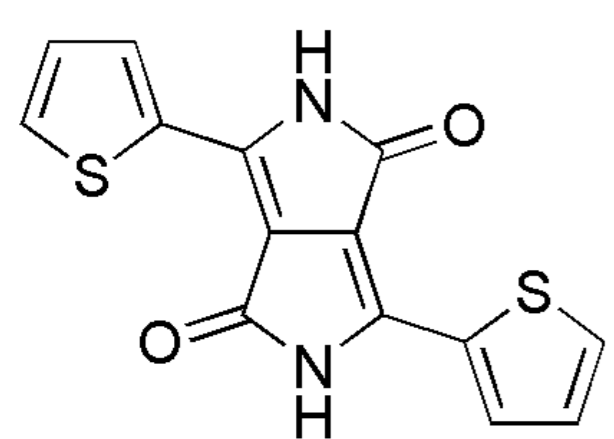


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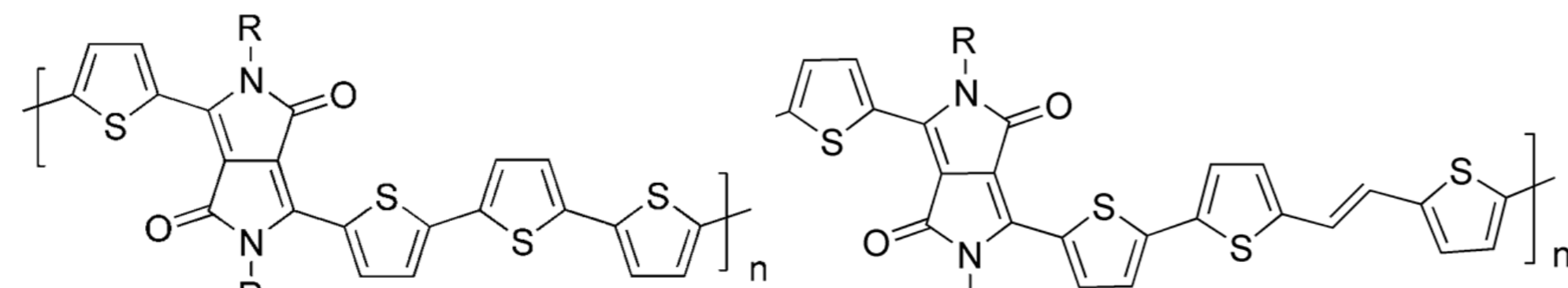
Introduction

High hole mobility diketopyrrolopyrrole (DPP)-based polymers



DPP

- Strong electron-deficient moiety
- Planar conjugated structure
- **Strong π - π interaction**



PDPPQT

$$\mu_h = 1.04 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$$

J. Am. Chem. Soc. 2011, 133, 10364

PDVT-10

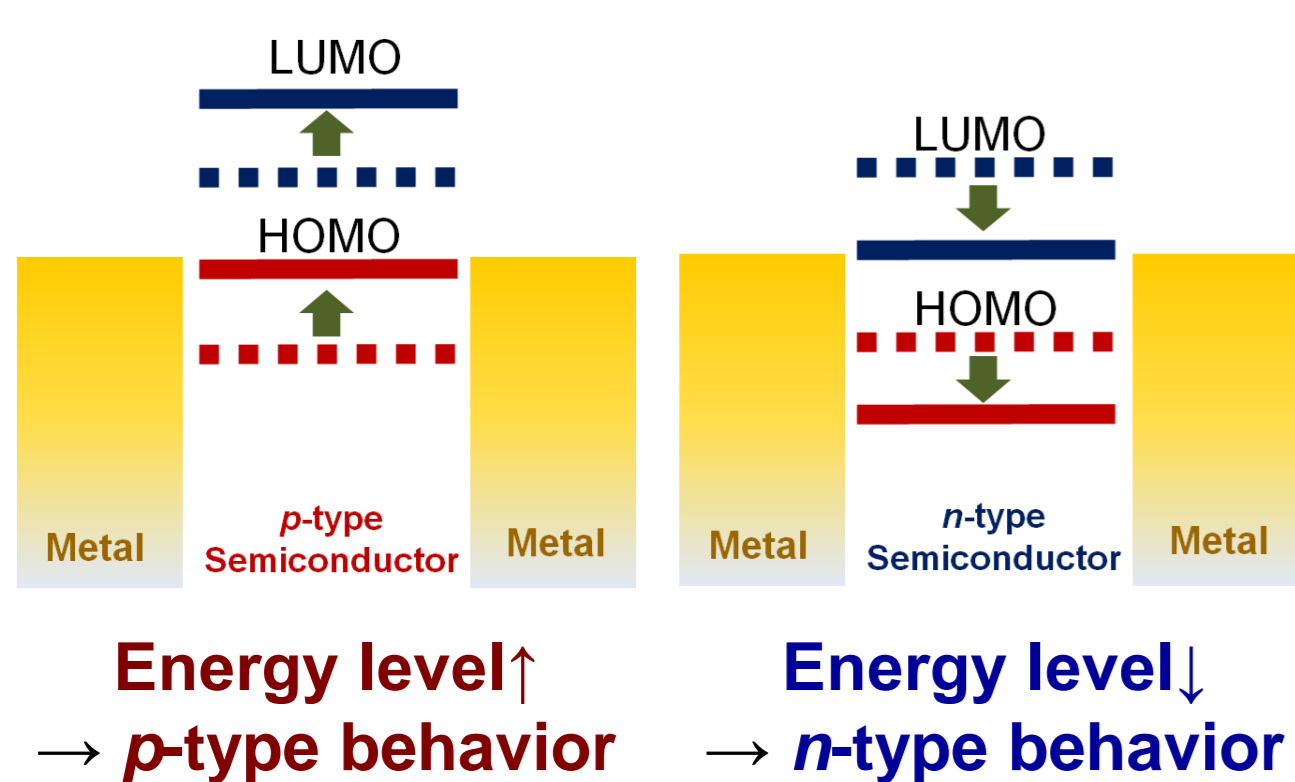
$$\mu_h = 4.0\text{--}8.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$$

