

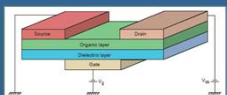
Synthesis and Properties of Indigo based Donor–Acceptor Conjugated Polymers

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Introduction

Organic thin-film transistors (OTFTs):

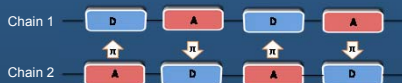


Transistors: work as electronic switches to control the electrical current between source / drain electrodes by applying an input voltage on "gate".

Transport holes or electrons, depending on the organic semiconductor.

Polymer semiconductors normally bearing donor-acceptor (D-A) structure synthesized by transition-metal catalyzed D-A units crossing-coupling reactions.

D-A Polymer:

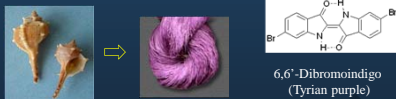


Donor: π -electron rich moiety
Acceptor: π -electron deficient moiety

Easy to tune the bandgap of resultant conjugated polymer

Making the polymer chains tightly packed along the π - π stacking direction

Indigo (ID) Molecule:



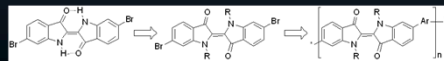
A natural dye indigo used as early as 1600 BCE.

A strong electron withdrawing unit, with a highly coplanar geometry.

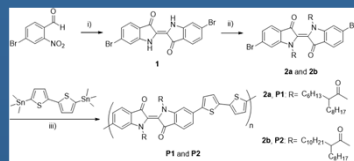
An isomer of isoindigo (IID), which shows good performance in OTFTs.

No report to make the molecule soluble for polymerization yet.

What if indigo molecule could be incorporated into polymers as an acceptor unit as below?



Polymer Synthesis



i) NaOH / acetone / rt.; ii) a) NaH / NMP / rt. b) RCOCl / rt.; iii) Pd₂(dba)₃ / P(o-tolyl)₃ / chlorobenzene / 90 °C.

Substitution: the nitrogen atoms of indigo molecule could be readily substituted with acyl groups by using the chemistry we used for diketopyrrolopyrrole (DPP) unit.

Long branched side chains: 2-hexyldecanoyl and 2-octyldecanoyl provide the desirable solution processability to PIDBT (P1 and P2).

Purification of PIDBT: by Soxhlet extraction method, finally dissolved in 130 °C 1,1,2,2-tetrachloroethane (TCE), both polymers obtained as a bluish film.

Polymer Characterization

Molecule Weight:

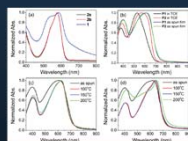
	Mn(kDa)	PDI	Mw(kDa)
P1 (TCE)	13.5	3.50	47.4
P2 (CHL)	12.4	10.6	130.6

Characterized by Gel Permeation Chromatography (GPC), by using polystyrenes as standards and chlorobenzene as an eluent at column temperature of 40 °C.

The molecular weight of P2 dissolved in TCE could not be measured because of its very poor solubility. However, we can reasonably assume that the molecular weight of P2 in the TCE fraction should be higher than that of P1. The results used for the following discussions were obtained using the fractions of P1 and P2 dissolved in TCE.

UV-vis Absorption:

The blue shift of ~10 nm for the λ_{max} for 2a and 2b with respect to compound 1 in TCE solution (a) is likely to be the result of the twisted indigo moiety caused by the acyl groups.

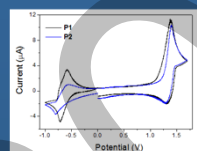


As-spun thin film (b): λ_{max} ~ 527 nm for P1 and ~ 572 nm for P2, blue shift is due to the higher molecular weight and thus the longer effective conjugation length of P2

P1 thin film annealed at 100 °C (c): λ_{max} red shifted to 626 nm. P2 thin film annealed at 100 °C, 150 °C and 200 °C (d): λ_{max} red shifted progressively to 639, 643 and 651 nm. Thermal annealing increased the chain ordering and led to more extended π -conjugation of the polymer backbone.

