

Modification of Metastable Phase in Organic Solar Cells

(Degree of Polymerization)

Jie Min

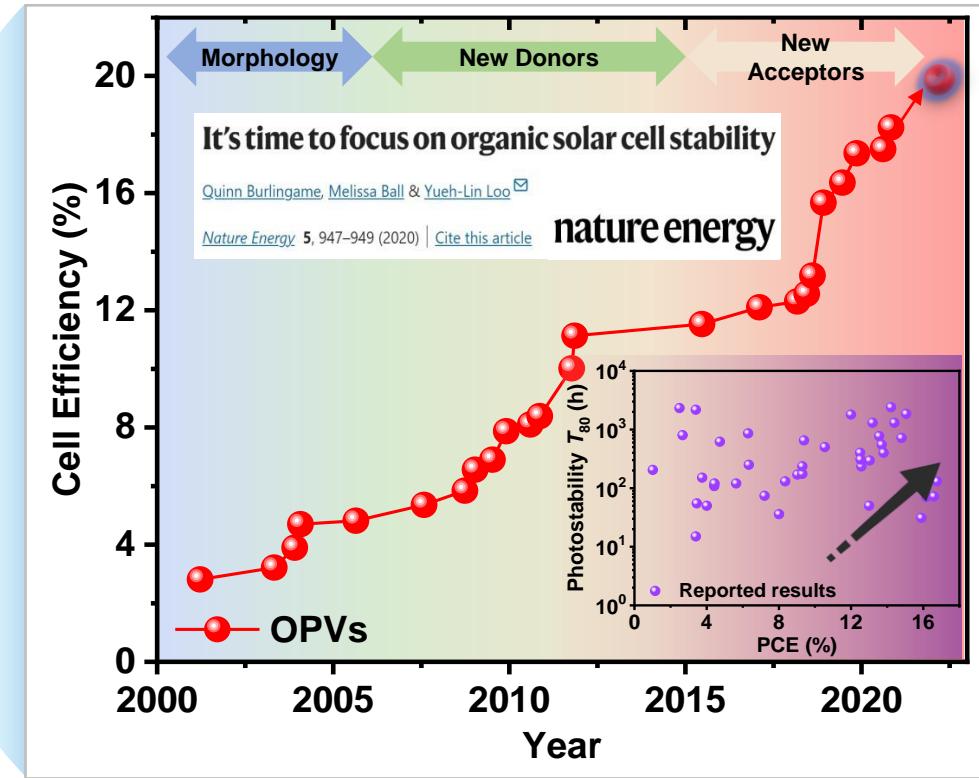
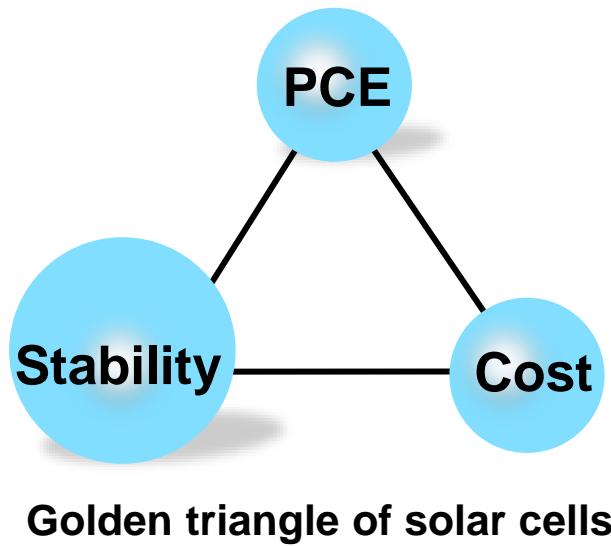
The Institute For Advanced Studies, Wuhan University



Research status

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Dramatic advances in PCEs achieved in these five years



A big lifetime issue:

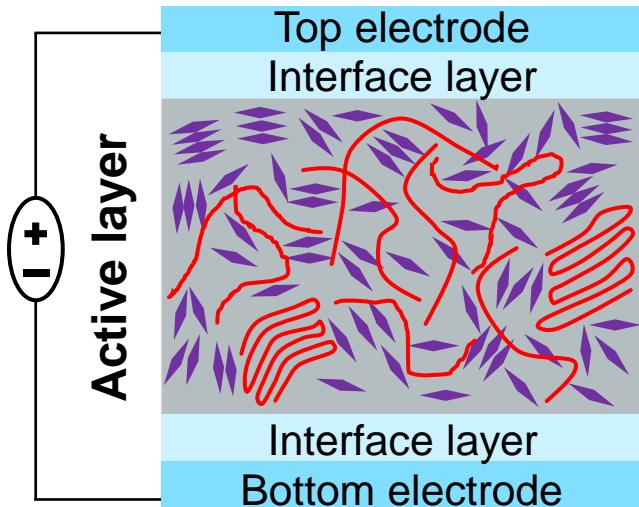
Current active layer systems can not meet the requirements for long-term operation

Key scientific issues

3

Key point: How to precisely regulate the metastable phase and suppress the phase evolution?

Device Structure



Notes:

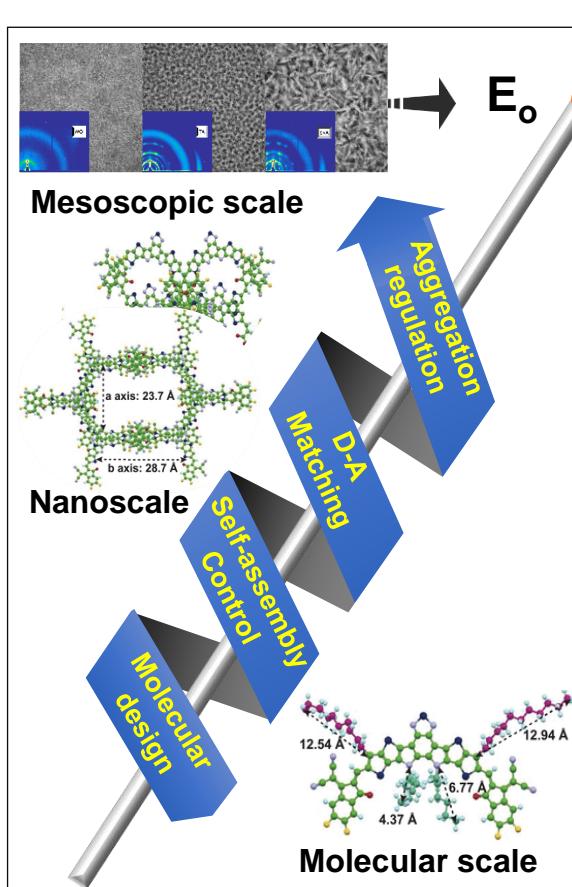
- Small molecular acceptor
- Polymer donor

Dynamic evolution of metastable phases (schematic video)

