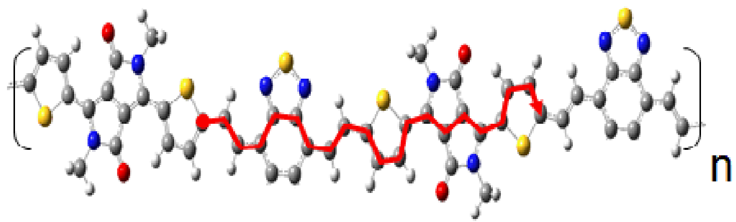

Tuning the Electronic and Structural Properties of Copolymers for Transistors and Photovoltaics

Kirsty Leong, Nick R. Myllenbeck, Michael E. Foster, Joseph G. Cordero

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Phoenix, AZ
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Introduction

Sandia National Laboratories

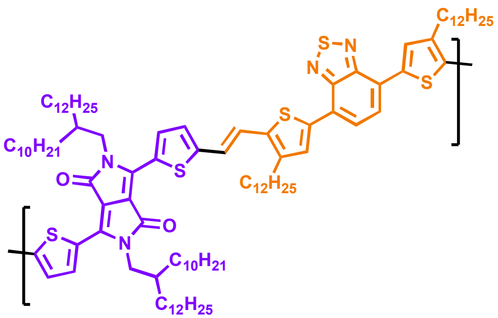
Effective strategies to tune materials' properties

(1) Choice of building block(s) for polymer backbone: electronic nature of monomer (donor/acceptor polymers, quinoidal *versus* aromatic)

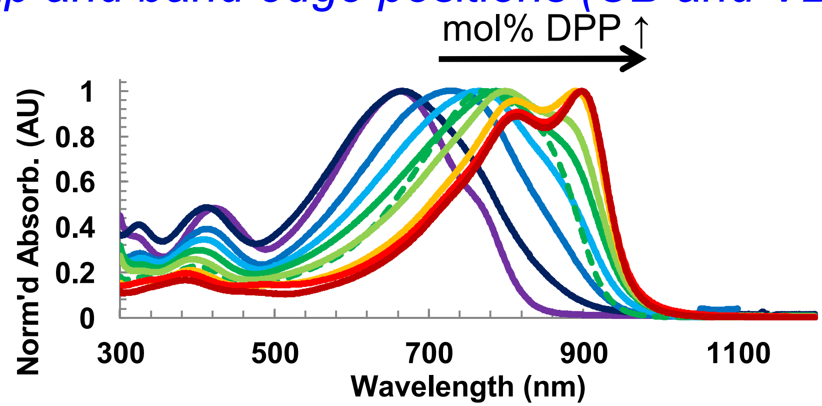
(2) Special designs alkyl chains

(3) (Co)monomer sequence: chain length, shape, substituting position.

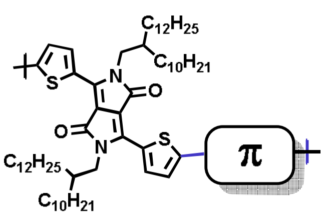
Demonstrate ability to tune band gap and band edge positions (CB and VB energy levels)

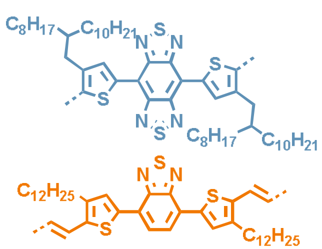


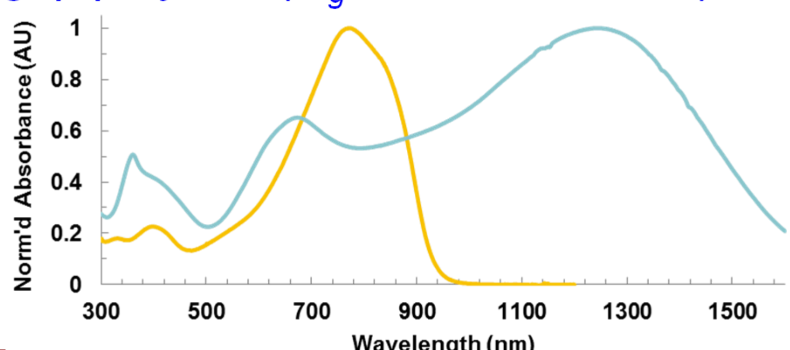
DPP BTDT-C_{12}



Apply above strategy to a low band gap polymer (E_g<1eV or 1240nm)

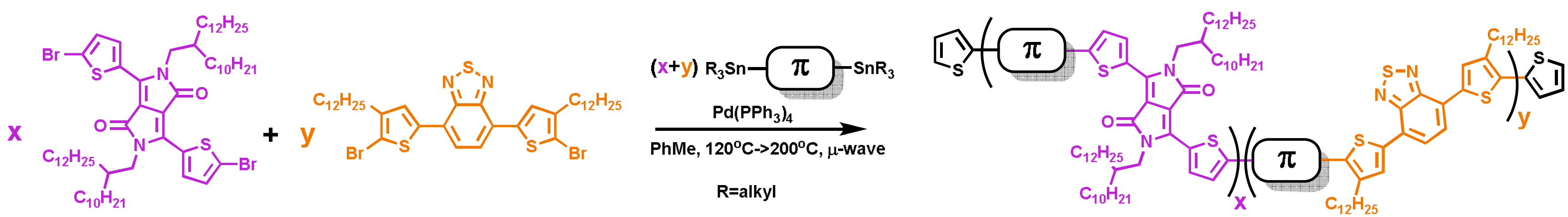


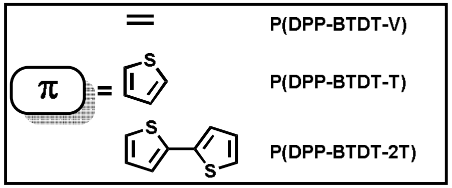




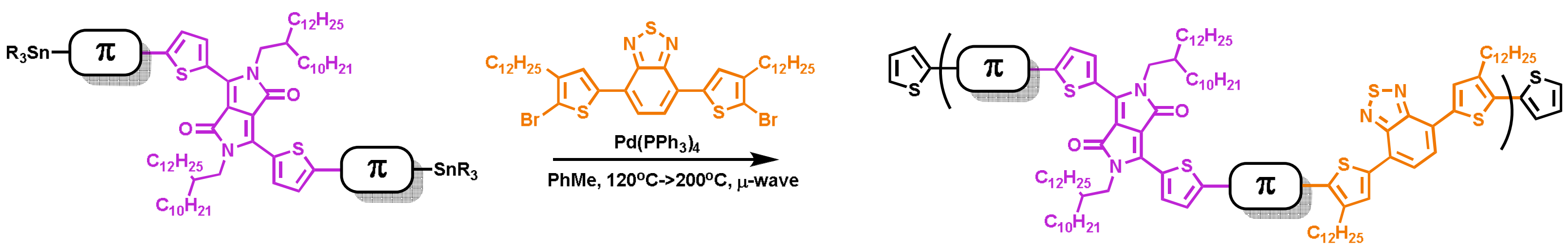
Copolymer Synthesis

Random Copolymer Synthesis





Alternating Copolymer Synthesis



- Series of DPP and BTDT based small band gap copolymers are synthesized by Pd-catalyzed Stille-coupling polymerization.
- Polymers contain extended aromatic π-conjugated segments to increase free energy for charge generation.
- Ratio of DPP and BTDT varied in the polymer backbone.
- Effects of the linkers on the electronic and optical properties.
- Polymer MW ~16.5-19 kDa and PDI range 1.54 -1.93.

