

Electronic and Optoelectronic Polymers -Polymer TFT (II): Examples

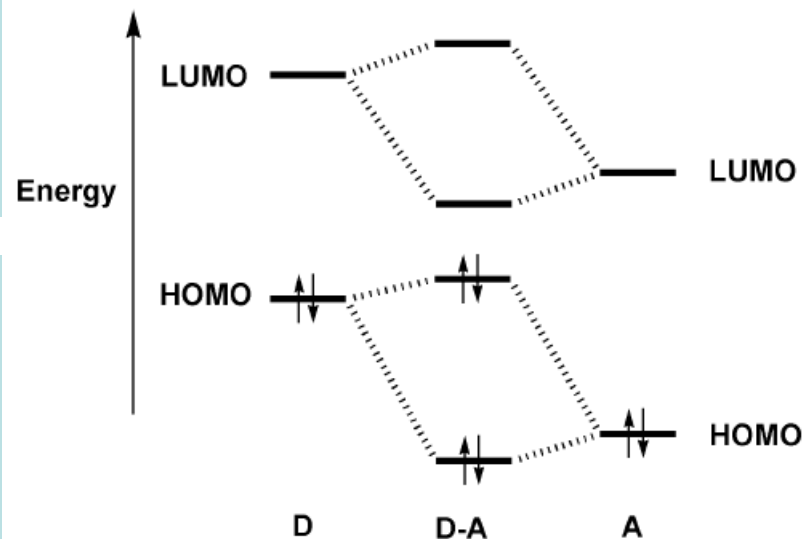
Wen-Chang Chen

Department of Chemical Engineering
Institute of Polymer Science and Engineering
National Taiwan University

Introduction of Donor-Acceptor Alternating Conjugated Polymers

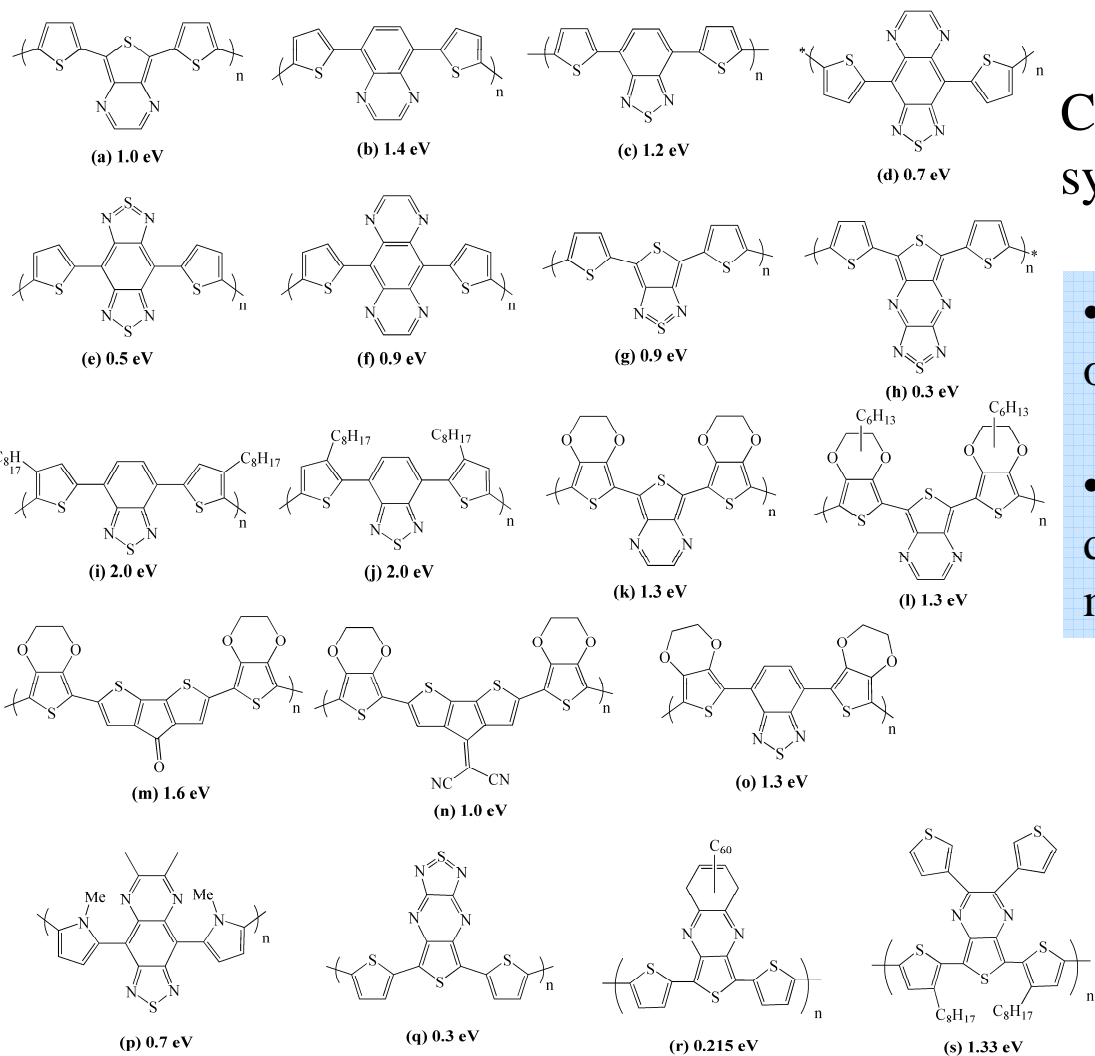
- Hybridization of the energy levels of a donor (D) and acceptor (A) fragments leads to a D-A monomer with an unusually narrow HOMO-LUMO energy separation.

- The interaction between a strong electron-donor (D) and a strong electron-acceptor (A) may give rise to an increased double bond character and are associated with such a mesomerism. ($D-A \longleftrightarrow D^+ = A^-$)



van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng. B* **2001**, 32, 1.

Donor-acceptor-donor Polymers



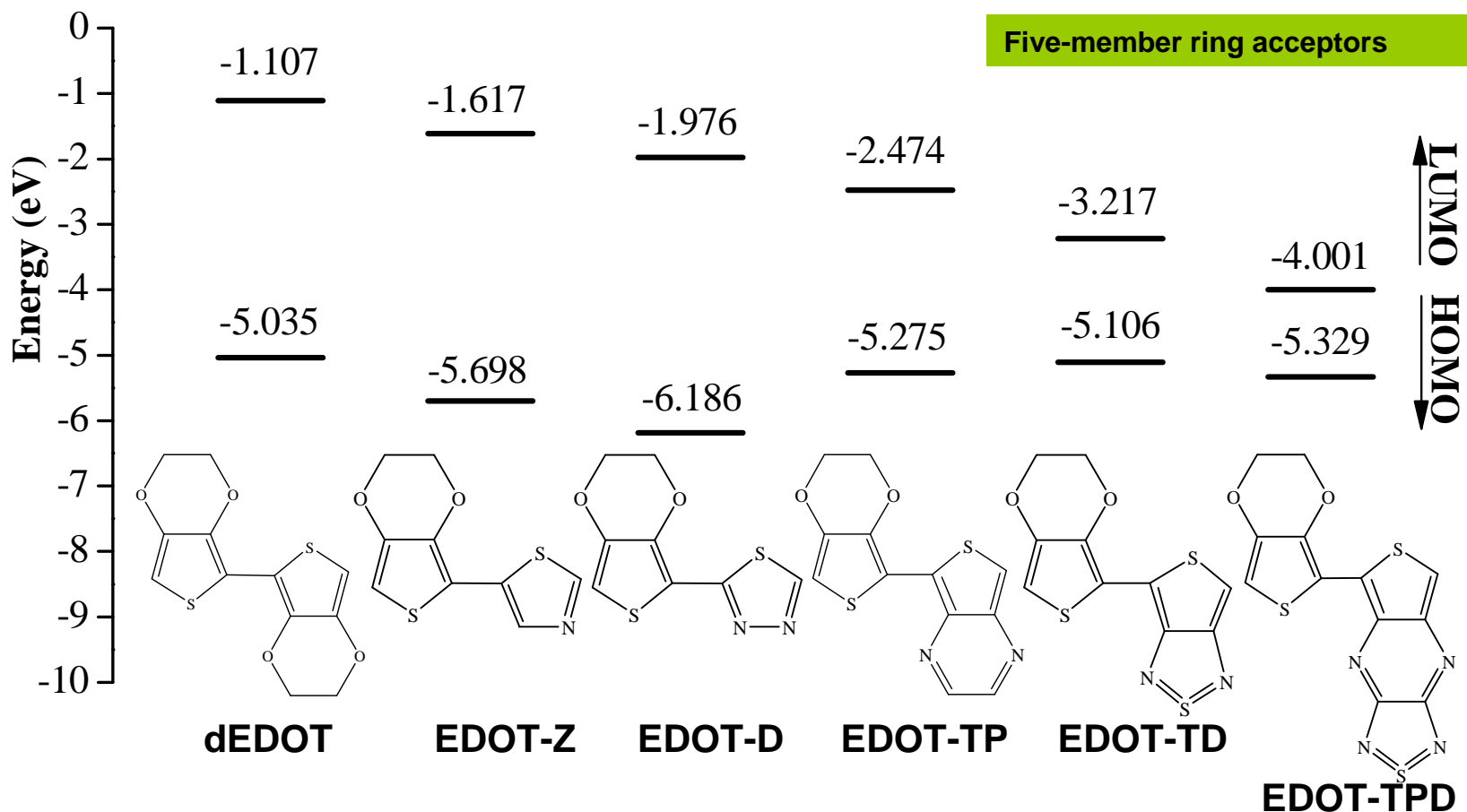
Construction of narrow-bandgap systems:

- copolymerization of aromatic and o-quinoid units
- alternation of strong electron-donating and electron-accepting moieties

[A-Q-A]

where **A** is a kind of aromatic-donor unit and **Q** is a kind of o-quinoid-acceptor unit

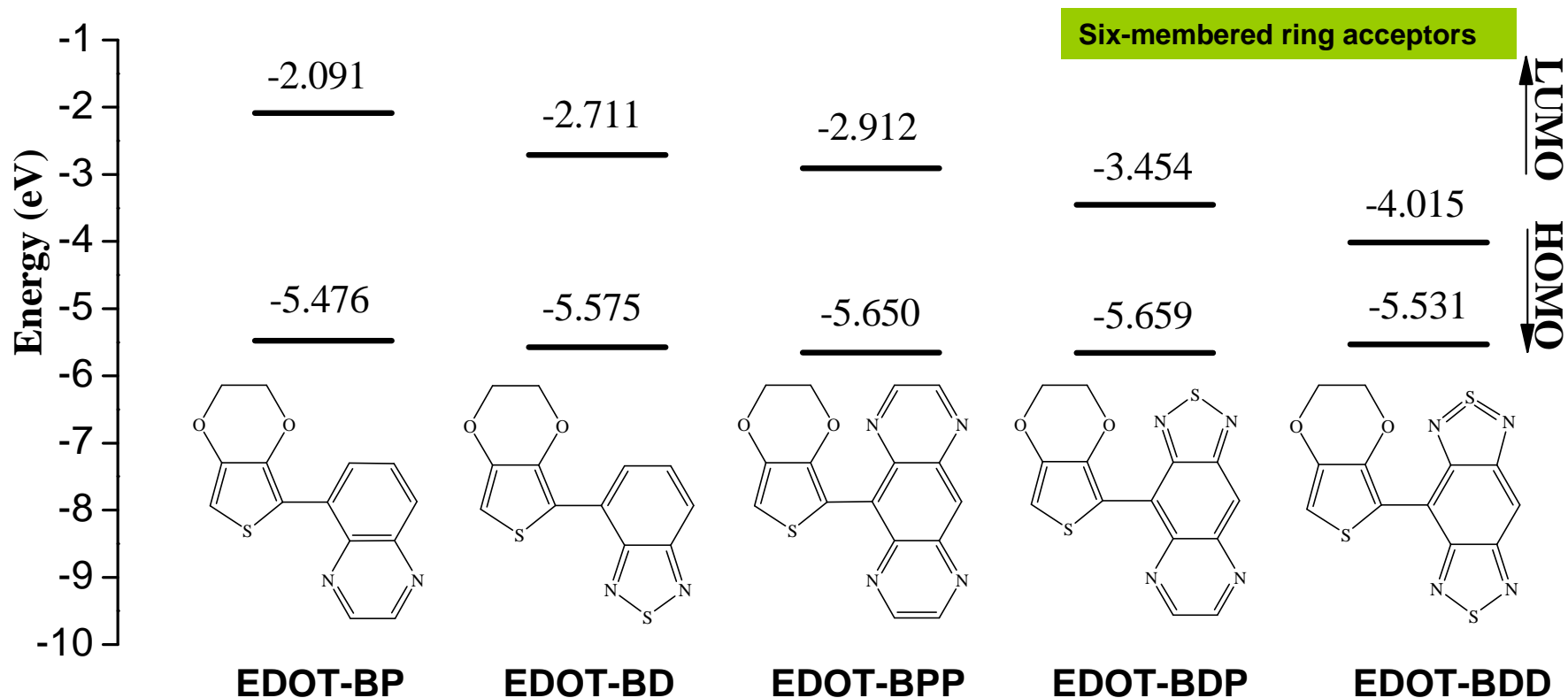
Optimized Electronic Properties



□ LUMO: **dEDOT < EDOT-Z < EDOT-D < EDOT-TP < EDOT-TD < EDOT-TPD** (the same as that of the acceptor strength)

□ HOMO: -5.035 ~ -5.329 eV except **EDOT-Z** and **EDOT-D** (carriers of the backbone nitrogen atom are localized within the ring, reduce the π -electron delocalization)

□ Lower E_g of the **EDOT-TP**, **EDOT-TD**, and **EDOT-TPD** than **dEDOT** → significant intramolecular charge transfer.

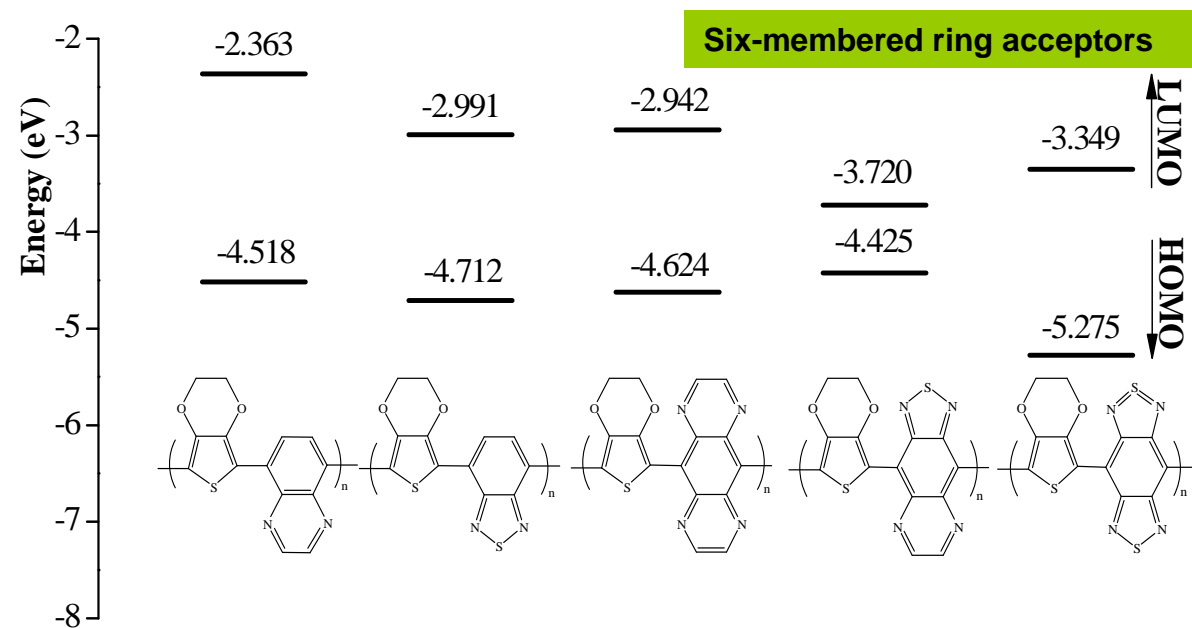
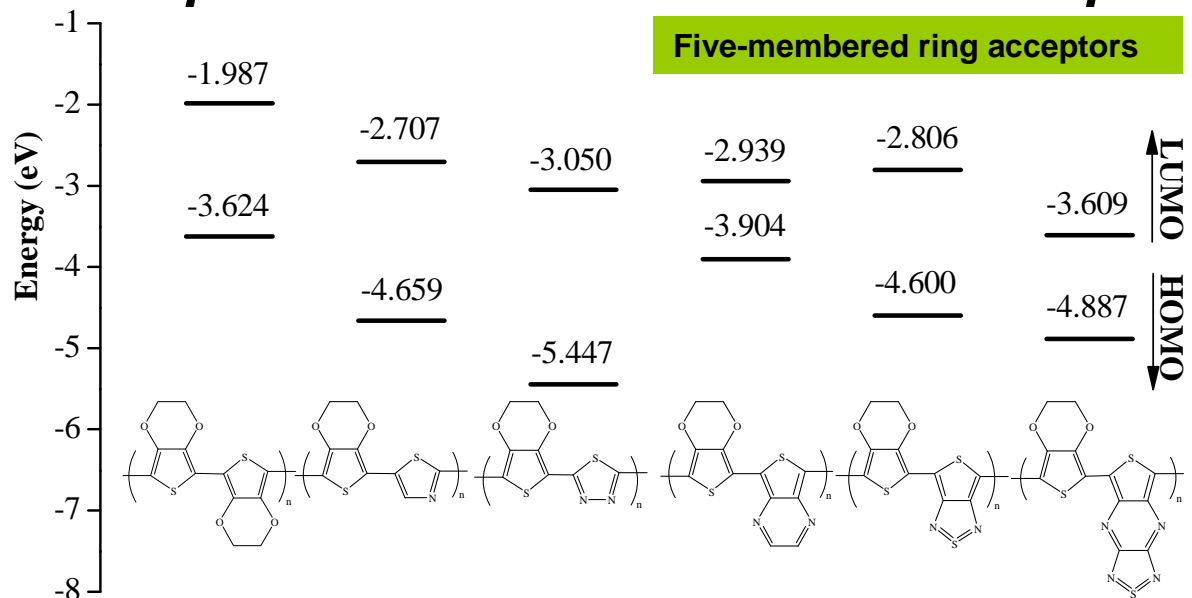


□ LUMO: **EDOT-BP < EDOT-BD < EDOT-BPP < EDOT-BDP < EDOT-BDD** (the same as the acceptor strength)

□ HOMO: -5.476 ~ -5.659 eV

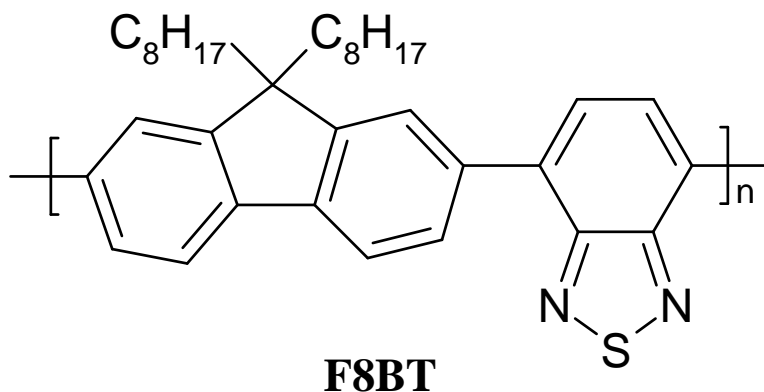
□ Eg: 1.516 ~ 3.385 eV, which is significantly lower than **dEDOT** (3.929 eV)

Optimized Electronic Properties



The different trend on the electronic properties of the studied polymers compared to those of the model compounds are probably contributed from the **geometrical effects** besides the acceptor strength.

