

A 3D molecular model showing a complex, interconnected network of yellow spheres (atoms) and grey rods (bonds) forming a dense, fibrous structure. The structure appears to be a supramolecular nanowire assembly of a conjugated polymer, with various loops and branches. The background is a light blue gradient.

Supramolecular nanowire assembly of conjugated polymer



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□ Aqueous self-assembly of rigid-flexible block molecules

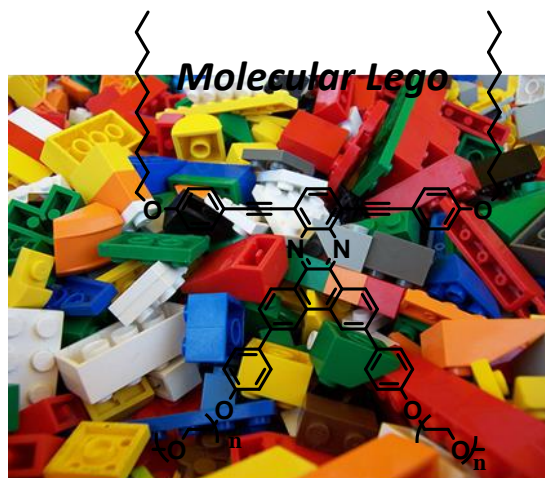
- Manipulation of desired nanostructures
- Stimuli-responsive dynamic nanostructures

□ Conjugated polymer self-assembly into nanowires and its applications

- Crystallization-driven self-assembly
- 3D morphological control for organic photovoltaics
- : Correlation of structure-property relationship
- For electro-optical and biomedical materials applications

*The role of direct visualization of controlled nanostructures
in developing intelligent bio- and electro-optical materials*

- Molecular self-assembly into architectures at the nanoscale

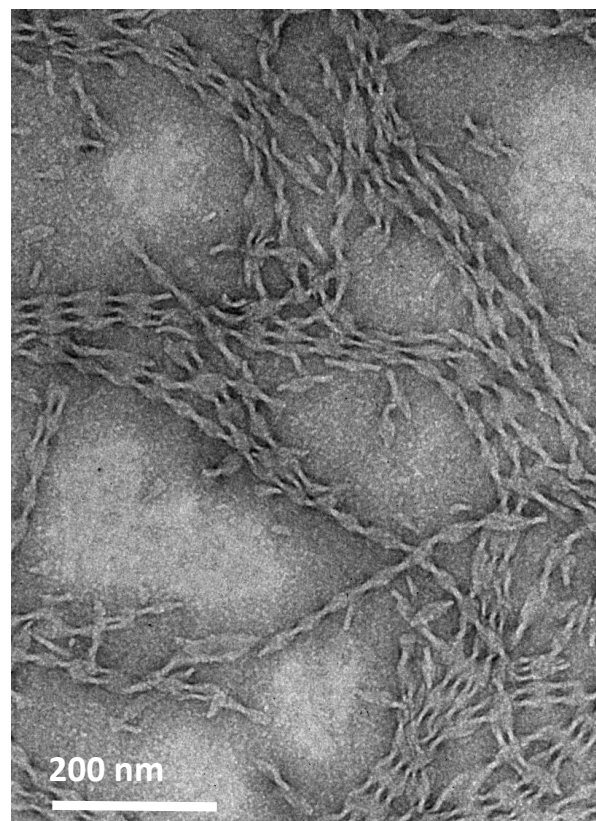


Weak interaction



Van der Waals,
capillary,
 $\pi - \pi$,
hydrogen bonds

*Rational design of
molecular building blocks*



- **Chemical polymerization (monomer → macromolecules)**

- Addition polymerization
- Condensation polymerization

- Step-growth polymerization
- Chain-growth polymerization

- **Physical polymerization**

Type of interaction or bonding	Strength (kJ mol ⁻¹)
Covalent bond	100-400
Coulomb	250
Hydrogen bond	10-65
Ion-dipole	50-200
dipole-dipole	5-50
Cation- π	5-80
π - π	0-50
van der Waals forces	<5
hydrophobic effects	difficult to assess
metal-ligand	0-400