Tuning the Optical Properties: *Vinylene Linker*

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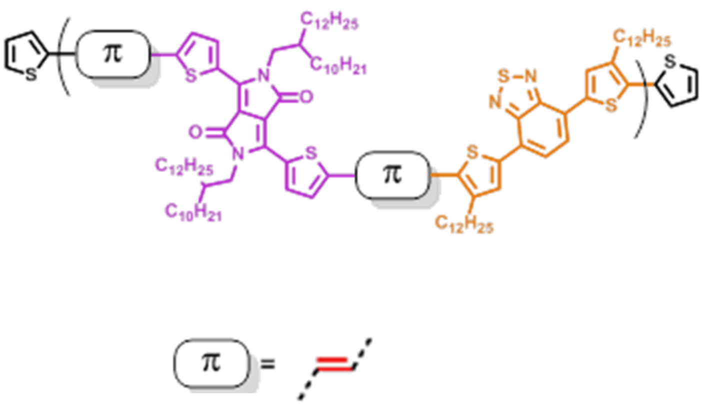
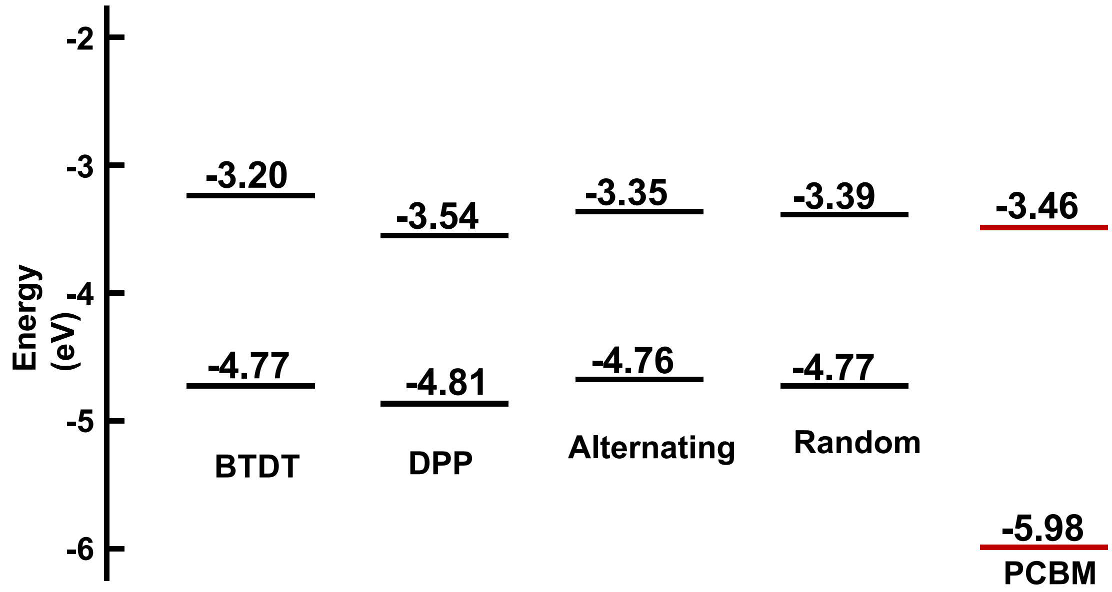
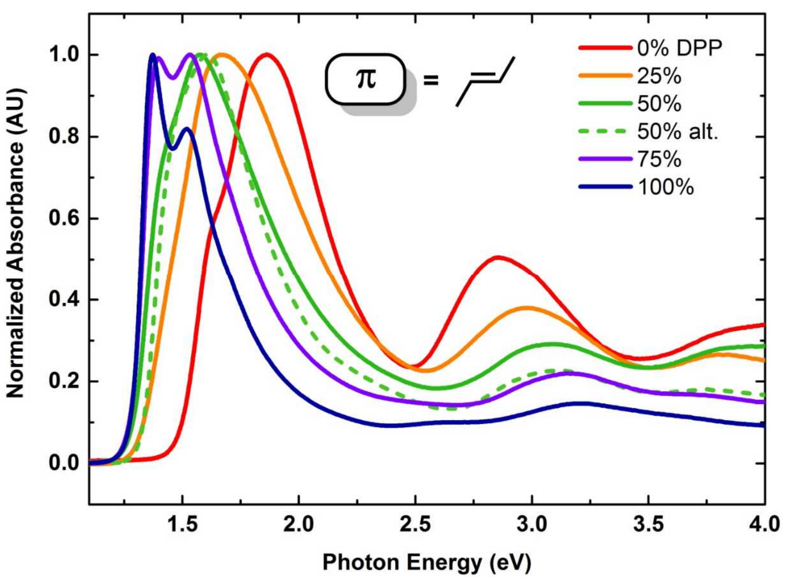
P(DPP-BTDT-V)