Donor-Acceptor Conjugated Polymers Based Thin Film Transistors

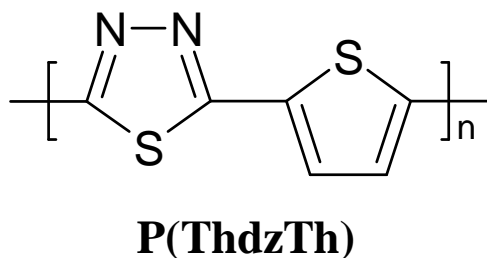


Hole Mobility: $3.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$

Electron Mobility: $5 \times 10^{-3} \text{ cm}^2/\text{Vs}$

Ref: 1.Zaumseil et al., *Adv. Mater.* **2006**, *18*, 2708.

2.Friend et al., *Nature* **2005**, *434*, 194.



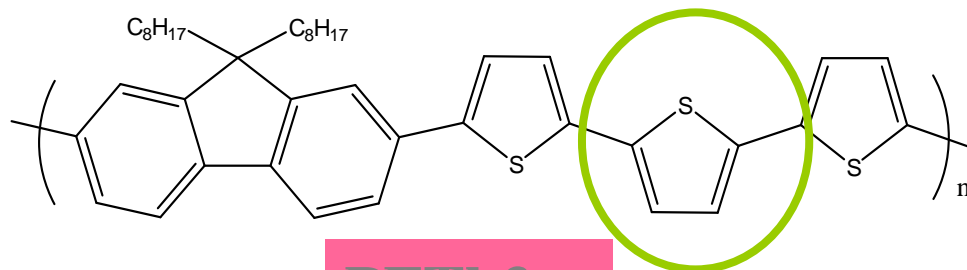
Hole Mobility: $3.4 \times 10^{-4} \text{ cm}^2/\text{Vs}$

Electron Mobility: $5.4 \times 10^{-3} \text{ cm}^2/\text{Vs}$

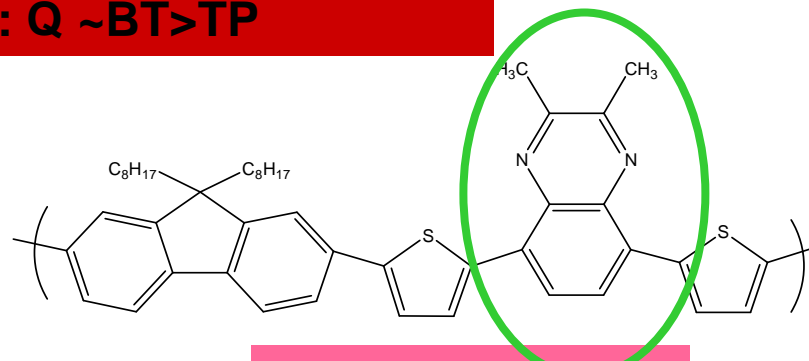
Ref: Yamamoto et al., *Macromol. Rapid. Commun.* **2005**, *26*, 1835 .

Effects of Acceptor Structures on the FET mobility of Fluorene based Donor-Acceptor Conjugated Polymers

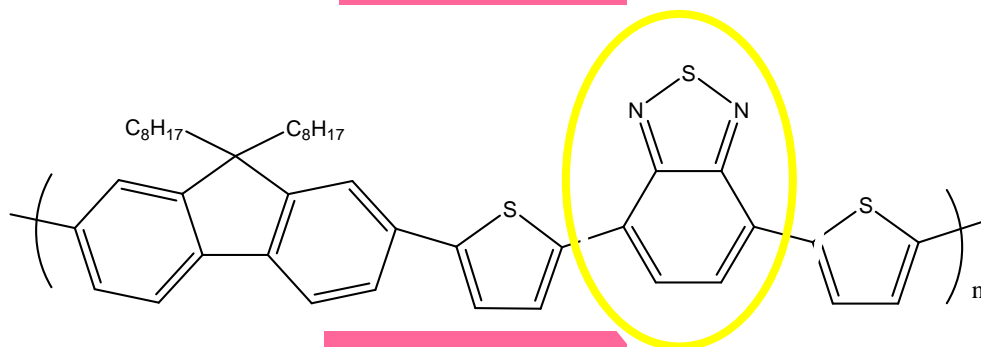
Acceptor strength : BT > TP > Q
Ring Torsional Angle: Q ~ BT > TP



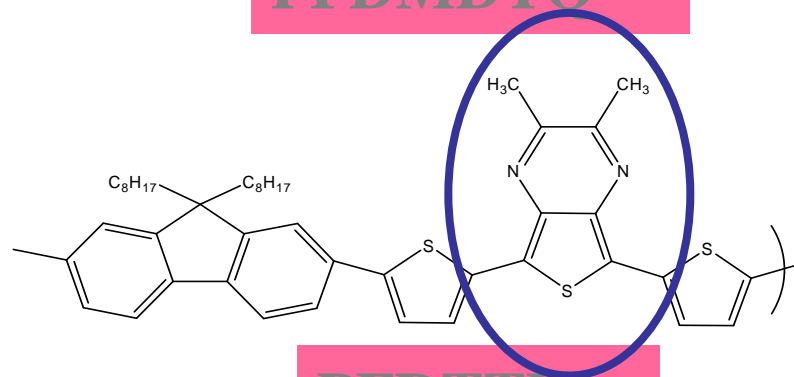
PFTh3



PFDMDTO

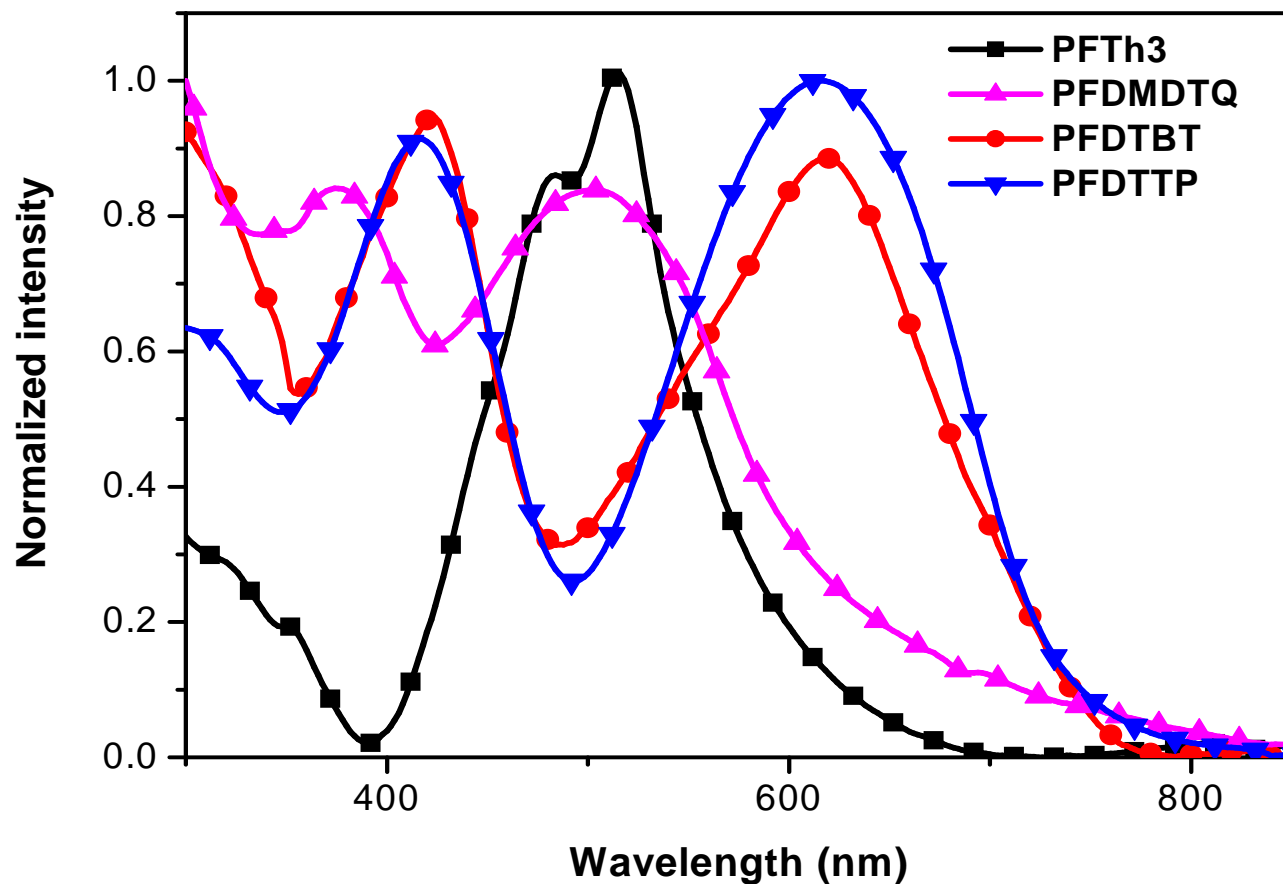


PFDTBT



PFDTTP

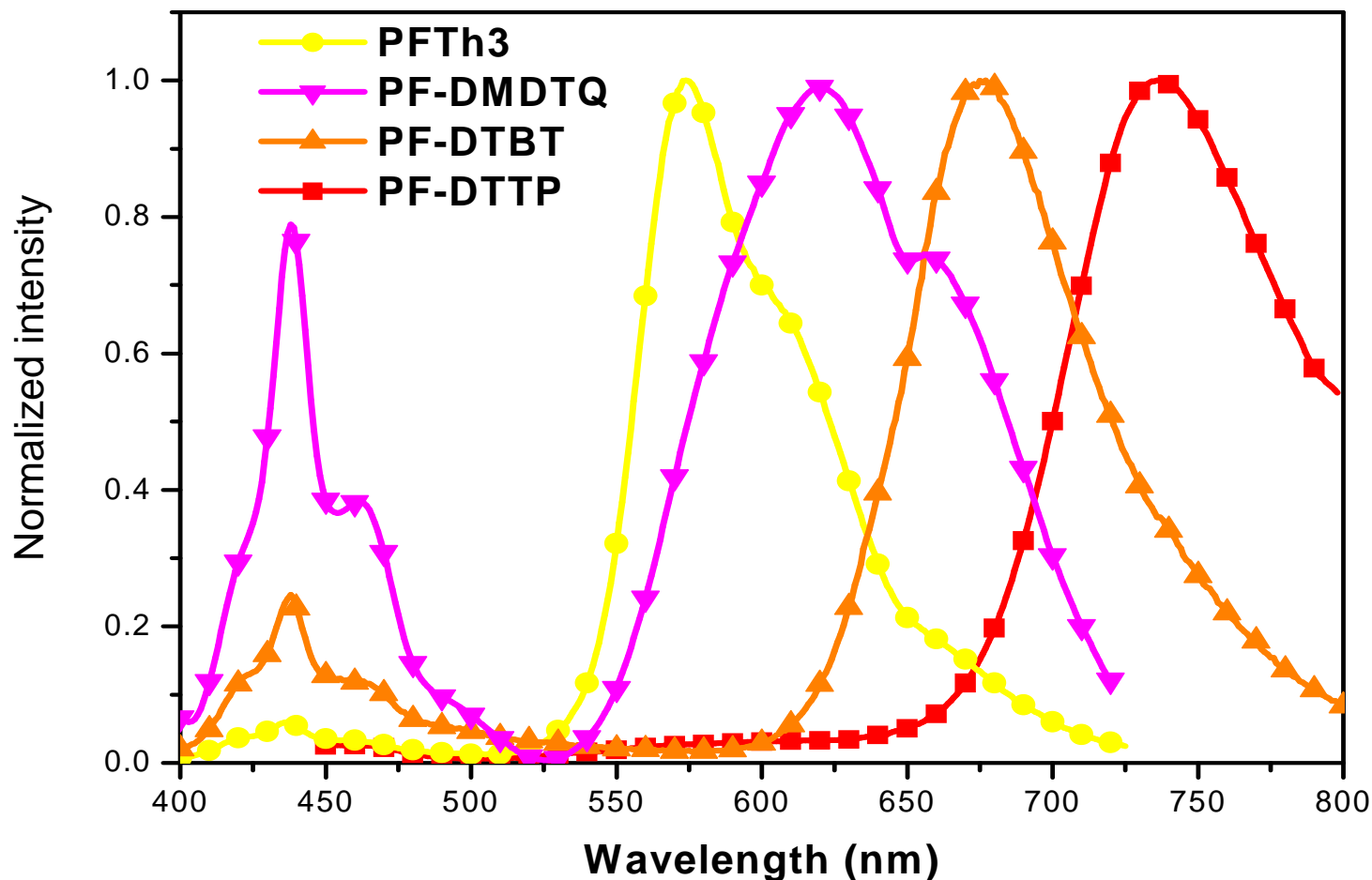
Electronic Properties of Fluorene Based Donor-Acceptor-Donor Conjugated Polymers



Band gaps : PFDTTP < PFDTBT < PFDMDTQ < PFTTh3

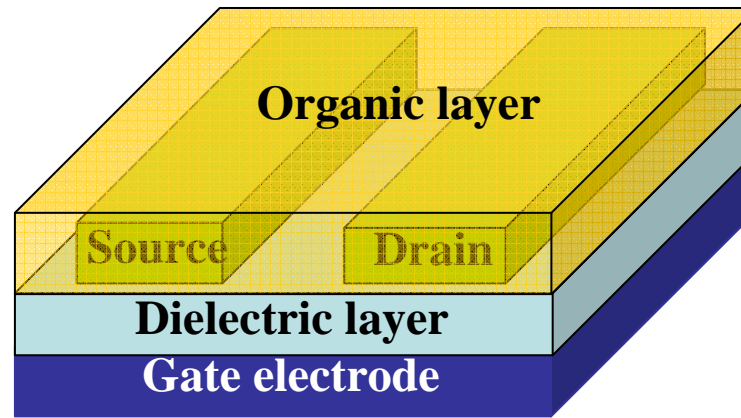
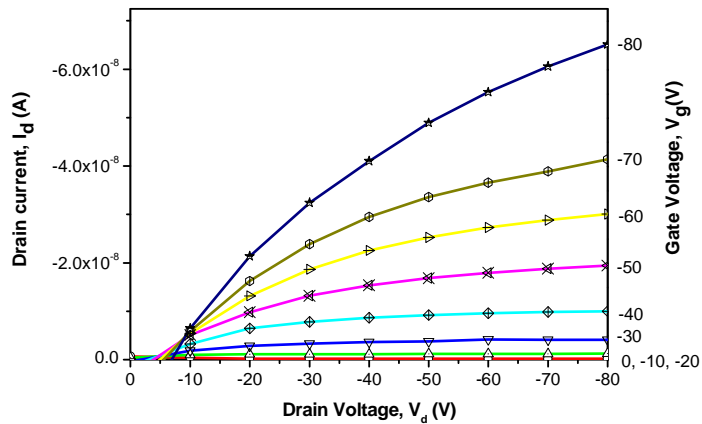
→ coplanarity : PFDTTP > PFDTBT

Photoluminescence Spectra of Fluorene-Acceptor Conjugated Copolymers



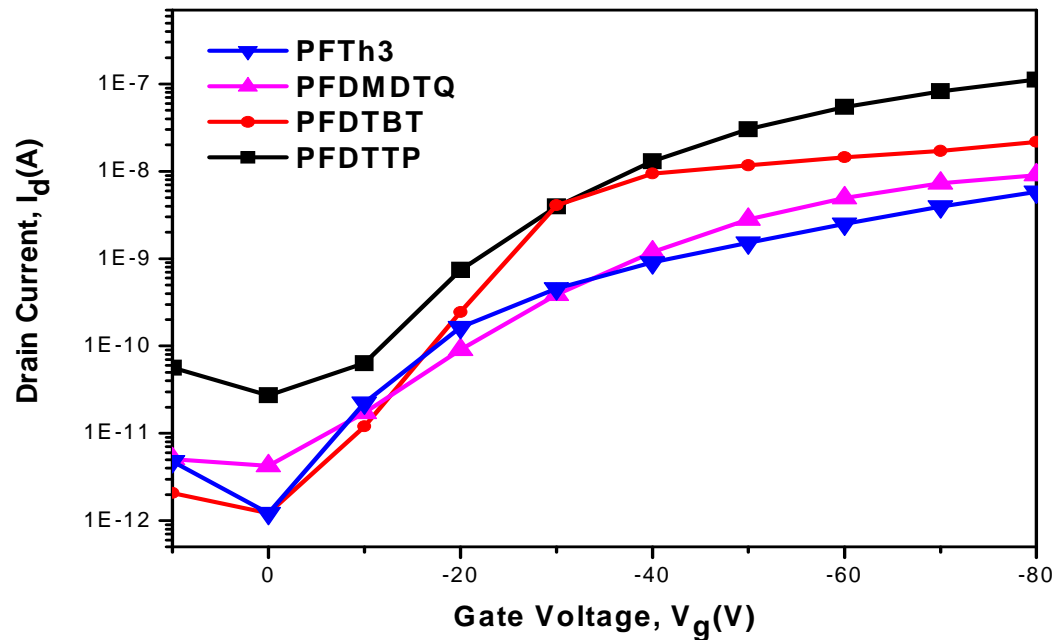
Yellow → purple → orange → red

The color tuning is feasible with various acceptor segments



■ Bottom Contact device structure

The output characteristics has good drain-current modulation and well-defined linear and saturation regions.