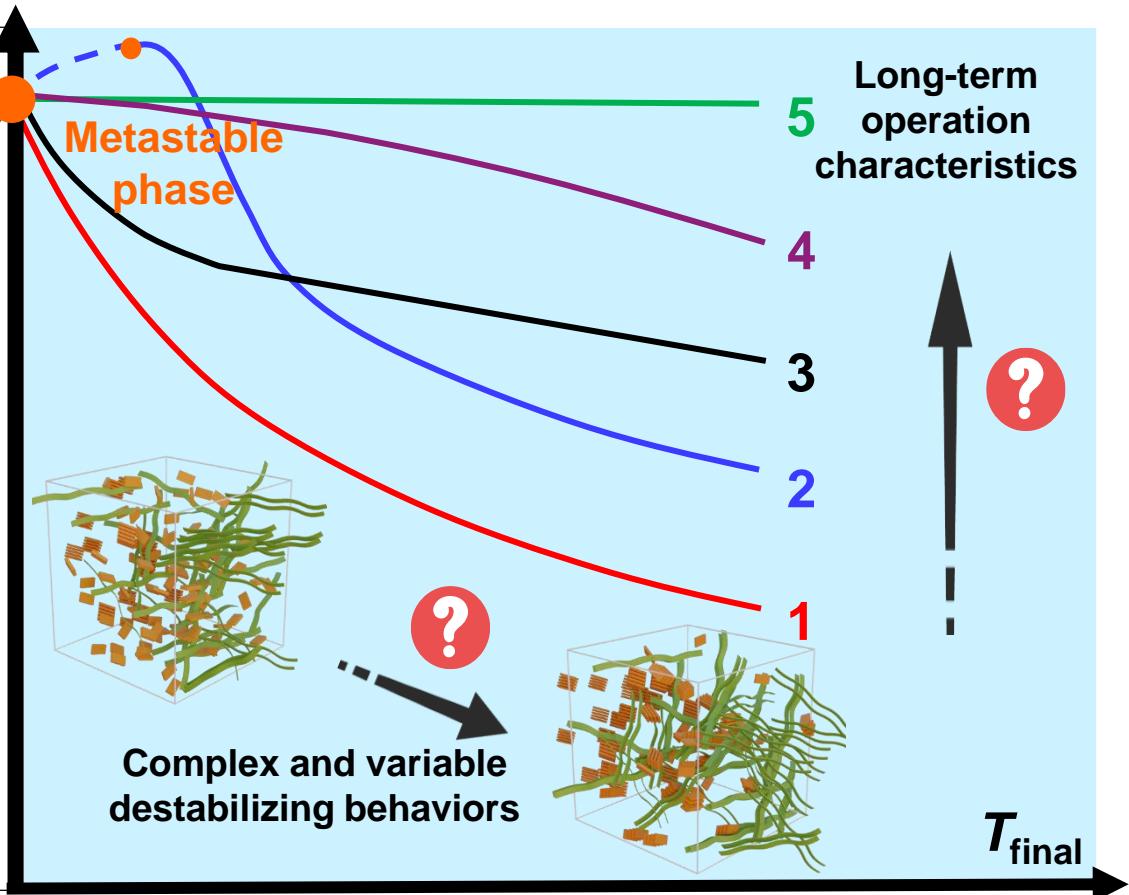
Metastable phase evolution mechanisms

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Aggregation regulation (material properties)

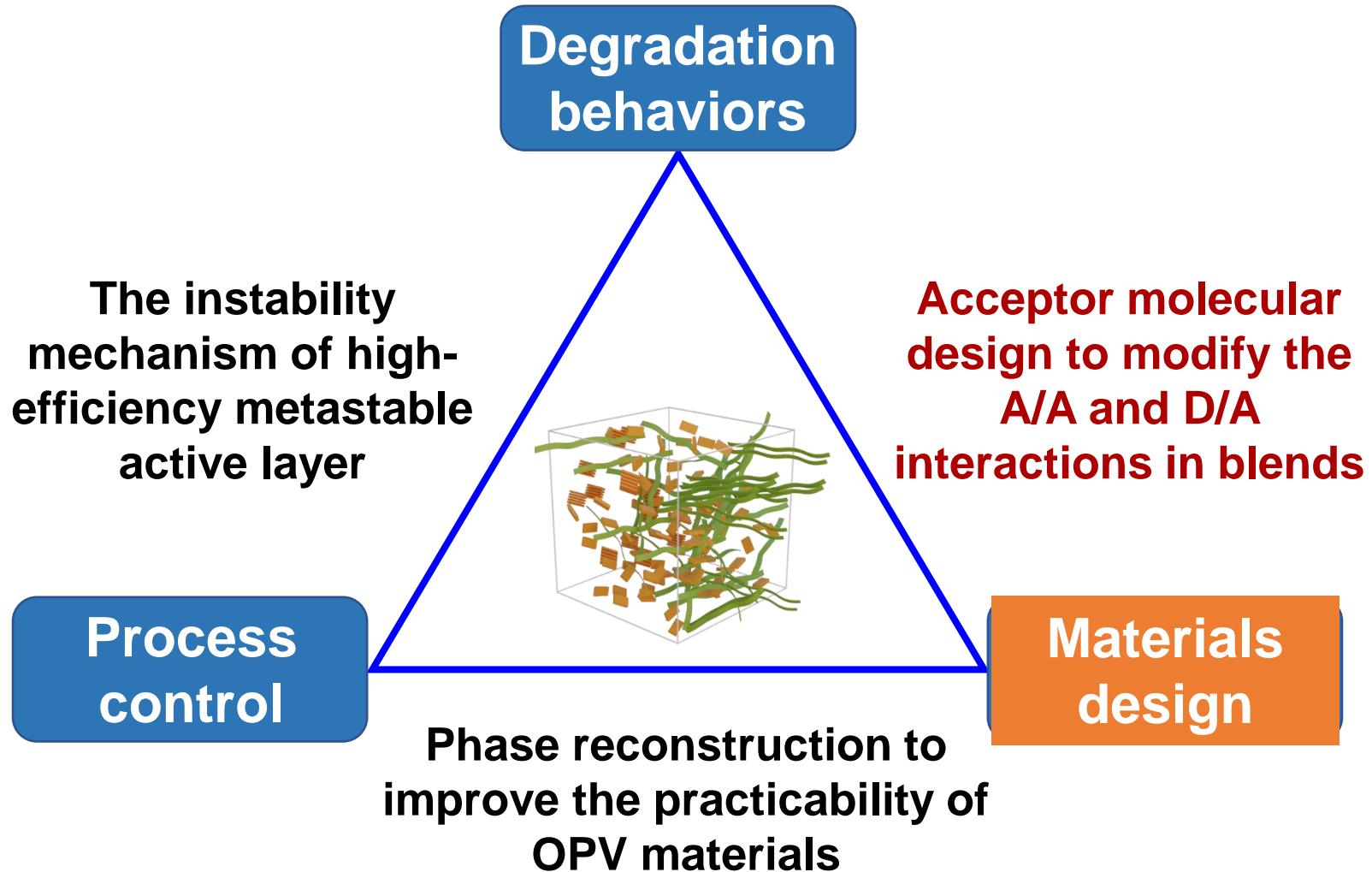


Metastable phase modification (mixed-phase domain)



Research idea: Understanding the destabilizing behaviors of ALs;
Guiding molecular design and morphology control

Research content



Morphological instability of mixed phase domain

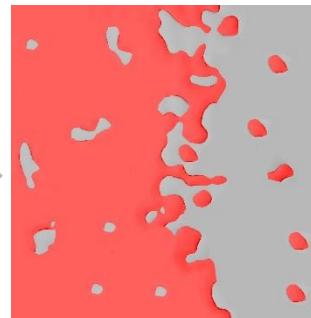
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Intrinsic factors: molecular structure and intermolecular interactions

Morphology evolution under operating conditions

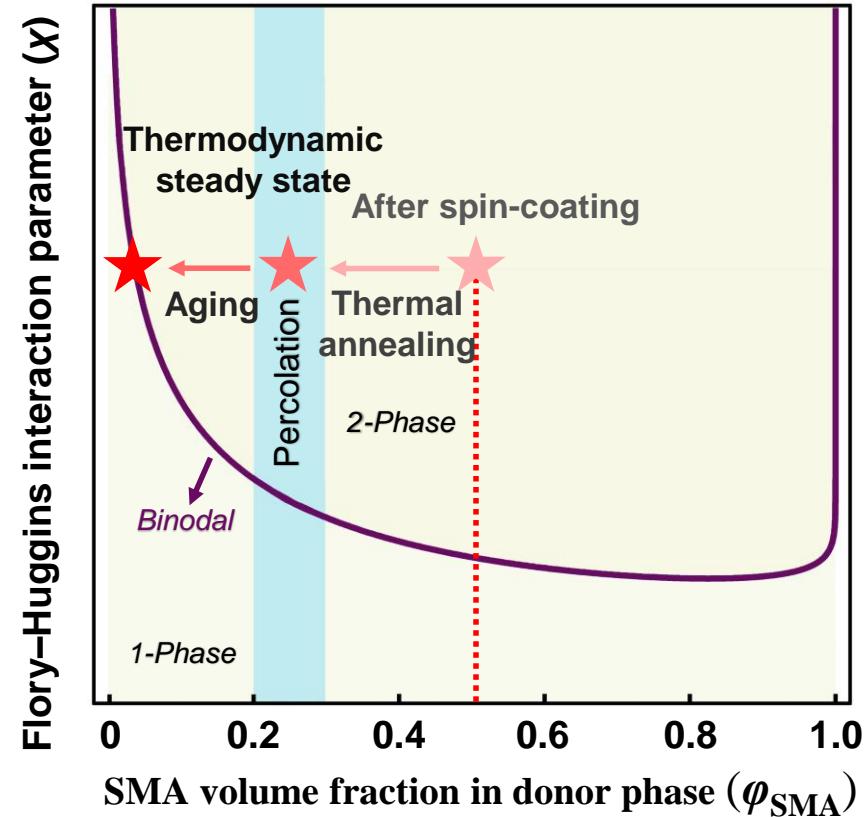


Aging



Bi-continue
interpenetrating
network structure

- ✓ Over-purified phase domain
- ✓ Large phase separation size



$$D(T) \propto \frac{1}{T_g} \quad D(T): \text{Molecular diffusion coefficient}$$

$T_g:$ Phase transition temperature

Relative miscibility (D/A)

$$\frac{\chi_{1,2}}{\chi_{\text{Spinodal}}} = \frac{2}{RT} \frac{(\delta_{T_1} - \delta_{T_2})^2}{\left(\frac{\rho_1}{M_1 \phi_1} + \frac{\rho_2}{M_2 (1-\phi_1)} \right)}$$