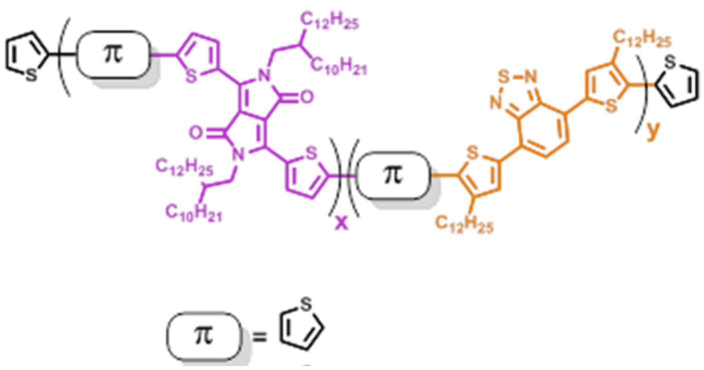


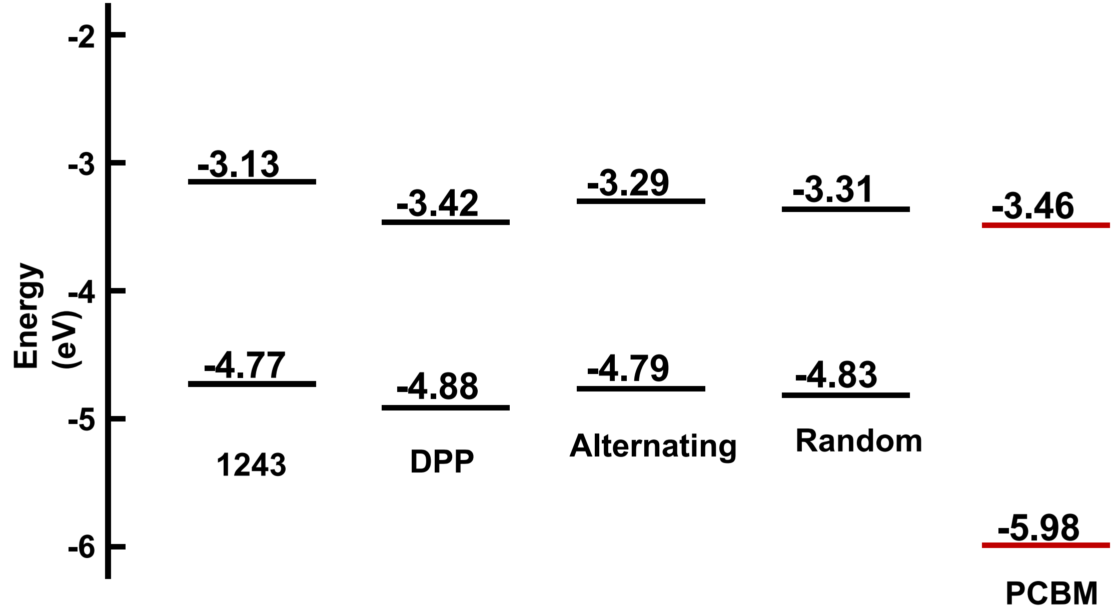


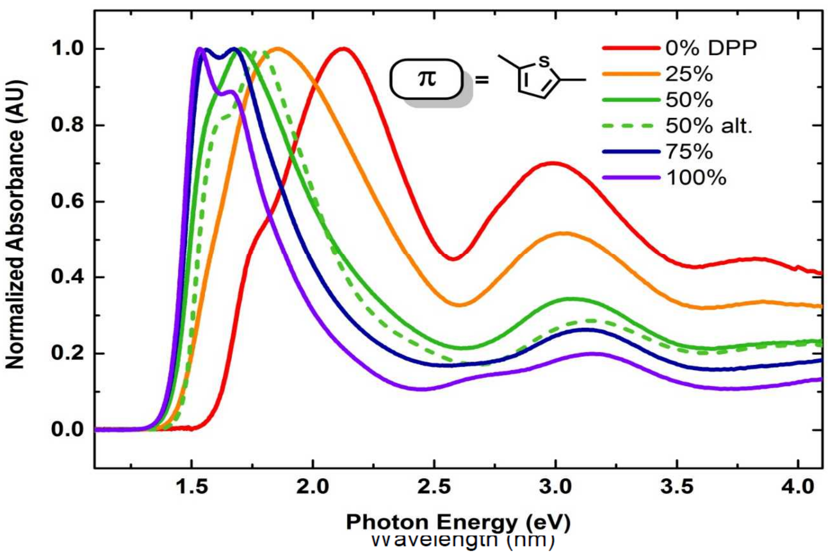
- Band gap: 1.57eV for BTDT, 1.27eV for DPP, 1.41eV for alt. DPP+1243, 1.38eV for rand DPP+1243.
- Absorption from visible to near-IR.
- Varying with the molar ratio of DPP and BTD, the absorption range and band gaps of polymers can be tailored.

Tuning the Optical Properties: *Thiophene Linker*

P(DPP-BTDT-T)



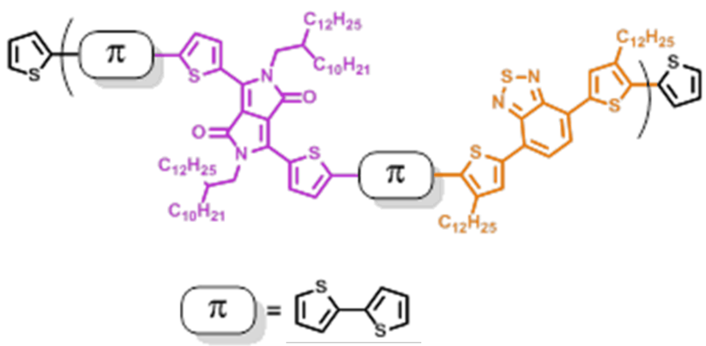


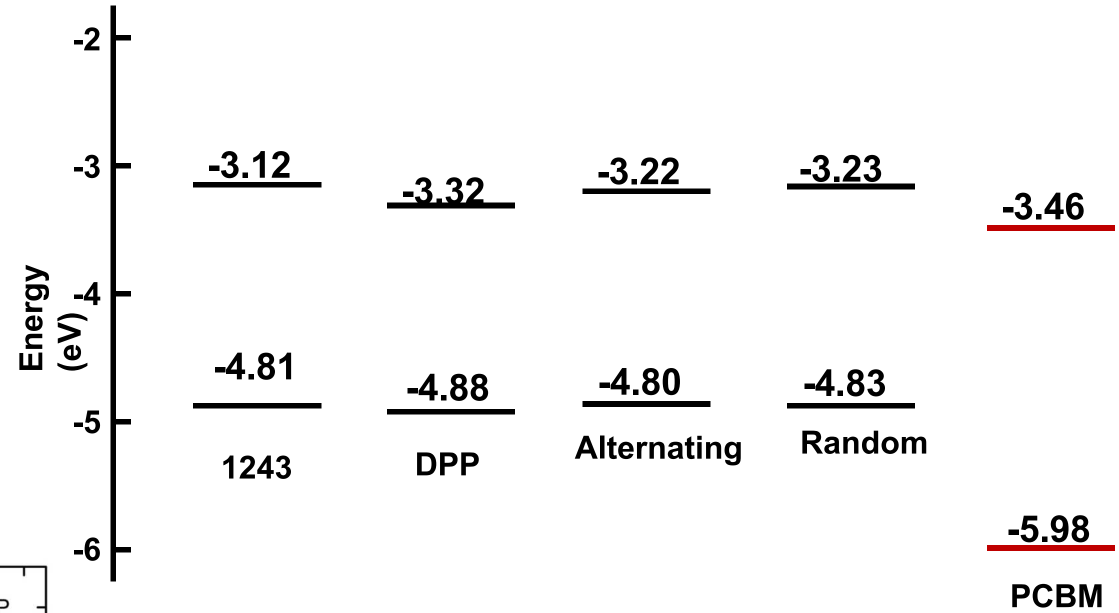


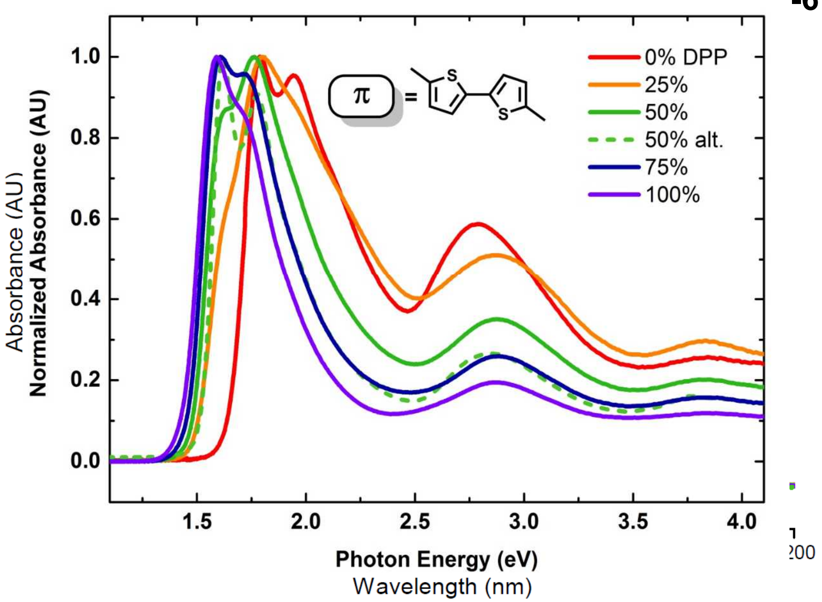
- Band gap: 1.64eV for BTDT, 1.46eV for DPP, 1.50eV for alt. DPP+1243, 1.52eV for rand DPP+1243.