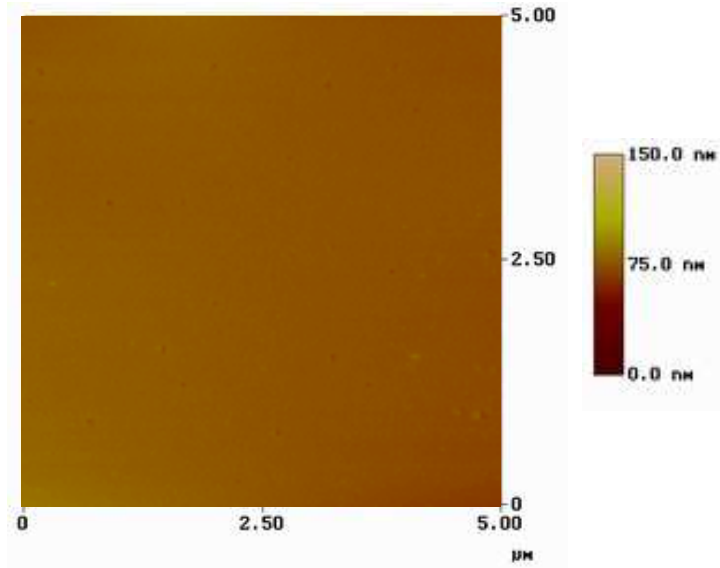


■ FET Mobility

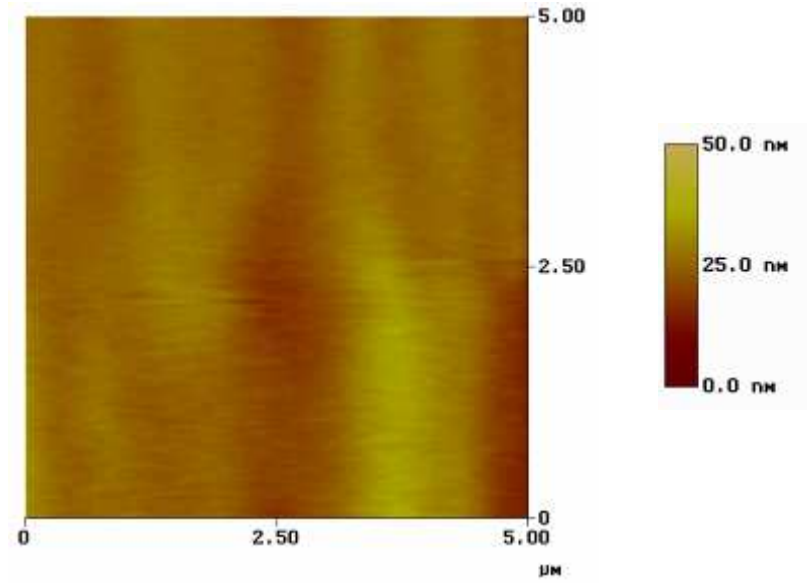
■ PFDTP > PFDTBT > PFDMDTQ > PFTh3

AFM image of Fluorene-Acceptor Copolymers

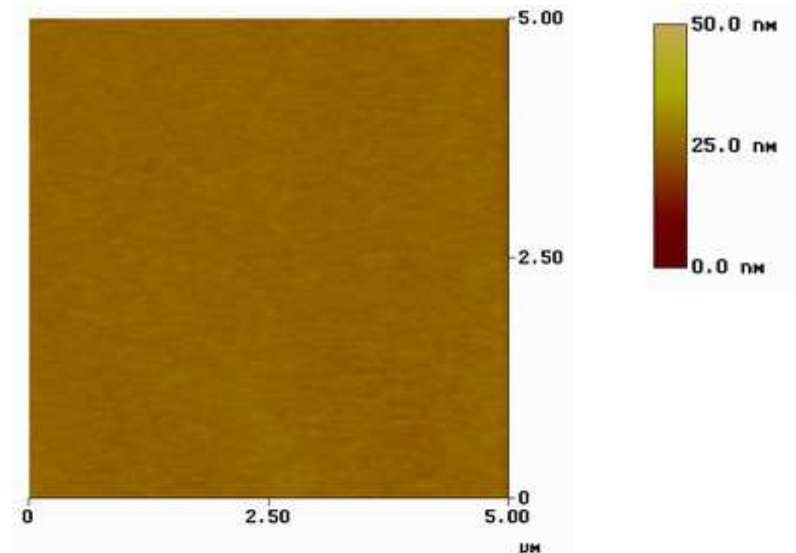
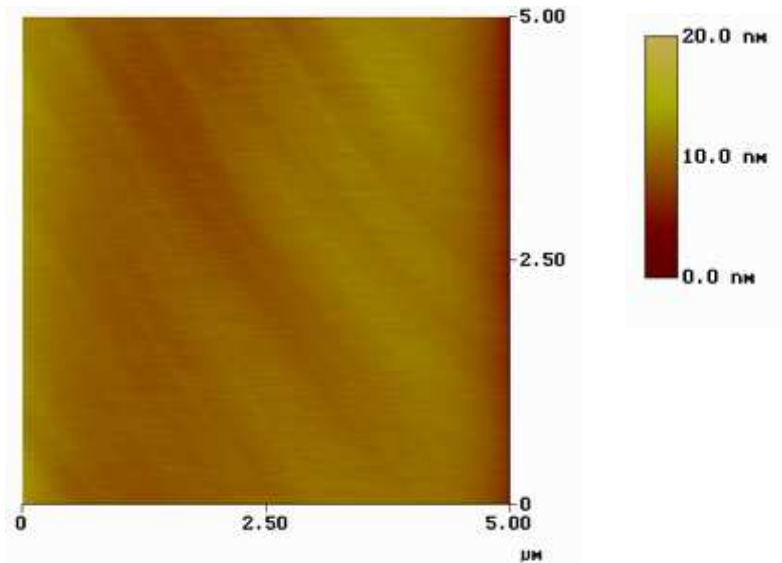
- PFDTTP (Dichlorobenzene)



- PFDMDTQ (Toluene)



-

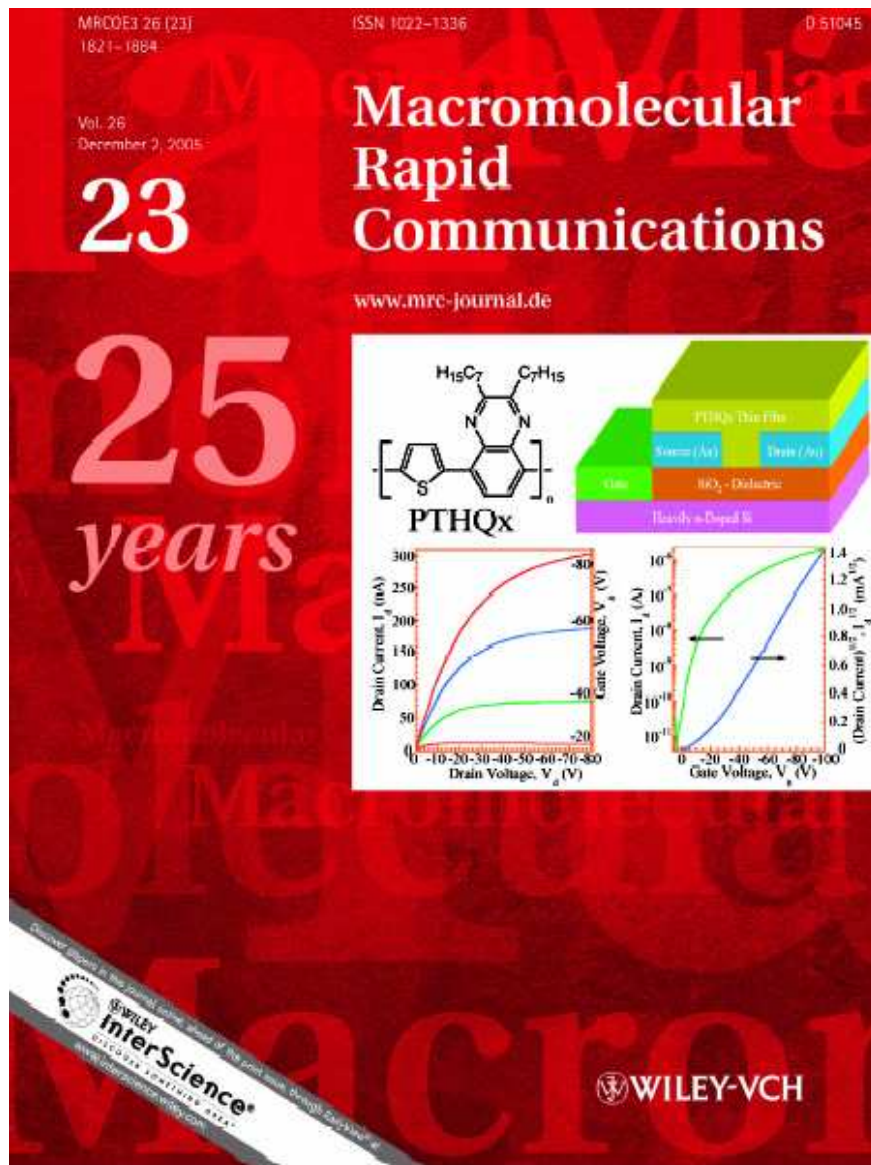


Electronic Properties of PFTh3, PFDMDTQ, PFDTBT, and PFDTTP

	Band gap ^{opt} (eV) ^a	LUMO (eV)	Mobility (cm ² v ⁻¹ s ⁻¹)	Thresho ld Voltage (V)	on/off
PF6Th3	2.05	-2.93 ^b	2.35×10 ⁻⁶	-3.7	1×10 ³
PF-DMDTQ	1.94	-3.17	5.44×10 ⁻⁶	-13.3	1×10 ³
PF-DTBT	1.68	↓ -3.19	4.87×10 ⁻⁵	↓ -12.8	2×10 ⁴
PF-DTTP	1.67	-3.60	5.52×10 ⁻⁵	-12.8	5×10 ³

🌐 The mobility could be enhanced incorporating the acceptor moiety into the donor-type polymer due to the **intramolecular charge transfer**.

New Donor-Acceptor Conjugated Materials for Organic Field Effect Transistors



Semiconductor properties

Bandgap~1.75eV

Unmodified SiO₂ dielectric

Mobility~ $2.7 \times 10^{-5} \text{cm}^2/\text{Vs}$

$I_{\text{on}}/I_{\text{off}} \sim 10^3$

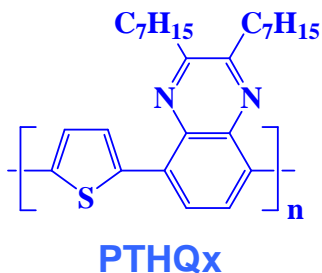
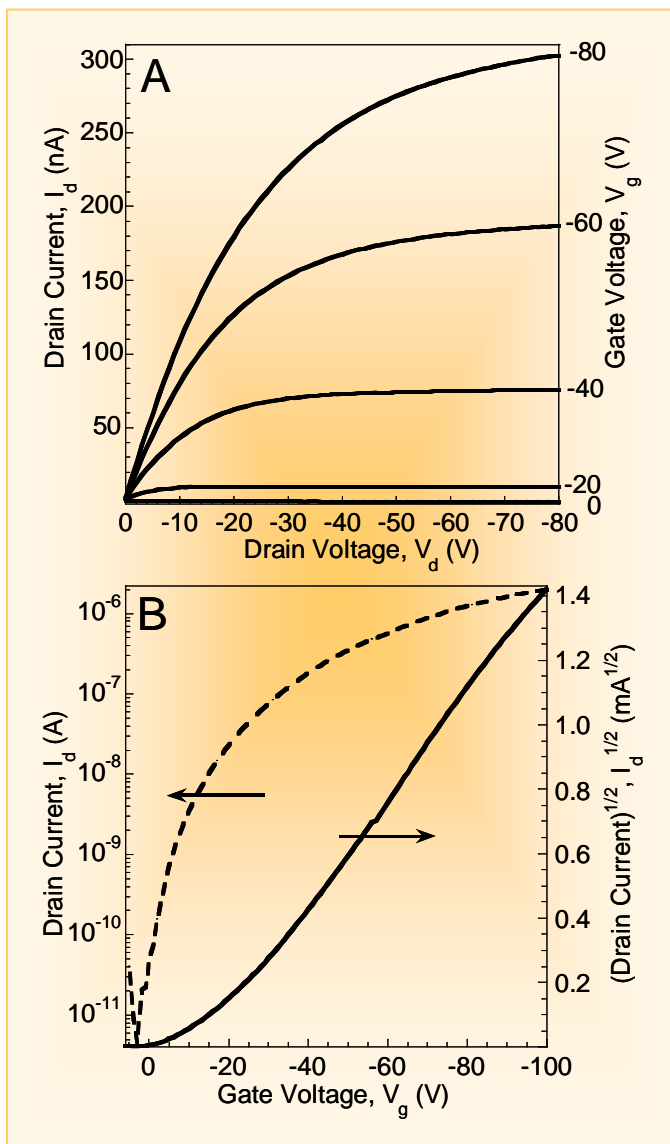
Modified by SAM OTS

Mobility~ $6 \times 10^{-3} \text{cm}^2/\text{Vs}$

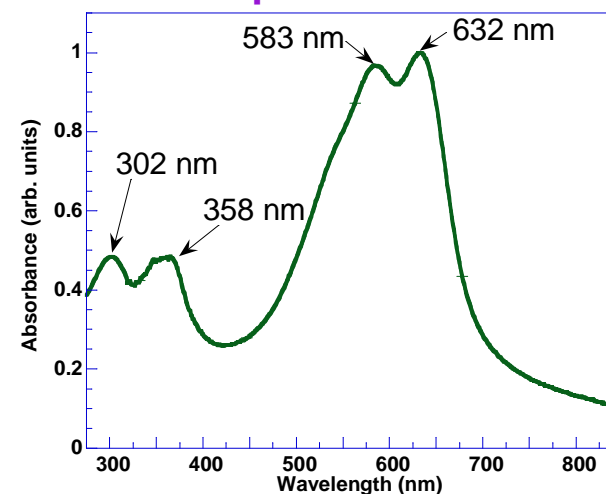
$I_{\text{on}}/I_{\text{off}} \sim 6 \times 10^5$

Chen and Jenekhe,
Macromol. Rapid Commun 2005., 26, 1835-1840.

Thiophene-Quinoxaline Copolymer Field-Effect Transistors



Absorption of PTHQx



- Donor-Acceptor Architecture

- Large Intramolecular Charge Transfer
- Small Band Gap (1.68 eV)

- OFETs

- Hole mobility:

Untreated SiO_2 : $\mu_h = 2.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$

$$I_{on}/I_{off} > 10^4$$

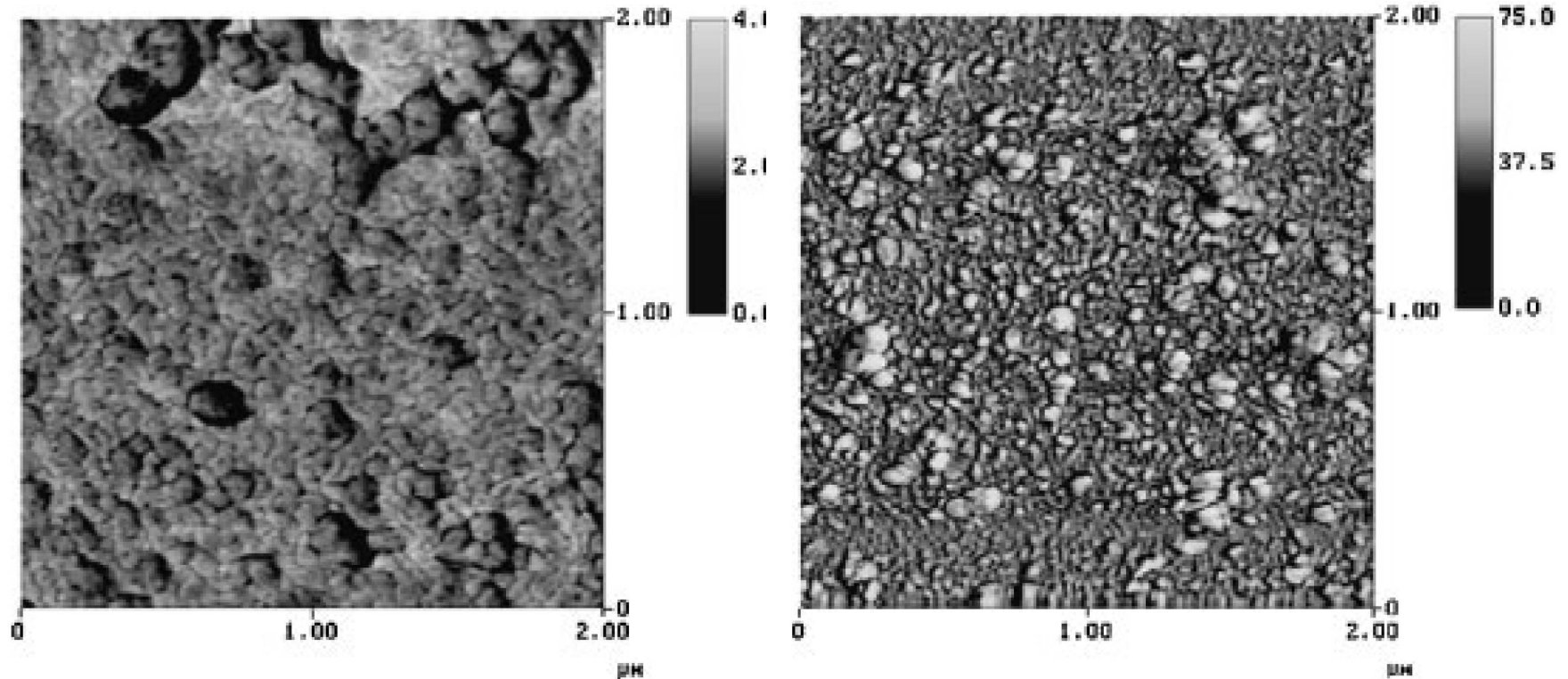
OTS-8 treated SiO_2 : $\mu_h = 3.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$

$$I_{on}/I_{off} > 10^5$$

- No electron transport even with top-contact Aluminum source/drain.

Champion, R. D.; Cheng, K.-F.; Pai, C.-L.; Chen, W.-C.; Jenekhe, S. A. *Macromol. Rapid Commun.* **2005**, *26*, 1835.

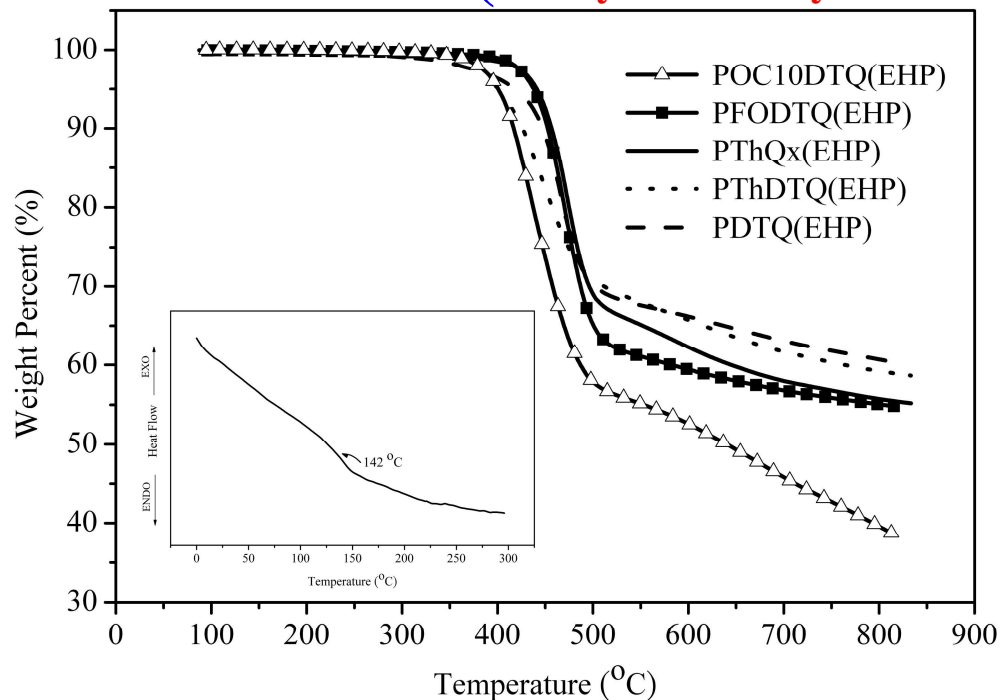
Phase AFM Images of PTHQ_x



The morphology of PTHQ_x thin films on an OTS modified SiO₂ dielectric consist of more densely packed crystalline spherical grains

Quinoxaline-Based Conjugated Copolymers

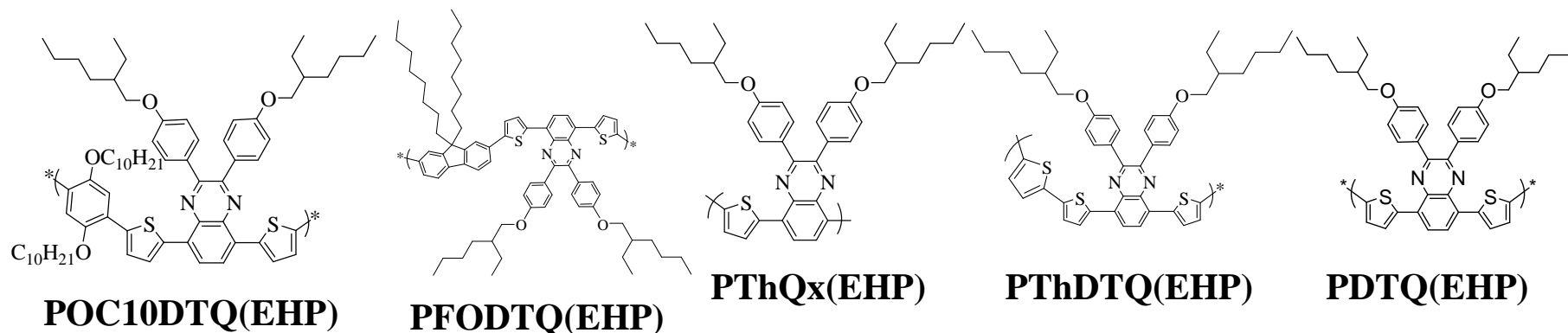
(*J. Polym. Sci. Polym. Chem.* 2009, 47, 973-958)