Adv. Mater. 2012, 24, 4618

- Until now, many superb *p*-type conjugated polymers based on DPP have been reported. However, there aren't almost represented *n*-type substance.

Effects of molecular energy level upon OFETs

- ✓ Transport behavior in organic materials
- ✓ Natural properties of fluorine atom

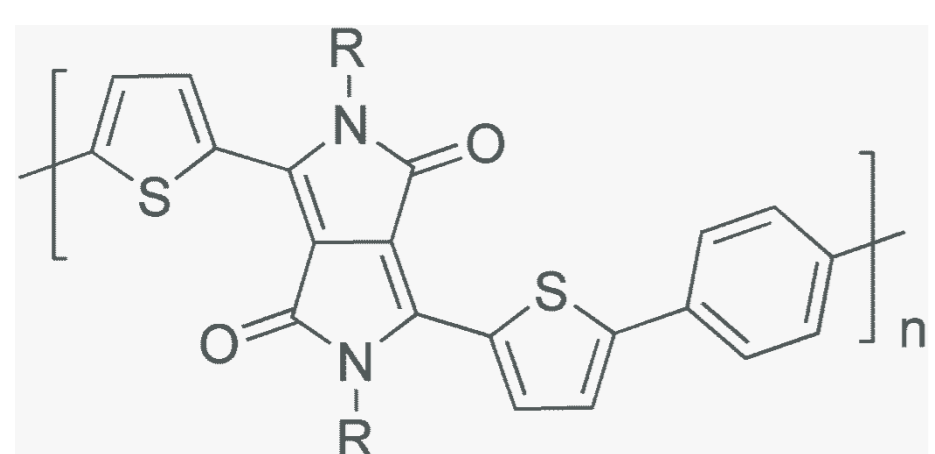


- Highest electronegativity

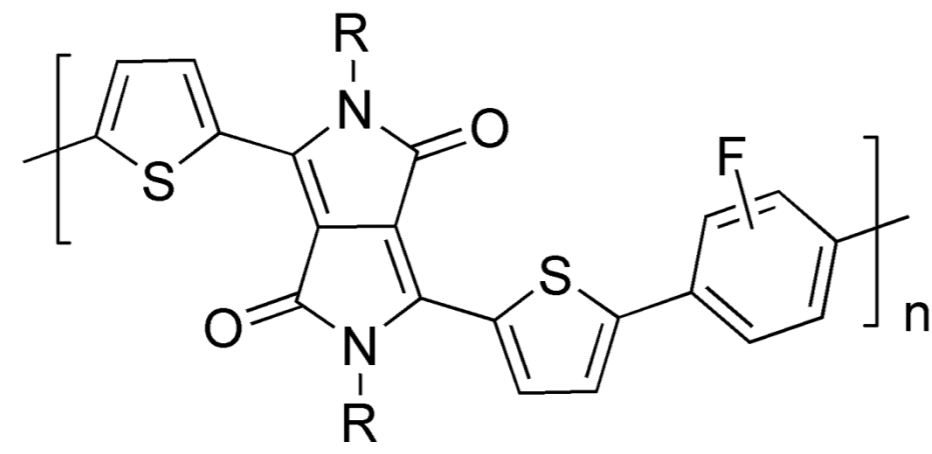


- Smallest electron-withdrawing group → less steric hindrance

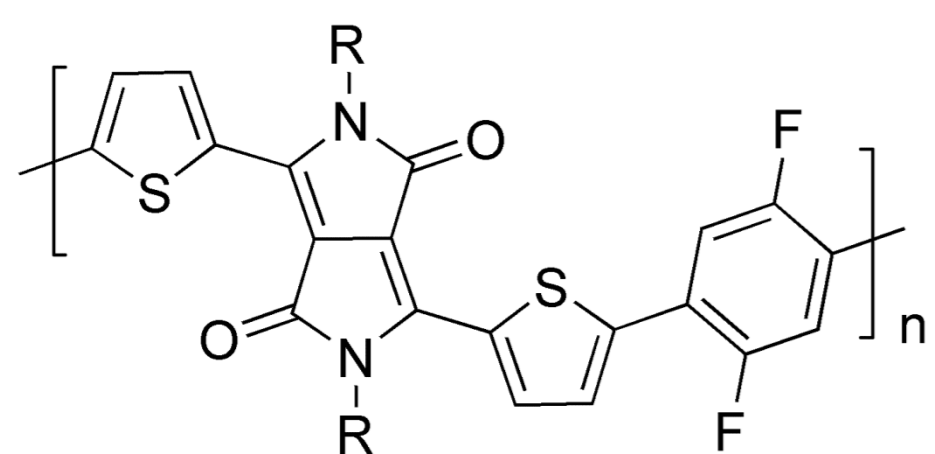
Molecular designs for *n*-type organic materials