Tuning the Optical Properties: Bit*hiophene Linker*

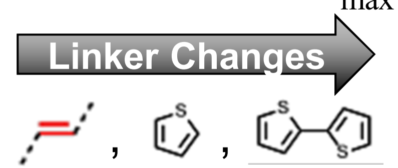
P(DPP-BTDT-2T)





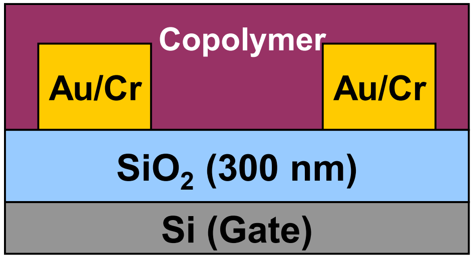


- Band gap: 1.69eV for BTDT, 1.56eV for DPP, 1.58eV for alt. DPP+1243, 1.60eV for rand DPP+1243.
- Bandgap increases and λ_{max} blue shifts as



OFET Mobility Measurements

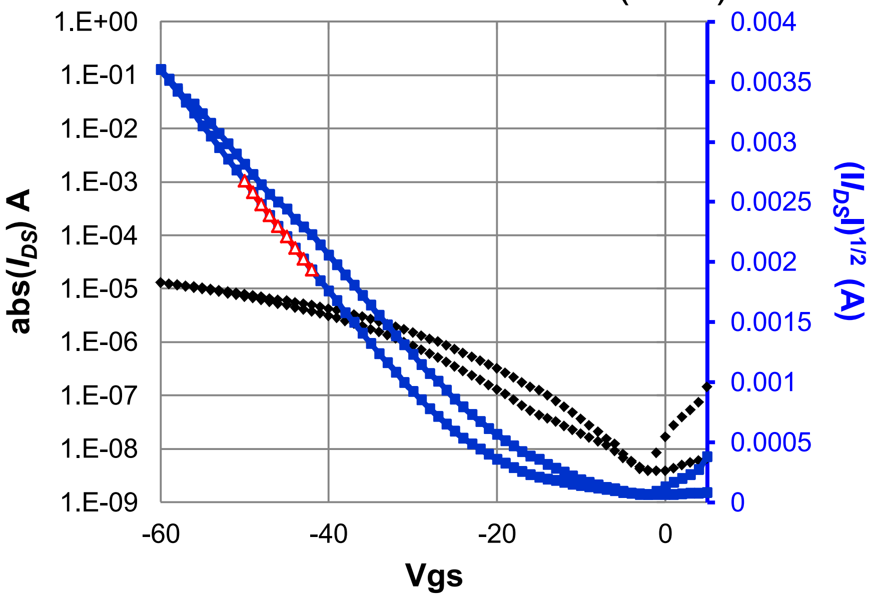
Bottom Contact Devices



Channel Dimensions
W = 20 μm L =1000 μm

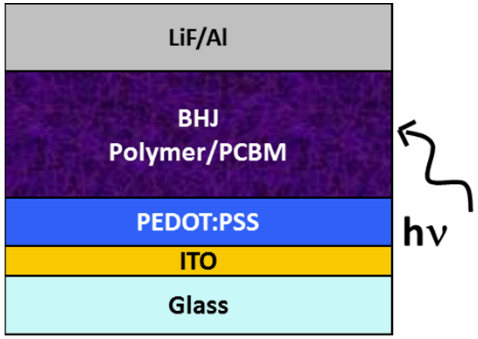
Mol% DPP	μ_{avg} (cm²/V•s) P(DPP-BTDT-V)	μ_{avg} (cm²/V•s) P(DPP-BTDT-T)	μ_{avg} (cm²/V•s) P(DPP-BTDT-2T)
0	n/a (not soluble)	5.33×10^{-6}	n/a (not soluble)
25	7.52×10^{-2}	4.21×10^{-3}	2.59×10^{-2}
50	1.62×10^{-2}	2.45×10^{-2}	3.41×10^{-2}
75	2.92×10^{-3} (p-type) 1.10×10^{-3} (n-type)	3.06×10^{-2}	5.73×10^{-2}
100	1.66×10^{-3} (p-type) 1.99×10^{-3} (n-type)	3.37×10^{-1}	2.26×10^{-1}

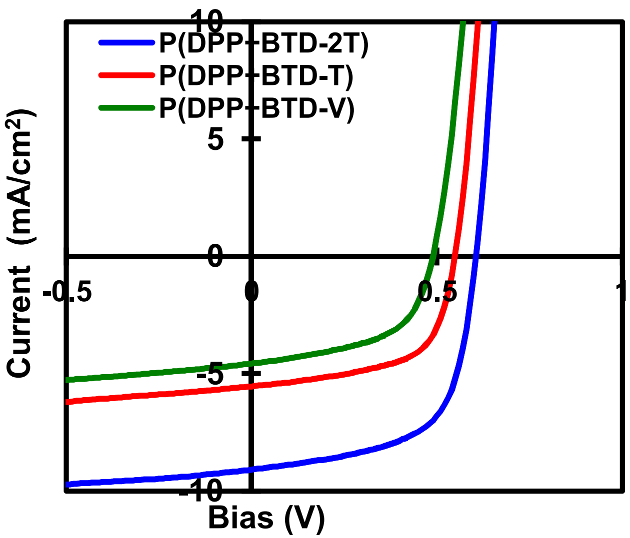
Transfer characteristics (5-63)



- Vinylene linked: Mobility decreases as the mol%DPP increases. At higher DPP ratio, the copolymer exhibits ambipolar behavior.
- Thiophene linked: Mobility increases as the mol% of DPP increases.
- DPP's ability to self-organized is disrupted by the presence of the BTDT units.
- Effects of linker on DPP's mobility: Mobility is highest with thiophene linker. Less intramolecular interactions within a polymer backbone with increasing linker lenghts. 2T has 4thiophene units separating DPP; 1T has 3T units separating the DPP units. Effective conjugation is broken with increasing thiophene units.

OPV Device Characteristic: Copolymers versus Homopolymer





P(DPP+BTDT-V)+PCBM	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	P_{max} (η%)
61.12 (25mol%DPP)	4.57	0.485	0.55	1.22
61.13 (50mol%DPP)	1.53	0.545	0.56	0.467
61.14 (75mol%DPP)	1.05	0.565	0.39	0.23
61.15 (100mol%DPP)	1.33	0.635	0.40	0.37

P(DPP+BTDT-T)+PCBM	Jsc	Voc	FF	Pmax
62.2 (0mol%DPP)	1.72	0.385	0.4	0.261
62.3 (25mol%DPP)	5.54	0.545	0.61	1.83
62.5 (50mol%DPP)	2.73	0.595	0.62	1.01
62.7 (75mol%DPP)	1.94	0.645	0.59	0.72
62.9 (100mol%DPP)	1.52	0.675	0.53	0.543

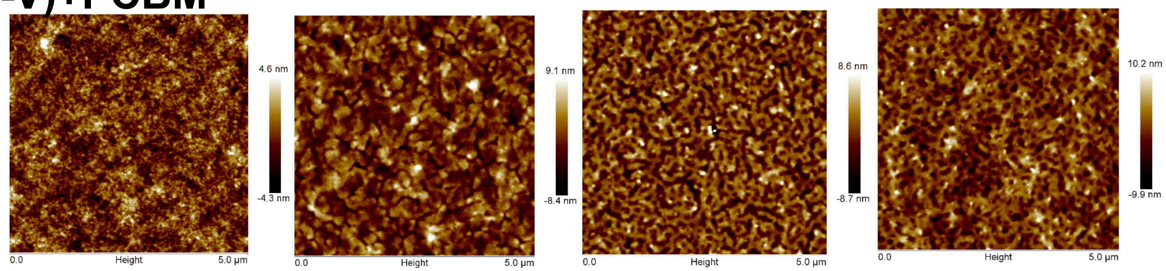
P(DPP+BTDT-2T)+PCBM	Jsc	Voc	FF	Pmax
63.3 (25mol%DPP)	6.06	0.535	0.58	1.88
63.5 (50mol%DPP)	6.06	0.525	0.6	1.92
63.7 (75mol%DPP)	9.08	0.605	0.62	3.43
63.9 (100 mol%DPP)	7.24	0.665	0.65	3.15

OPV device performances are higher with copolymers DPP and BTDT, as oppose to homopolymer (eg. pure DPP or 1243).