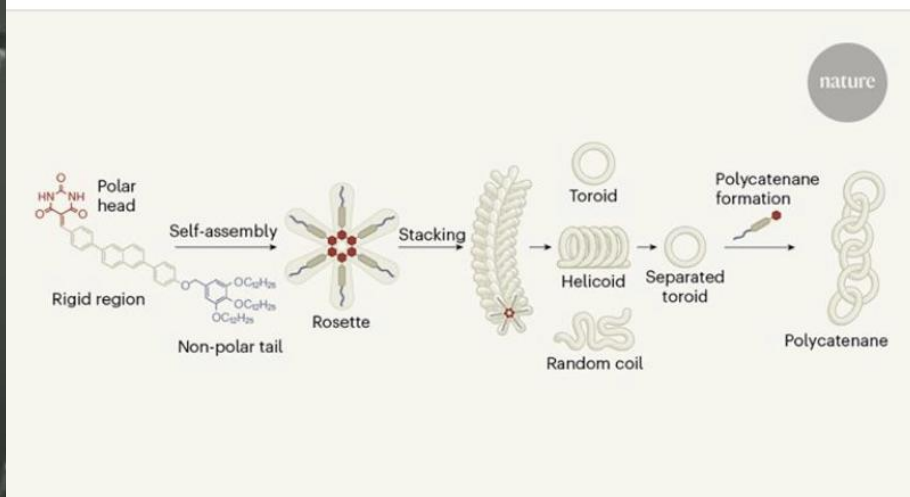
Nature Chemistry

Yesterday at 20:33 ·

...

News & Views in Nature:

Non-covalent interactions can assemble molecules into complex architectures, but with limited control of the resulting topology. A method for assembling nanoscale chains shows how specific architectures can be targeted.



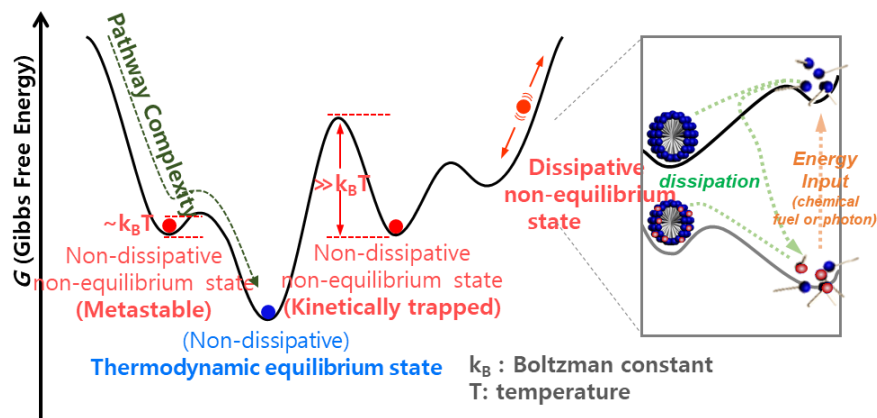
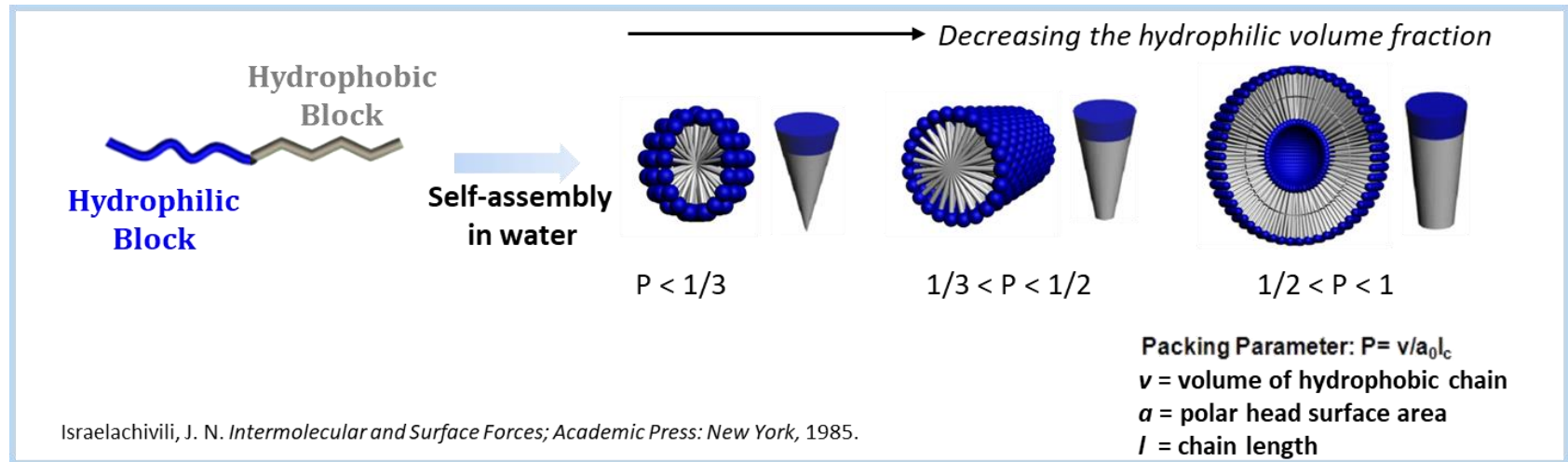
NATURE.COM