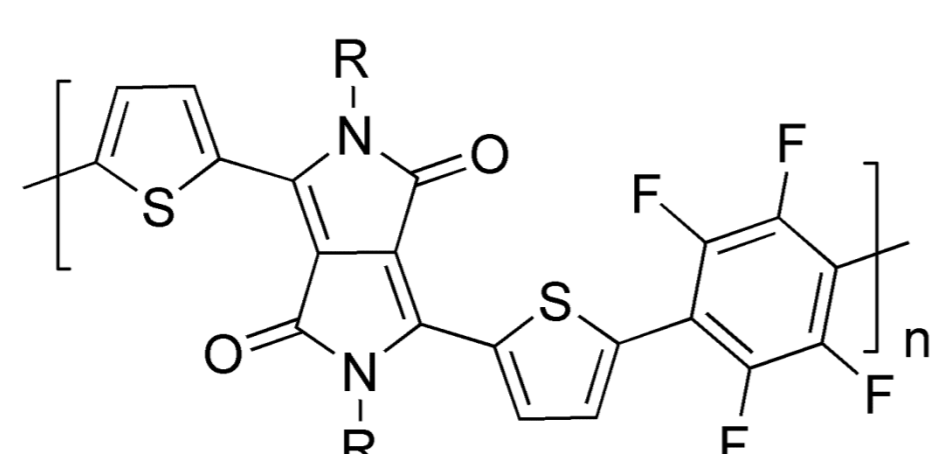
DPPP0FP



DPPPT1FP



DPPPT2FP



DPPPT4FP

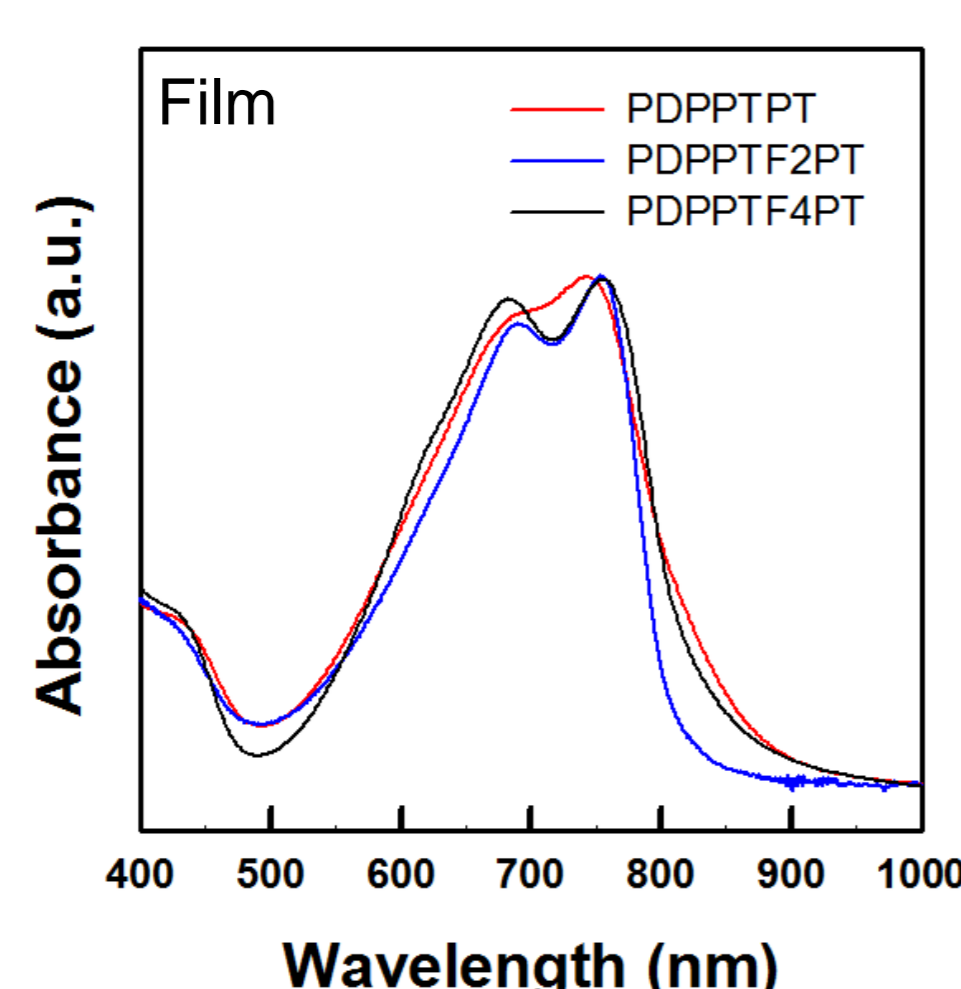
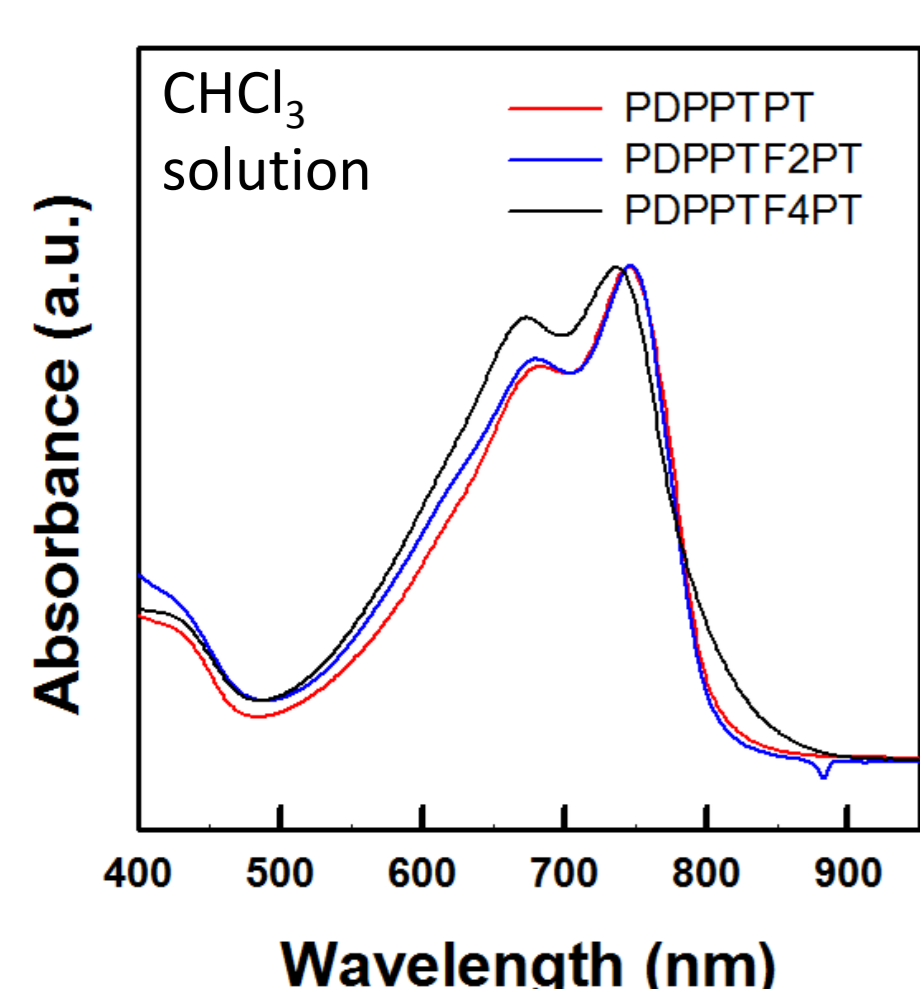
Objectives

- To lower the energy level of the polymer by introducing electron-withdrawing fluorine atoms to phenylene unit that is copolymerized with diketopyrrolo[3,4-*c*]pyrrole (DPP)
- To investigate the effect of fluorine substitution on organic field-effect transistor properties of solution-processable polymers