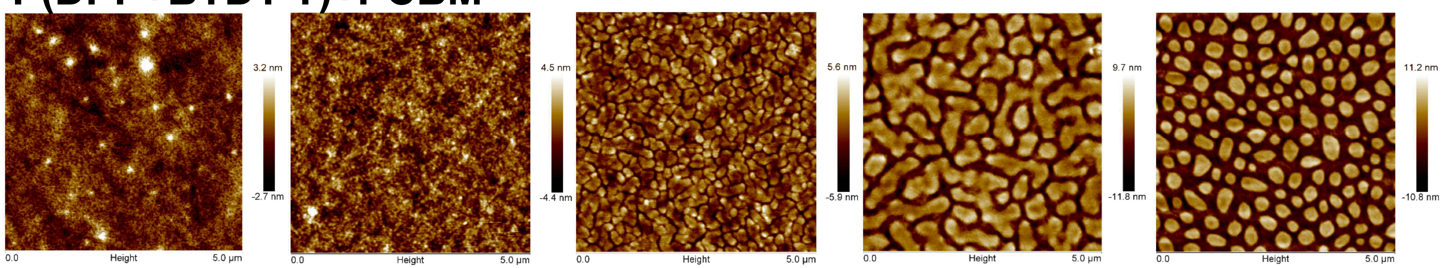
Morphology Characterization: OPV Film

Increasing mol% DPP : 0% to 100%

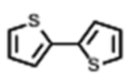
P(DPP+BTDT-V)+PCBM

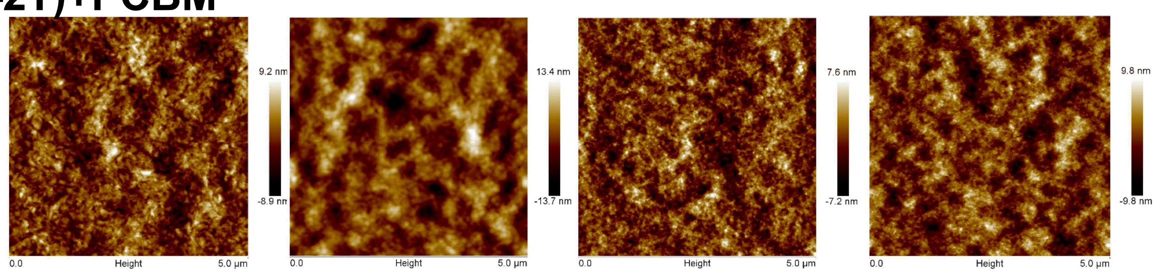


P(DPP+BTDT-T)+PCBM



P(DPP+BTDT-2T)+PCBM





Increasing mol% of DPP in the copolymer results in an increase in phase segregation for vinylene and thiophene linkers; effectively decreasing device performance. However, using bithiophene linkers, phase segregation is reduced and highest η.

Conclusions

- Optical properties of copolymers are effectively tuned by varying the composition’s concentration.
- BTDT disrupts the self-organization of DPP resulting in decrease mobility.
- *OPV device performances are higher with copolymers DPP and BTDT, as oppose to homopolymer*
- Linker effects the mobility and efficiency

Acknowledgements

- Michael Foster (Modeling)
- Nick Myllenbeck (Synthesis)
- Dustin Murtagh
- Eric Brown
- Molecular Foundry, LBNL

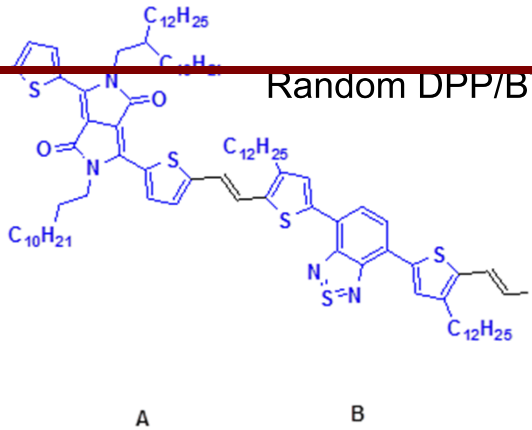
Funding

- **Sandia Laboratory Directed Research and Development Program**

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Random Polymers: OPV and OFET Characteristic Summary

Random DPP/BT/vinylene

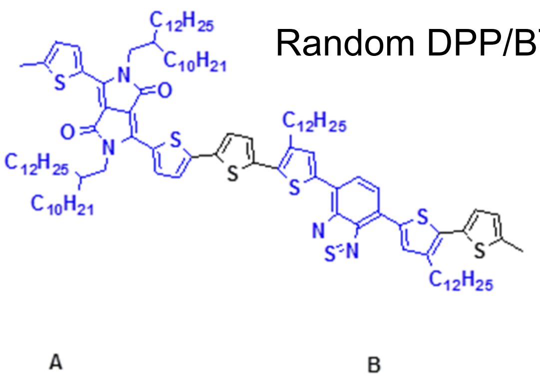


Mol % DPP	Highest Mobility, μ $cm^2/V{\bullet}s$	PCE (η %)
0	n/a (not soluble)	–
25	7.52×10^{-2}	1.19
50	1.62×10^{-2}	0.458
75	2.92×10^{-3} (p-type) 1.10×10^{-3} (n-type)	0.220
100	1.66×10^{-3} (p-type) 1.99×10^{-3} (n-type)	0.294

Increasing

Increasing

Random DPP/BT/thio

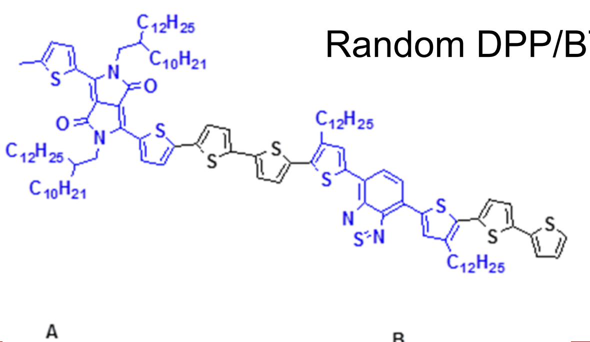


Mol % DPP	Highest Mobility, μ $cm^2/V{\bullet}s$	PCE (η %) Nov 17	PCE (η %) Dec 9
0	5.33×10^{-6}	0.438	0.261
25	4.21×10^{-3}	1.41	1.83
50	2.45×10^{-2}	0.844	1.01
75	3.06×10^{-2}	0.720	0.72
100	3.37×10^{-1}	0.458	0.543

Increasing

Increasing

Random DPP/BT/Bi-thio



Mol % DPP	Highest Mobility, μ $cm^2/V{\bullet}s$	PCE (η %)	PCE (η %) Dec 9
0	n/a (not soluble)	-	-
25	2.59×10^{-2}	1.88	1.29
50	3.41×10^{-2}	1.92	1.09
75	5.73×10^{-2}	2.45	3.43
100	2.26×10^{-1}	2.51	3.15