Simple molecules self-assemble into the links of a nanoscale chain

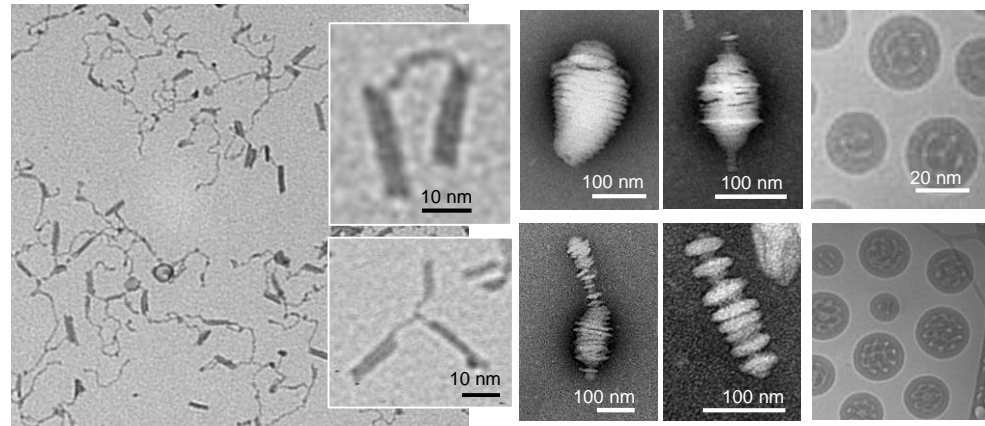
Reversible and dynamic molecular assembly

Aqueous self-assembly of amphiphilies

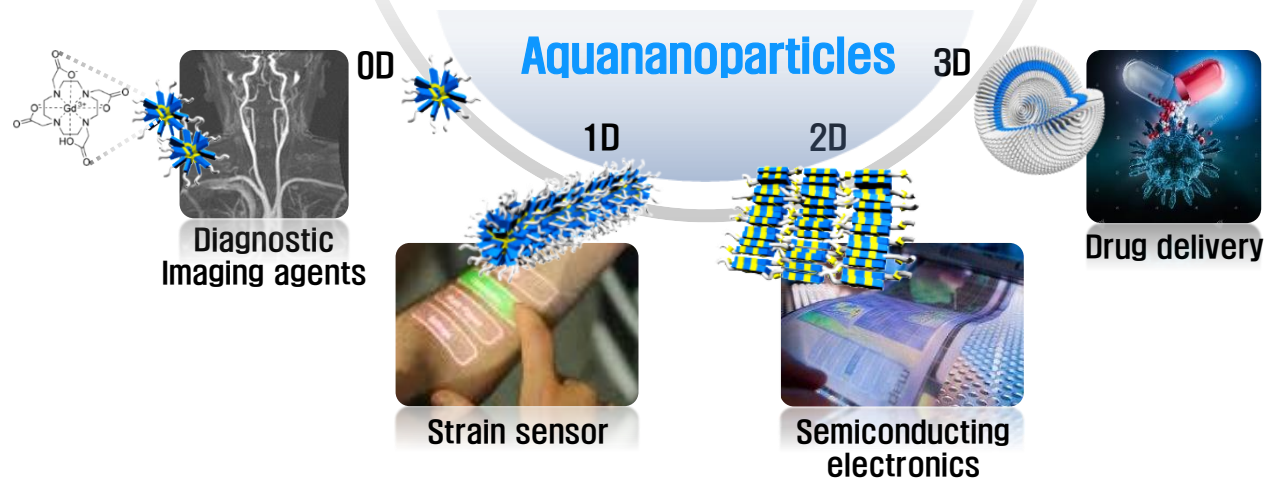
5



A. Sorrenti *et al.*, *Chem. Soc. Rev.*, 2017, 46, 5476



Hybrid nanomaterials



Hybrid

organic-inorganic

biomolecular-inorganic
polymeric-inorganic
biomolecular-polymeric
organic-biomolecular
inorganic-inorganic