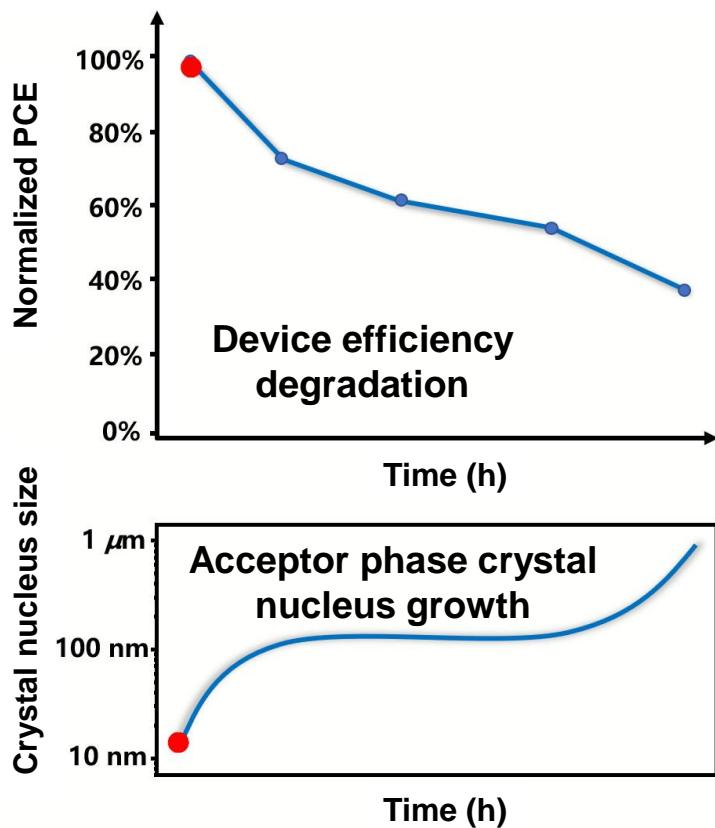
Destabilization mechanism of PD:SMA

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1. Amorphous mixed phase demixing

2. Small isolated domain formation

3. Donor/acceptor crystal phase separation

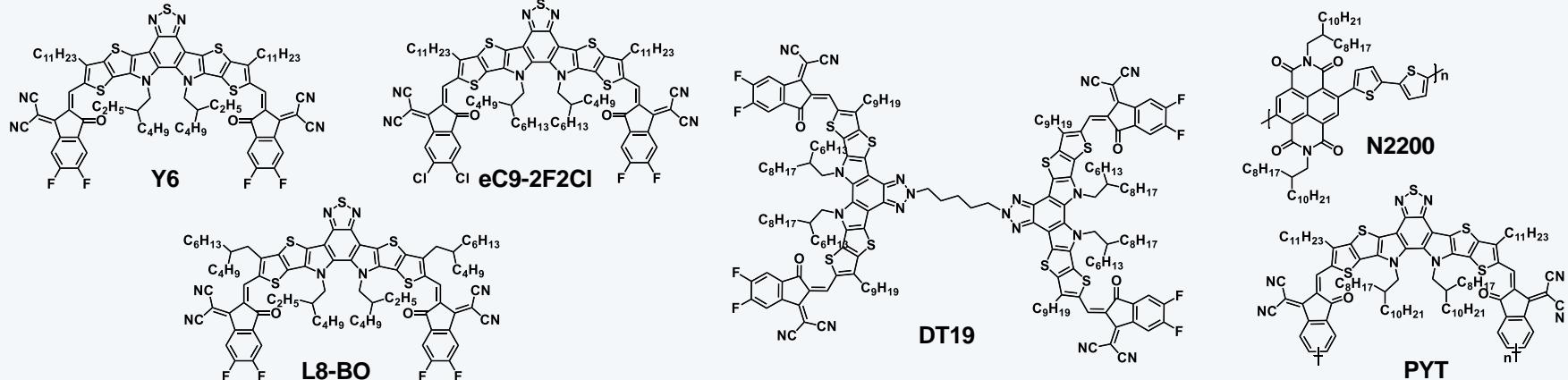
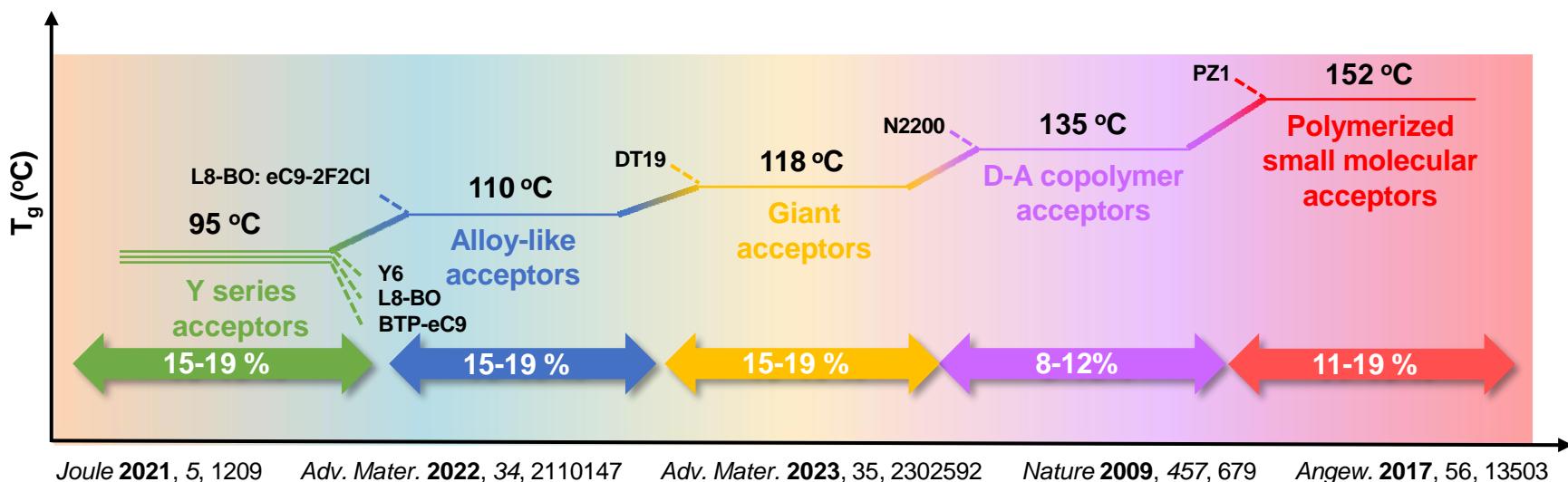


Metastable phase evolution
Recorded by optical
microscope

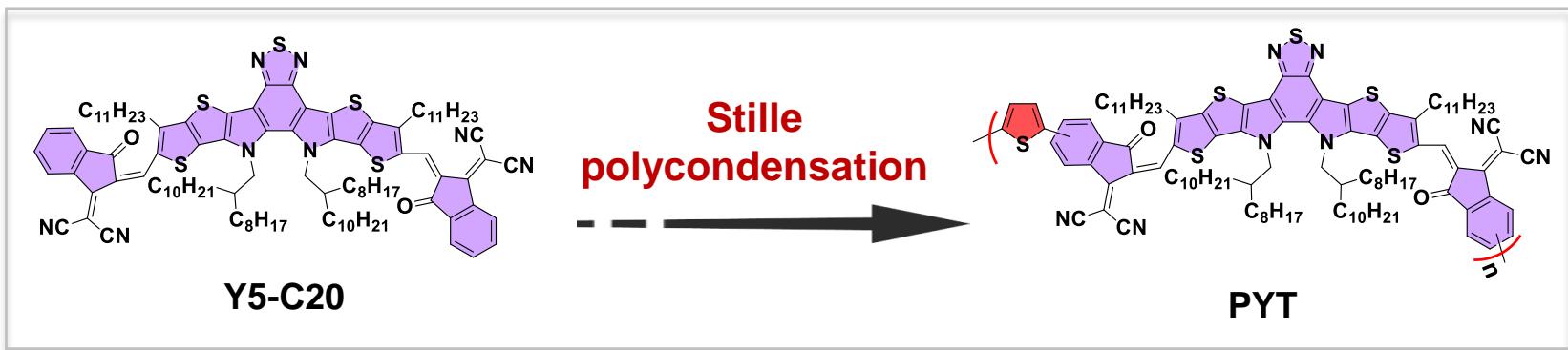
Explore the evolution mechanisms of blend phase