Increasing

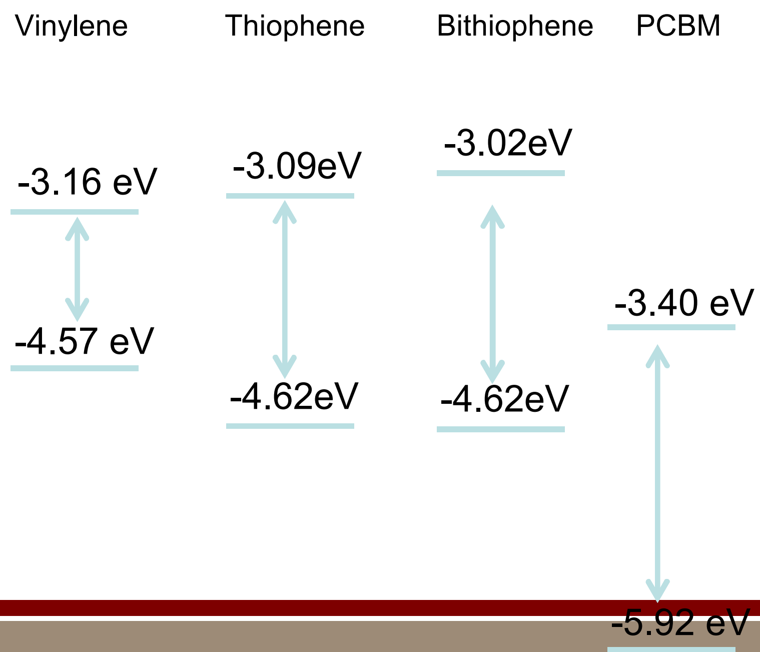
Increasing

Increasing

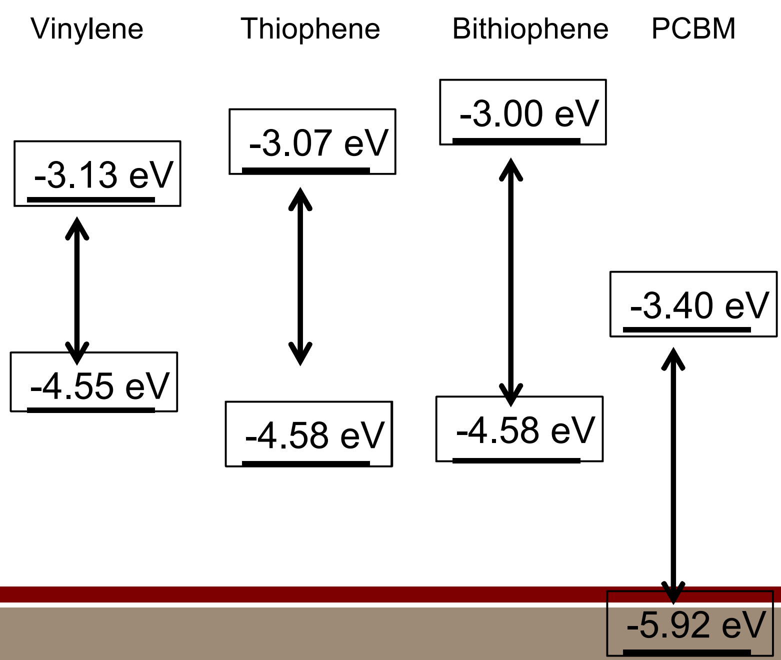
Synthetic Efforts for Higher Mobility and Efficiencies: Random Vs. Alternating

Mol 50% DPP+BTDT+ *linker*	HOMO Random (eV)	LUMO Random (eV)	HOMO Alternating (eV)	LUMO Alternating (eV)	BG Random (eV)	BG Alternating (eV)
vinylene	-4.55	-3.16	-4.55	-3.13	1.39	1.42
thiophene	-4.62	-3.09	-4.58	-3.07	1.53	1.51
bithiophene	-4.62	-3.02	-4.58	-3.00	1.60	1.58

Random



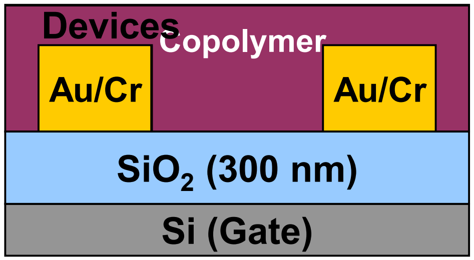
Alternating



OFET Characteristics

Table #. Transistor Performance Parameters.

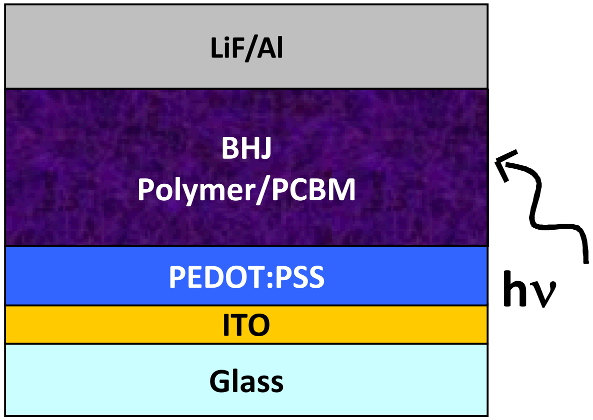
Bottom Contact Devices



Channel Dimensions
W = 20 μm L =1000 μm

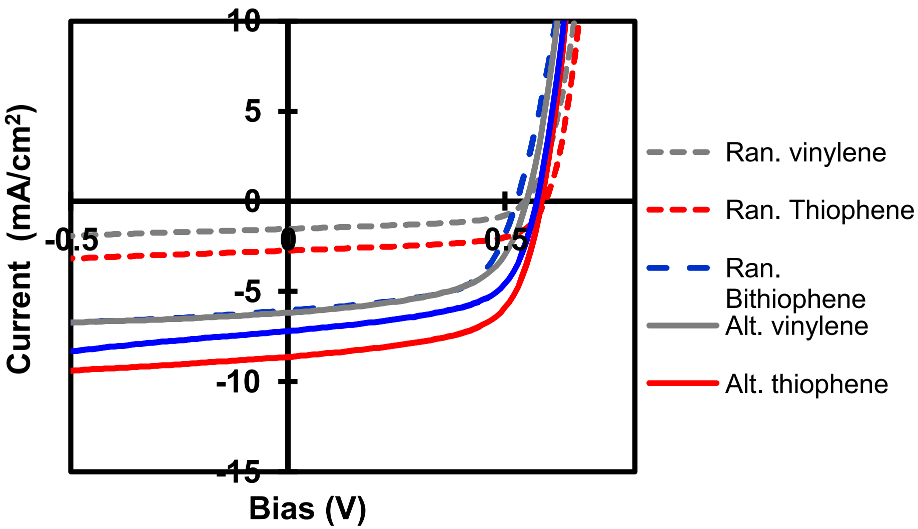
Mol 50% DPP+BTDT+ *linker*	μ_{avg} (cm^2/V•s)	I_{ON} /$I_{OFF, Avg}$	$V_{TH, Avg}$
Vinylene *Random* *Alternating*	1.62×10^{-2} 7.30×10^{-2}		
Thiophene *Random* *Alternating*	2.45×10^{-2} 6.50×10^{-2}		
Bithiophene *Random* *Alternating*	3.41×10^{-2} 2.62×10^{-2}		