chemical strategies
(**self-assembly**,
nanobuilding block approaches,
hybrid MOF)
integrative synthesis
coupled processes
bio-inspired strategies, etc.
in a nanoscale manner

optics
ionics
mechanics
energy
environment
biology
medicine

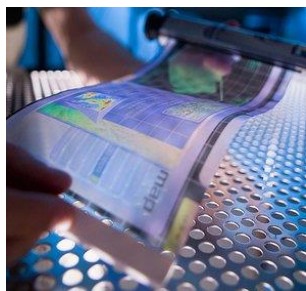
It can open new perspectives towards the design of materials with desired features and functions. 6

Conducting polymers with π -conjugated backbone

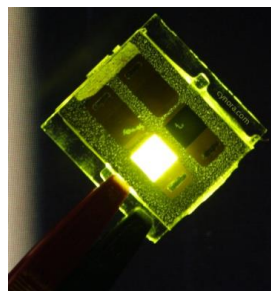
7

Possessing unique electro-optical properties

for use as an active materials in **low-cost, large-area, and flexible** devices



OTFT



OLED



OPV

Nano Energy **2020**, accepted
Nano Energy **2020**, 104708
J. Mater. Chem. A **2019**, 7, 24992
J. Mater. Chem. A **2019**, 7, 2027

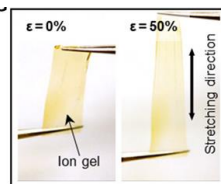
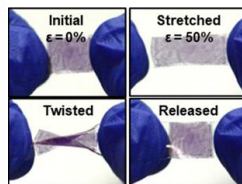
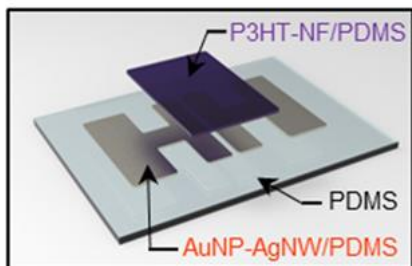
ACS Nano **2016**, 10, 4954
ACS Appl. Mater. Interfaces **2018**, 10, 29284

Source: Konarka

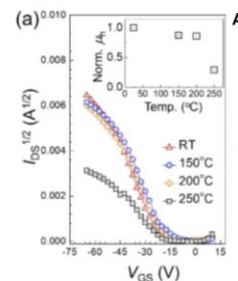
π -conjugated polymer: poly(*p*-phenylene)(ppp), poly(*p*-phenylene vinylene)(PPV)
 polyfluorene (PF), **poly(3-hexylthiophene) (PT)**

Adv. Mater. **2020**, under review
Polymer **2019**, 175, 49
Adv. Funct. Mater. **2016**, 26, 3226
Polym. Chem. **2018**, 9, 3279
J. Am. Chem. Soc. **2015**, 137, 12394
J. Am. Chem. Soc. **2014**, 136, 2767
J. Am. Chem. Soc. **2011**, 133, 10390