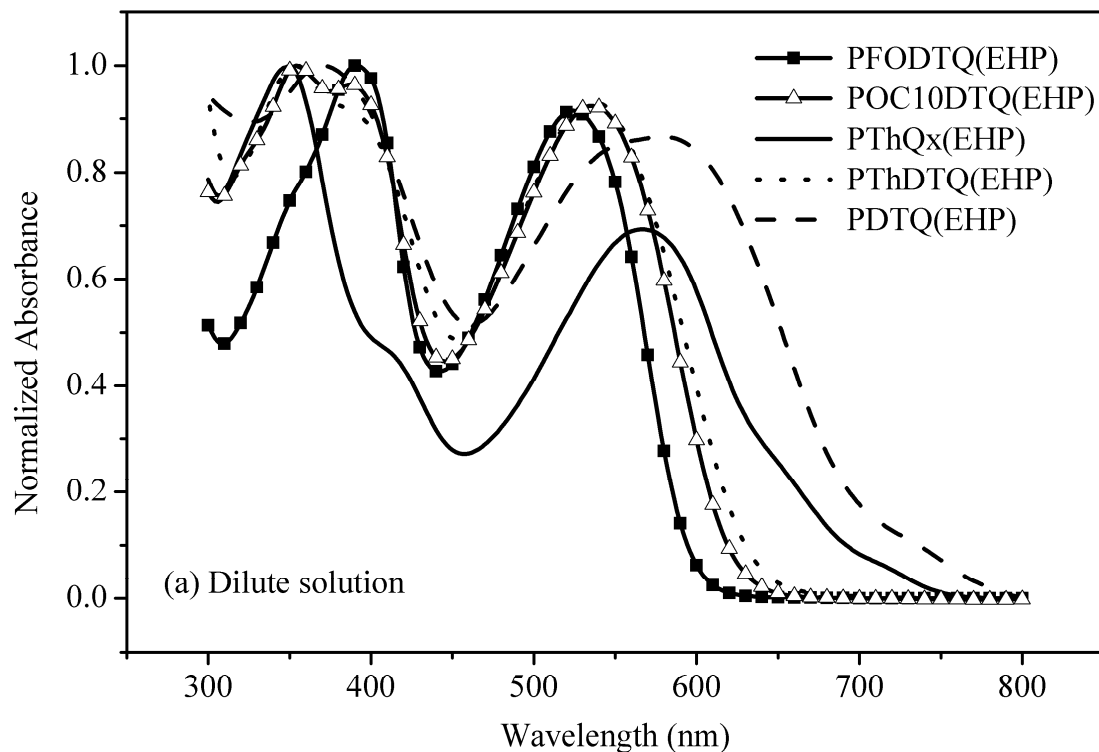
	M_n	PDI	T_g (°C) ^a	T_d (°C)
POC10DTQ(EHP)	8590	1.67	NA	400
PFODTQ(EHP)	22300	2.38	142	437
PThQx(EHP)	4003	1.26	NA	441
PThDTQ(EHP)	1781 ^b	1.11	NA	400
PDTQ(EHP)	6880	1.68	NA	418

a: 95 wt% residue temperature.

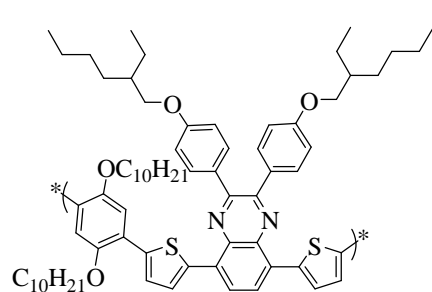
b: polymer is only partially soluble in THF.



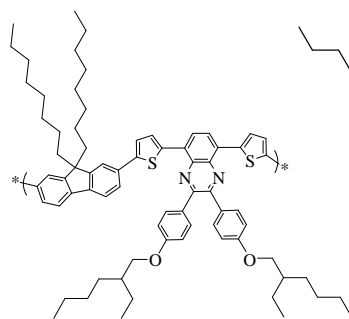
UV-visible spectrum-solution



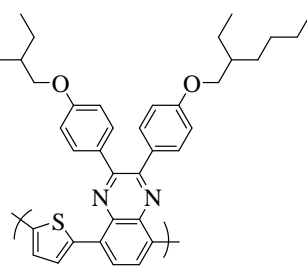
	$\lambda_{\max}^{\text{abs}}$ (soln) (nm)
PFODTQ(EHP)	390, 524
POC10DTQ(EHP)	356, 388*, 536
PThQx(EHP)	350, 566
PThDTQ(EHP)^c	352, 538
PDTQ(EHP)	366, 586



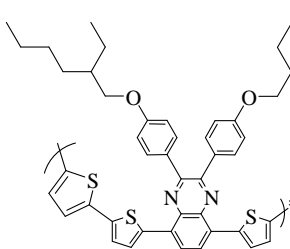
POC10DTQ(EHP)



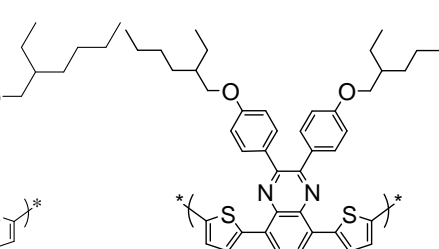
PFODTQ(EHP)



PThQx(EHP)

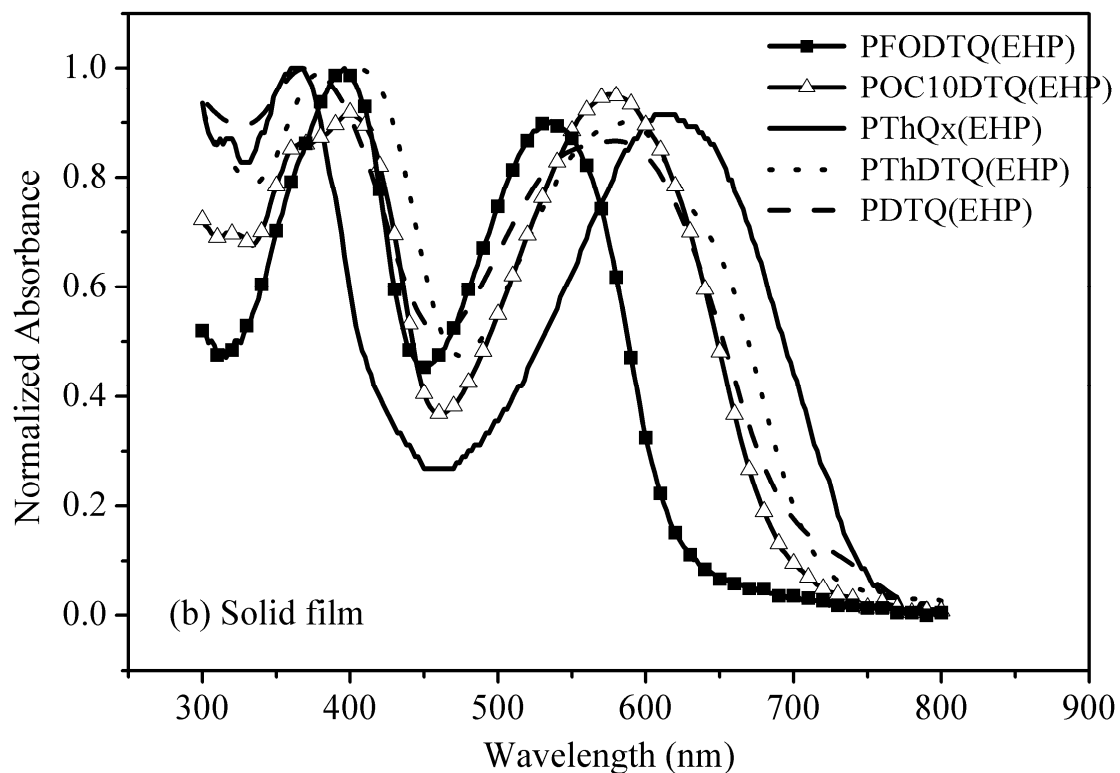


PThDTQ(EHP)



PDTQ(EHP)

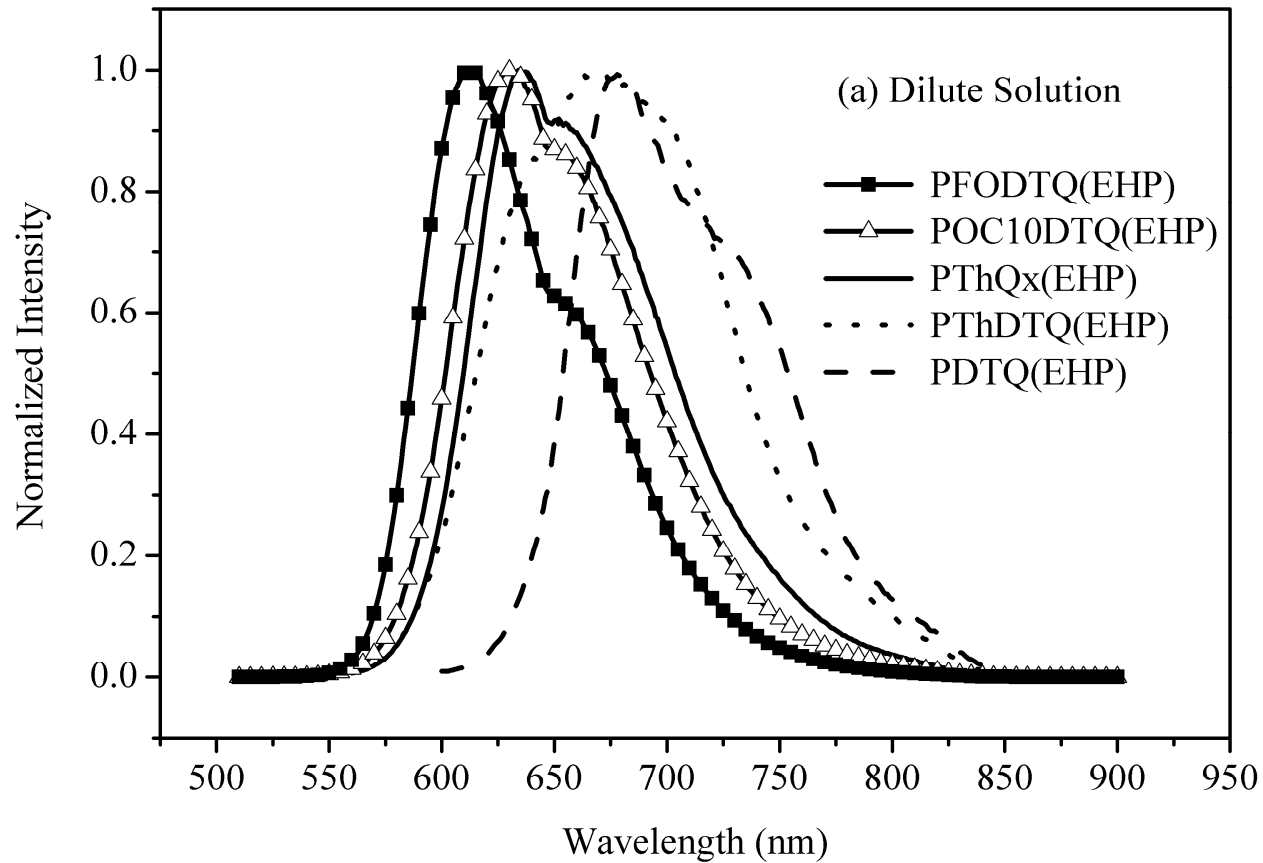
UV-visible spectrum-film



	$\lambda_{\max}^{\text{abs}}$ (film) (nm)	E_g^{opt} (eV) ^a
PFODTQ(EHP)	396, 538	1.92
POC10DTQ(EHP)	368*, 400, 576	1.77
PThQx(EHP)	364, 612	1.57
PThDTQ(EHP)^c	376, 410, 586	1.65
PDTQ(EHP)	386, 586, 717*	1.65

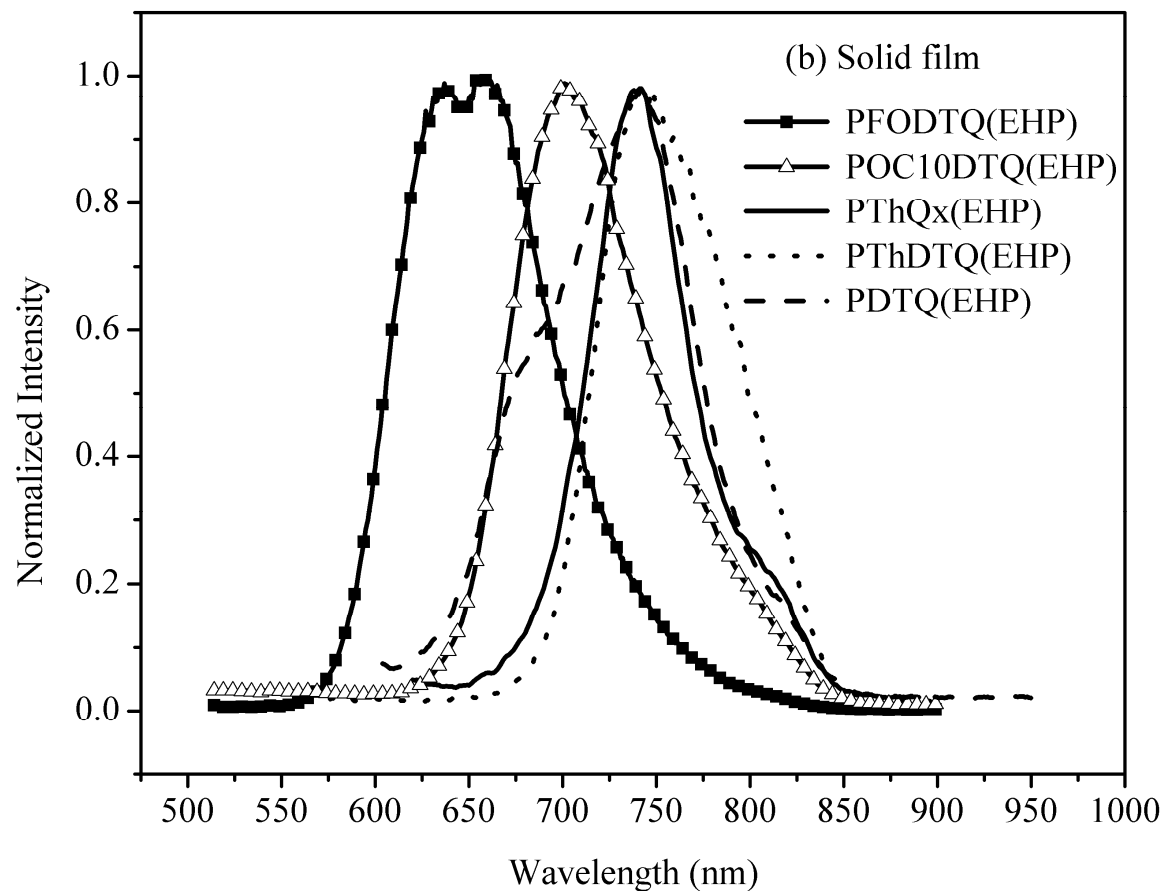
- Donor strength : thiophene > phenylene > fluorene
- When thiophene : quinoxaline = 1 : 1, the intramolecular charge transfer effect is most remarkable.

Photoluminescence spectrum-solution



	$\lambda_{\max}^{\text{PL}}$ (soln) (nm)
POC10DTQ(EHP)	630, 652*
PFODTQ(EHP)	612, 655*
PThQx(EHP)	636
PThDTQ(EHP)^c	666
PDTQ(EHP)	678

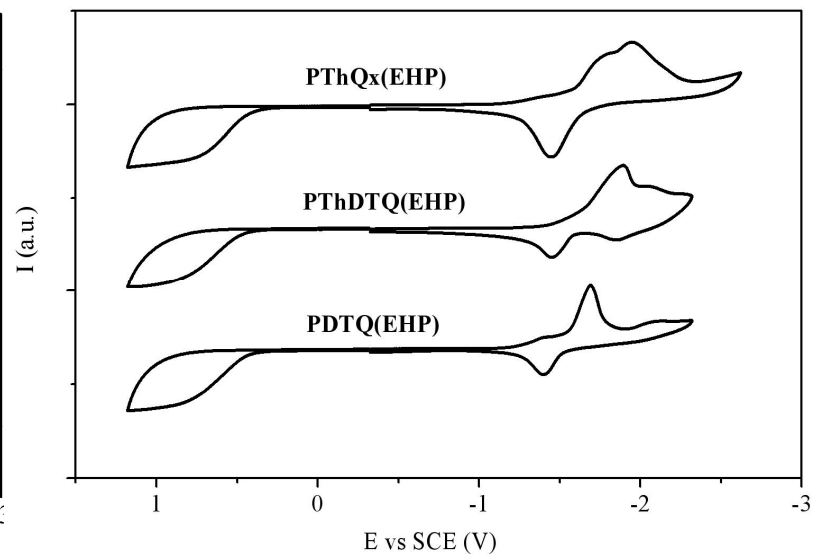
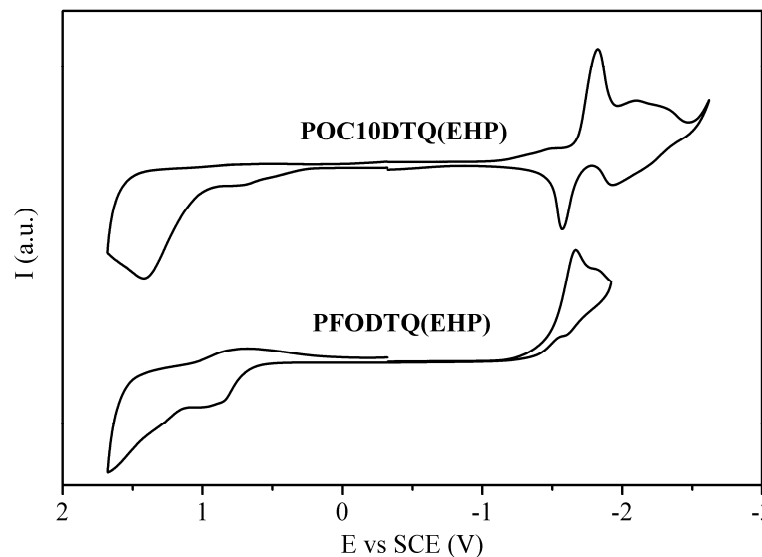
Photoluminescence spectrum-film



	$\lambda_{\max}^{\text{PL}}$ (film) (nm)
POC10DTQ(EHP)	702
PFODTQ(EHP)	636, 658
PThQx(EHP)	740
PThDTQ(EHP)	744
PDTQ(EHP)	742

Red shifts of spectra in solid state than in solution, suggesting changes in electronic states of the polymer molecules by interaction with neighboring polymers in the film also concerning the **intermolecular charge transfer interaction**.