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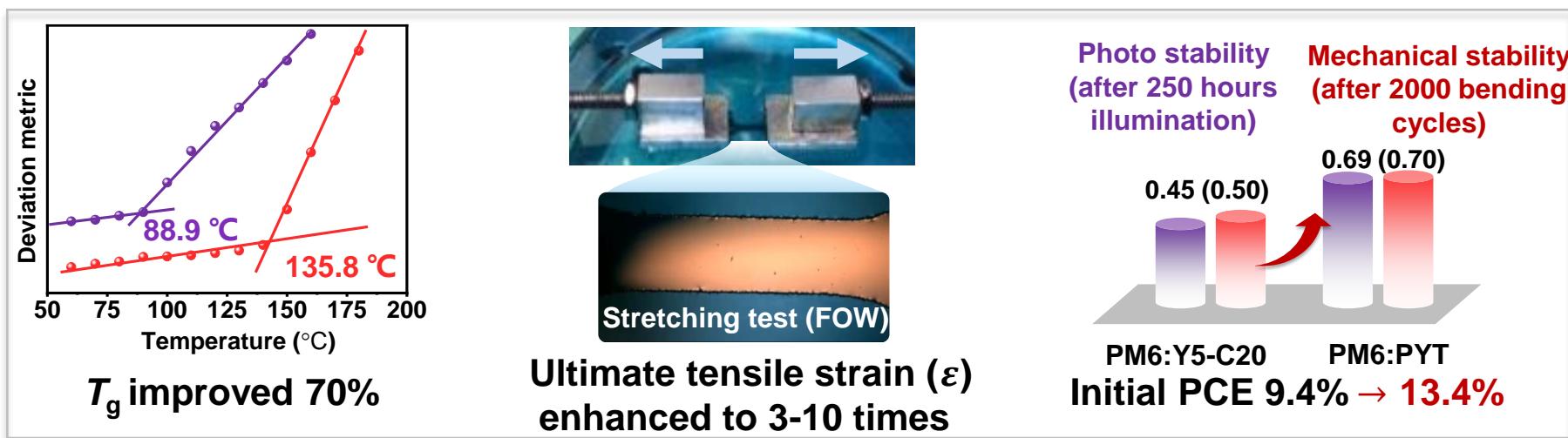
The analysis focused on the T_g of various acceptor materials



Design and synthesis of PSMAs



First group to introduce Y-series acceptor into polymer acceptors

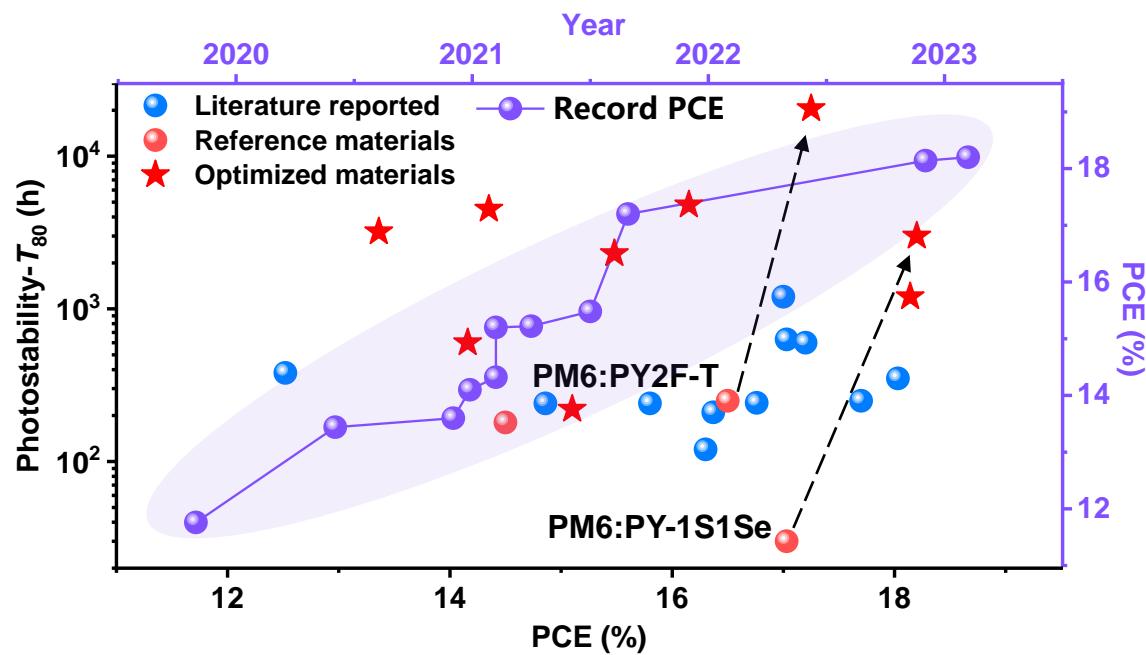
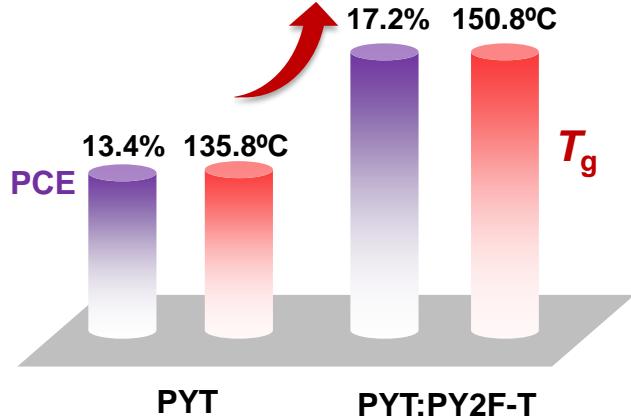


High $M_w \rightarrow$ Viscoelastic effect
enhancing T_g values, mechanical and operational stability

Efficient and stable all-polymer systems

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Multiple strategies: increasing the T_g of A materials
optimizing the metastable morphology

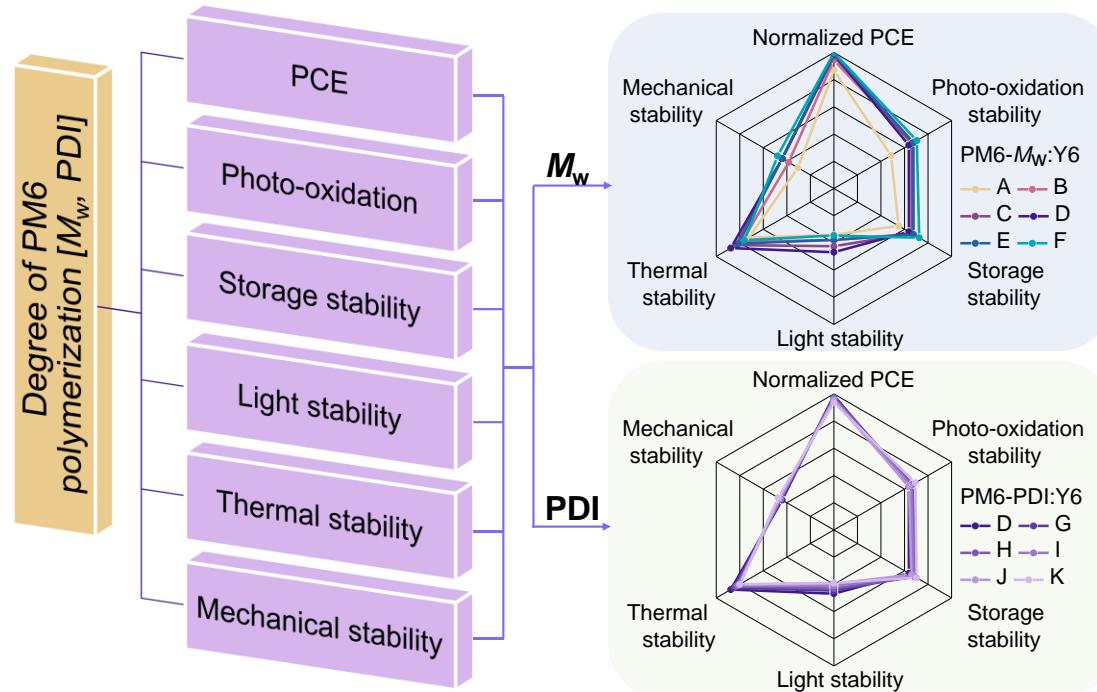
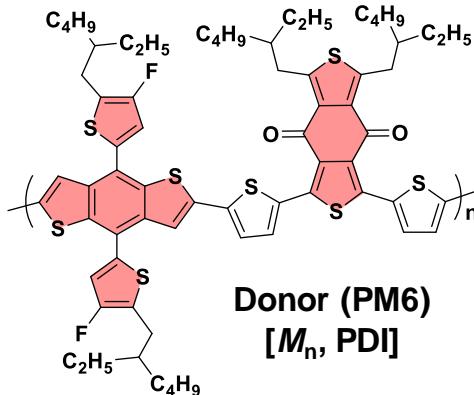


PCE (11.7%→19.0%) and operational stability ($T_{80}=35,000$ hours)