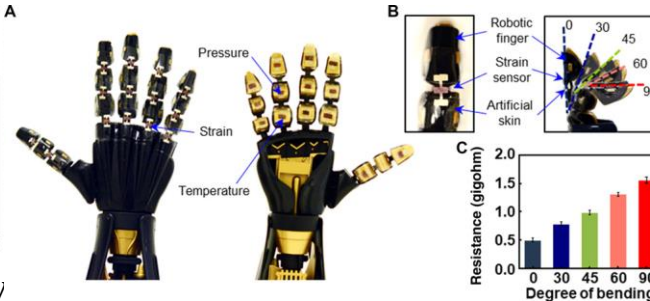
Rubbery electronics and sensors



Mechanical stretchability



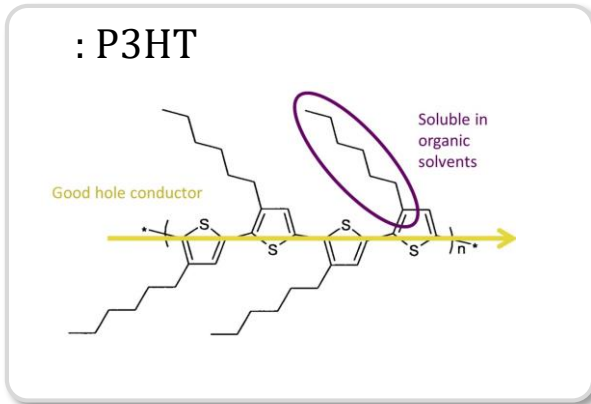
Thermal stability



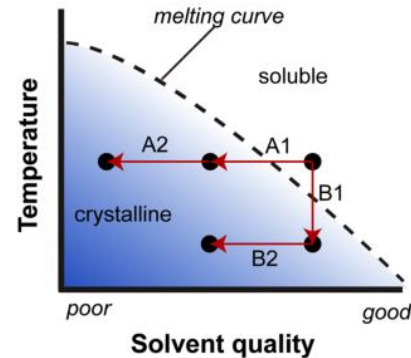
Organic scaffold: semicrystalline block macromolecules

• Amphiphilic block molecules + crystallization assembly

→ P3AT-based amphiphilic block molecules



crystallization controlled by



1. Synthetic effects

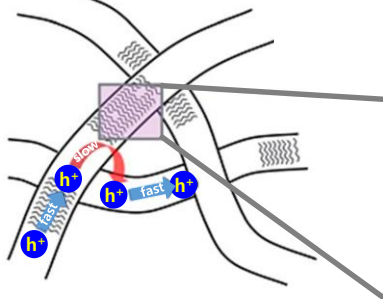
- Molecular weight
- Regioregularity
- Polydispersity...

2. Solution-processing effects

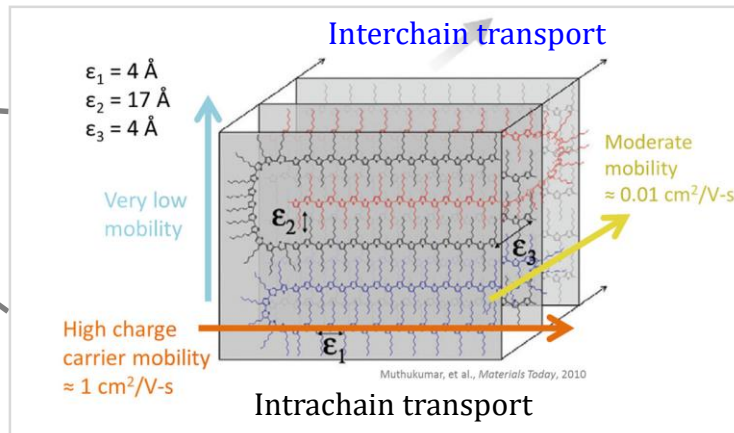
- Polymer concentration
- Solvent quality
- Thermal or Solvent annealing...