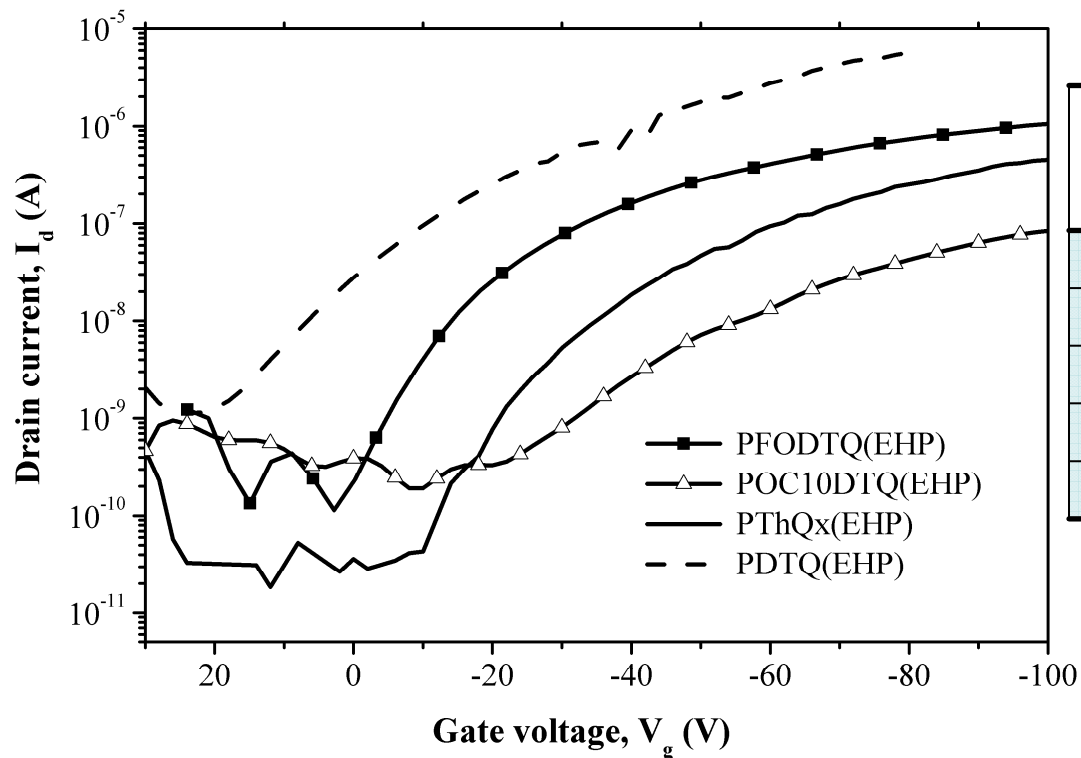
Electrochemical Characteristics



	Oxidation (vs SCE)		Reduction (vs SCE)	
	E_{onset} (V)	HOMO (eV)	E_{onset} (V)	LUMO (eV)
POC10DTQ(EHP)	0.23	-4.63	-1.67	-2.73
PFODTQ(EHP)	0.68	-5.08	-1.46	-2.94
PThQx(EHP)	0.42	-4.82	-1.55	-2.85
PThDTQ(EHP)	0.45	-4.85	-1.57	-2.83
PDTQ(EHP)	0.43	-4.83	-1.53	-2.87

• Donor strength :
thiophene > phenylene > fluorene

TFT Application-2

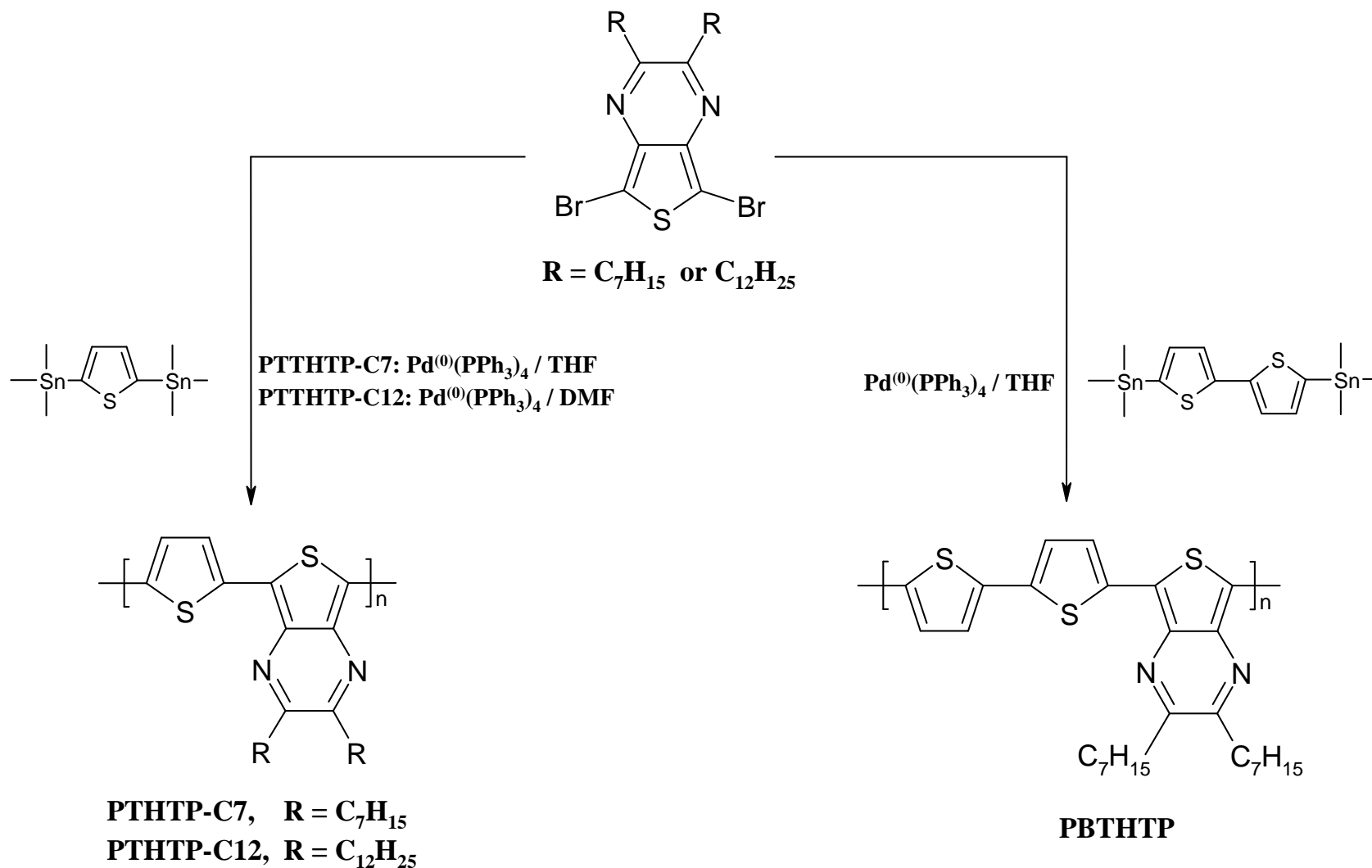


	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	On/Off	RMS (nm)
POC10DTQ(EHP)	4.7×10^{-5}	4.1×10^3	0.18
PFODTQ(EHP)	9.3×10^{-4}	2.3×10^4	0.61
PThQx(EHP)	2.5×10^{-4}	2.00×10^4	1.68
PThDTQ(EHP)	-	-	-
PDTQ(EHP)	4.3×10^{-3}	2.66×10^3	1.96

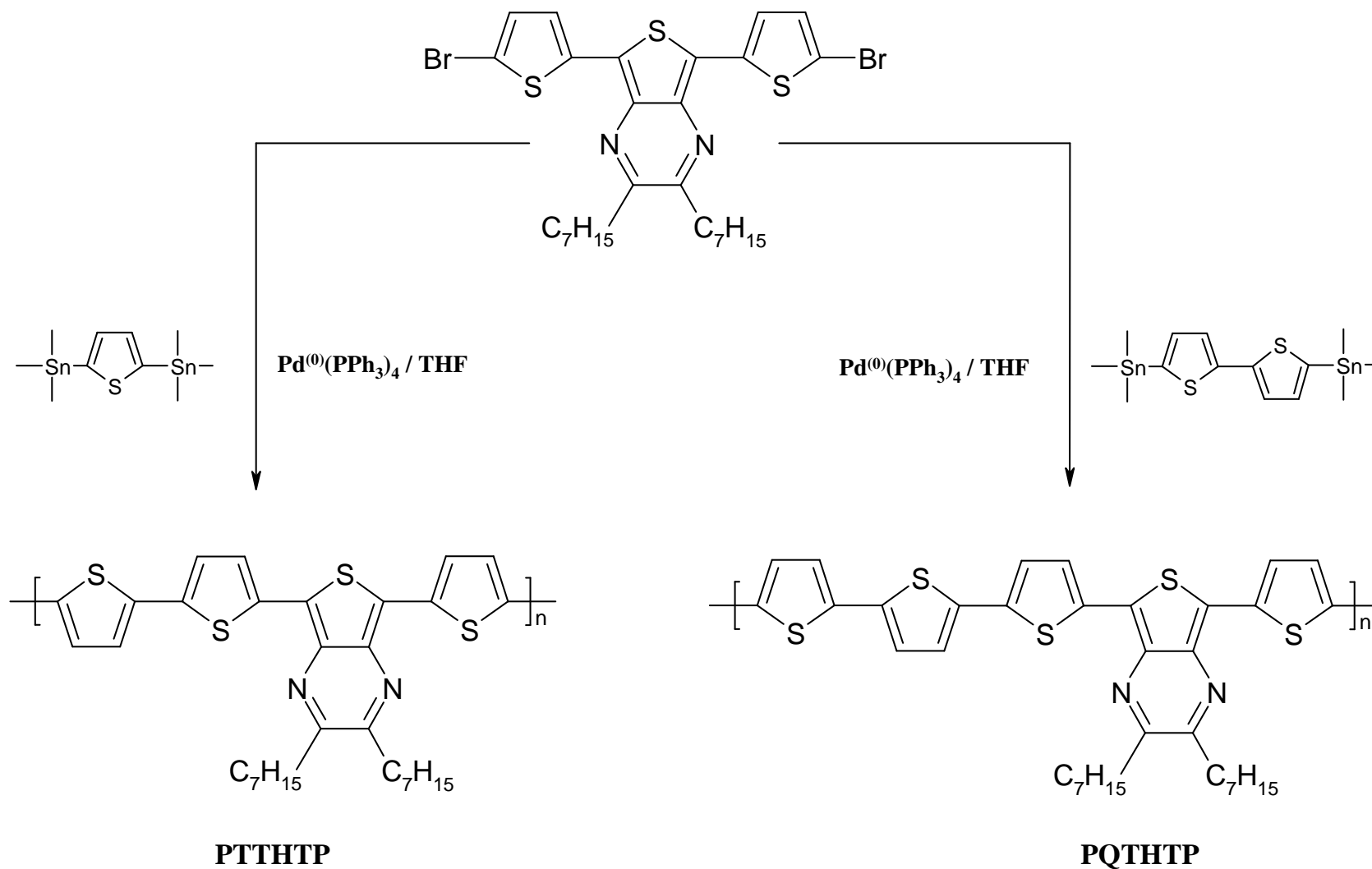
The PDTQX (EHP) shows a high mobility than PTHQx due to its higher molecular weight. The relatively low mobility of polymers **POC10DTQ(EHP)** may be account for the high-lying HOMO energy levels of the polymers, and therefore the ambient oxygen doping of the organic semiconductor.

Thiophene-TP Alternating Copolymers :

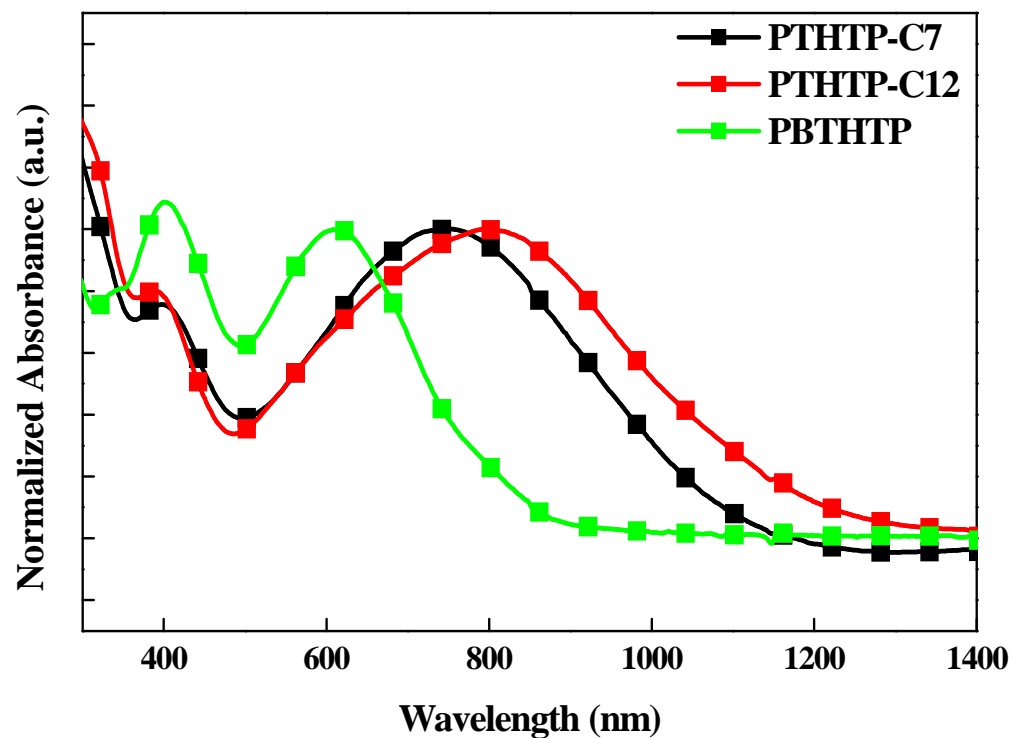
TP is a stronger donor than Q



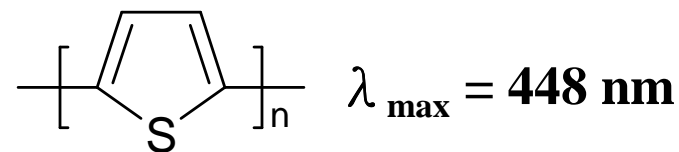
Thiophene-TP Alternating Copolymers



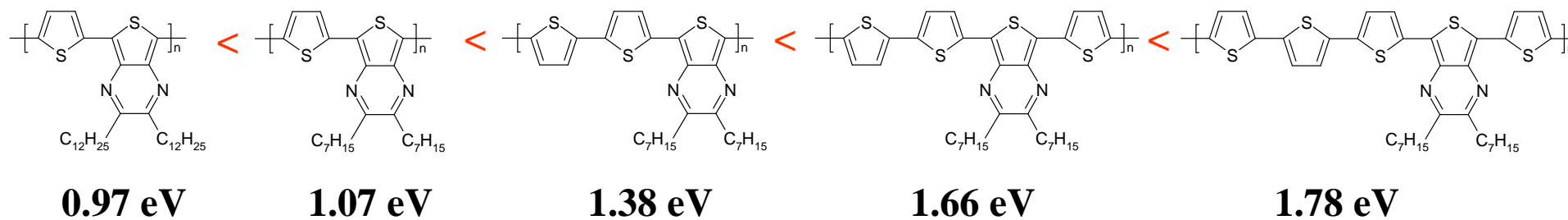
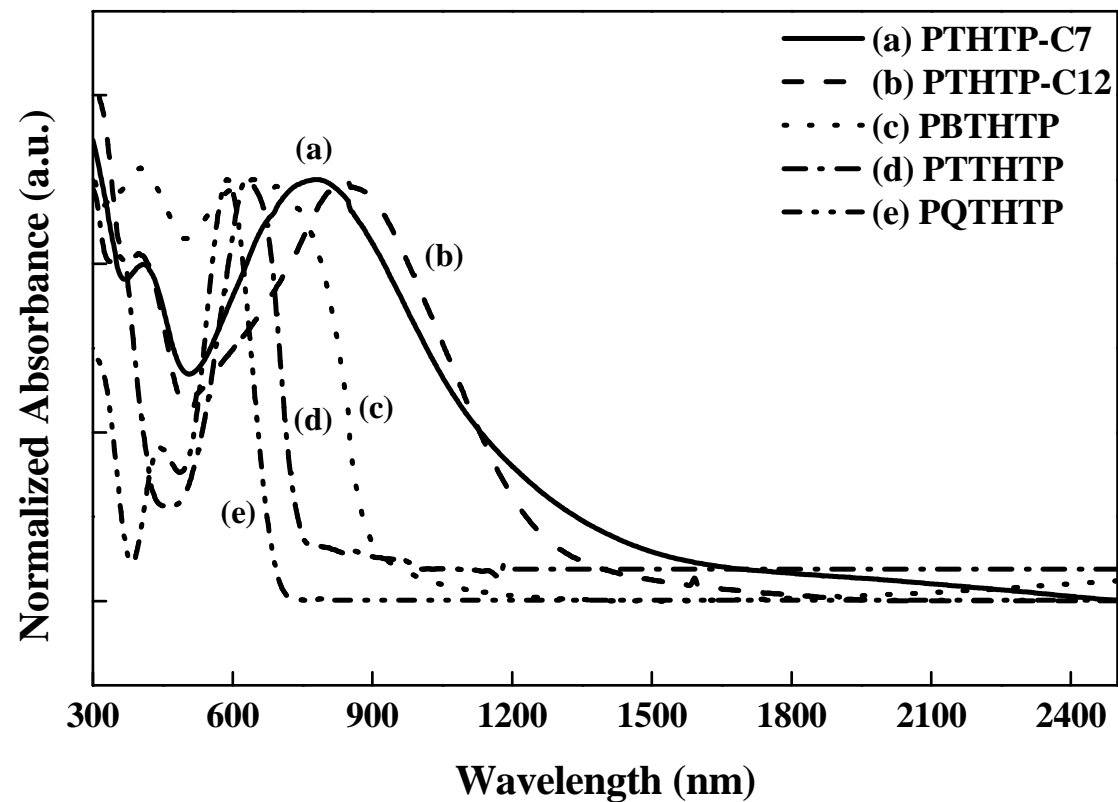
Solid State Optical Absorption Spectrum & Intramolecular Charge Transfer of Thiophene-TP Alternating Copolymers



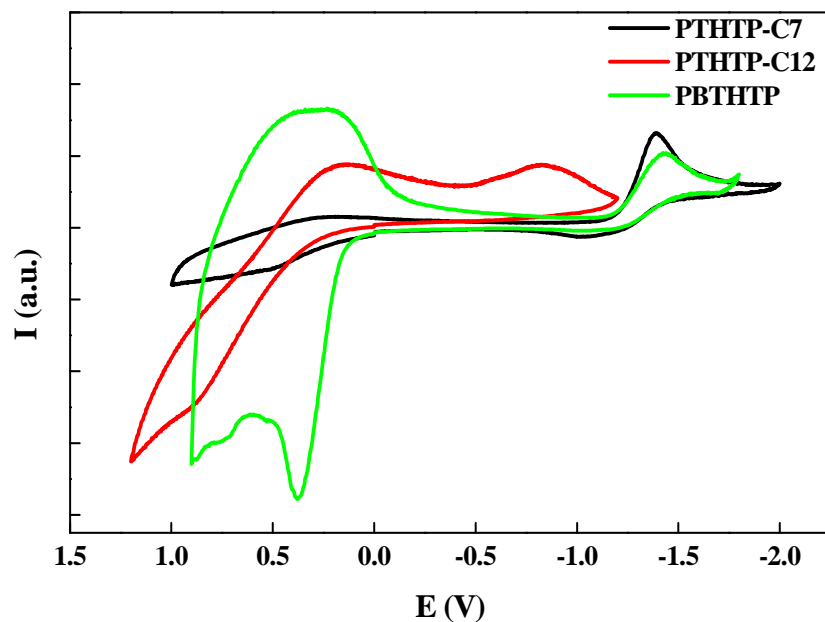
	λ_{\max} solution (nm)
PTHTP-C7	748
PTHTP-C12	774
PBTHTP	610



Solid State Optical Absorption Spectrum & Optical Band Gaps of Thiophene-TP Alternating Copolymers



CV & Electronic Structures of Thiophene-TP Alternating Copolymers



	Oxidation (vs SCE)		Reduction (vs SCE)		E_g^{ec} (eV)
	E_{onset} (V)	HOMO (eV)	E_{onset} (V)	LUMO (eV)	
PTHTP-C7	0.05	-4.45	-1.15	-3.25	1.20
PTHTP-C12	0.30	-4.70	-0.48	-3.92	0.78
PBTHTP	0.15	-4.55	-1.19	-3.21	1.34