Degree of polymerization → Intermolecular interactions

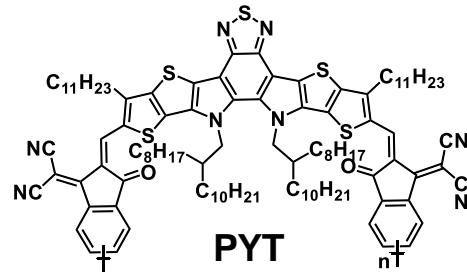
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**DP control: modify D/D and D/A interactions
control active layer morphology**

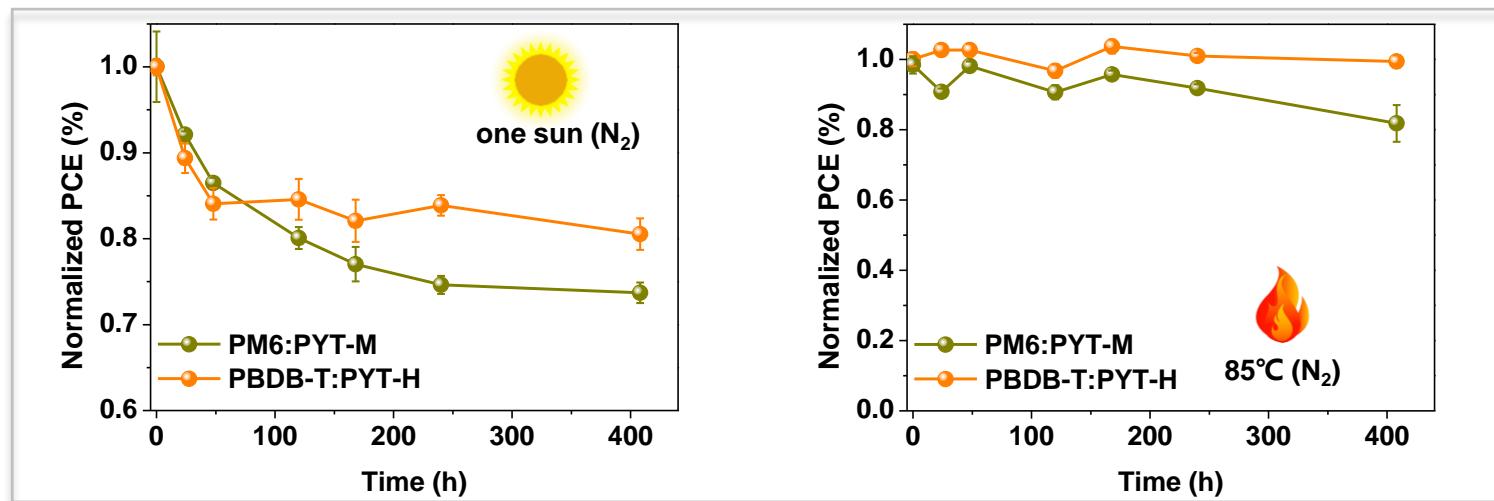
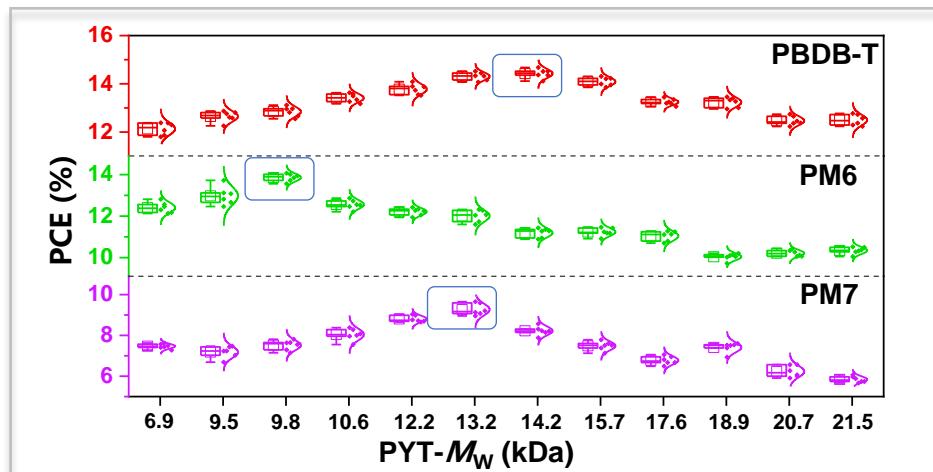


| Batch | A | B | C | D | E | F | G | H | I | J | K |
|-------------|------|------|------|------|------|------|------|------|------|------|------|
| M_n [kDa] | 28.1 | 44.1 | 68.7 | 73.8 | 80.8 | 97.6 | 72.3 | 73.9 | 71.6 | 75.5 | 74.0 |
| PDI | 2.68 | 2.63 | 2.29 | 2.16 | 2.12 | 2.07 | 2.36 | 2.59 | 2.74 | 3.05 | 3.60 |

M_w : modify D/A miscibility, determine device efficiency and stability

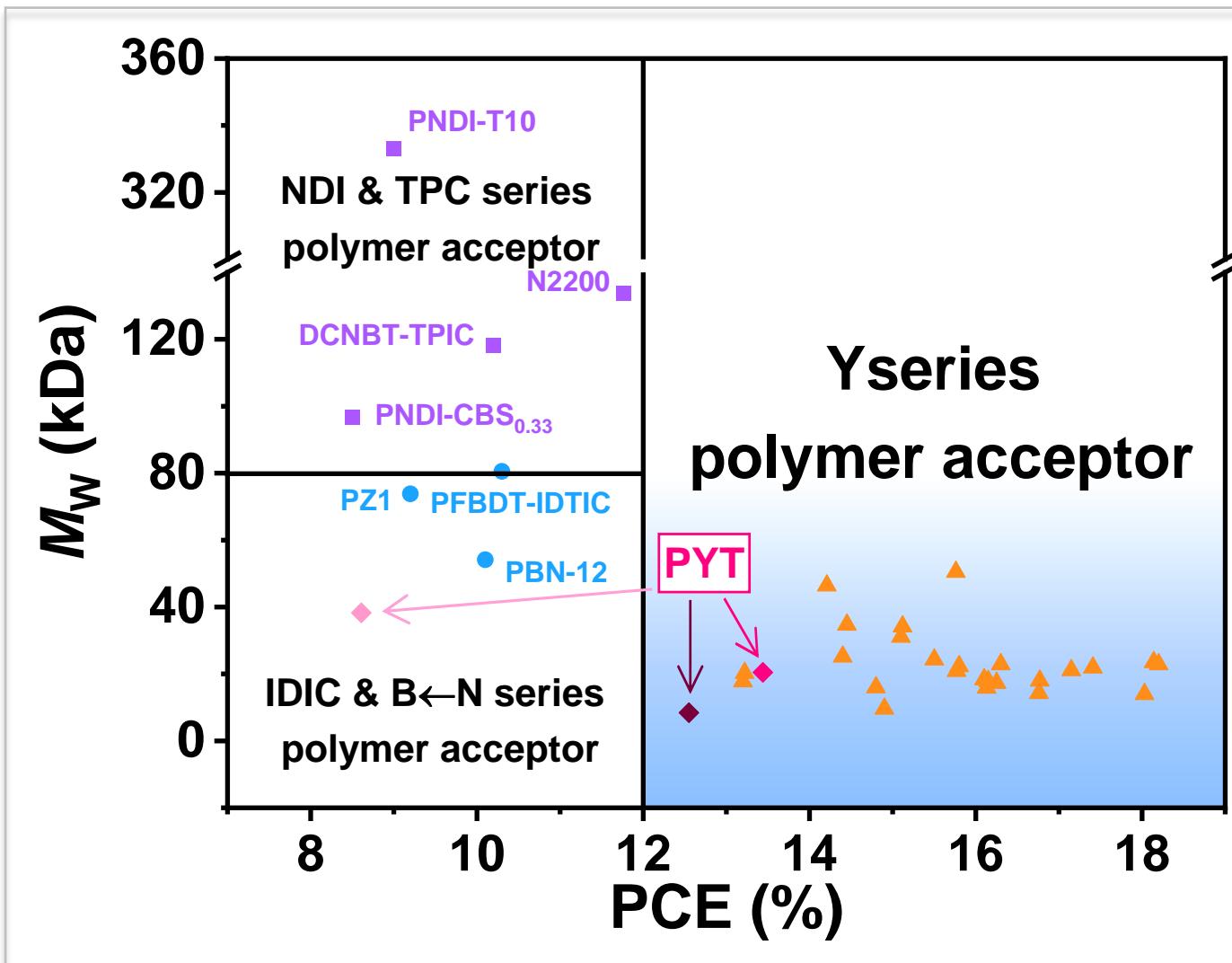


Influence of M_w s on device performance



Precision synthesis (Fronting phase regulation)