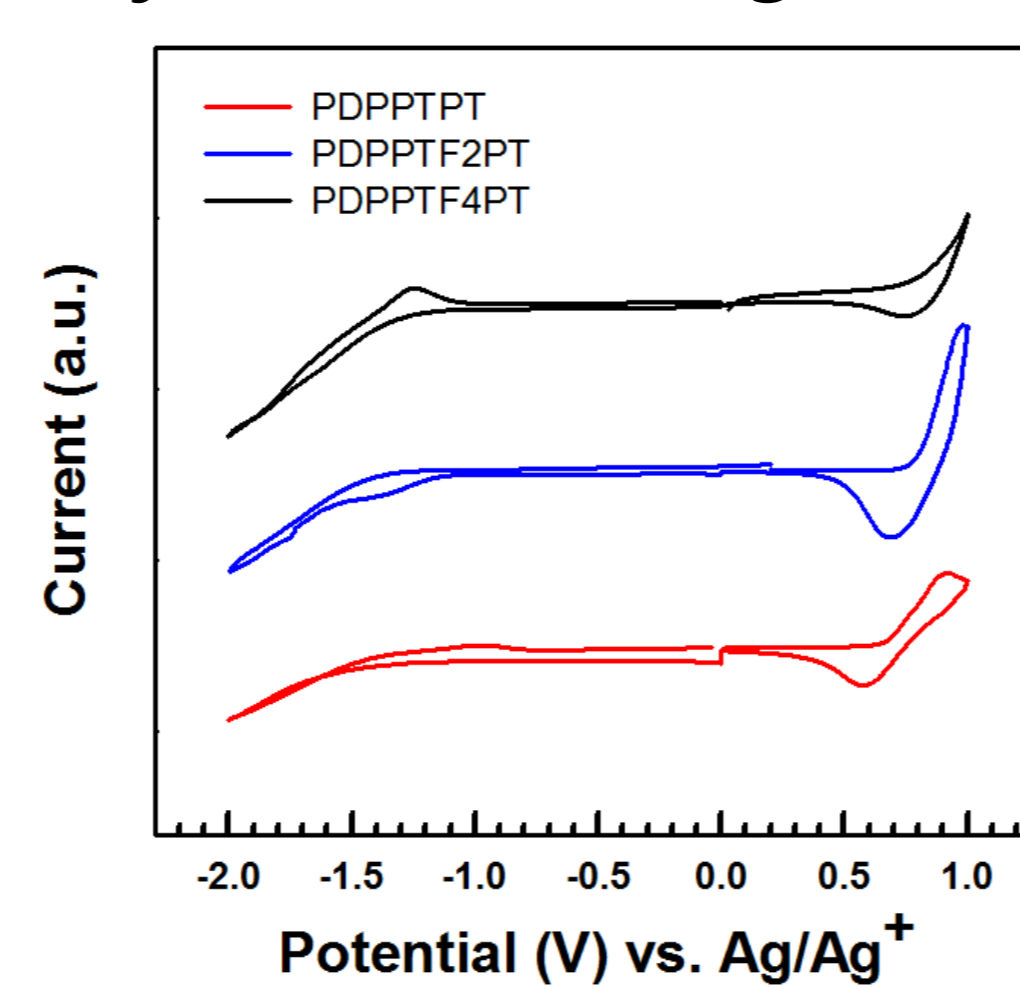
Results

Optical and electrochemical characteristics of the polymers

Absorption spectra



Cyclic voltammograms



Polymer	M_n (kg mol ⁻¹)	PDI	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
PDPP0FP	17.4	2.01	745, 683	744, 700	1.38	-5.36	-3.56	1.8
PDPP2FP	18.8	1.73	747, 680	754, 690	1.45	-5.57	-3.56	2.0
PDPP4FP	16.3	1.79	743, 674	756, 683	1.33	-5.65	-3.64	2.0