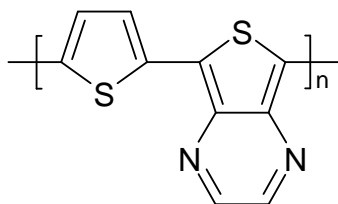
PTH : HOMO(-4.9eV) LUMO(-2.9eV)

Incorporation of TP → HOMO ↑ , LUMO ↓

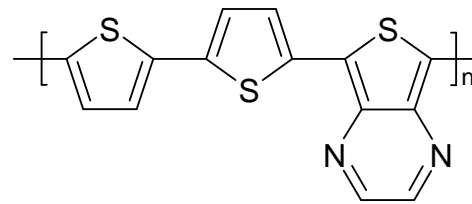
Band gap: PTHTP-C12 < PTHTP-C7 < PBTHTP

Theoretical Analysis on Thiophene-TP

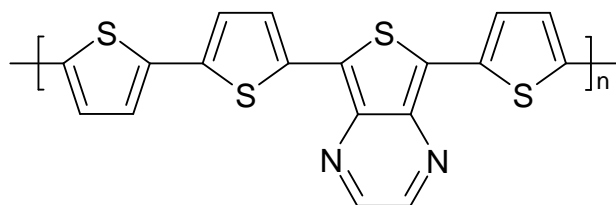
Alternating Copolymers



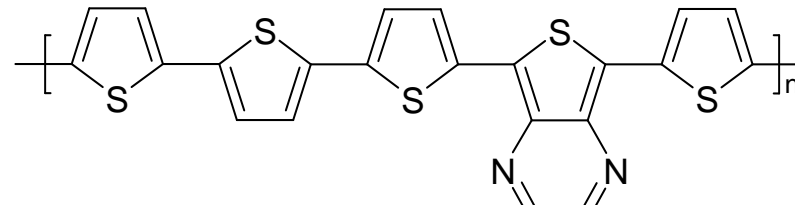
PTHTP



PBTHTP



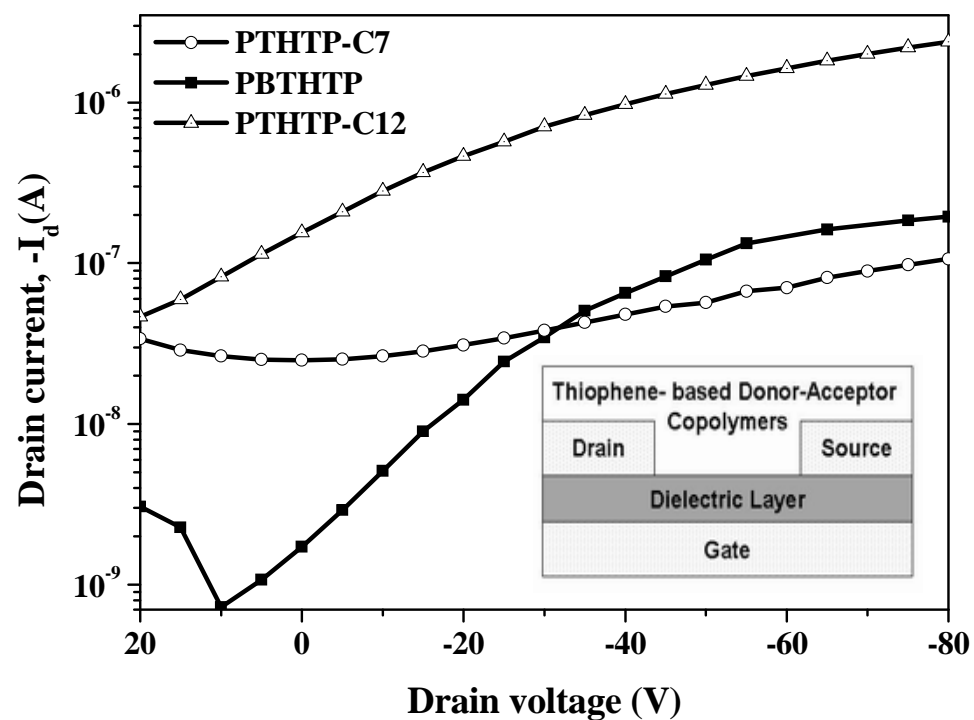
PTTHTP



PQTHTP

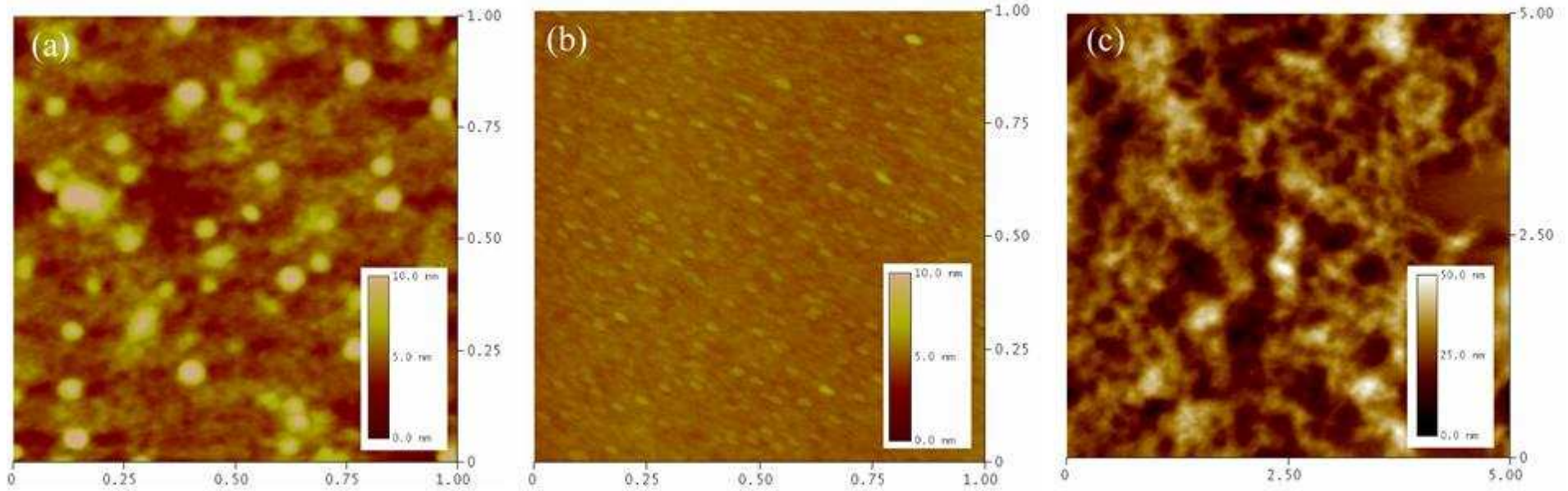
Polymer	L_B (Å)	δ_D (Å)	δ_A (Å)	IP (eV)	EA (eV)	E_g (eV)
PTH	1.441	0.031	-	-4.62	-2.55	2.07
PTP	1.373	-	0.026	-4.40	-3.07	1.32
PTHTP	1.426	0.005	0.030	-4.20	-3.30	0.90
PBTHTP	1.429	0.016	0.037	-4.36	-3.15	1.21
PTTHTP	1.430	0.019	0.038	-4.42	-3.06	1.36
PQTHTP	1.431	0.021	0.039	-4.46	-3.01	1.45

Field-Effect Transfer Characteristics of Thiophene-TP Copolymers



	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	On/off ratios
PTHTP-C7	3.6×10^{-5}	3
PTHTP-C12	1.1×10^{-3}	70
PBTHTP	1.2×10^{-4}	300

Topographical AFM images of PTHTPs

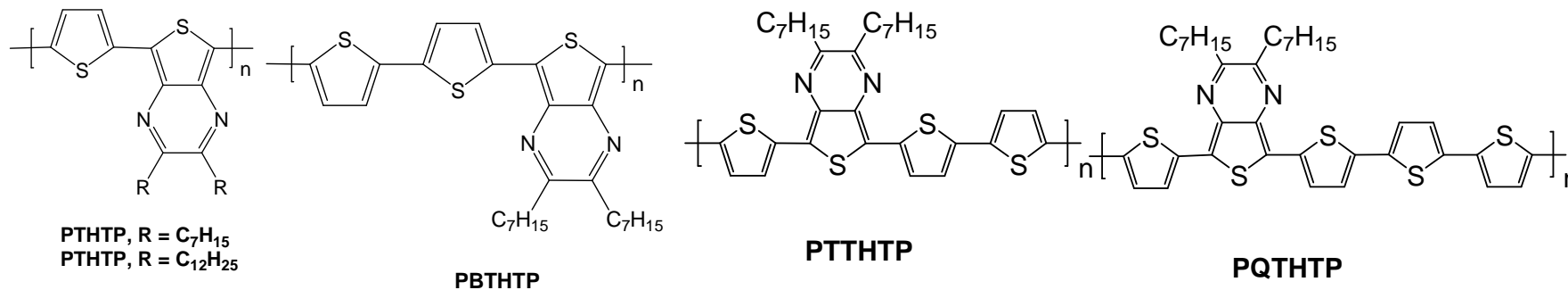


PTHTP-C7

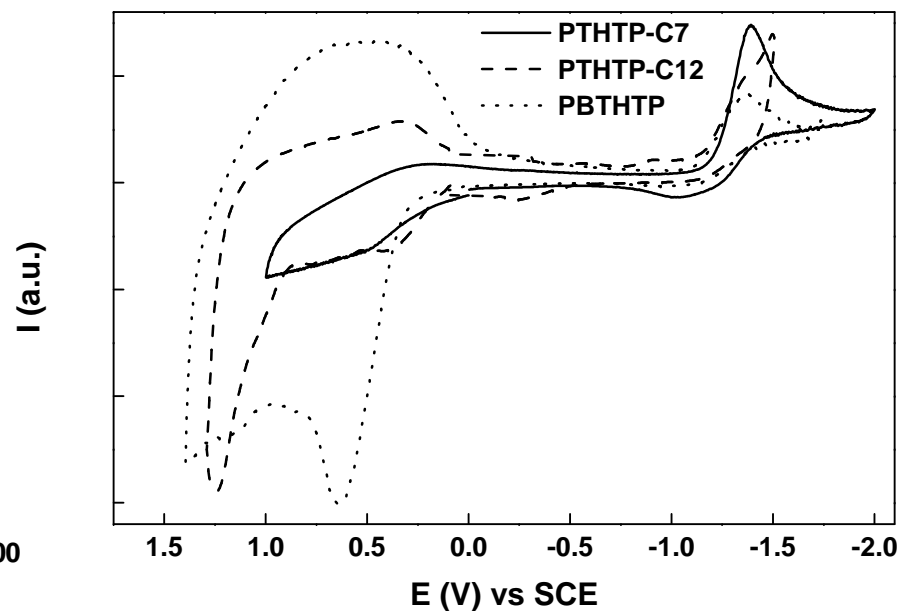
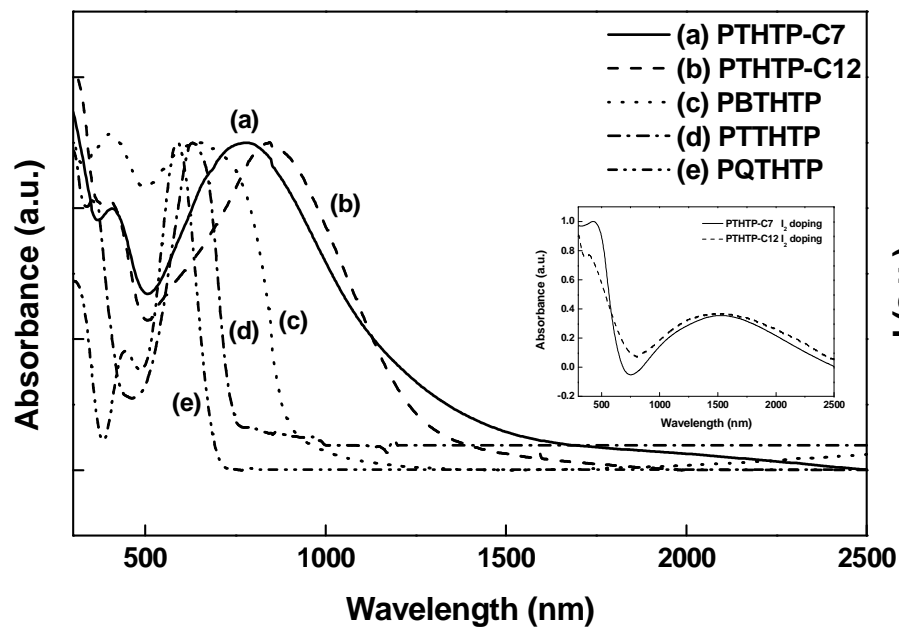
PBTHTP

PTHTP-C12

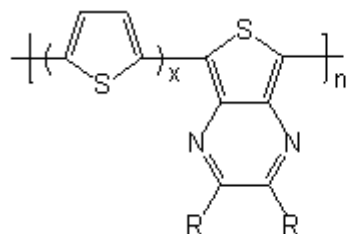
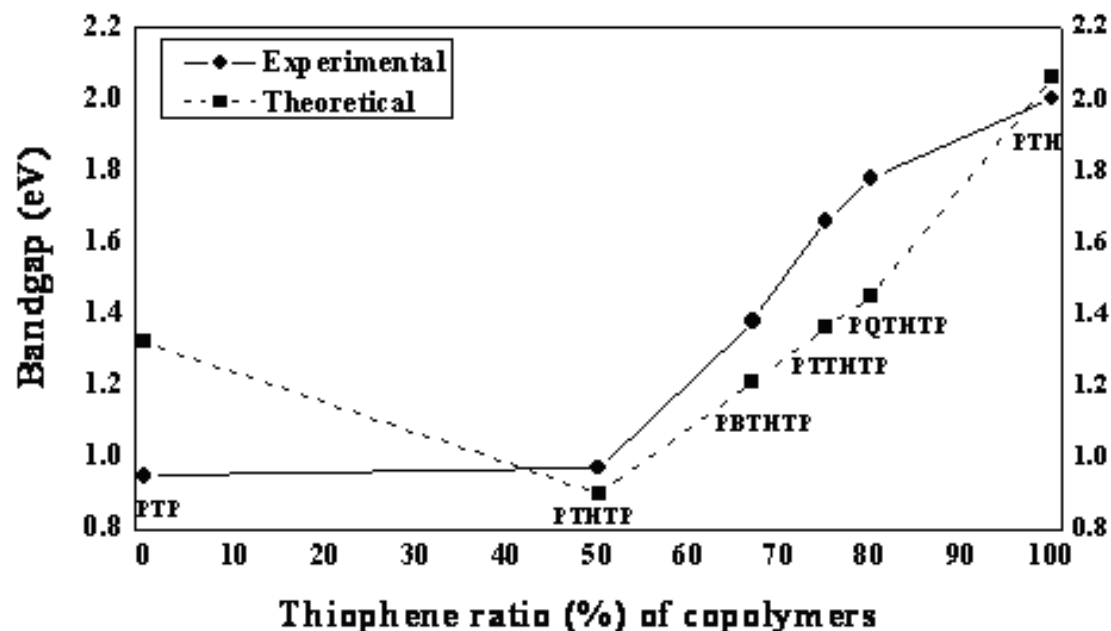
Small Band Gap Conjugated Polymers Based on Thiophene-Thienopyrazine Copolymers



0.97 eV(opt)
0.78 (EC)



Correlation of Optical band Gap with Donor/acceptor Ratio

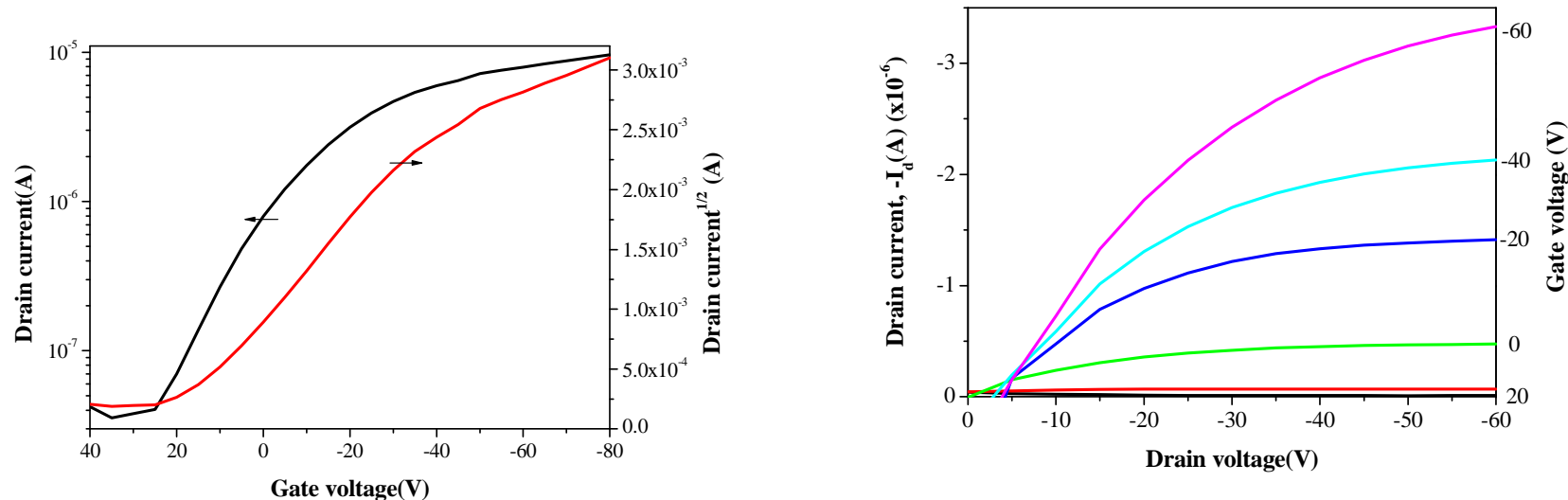


- x = 1 PTHTP
- x = 2 PBTHTP
- x = 3 PTTHTP
- x = 4 PQTHTP

The band gaps of the thiophene (TH)-thienopyrazine (TP) conjugated copolymers were varied significantly by the thiophene content due to the effects of **bond length alternation** and **intramolecular charge transfer**.