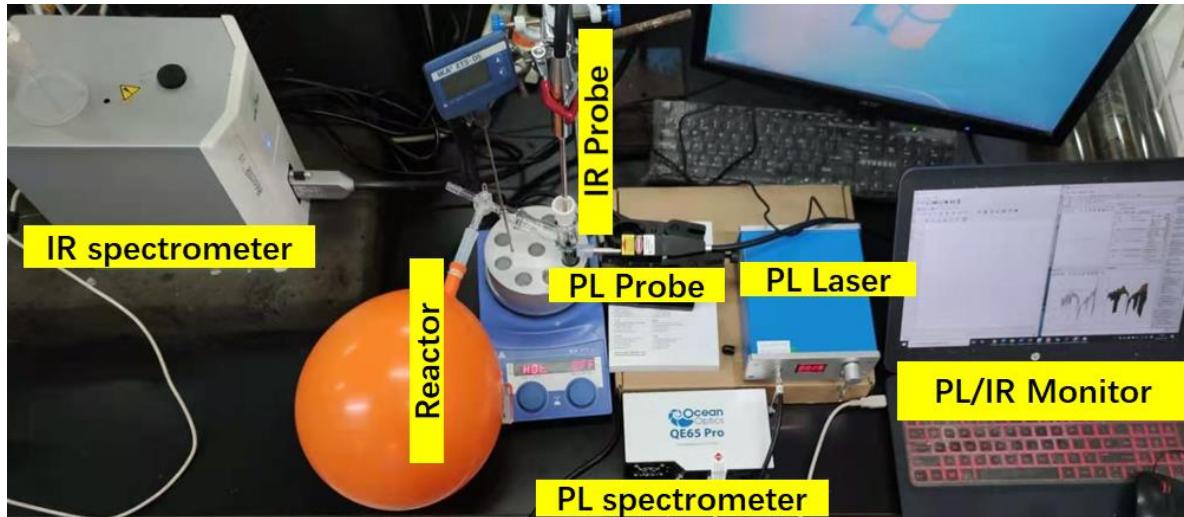
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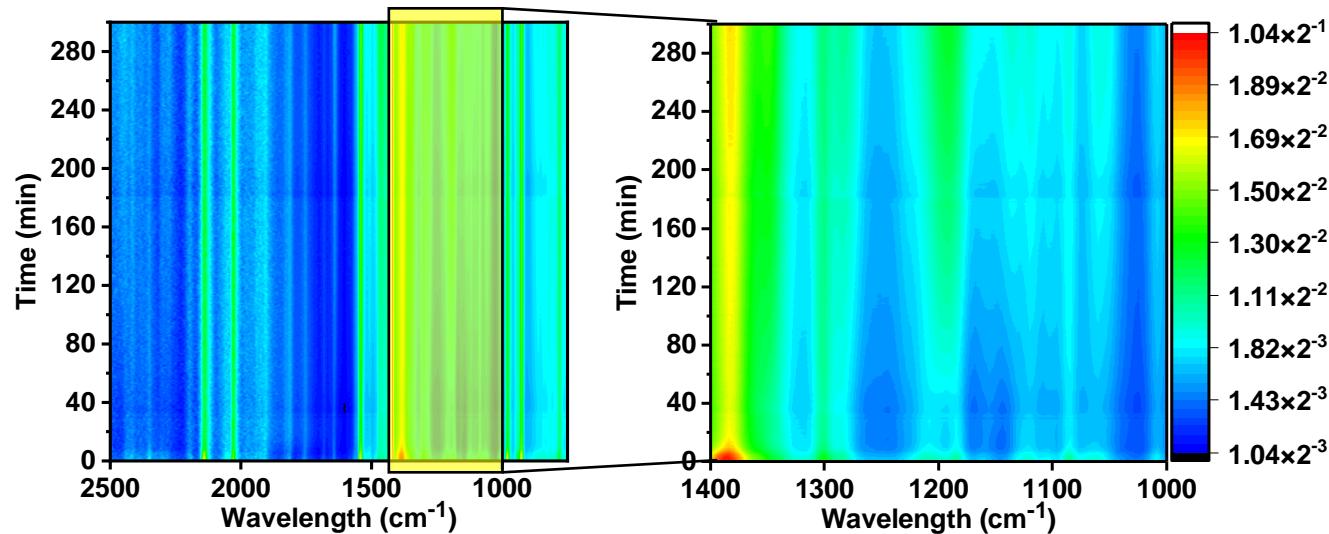
Development of a real-time polymerization detection system

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Methods: Combined *in-situ* FTIR and PL spectroscopy (process control)



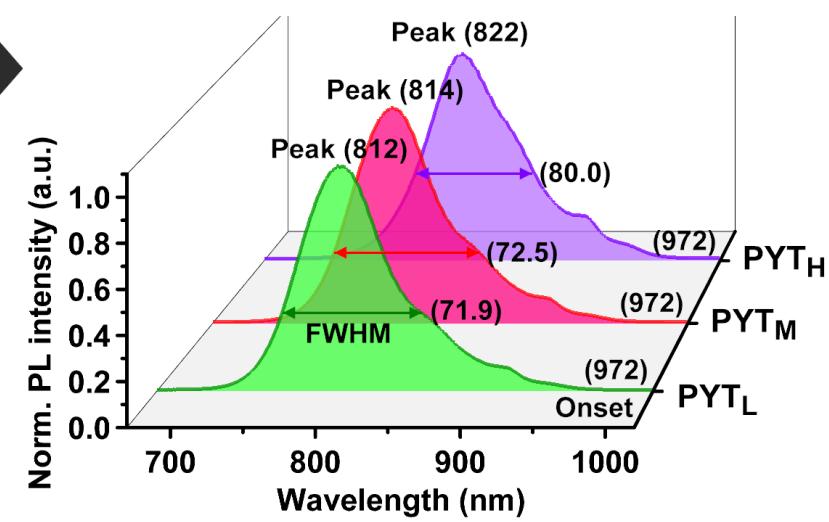
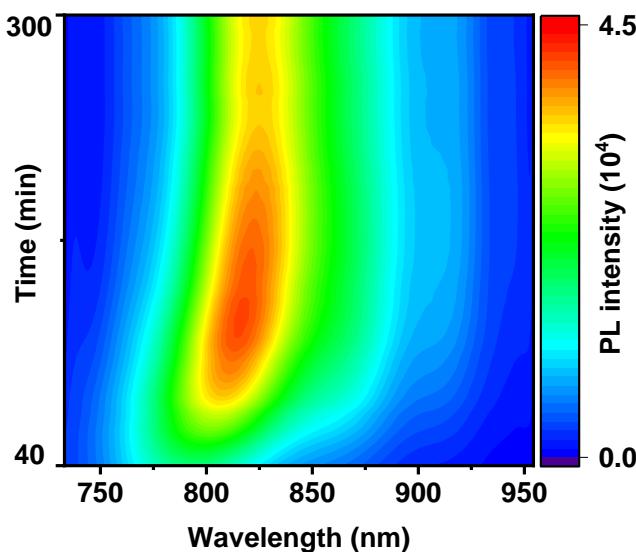
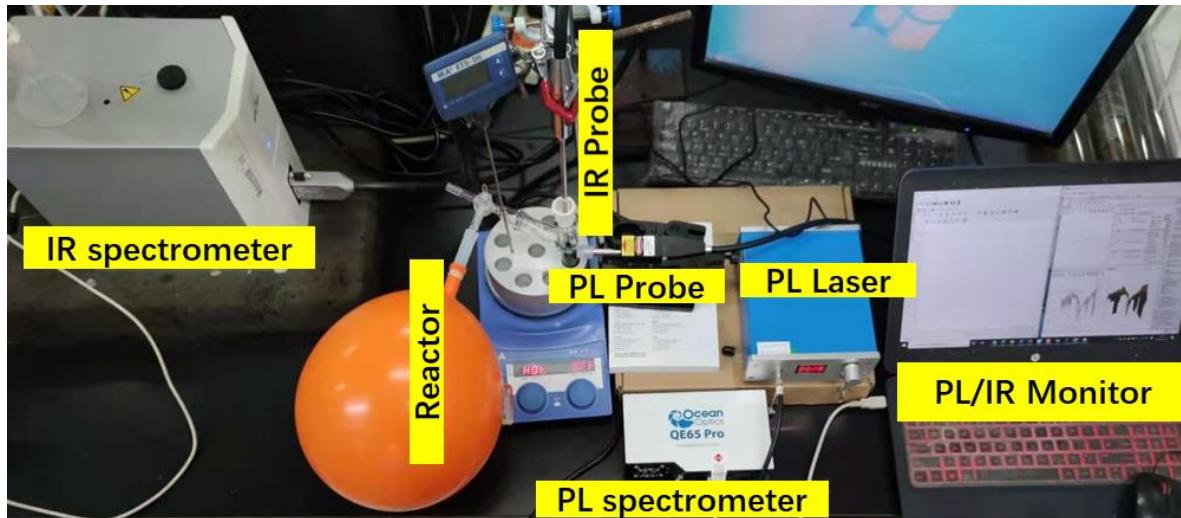
***In-situ* FTIR spectrum**