- Substituted number of fluorine atoms \uparrow → energy levels \downarrow

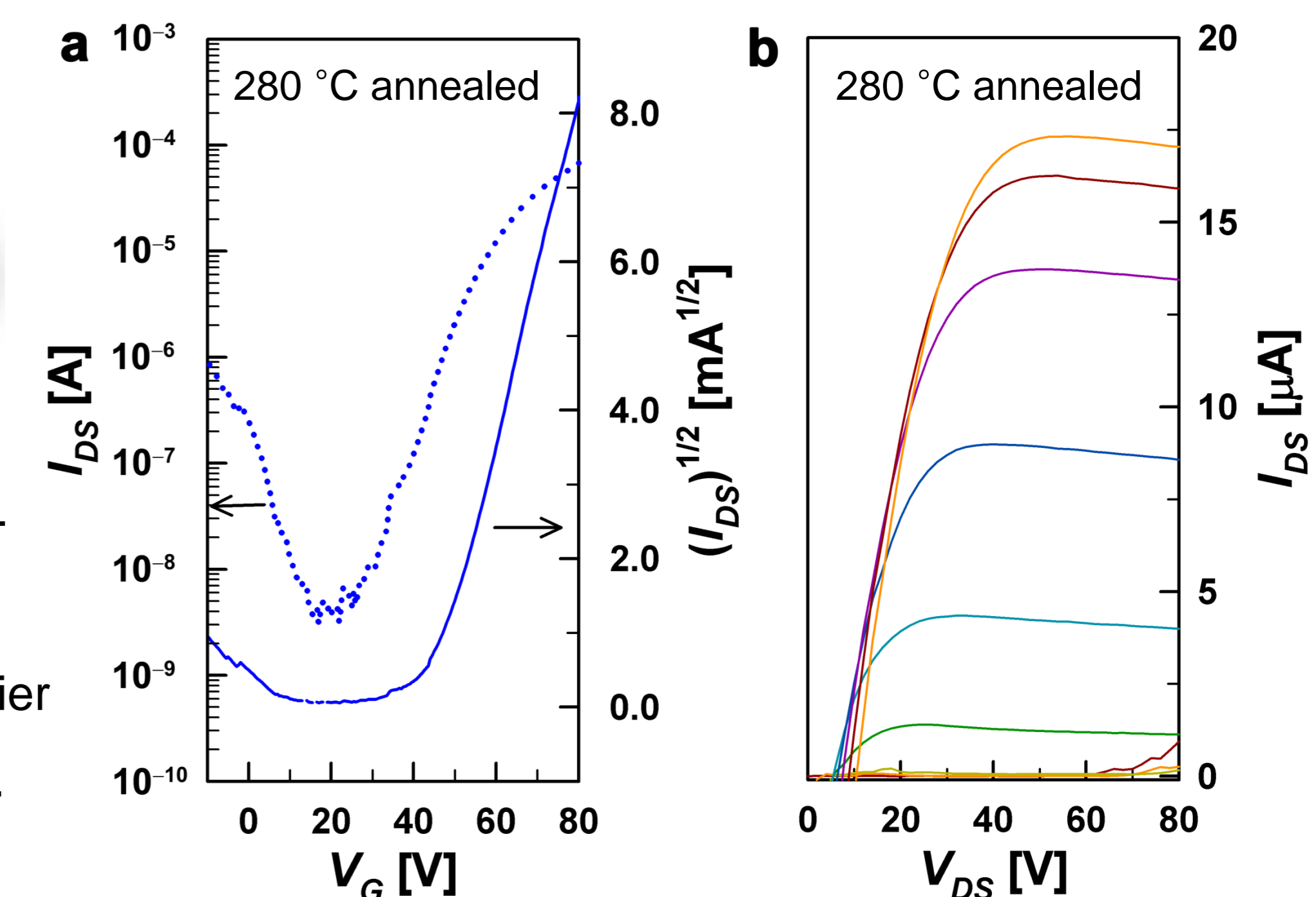
Organic field-effect transistor

Device structure



- Increased F atoms within DPP-based on conjugated polymer change the type of charge carrier transport from *p*-type to *n*-type.