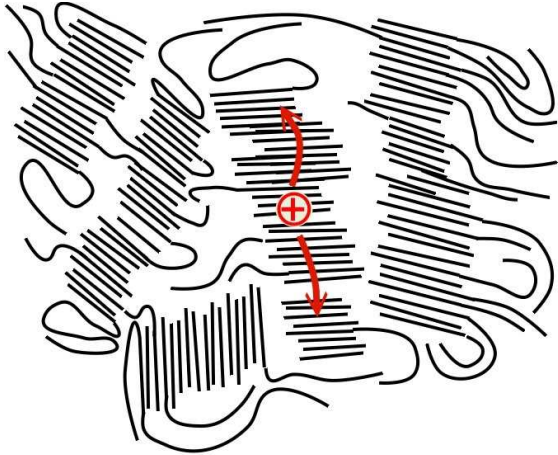
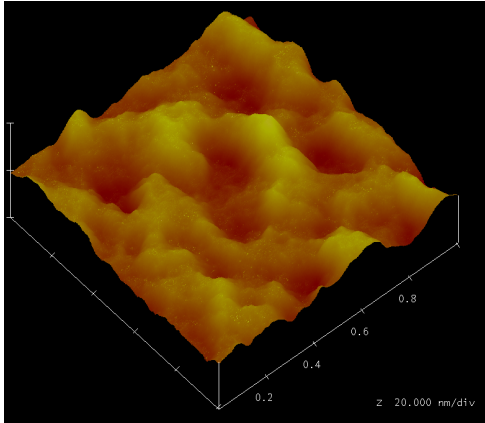
FET characteristics of Thiophene-Thienopyrazine Copolymers

(unpublished results)

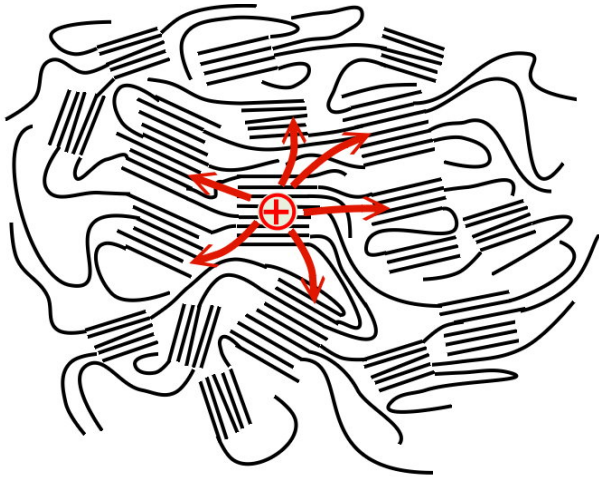
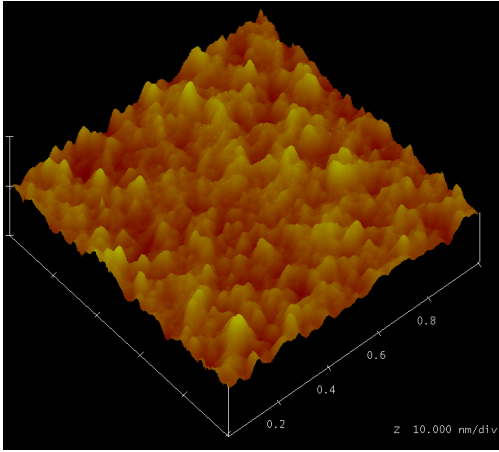


	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	Mobility (cm²V⁻¹s⁻¹)	On/off ratios	RMS roughness (nm)
PTHTP-C7 (HMDS)	1.07	-4.64	-3.22	3.6 × 10⁻⁵	3	2.21
PBTHTP -C7 (HMDS)	1.38	-4.73	-3.26	1.2 × 10⁻⁴	300	0.94
PTHTP-C12 (HMDS)	0.97	-4.64	-3.25	1.1 × 10⁻³	70	7.37
PTHTP-C12 (OTS, 60°C)				6.1 × 10⁻³	60	2.05
PTHTP-C12 (OTS, 60°C)				1.1 × 10⁻²	227	0.99

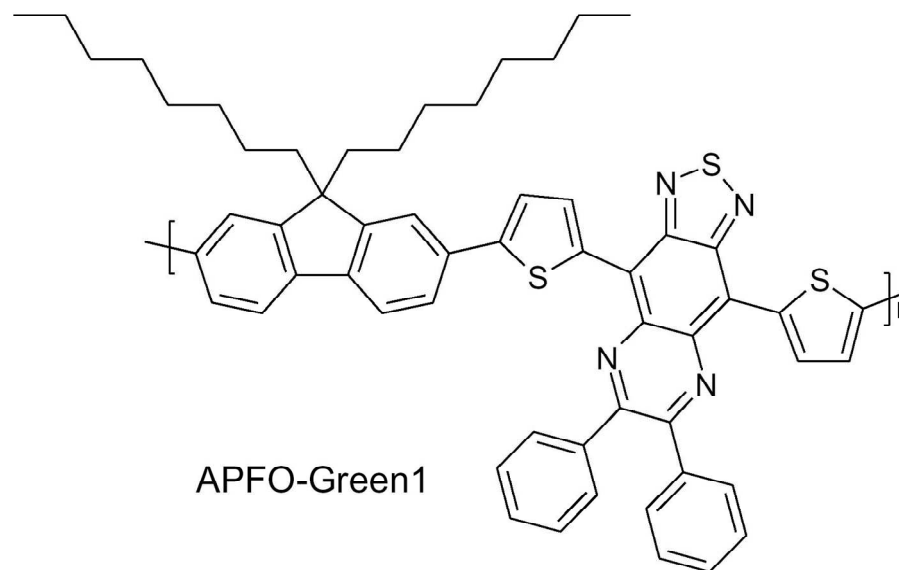
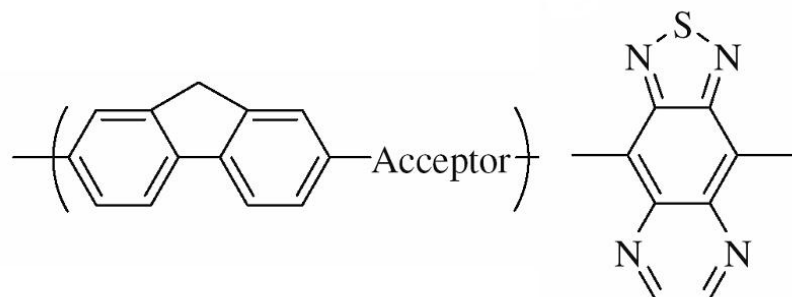
HMDS modified Surface



OTS modified Surface



Literature Review of TQ-Based Conjugated Polymer



Polymer	L_B (Å)	IP (eV)	EA (eV)	E_g (eV)
P(F-TQ)	1.478	-5.16	-3.51	1.64

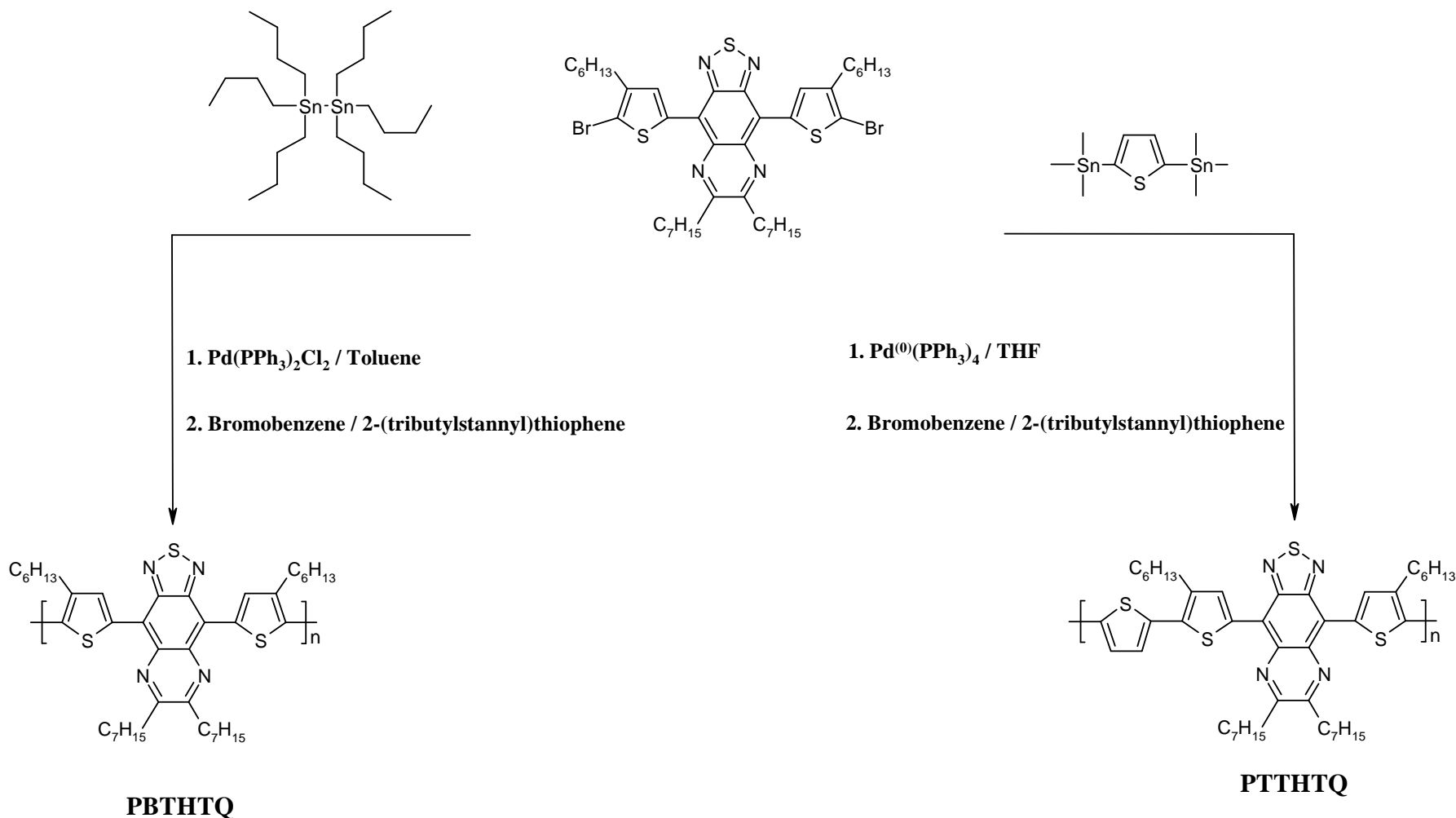
Band gap = 1.3 eV
Hole Mobility: $3 \times 10^{-2} \text{ cm}^2/\text{Vs}$

Ref: (1) Wu et al., *Journal of Polymer Research* **2006**, *13*, 441.

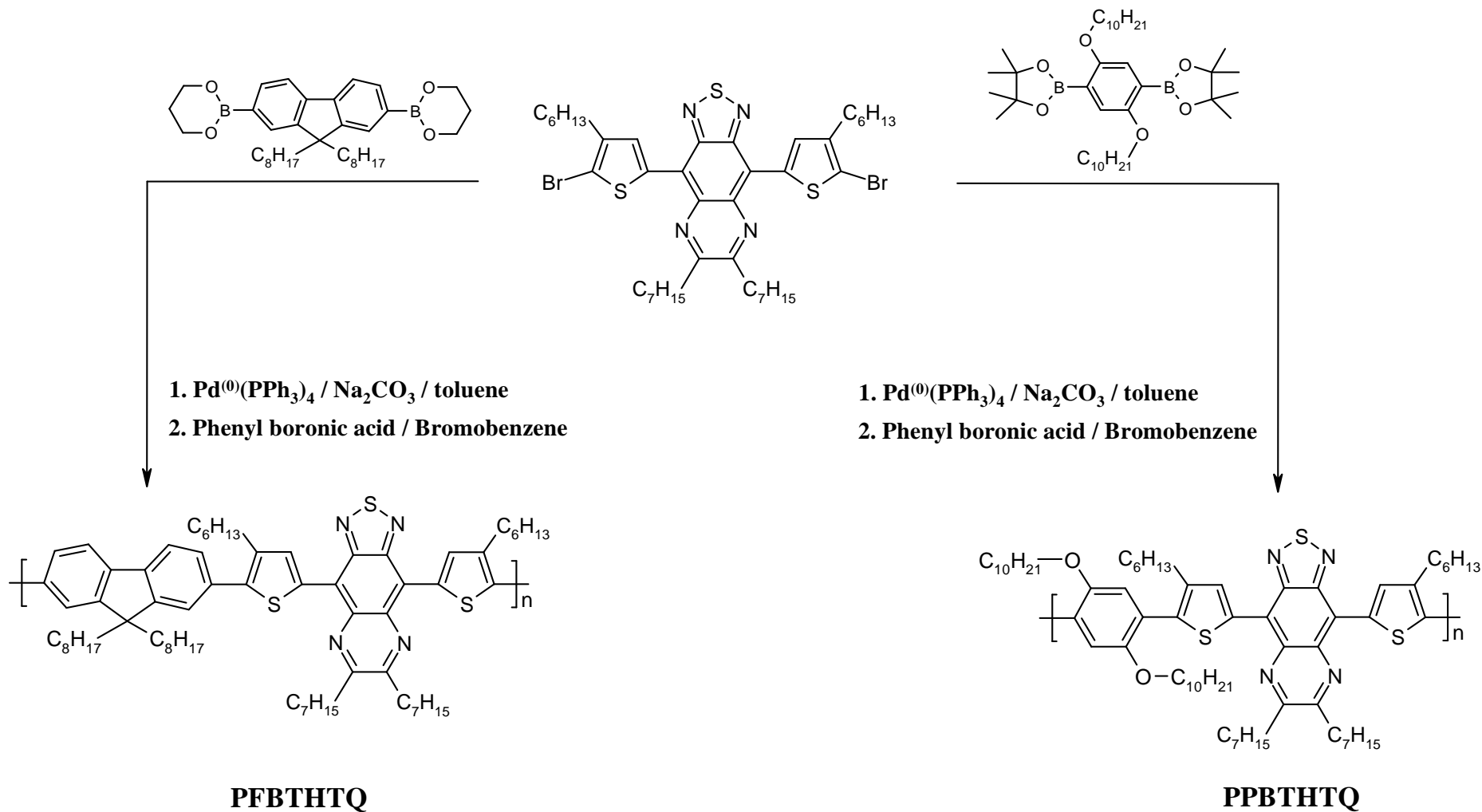
(2) Perzon et al., *Appl. Phys. Lett.* **2005**, *87*, 252105.

(3) Perzon et al., *Polymer*. **2006**, *47*, 4261.

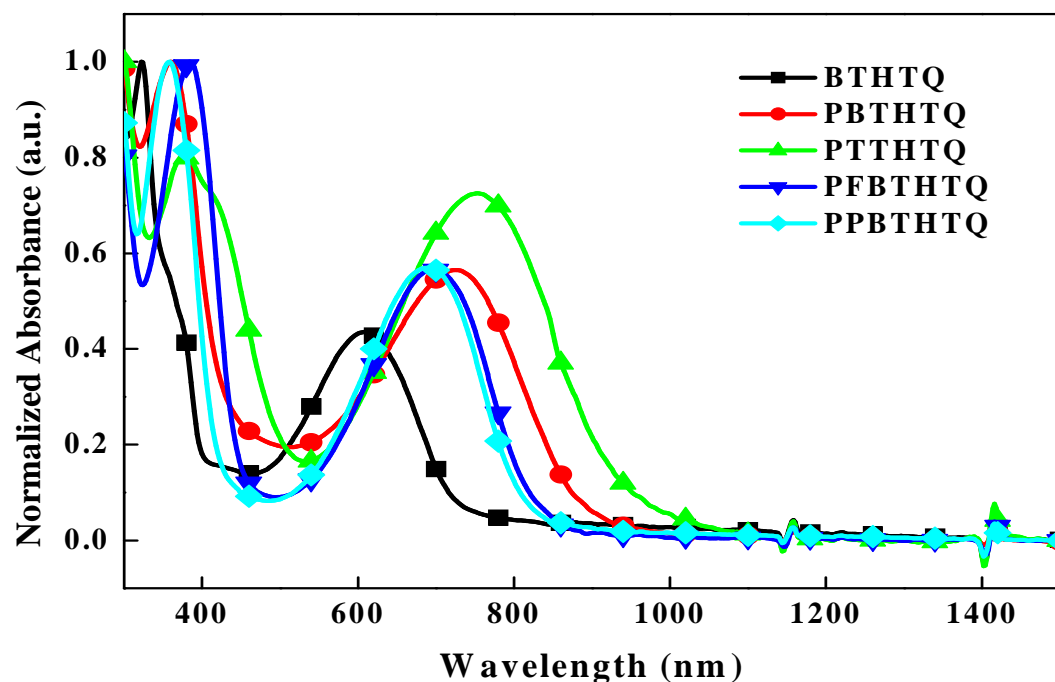
Synthesis of TQ Based Donor-Acceptor Alternating Copolymers (I)



Synthesis of TQ Based Donor-Acceptor Alternating Copolymers (II)



Solution State Optical Absorption Spectra & Intramolecular Charge Transfer



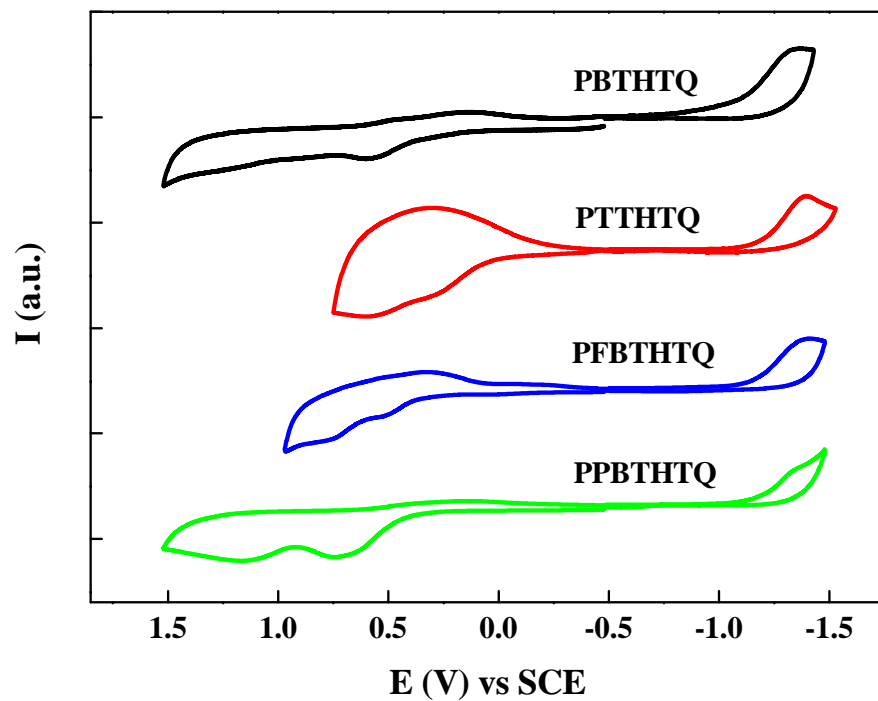
	λ_{max} solution (nm)
BTHTQ	608
PBTHHTQ	727
PTTHTQ	752
PFBTHHTQ	695
PPBTHHTQ	686

ICT: **PTTHTQ > PBTHHTQ > PFBTHHTQ, PPBTHHTQ**

Electron donating ability: **Thiophene > Fluorene, Phenylene**

Steric Hindrance: **PBTHHTQ > PTTHTQ**

CV & Electronic Structures



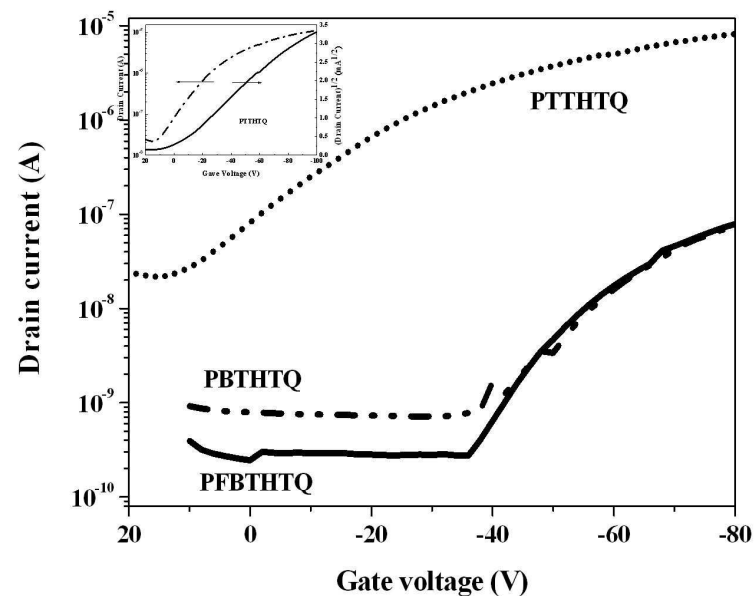
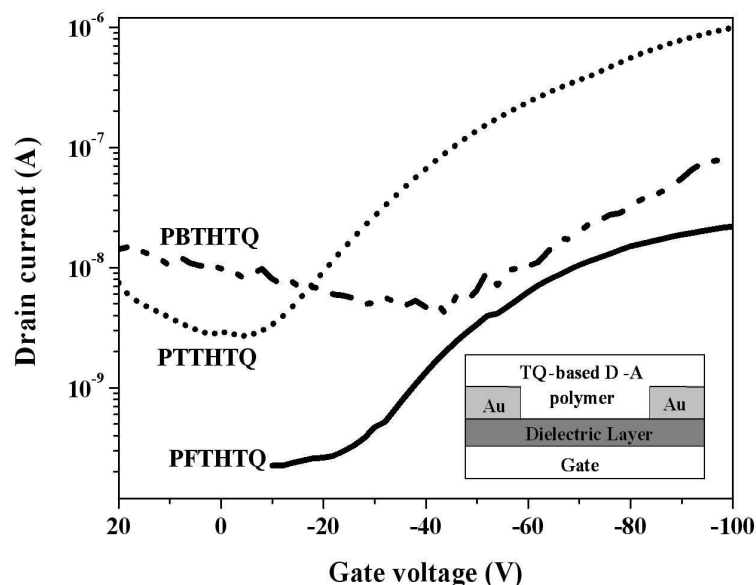
	Oxidation (vs SCE)		Reduction (vs SCE)		E_g (eV)
	E_{onset} (V)	HOMO (eV)	E_{onset} (V)	LUMO (eV)	
PBTHTQ	0.26	-5.06	-1.05	-3.75	1.31
PTTHTQ	0.04	-4.84	-1.17	-3.63	1.21
PFBTHTQ	0.34	-5.14	-1.14	-3.66	1.48
PPBTHTQ	0.40	-5.20	-1.17	-3.63	1.57