Development of a real-time polymerization detection system

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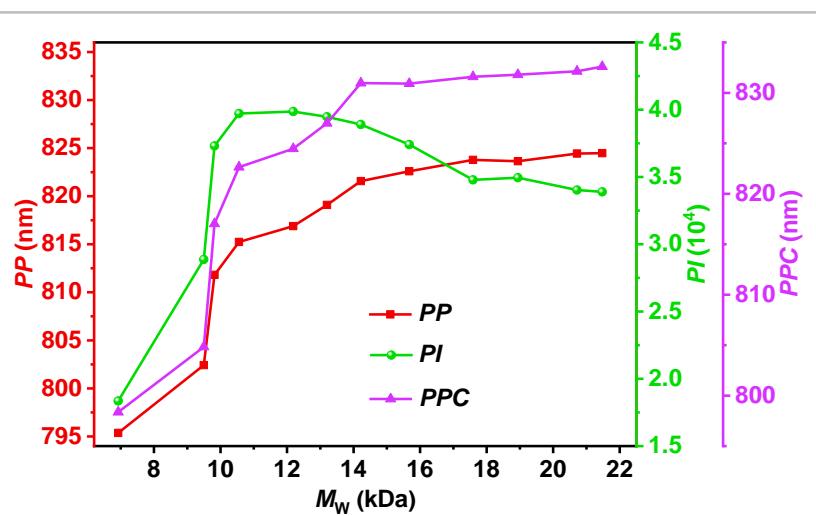
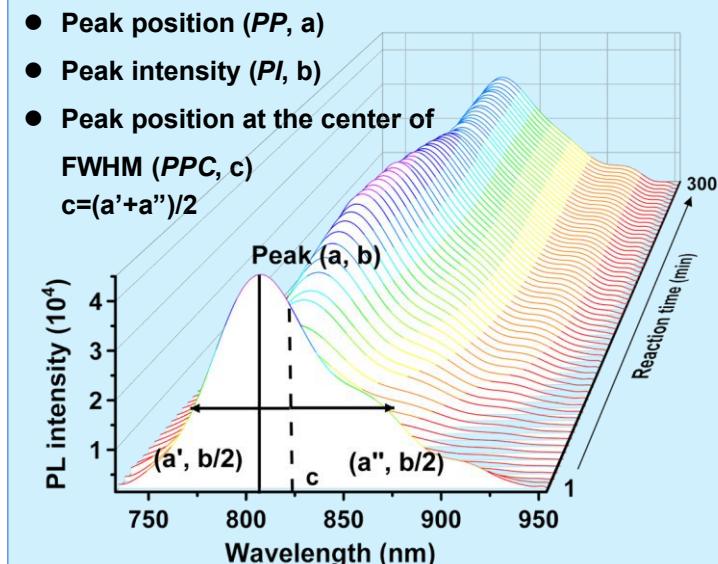
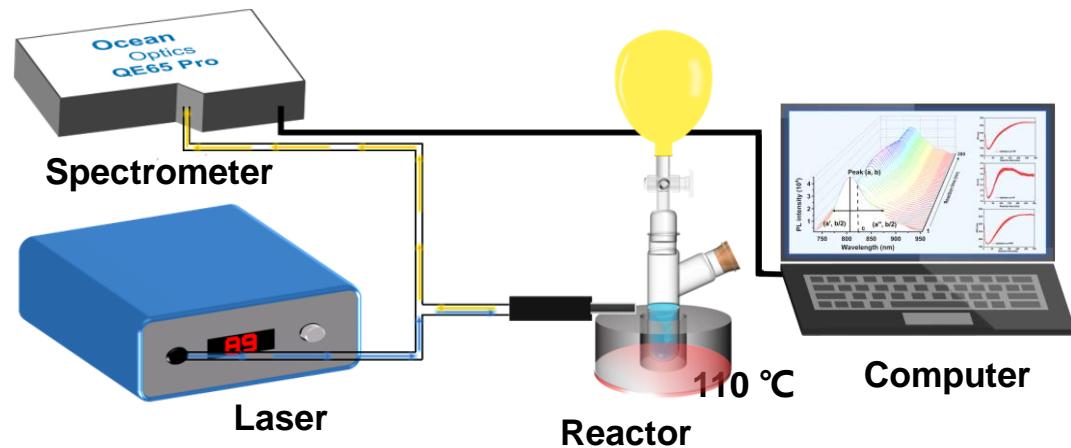
Methods: Combined *in-situ* FTIR and PL spectroscopy (process control)



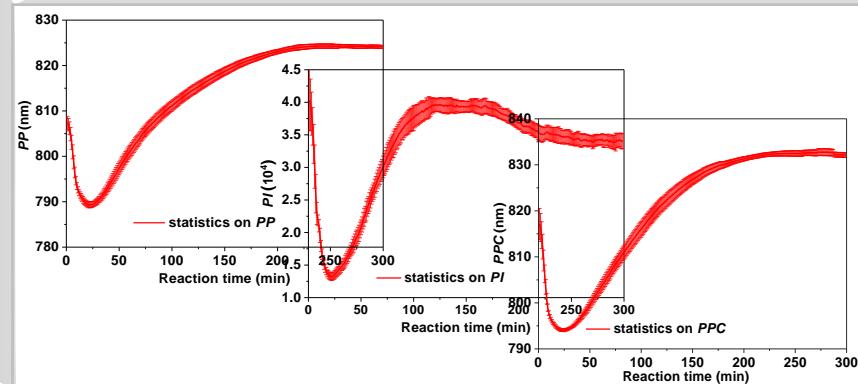
Development of a real-time polymerization detection system

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Method: Automatic polymerization monitoring technology



Establishing a correlation between PL spectral parameters and M_W

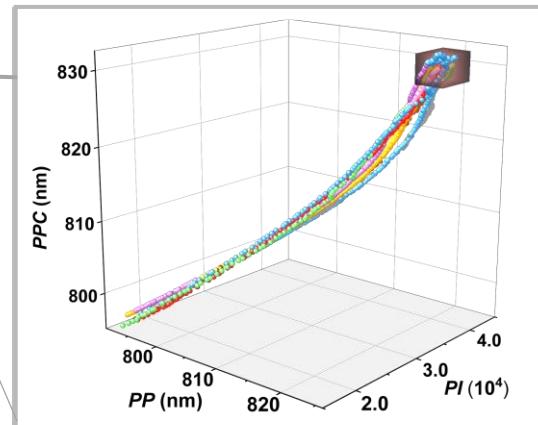
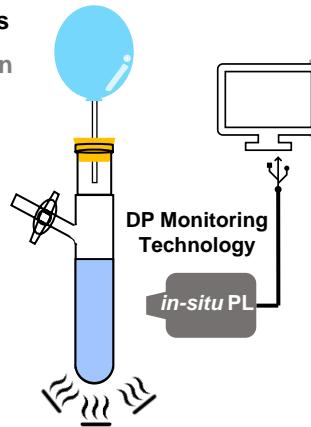


Technical verification: PYT precision synthesis

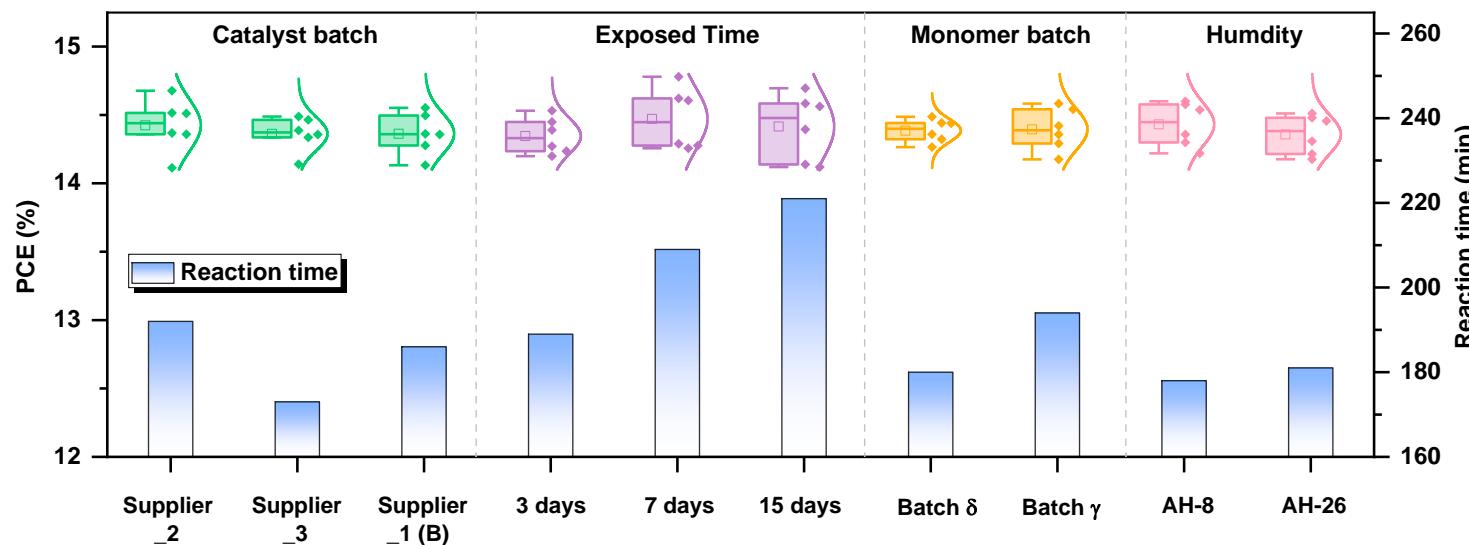
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Fixed reaction conditions