: Structuring factors influencing the charge transport of P3HT aggregation

1D crystallization of P3HT

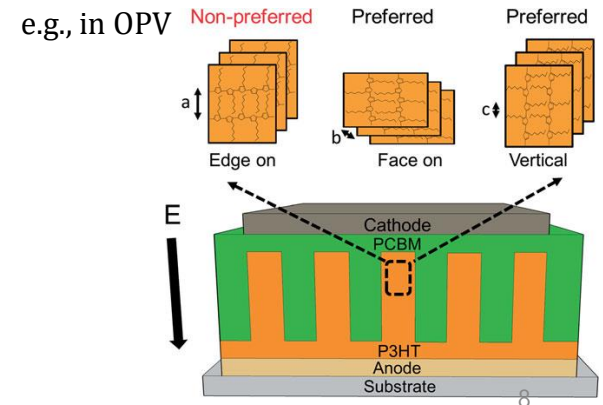


Intrachain transport
Interchain transport
Inter-grain transport



Wang, H. et al. *polymers*. **2013**, 5, 1272

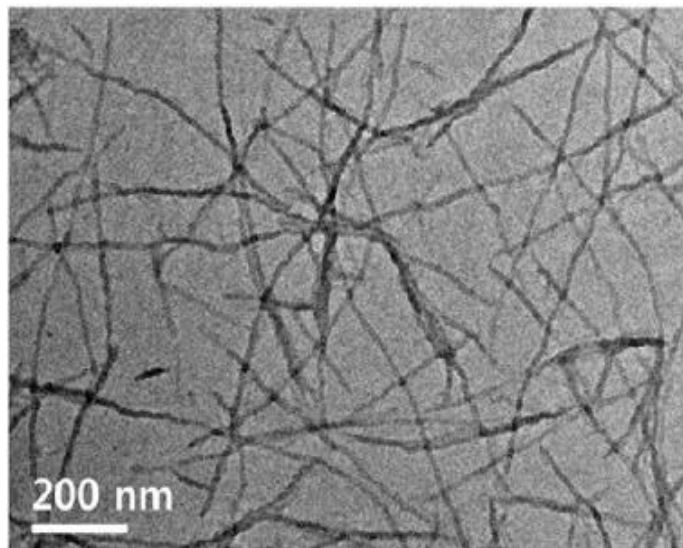
Device performance



Crystallization-driven self-assembly

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Crystallization assembly of macromolecules



Disentanglement → *Coil-to-rod transition* → *Nucleation and Growth*



- Good solvent
- Filtration
- Ultrasonic
- Additives
- ...



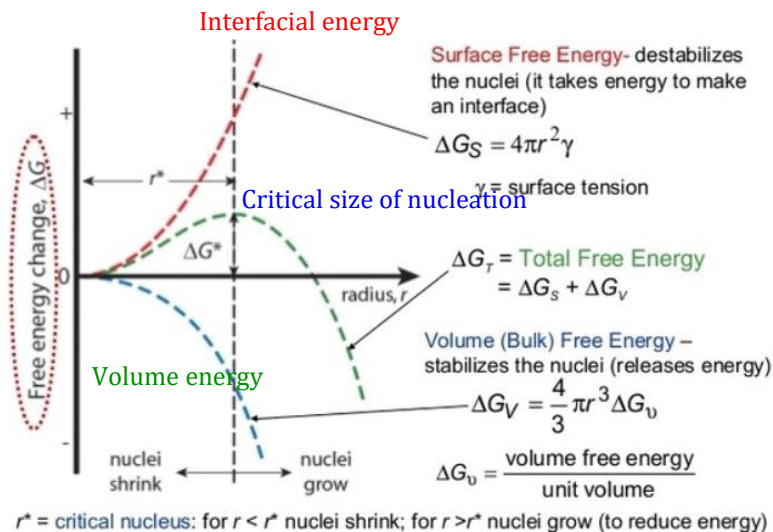
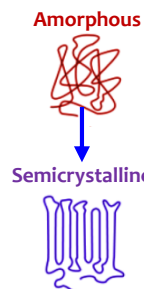
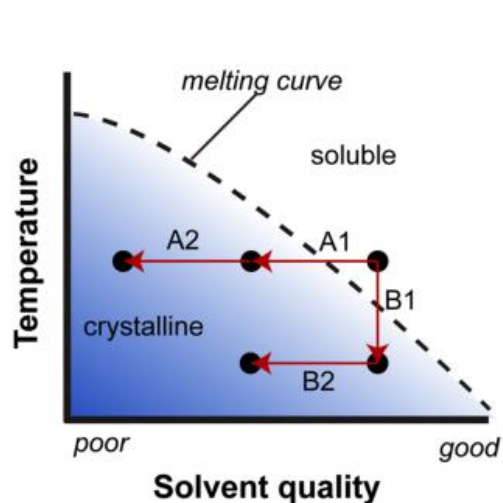
- Decreasing solubility
- Lowering temperature
- Aging
- ...



- Self-seeding (temperature, solubility, vapor pressure)
- Step nucleation (solubility)
- Dispersed nucleation (blending)
- Aging and evaporation kinetics