PTH (-2.9eV) PF (-2.12eV) PPP (-1.67eV)

Incorporation of Acceptor → LUMO ↓

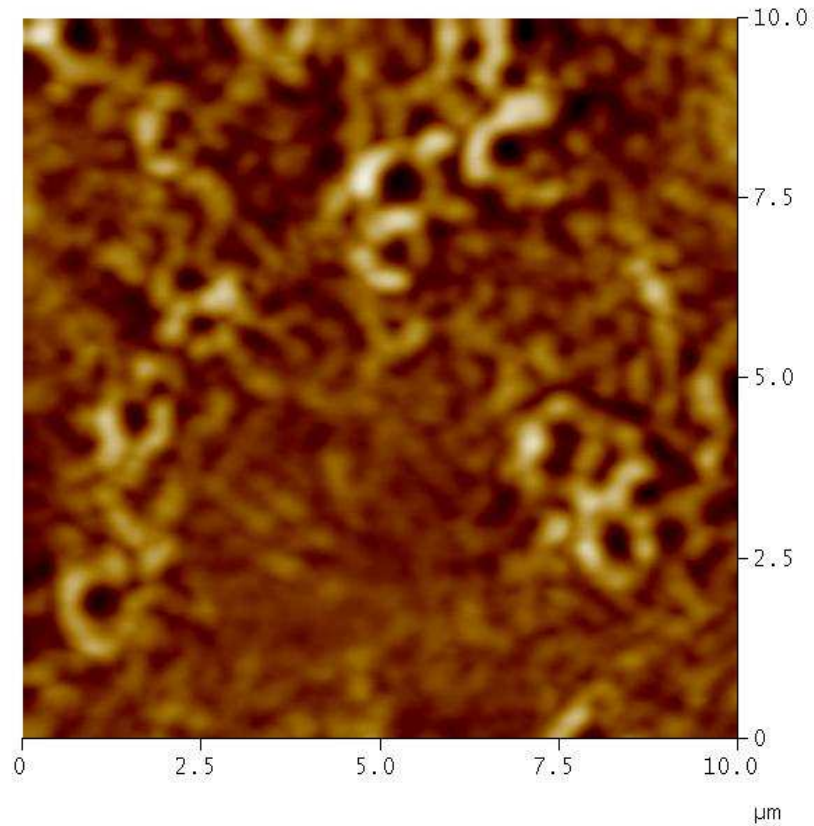
Band gap: PTTHTQ < PBTHTQ < PFBTHTQ < PPBTHTQ

Field-Effect Transfer Characteristics

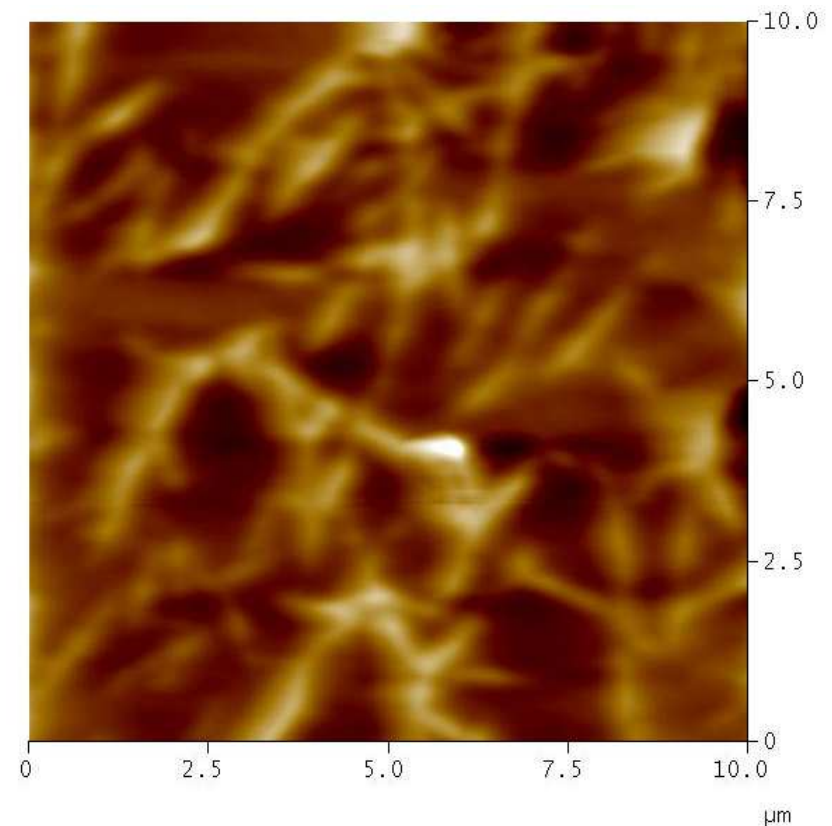


	CHCl ₃ , 100 °C, overnight		CB, 100 °C, overnight	
	Mobility	On/Off	Mobility	On/Off
PBTHTQ	8.53E-05	23	1.62E-04	215
PTTHTTQ	8.54E-04	358	3.83E-03	505
PFBTHTQ	2.77E-05	101.7	1.49E-04	324
PPBTHTQ	---	---	---	---

Topographical AFM Images of PTTHTQ

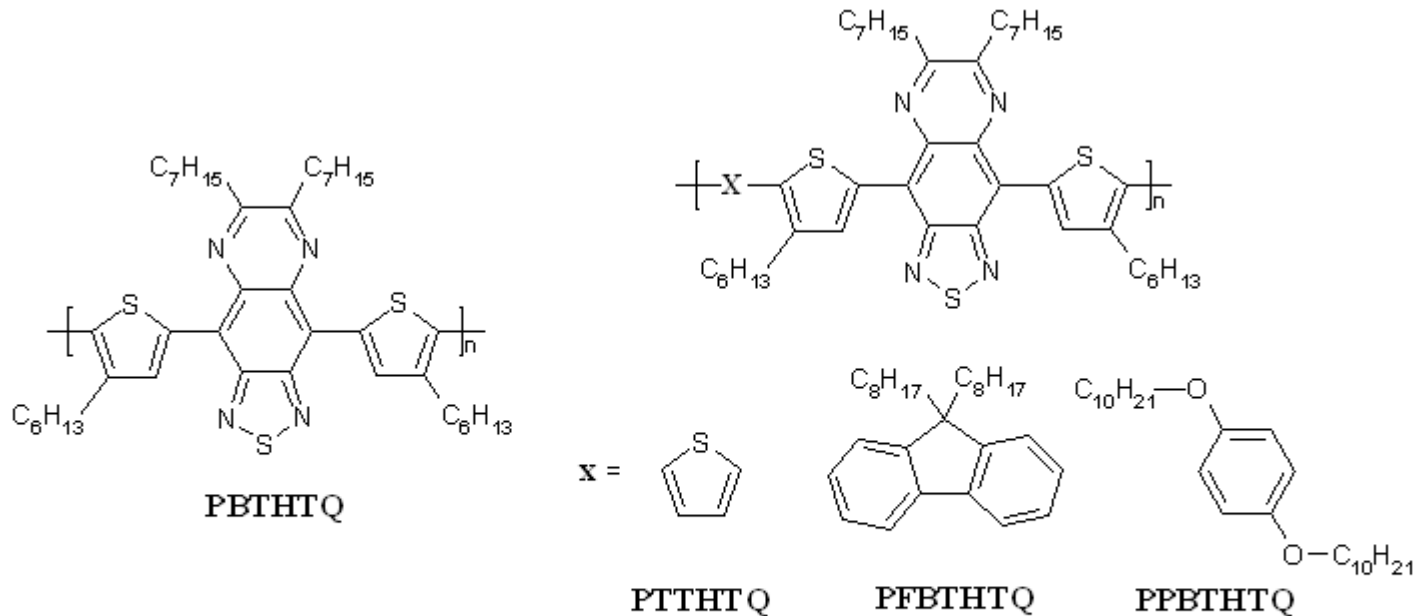


From chloroform



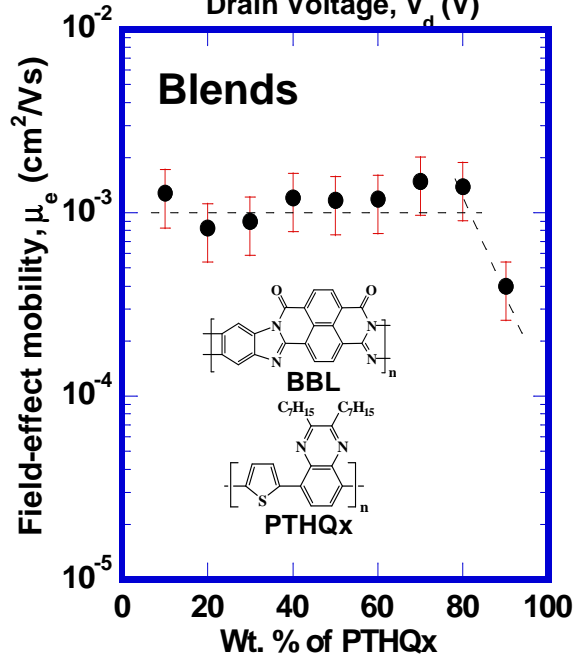
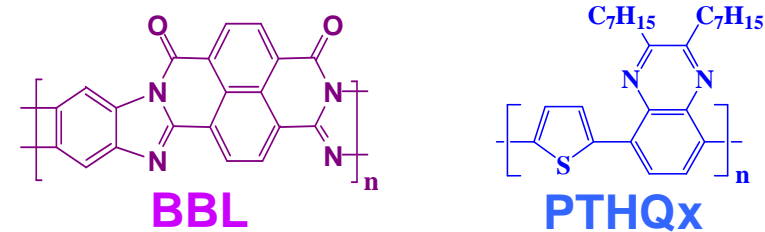
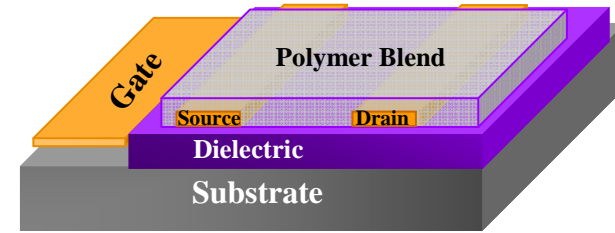
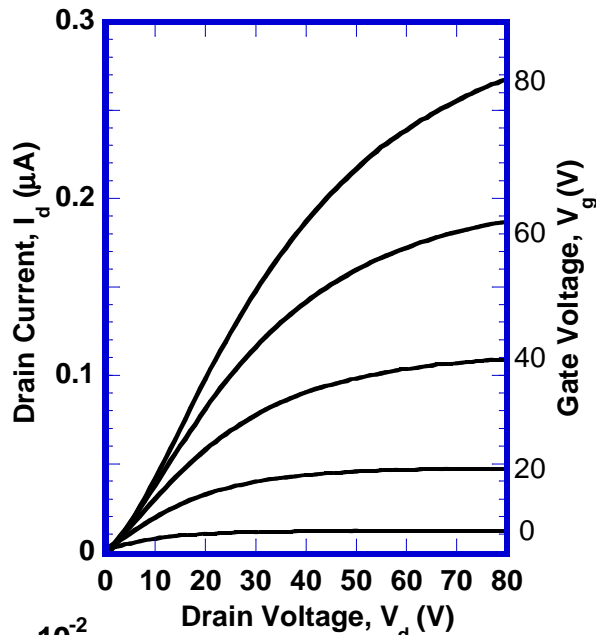
From chlorobenzene

Conclusion



- ICT: **PTTHTQ** > **PBTHTQ** > **PFBTHTQ**, **PPBTHTQ**
- The higher hole mobility of **PTTHTQ** than the other copolymers was attributed from its smaller band gap or ordered morphology

High Electron Mobility in BBL-PTHQx Blends

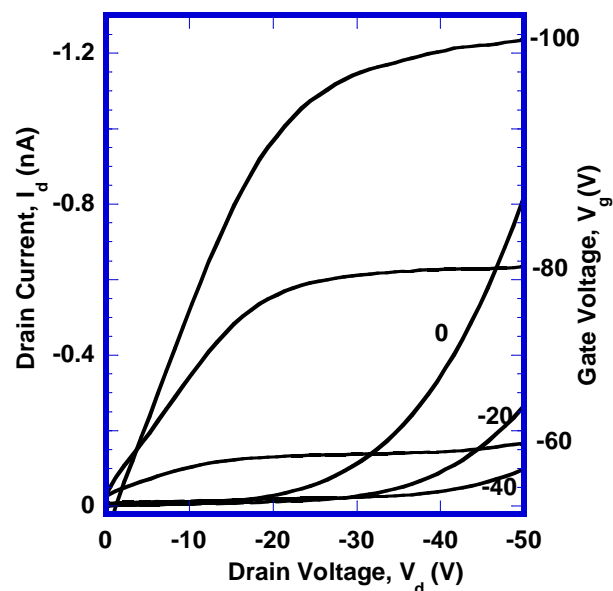
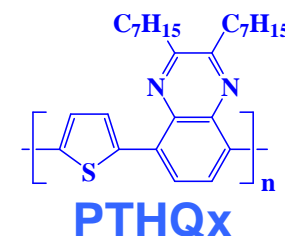
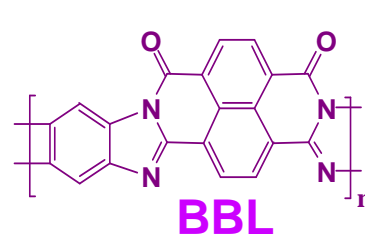
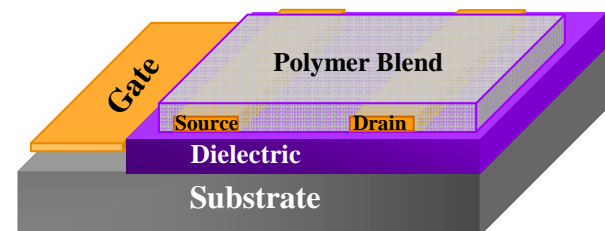
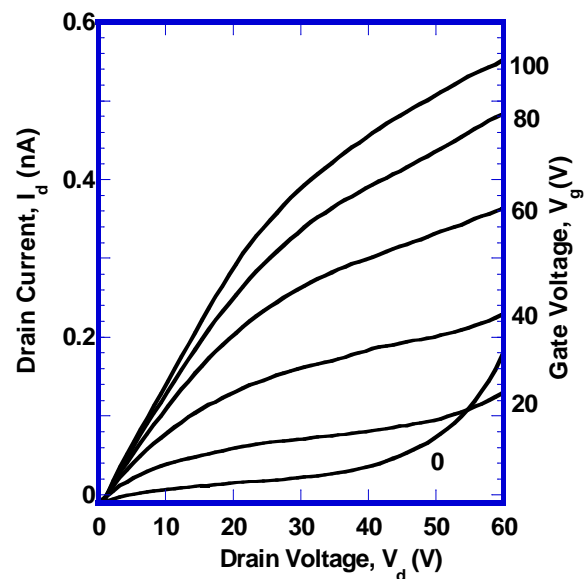


- High unipolar electron mobility observed in most of the BBL-PTHQx blends (10-80 wt%).

- $\mu_e = 1 \times 10^{-3}$ cm^2/Vs .

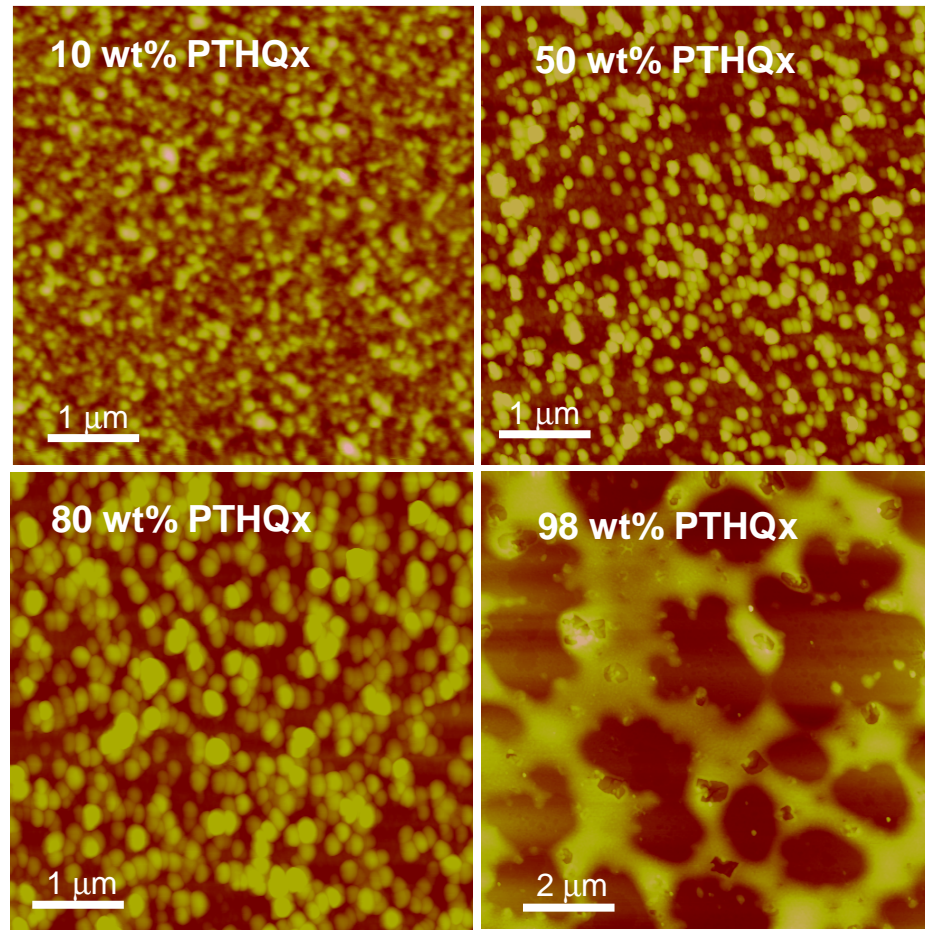
- Decrease in electron mobility at 90 wt% PTHQx blend FETs.

Ambipolar FETs from Blends of BBL and PTHQx



- Ambipolar charge transport was observed for >90 wt% PTHQx blends.
- $\mu_h = 1.4 \times 10^{-5}$ to 2.0×10^{-4} cm^2/Vs .
- $\mu_e = 2.4 \times 10^{-6}$ to 1.4×10^{-5} cm^2/Vs .
- A Non-Linear Drain Current at Low Gate Voltages Due to the Presence of Both Charge Carriers in FET Channel

Morphology of BBL-PTHQx Blends: AFM Images



- **Phase-separated Morphology.**
- **Phase-separated domain sizes increase with the PTHQx content from 50-300 nm.**
- **Interpenetrated bicontinuous network is observed in 98 wt% blend.**