- Solution Concentration
- Catalyst Loading
- Solvent
- Temperature
- Catalyst Batch
- Catalyst Aged Time
- Monomer Batch
- Humidity



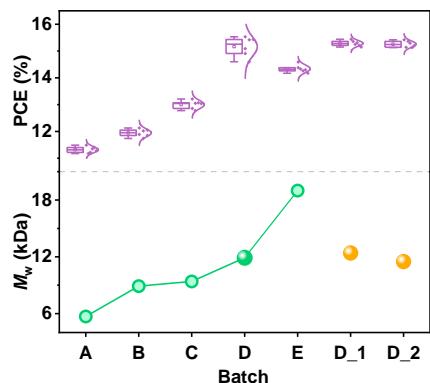
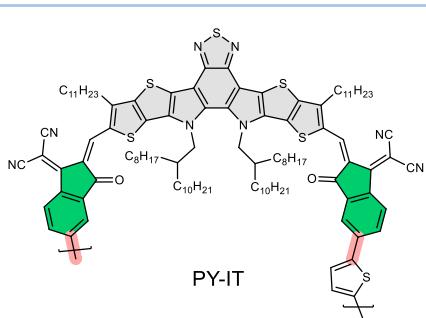
```
# Dataimport.py
# 0> cat > Dataimport.py <
# 1> import os
# 2> import numpy as np
# 3> import winsound
# 4> import time
# 5> import matplotlib.pyplot as plt
# 6>
# 7>
# 8> #!/usr/bin/python
# 9> # encoding: utf-8
# 10> # 4 start: 读取文件路径，确认是否
# 11> # stop: 读取的停止，确认是否
# 12> # div: 分割数，(PCA 900-4000)
# 13> # get_datafile_path, start=5000, stop=8000, div=0.001):
# 14> # with open(file_path, "r", encoding="gbk") as f:
# 15> #     data_all = f.readlines()
# 16> #     data = []
# 17> #     for s in data_all:
# 18> #         if >>>begin Spectral Data<<< in s:
# 19> #             l = s.replace("\n", "")
# 20> #             data.append(l.split("\t"))
# 21> #     x = np.array([float(i[0]) for i in data[start:stop]])
# 22> #     y = [float(i[1]) for i in data[start:stop]]
# 23> #     xt = x
# 24> #     m = x[0]
# 25> #     while m < x[-1]:
# 26> #         m += div
# 27> #         n += div
# 28> #     return [x, y, m, n]
# 29>
# 30>
# 31> # power: 固体曲线的基底
# 32> # Y error: 测量的基底
# 33> # GIV: 基底的基底
# 34> # fit: 拟合的基底
# 35> # del_data: 去除的数据
# 36> # del_data: array(data[0])
# 37> # x1 = np.array(data[1])
# 38> # y = np.array(data[2])
# 39> # m = np.polyfit(x1, y, power)
# 40> # result = np.polyval(m, x2)
# 41>
# 42>
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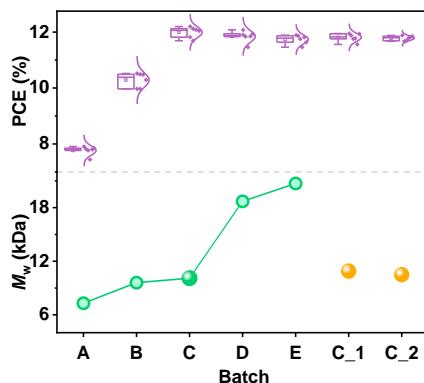
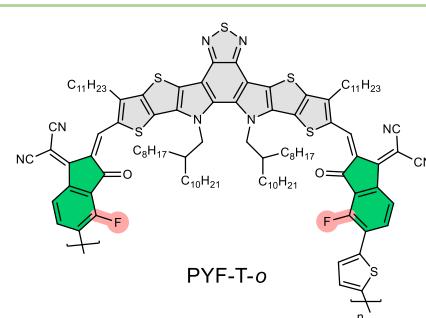
Technical verification: oligomer precision synthesis

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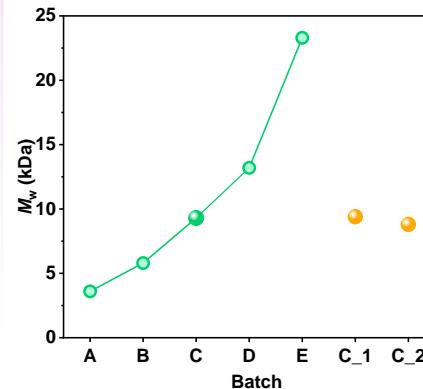
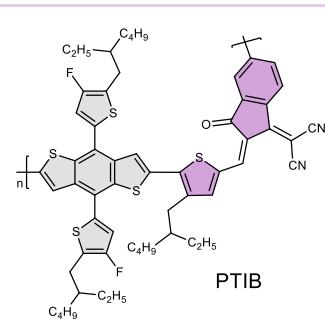
Universality testing based on different P_A materials



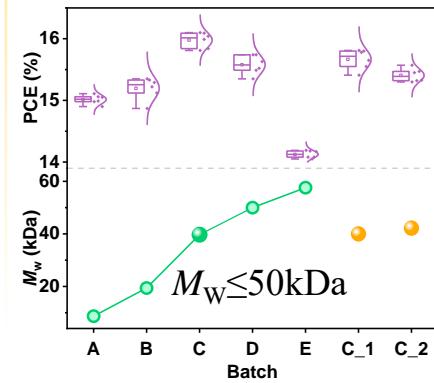
PSMA materials PYT derivatives



D-A copolymer acceptor



The chemical structure of PM6 is shown as a repeating unit in brackets with a subscript 'n'. It features a central benzene ring fused with two thiophene rings. The top position of the central ring has a substituent consisting of a C_4H_9 group attached to a C_2H_5 group, which is further attached to a fluorine atom (F). The bottom position of the central ring has a substituent consisting of a C_2H_5 group attached to a C_4H_9 group. A long chain of alternating C_4H_9 and C_2H_5 groups extends from the right side of the central ring. This chain is linked via a carbonyl group ($=O$) to another thiophene ring. This second thiophene ring is also fused with a central benzene ring, which is further fused with a third thiophene ring. This third thiophene ring is substituted at its top position with a C_2H_5 group attached to a C_4H_9 group. The bottom position of this third thiophene ring is substituted with a C_2H_5 group attached to a C_4H_9 group. The entire polymer chain ends with a $-C_2H_5$ group.



D-A copolymer donor

Multi-type strategies to achieve highly stable active layer system

Mechanism

Shed light on the destabilization mechanisms in relation to molecular diffusion coefficients and T_g values

Materials

Developed the PSMA strategy and fabricated efficient and stable all-polymer systems with enhanced phase change temperature

Precision synthesis of low and medium M_w polymers to eliminate batch-to-batch variations and keep device performance

Acknowledgements

20

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Professor Christoph Brabec (FAU)

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Professor Fei Huang (SCUT)

Professor He Yan (HKUST)

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Professor Chuluo Yang (SZU)

Professor Zhen Li (WHU)

Research fellow Xiaozhang Zhu (ICCAS)

Research fellow Erjun Zhou (NCNST)

Professor Tao Wang (WUT)

Professor Weihua Tang (NJUST)

Professor Zhiguo Zhang (BUCT)

Professor Xiaotao Hao (SDU)

Professor Haiming Zhu (ZJU)

Professor Yang Yang (ZJU)

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Thank you for your attention!



Jie Min Wuhan University
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