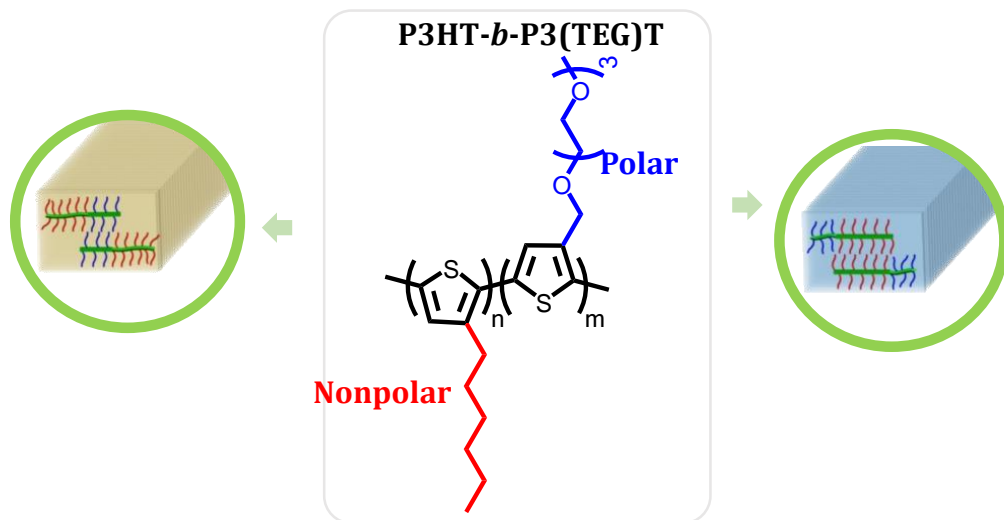


Free energy change by nucleation



Molecular design of P3HT-*b*-P3TEGT

- P3HT has a low solubility, so...



Denotation	P3HT:P3(TEG)T weight ratio	M_n (Kg·mol ⁻¹)	PDI
H1T1	1.1:1	18 000	1.7
H2T1	2.2:1	16 000	1.7
H4T1	4.0:1	18 000	1.5

^a determined from ¹H-NMR.

^b Estimated by GPC. GRIM: Grignard metathesis.

Two distinct advantages for solution-state assembly

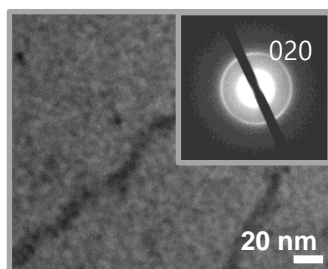
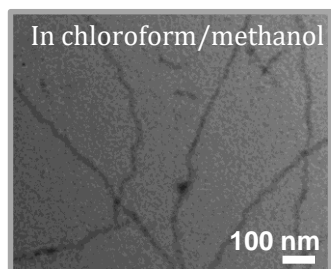
- **large contrast in solubility** between the blocks
- ability of the oligoether chains to **complex alkali metal ions**

Additional driving force for self-organization
Wide range of solvents for aggregation formation
Improvement of tunability of morphology

- Self-assembly behavior in mixed solvent**

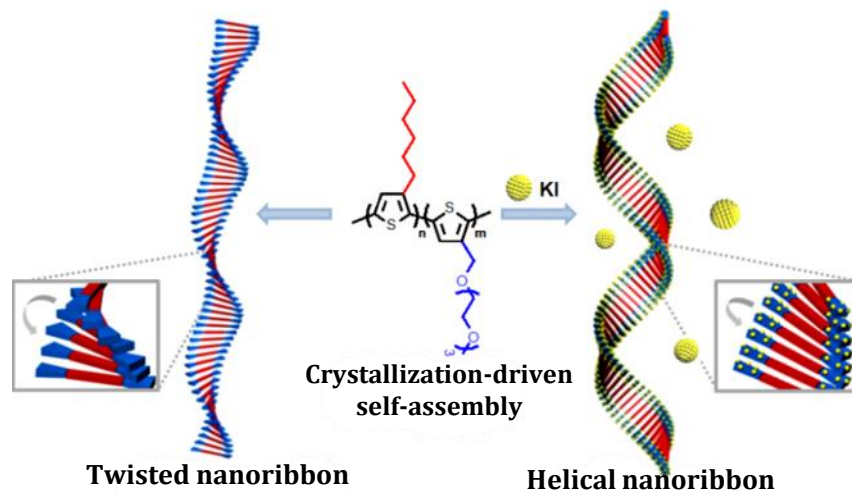
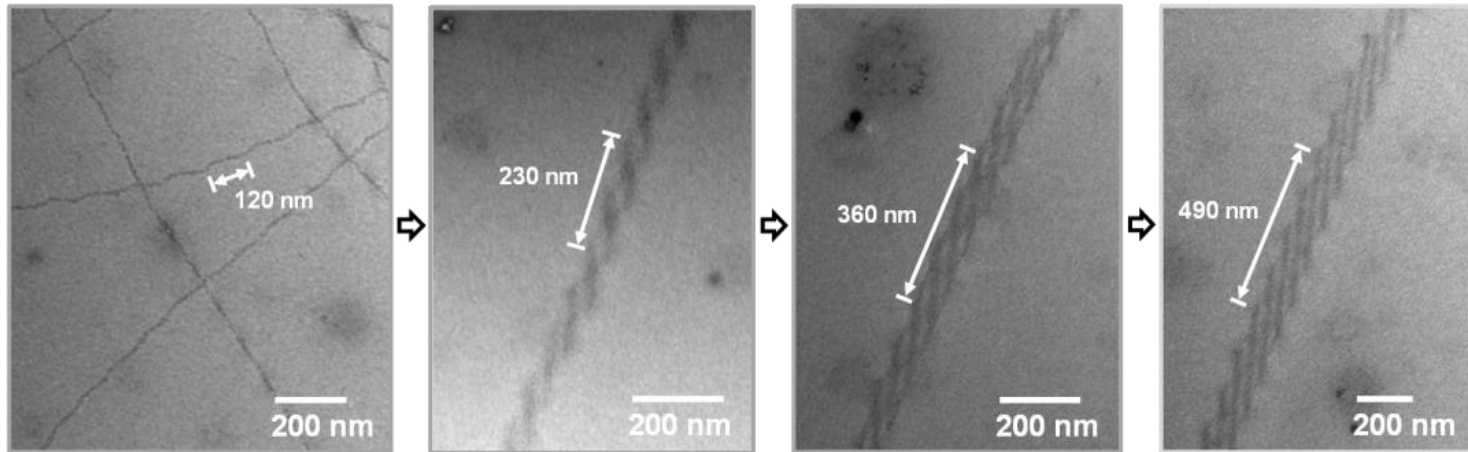
Fibrils formed in the mixed solvent of chloroform/methanol