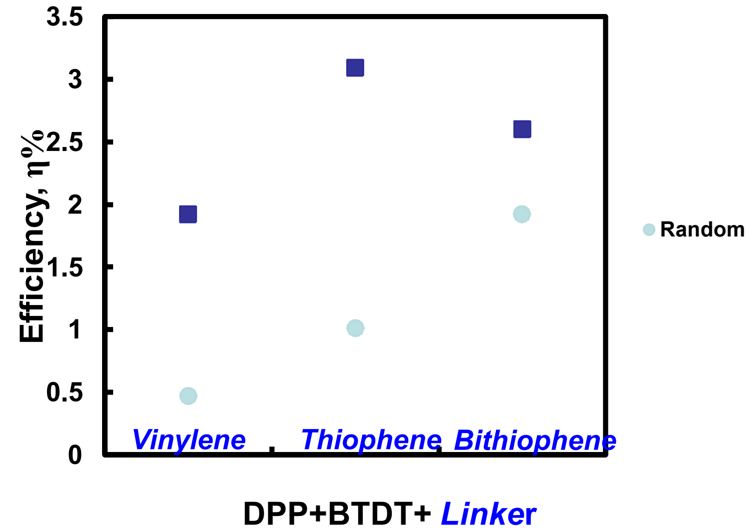
OPV Device characteristics



Mol 50% DPP+BTDT+ *linker*	J_{sc} (mA/cm^2)	V_{oc} (V)	η (%) mW/cm^2	FF
Random *vinylene*	1.53	0.545	0.467	0.56
Alternating vinylene	6.18	0.555	1.92	0.56
Random *thiophene*	2.73	0.59	1.01	0.62
Alternating thiophene	8.65	0.585	3.09	0.61
Random *bithiophene*	6.06	0.525	1.92	0.60
Alternating bithiophene	7.34	0.575	2.60	0.62

[1] Films are cast from DCB at a 1:1 ratio with PCBM





- Alternating copolymers have higher OPV performances compared to random polymers.
- Thiophene linked DPP+BTDT has the highest efficiency due to most favorable band alignment

OPV Morphology Characterization

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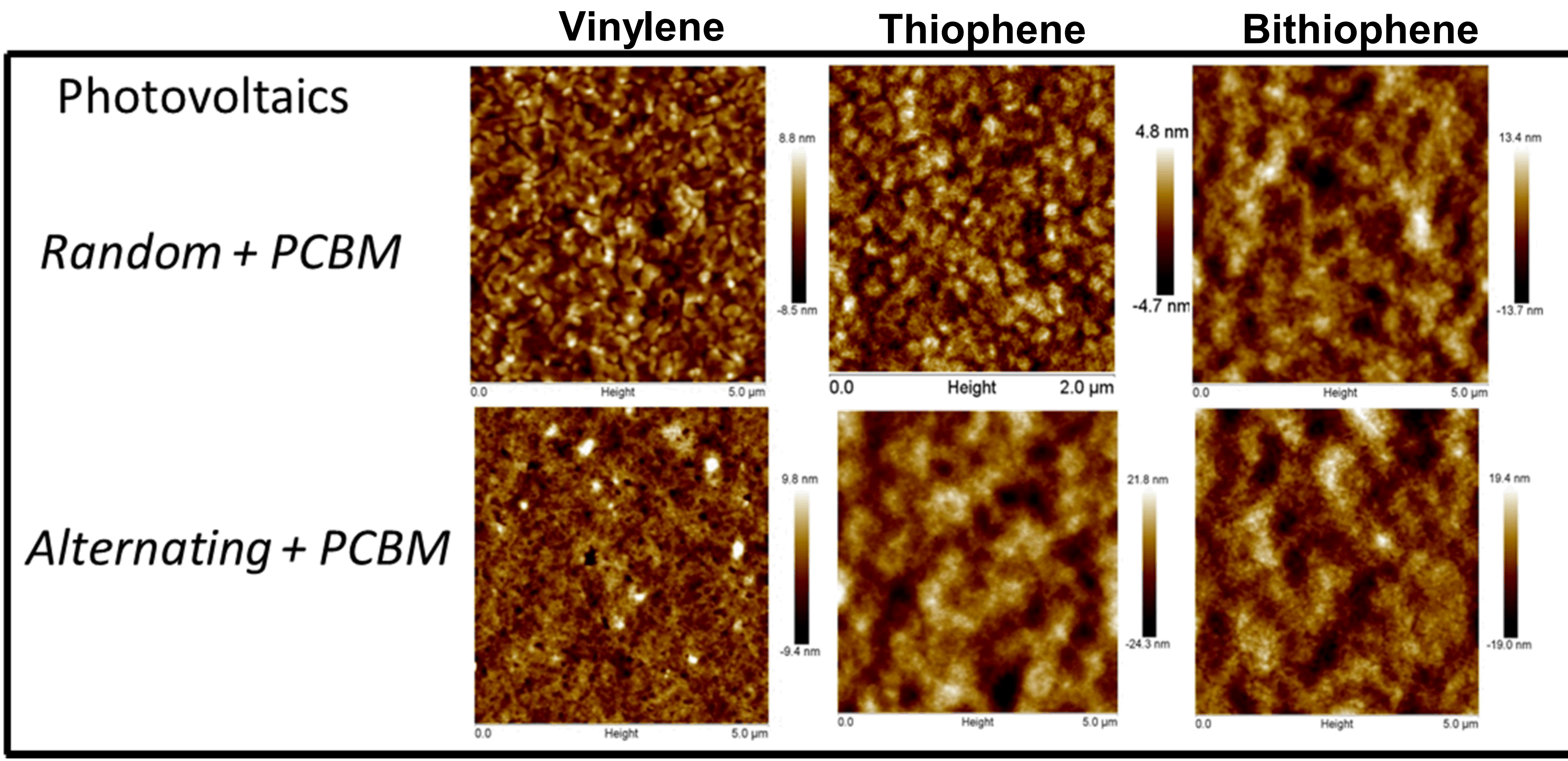
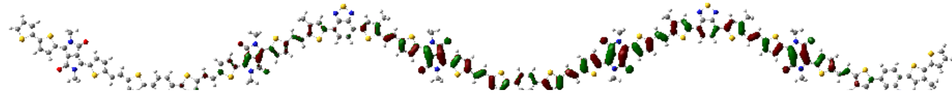


Alternating DPP+BTDT thiophene linked has the highest efficiency. This copolymer has the most favorable band alignment with PCBM.

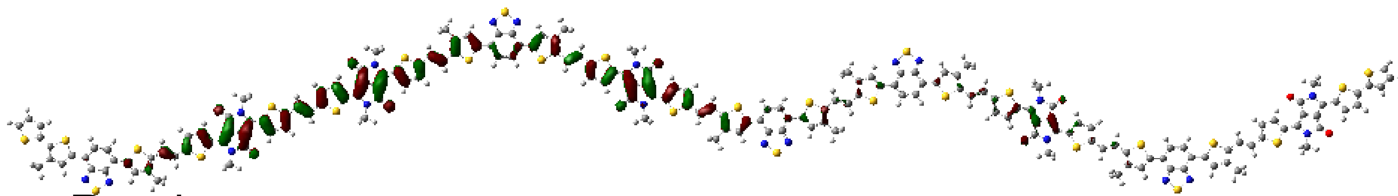
Abstract

The effects of polymer composition, monomer sequence, and linker identity on the electronic, physical, and transistor properties of donor-acceptor polymers incorporating dithienyldiketopyrrolopyrrole (DPP) and dithienylbenzothiadiazole (BTDT) are investigated. In comparison to the perfectly alternating analog, the stoichiometric equivalent random terpolymer exhibits an increased absorbance on-set wavelength and bandwidth. This trend is supported computationally; moreover, it was identified that a minimum of four consecutive BTDT units are needed to achieve a narrow optical gap than the perfectly alternating analog. In addition, the mobility of these terpolymers in field-effect transistors increases as the ratio of DPP:BTDT increases. Meanwhile, bulk heterojunction solar cells using the terpolymers as the donor and $PC_{61}BM$ as the acceptor show an increase in power conversion efficiency as the ratio of DPP:BTDT decreases. These trends are attributed to variations in molecular packing and thin film morphology. The effect of the coordinating linker (ethylene, thiophene and dithiophene) has also been experimentally and computationally explored. By varying the polymer composition and linker identity, the crystallinity of thin film devices is effectively tuned. Finally, we observe reversible thermochromism that is sensitive to polymer composition and linker identity. This behavior is the subject of future study on the molecular engineering of thermochromic, optoelectronic switches