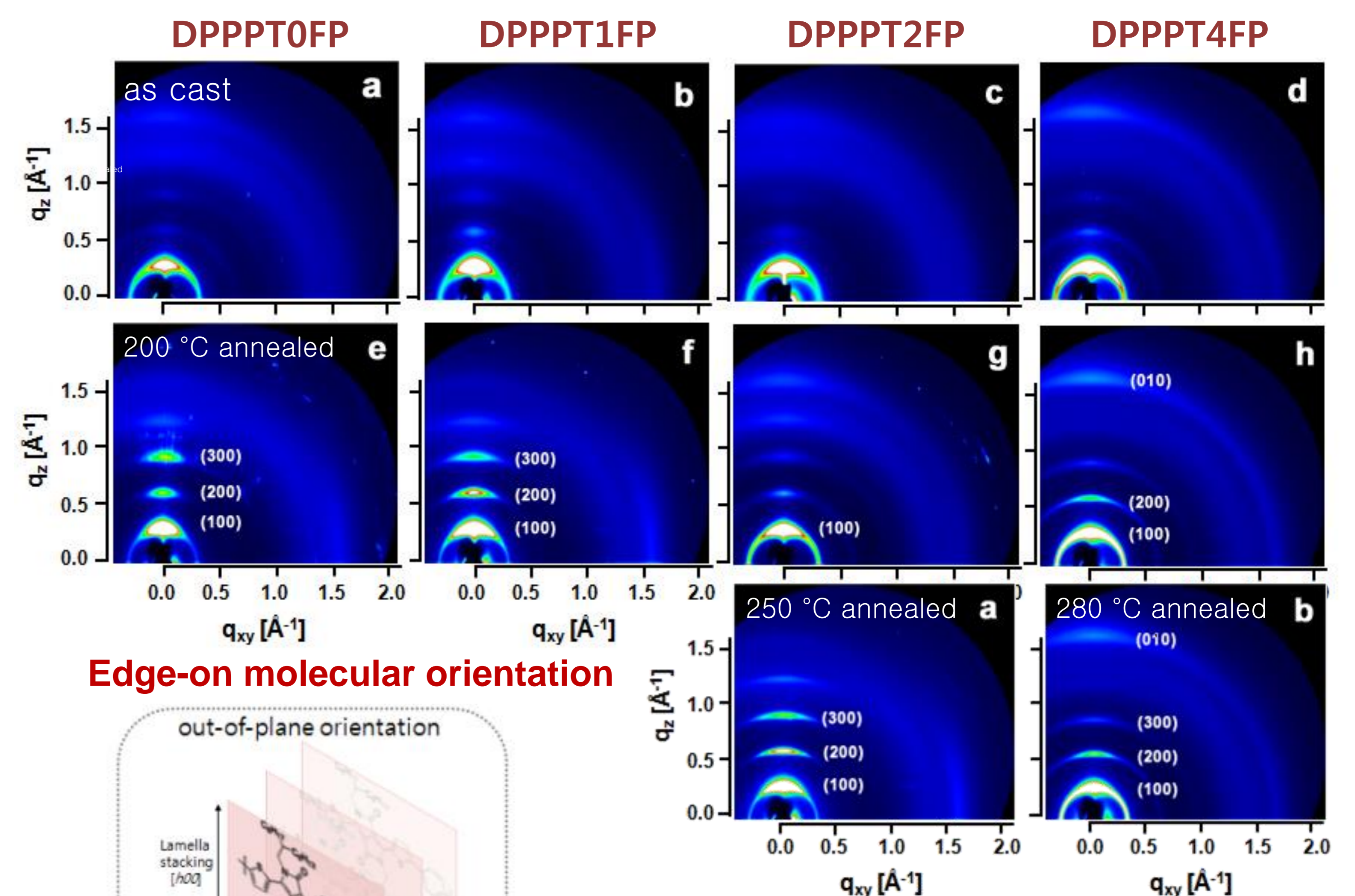
PDPP4FP OFETs properties



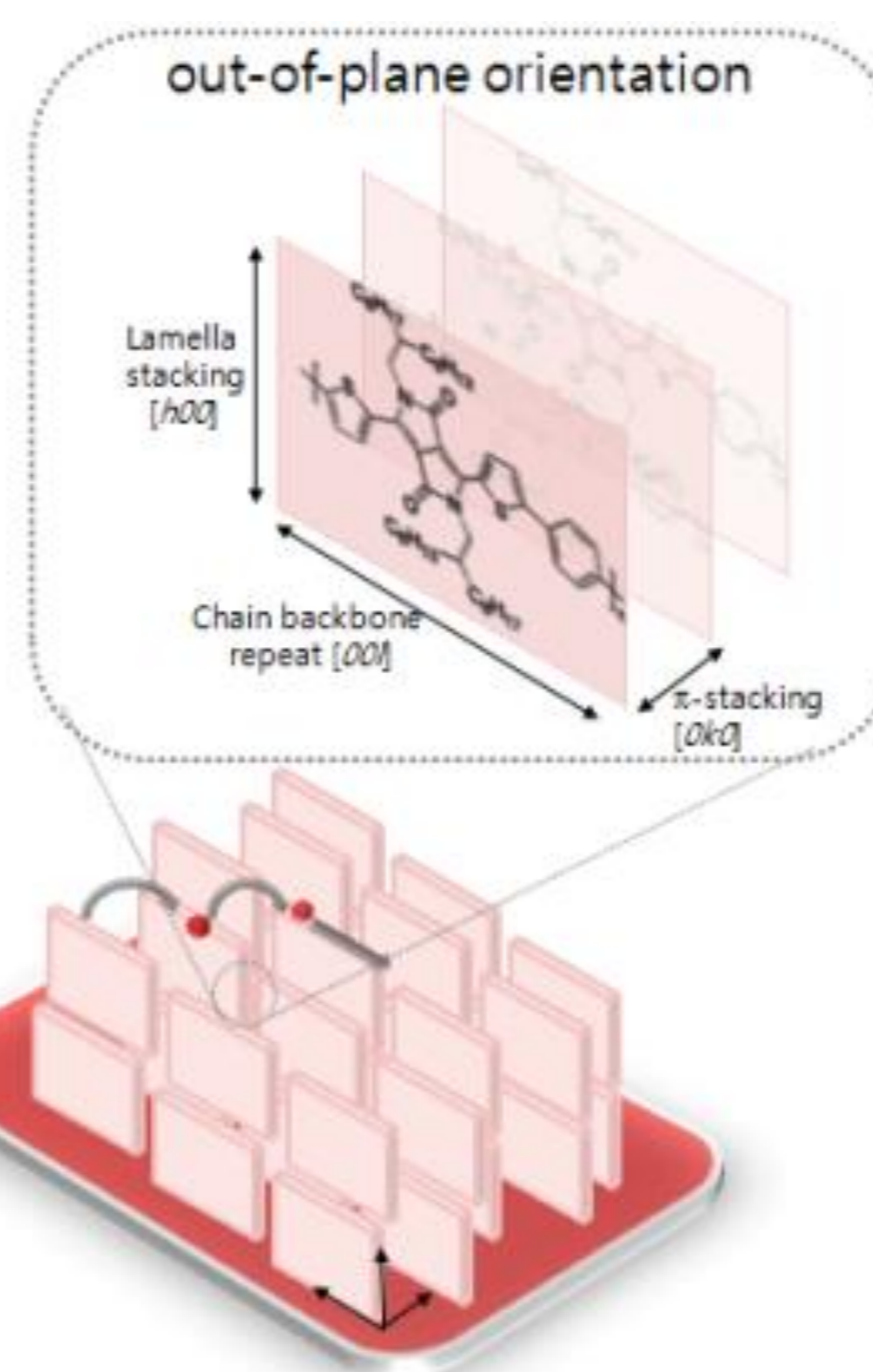
Polymer	Annealing temperature	$\mu_{h,\text{avg}} (\mu_{h,\text{max}})$ (cm ² V ⁻¹ s ⁻¹)	$\mu_{e,\text{avg}} (\mu_{e,\text{max}})$ (cm ² V ⁻¹ s ⁻¹)
DPPP0FP	100 °C	0.06 (0.07)	–
	200 °C	0.34 (0.37)	0.23 (0.24)
	250 °C	0.26 (0.40)	0.08 (0.08)
DPPP1FP	100 °C	0.07 (0.08)	–
	200 °C	0.21 (0.30)	0.21 (0.26)
	250 °C	0.22 (0.23)	–
DPPP2FP	100 °C	0.03 (0.03)	0.08 (0.09)
	200 °C	0.02 (0.02)	0.09 (0.12)
	250 °C	0.03 (0.03)	0.06 (0.08)
DPPP4FP	100 °C	0.03 (0.04)	0.69 (0.80)
	200 °C	0.15 (0.16)	0.90 (0.99)
	250 °C	0.17 (0.19)	1.25 (1.35)
	280 °C	0.23 (0.25)	2.00 (2.36)