Electrochemistry and energy levels of

PIDBT:



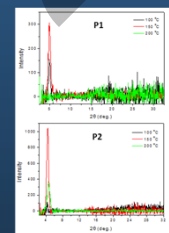
E_{HOMO} calculated from the oxidative onset potential: -5.69 eV for P1 and -5.78 eV for P2 (ferrocene as the standard).

Lower E_{HOMO} of P2 than that of isoindigo based polymers, due to the strong electron-withdrawing effect of indigo unit.

$E_{LUMO} = E_{HOMO} + E_{g}^{opt}$, the obtained values are closed to those calculated from the reductive onset potential.

	E_g	HOMO	LUMO (CV based)	LUMO (UV based)
P1	1.69eV	-5.69eV	-4.00eV	-4.00eV
P2	1.69eV	-5.78eV	-4.02eV	-4.10eV

XRD patterns of PIDBT film:

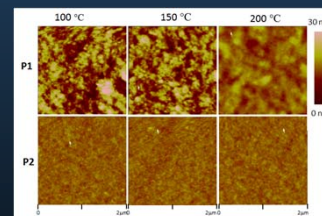


Thin film of both polymers showed much intensified peaks when annealed at 150 °C, manifesting improved crystallinity.

The corresponding d-spacing was calculated to be ~18.4 Å for P1 and 20.2 Å for P2, respectively.

Increasing the annealing temperature to 200 °C, the intensity of the primary peak decreased and the d-spacing further decreased, due to the loss of the side chains as corroborated by the thermal analysis data.

Thin film AFM images:



the 100 °C - and 150 °C -annealed P1 thin films contain large grains.

The 200 °C -annealed P1 thin film became more uniform, probably due to the removal of the side chains.

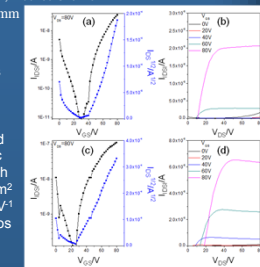
all of the P2 thin films are very smooth and the surface morphology was not much influenced by thermal annealing.

Characterization of OTFTs:

Gate
Semiconducting
Source
Drain

$L = 30$ mm;
 $W = 1000$ mm

Transfer and output curves of OTFT devices with P1 (a and b) and P2 (c and d) thin films annealed at 150 °C for 20 min.



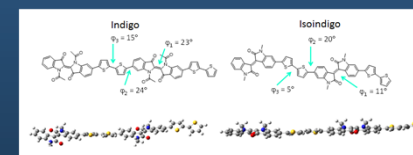
Devices with P1 or P2 thin films annealed at 100 °C showed no field effect performance.

Devices with thin films annealed at 150 °C showed characteristic electron transport behaviour with a mobility as high as 6.6×10^{-4} cm² V⁻¹ s⁻¹ for P1, and 1.1×10^{-3} cm² V⁻¹ s⁻¹ for P2. (current on-to-off ratios of ~10⁴).

Further increasing the annealing temperature to 200 °C resulted in the absence of field effect performance for both polymers, due to the deteriorated molecular ordering caused by thermal decomposition of the side chains.

The observed mobility values are much lower in comparison to isoindigo counterpart.

Simulated geometry of ID and IID:



The dihedral angle between the two indol moieties (ϕ_1), as well as that between two thiophen units (ϕ_3) of ID based polymers are greater than those of IID based polymers, according to the simulated results.

The backbone twisting led to the poor main chain conjugation, then resulted in the relatively low mobility.

Conclusions

For the first time, the novel D–A polymers based on indigo as acceptor, were synthesized and applied as organic semiconductor in OTFTs.

The low-lying HOMO/LUMO levels and rather low band gap manifested the strong electron withdrawing capability of the indigo moiety.

P1 and P2 showed characteristic electron transport performance in OTFTs with electron mobilities of up to 6.6×10^{-4} cm² V⁻¹ s⁻¹ for P1 and 1.1×10^{-3} cm² V⁻¹ s⁻¹ for P2, respectively.

The lower than expected field effect performance of these polymers in comparison to their counterpart isoindigo polymers was considered to be due to the backbone twisting according to the simulation result, which is undesirable for extended delocalization of electrons.

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