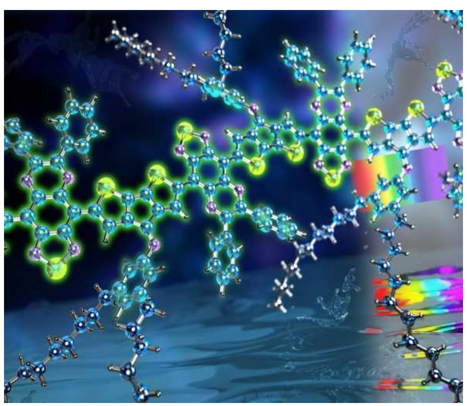
HOMO

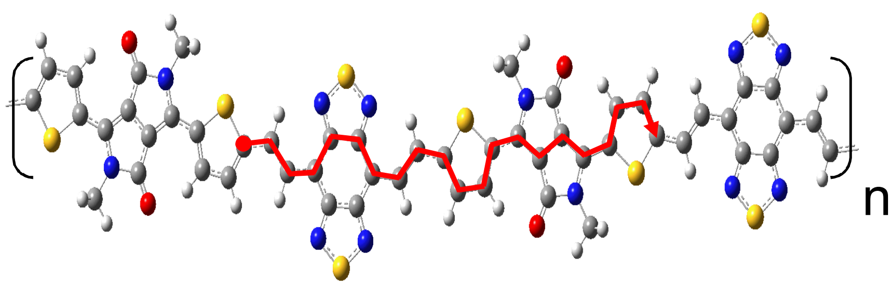


alt



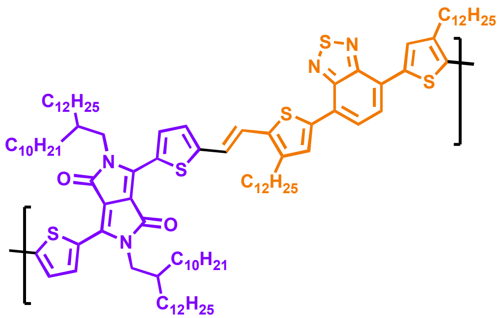
Random
1



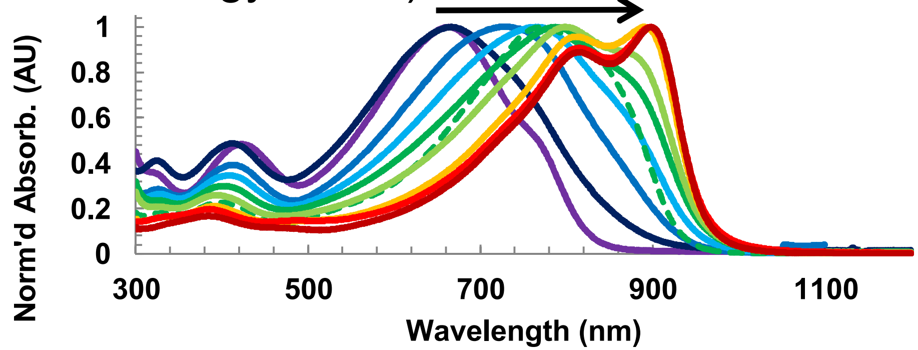


Goal A (Proof of Concept): Demonstrate ability to tune band gap and band edge positions (CB and VB energy levels)

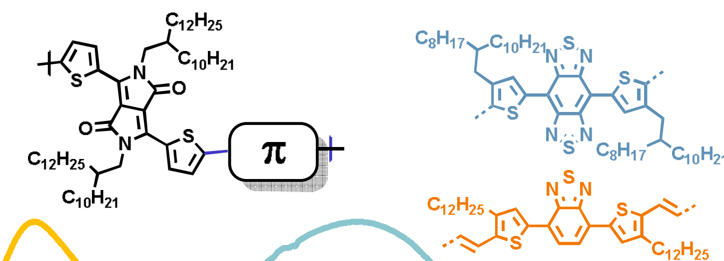
mol% DPP ↑

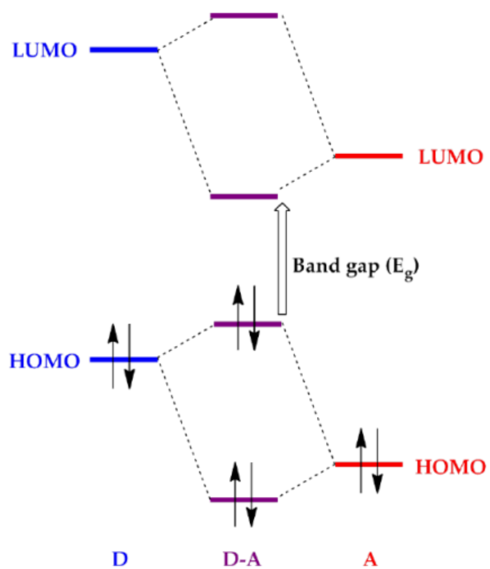


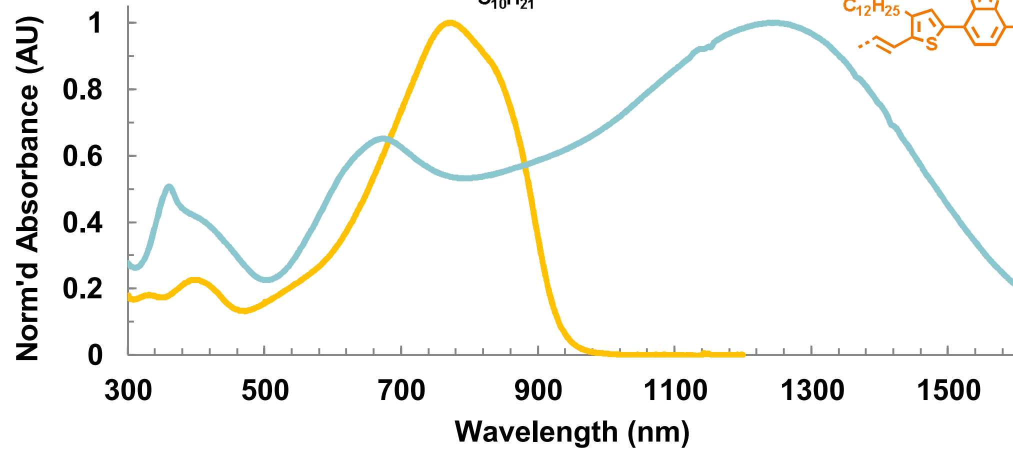
DPP BTDT-C_{12}



Goal B(extension to low E_g materials): Apply above strategy to a low band gap polymer (E_g<1eV or 1240nm)







(Extension to low E_g materials): ***Apply above strategy to a low band gap polymer (E_g<1eV or 1240nm)***

Effects of homopolymer versus copolymers using varying linker units.