Molecular Orientation

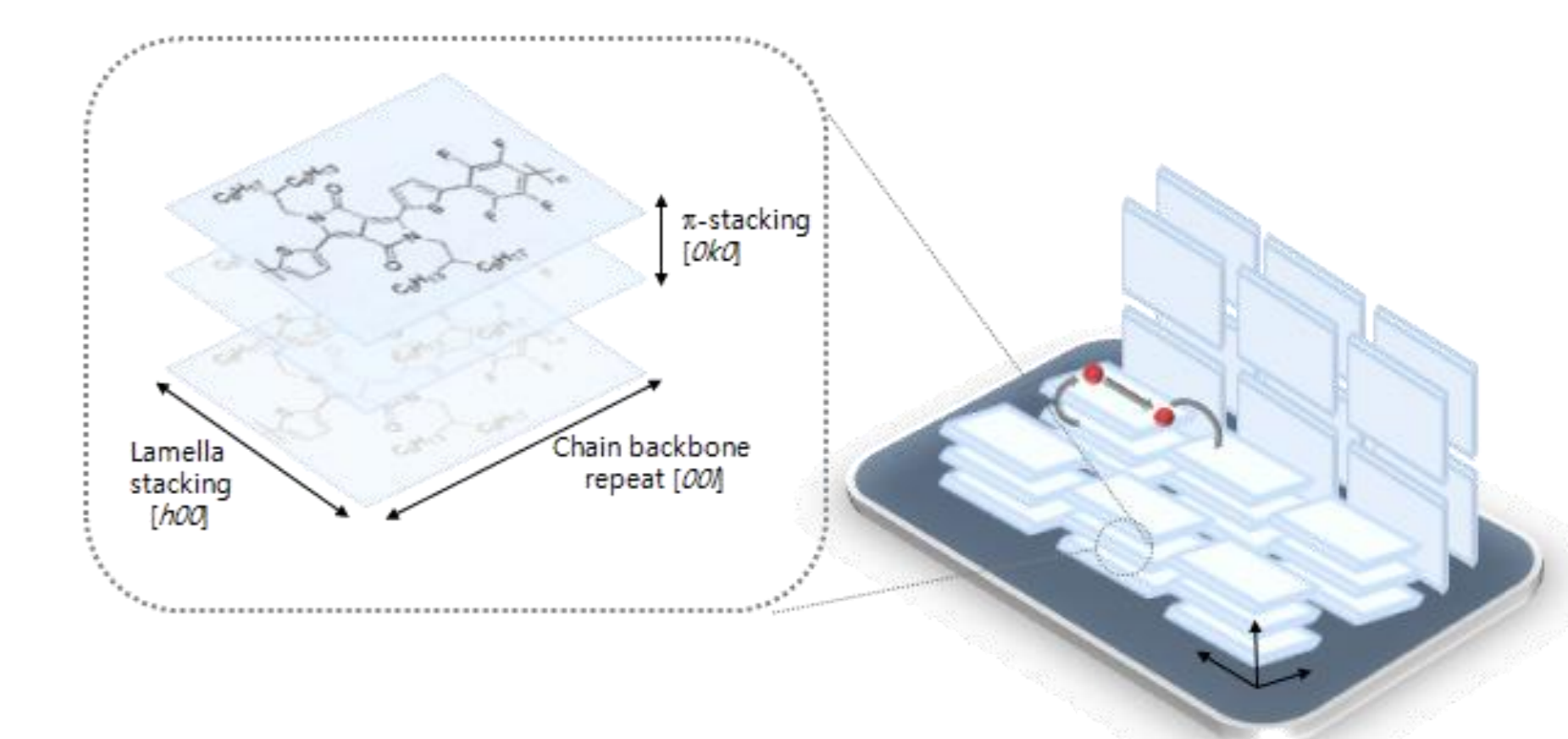
GIXD patterns



Edge-on molecular orientation



Face-on molecular orientation



Conclusions

- Polymers substituted with fluorine atoms, DPPPT4F, the best *n*-type charge transporting behavior with an μ_e of 2.36 cm²V⁻¹s⁻¹.
- Fluorination on the polymer backbone effectively controls the HOMO and LUMO energy levels and the transfer behavior of the conjugated polymers.