped DPP



PDPP3T

HOMO = −5.17 eV V_{OC} = 0.68 V

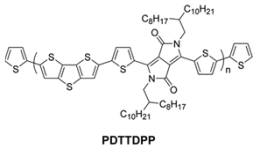
Janssen *et al*, *J. Am. Chem. Soc* **2009**, *131*, 16616



PTPT

HOMO = −5.35 eV V_{OC} = 0.80 V

Janssen *et al*, *Adv. Mater.* **2010**, *22*, E242



PDTTDPP

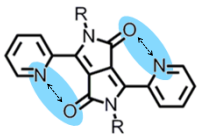
HOMO = −5.19 eV V_{OC} = 0.66 V

W. H. Jo *et al*., *Energy Env. Sci.* **2012**, *5*, 6857

✓High-lying HOMO level of conjugated polymer based on thiophene-capped DPP
✓Low V_{OC} of polymer solar cells due to high-lying HOMO level

⇒ Enhancement of V_{OC} of polymer solar cells by lowering the HOMO level of DPP-based SCPs is an important issue.

❖Pyridine: A novel candidate as a flanking group of DPP



structure of pyridine-capped DPP

Advantage of pyridine-capped DPP

→ Imine (C=N) group in pyridine pulls electrons because of strong electronegativity of nitrogen atom
→ PyDPP becomes stronger electron-accepting group and thus lowers the HOMO level of SCPs.
→Reduced repulsive interaction enhances planarity of polymer backbone

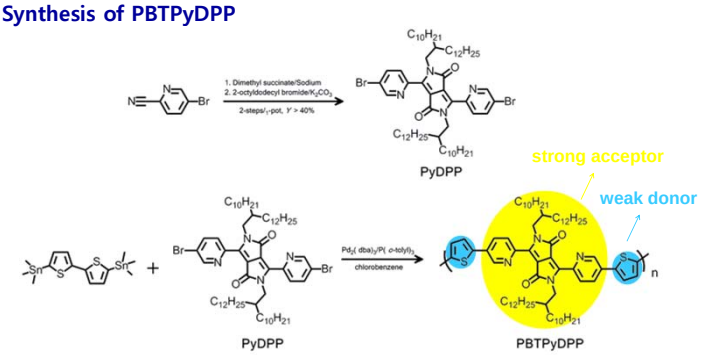
Objectives

❖ To introduce the pyridine as a flanking group of DPP, and utilize of PyDPP as a strong electron-accepting unit for synthesizing a D−A type low band-gap copolymer

❖ To investigate the photovoltaic properties of polymer solar cells based on PBTPyDPP

Results

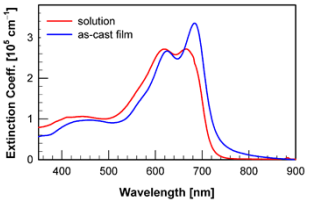
❖ Synthesis of PBTPyDPP

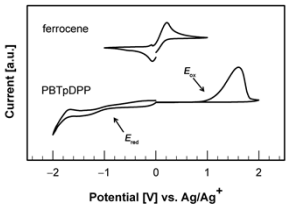


Polymer	M_n [kDa]	M_w [kDa]	PDI	HOMO [eV]	LUMO [eV]	$E_{g,ele}$ [eV]	$E_{g,opt}$ [eV]
PBTPyDPP	18	22	1.22	−5.75	−3.86	1.89	1.71

Results

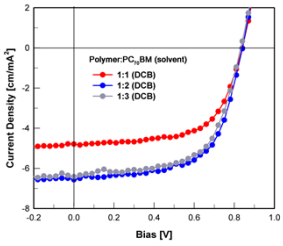
❖ UV-Vis Absorption Spectra and cyclic voltammetry of PBTPyDPP

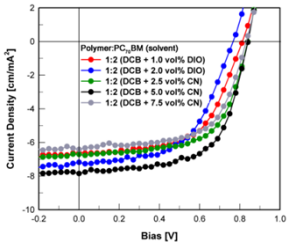




✓PBTPyDPP exhibits red-shift of absorption spectra in film state.
✓Low-lying HOMO level of PBTPyDPP is expected to afford high V_{OC} of solar cell.

❖ Photovoltaic Performance of PBTPyDPP and $PC_{71}BM$

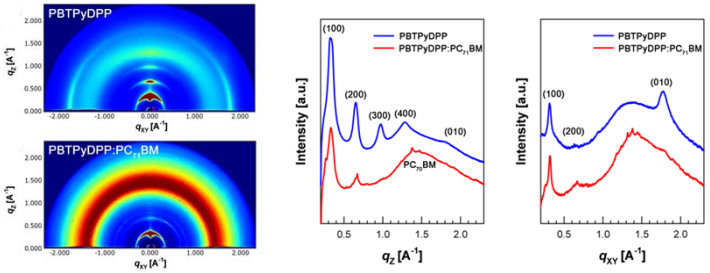




PBTPyDPP:$PC_{71}BM$	Solvent	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
1:1	DCB	0.91	4.79	62.4	2.7
1:2	DCB	0.91	6.57	61.5	3.7
1:3	DCB	0.90	6.41	60.8	3.5
1:2	DCB + 1.0 vol% DIO	0.86	6.61	58.8	3.3
1:2	DCB + 2.0 vol% DIO	0.82	7.18	56.1	3.3
1:2	DCB + 2.5 vol% CN	0.89	6.61	59.1	3.5
1:2	DCB + 5.0 vol% CN	0.92	7.96	65.8	4.9
1:2	DCB + 7.5 vol% CN	0.90	7.63	57.8	4.0

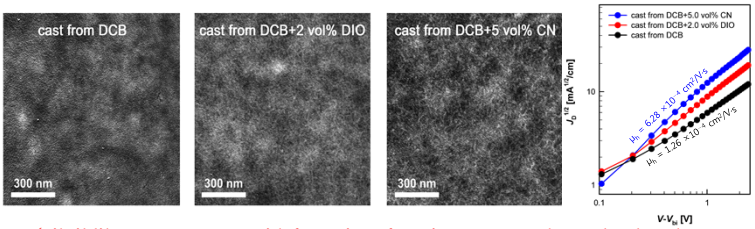
✓PBTPyDPP yields high V_{OC} over 0.9 V and promising high PCE up to 4.9%.

❖Grazing-incident wide angle X-ray spectroscopy of PBTPyDPP and $PC_{71}BM$



✓Highly crystalline lamellar structure with both face-on and edge-on orientation

❖ Morphology of PBTPyDPP and $PC_{71}BM$



✓Fibril-like nanostructures with formation of continuous network was developed.

Conclusions

❖ A new building block, PyDPP, was synthesized for constructing semiconducting conjugated polymers, PBTPyDPP.

❖ The PSCs fabricated from PBTPyDPP exhibited a promising PCE of 4.9% with a high VOC of 0.92 V, suggesting that PyDPP can be used as a novel building block for design of high-performance SCPs.