TEM images

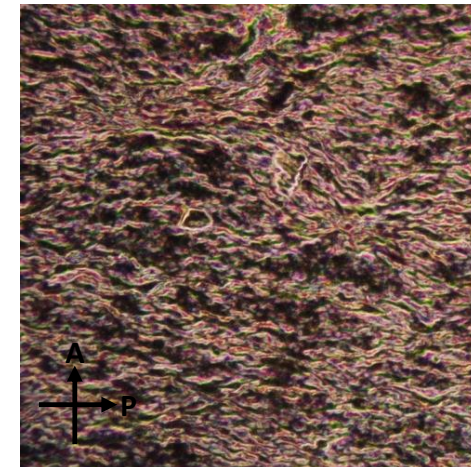


**Salt-induced helical assembly
of conjugated polymer**

KI addition



POM



Combination of crystallization-driven self-assembly and electrostatic interaction

→ Helical structure formation

→ Chiral Plasmonics, Chiroptics

Global issue

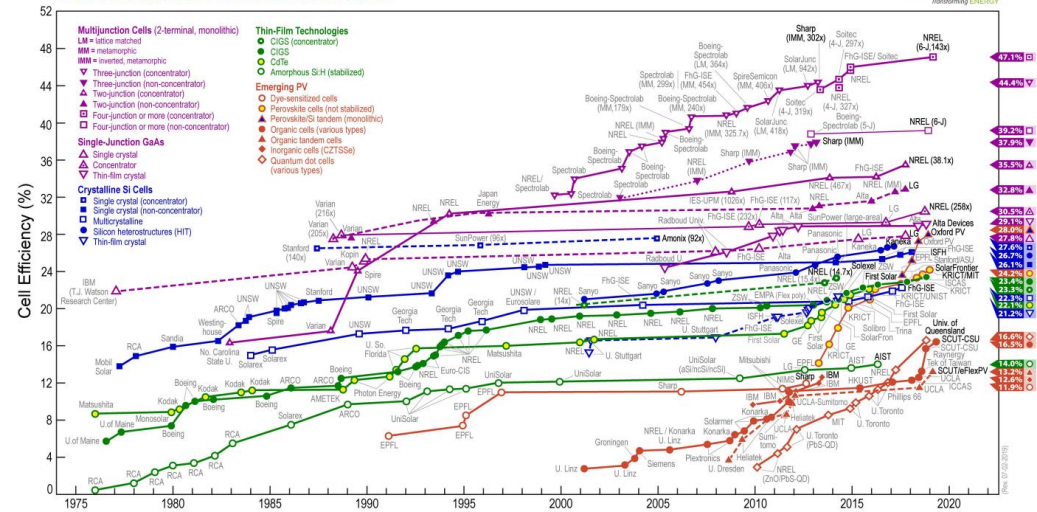
- Climate change response plan



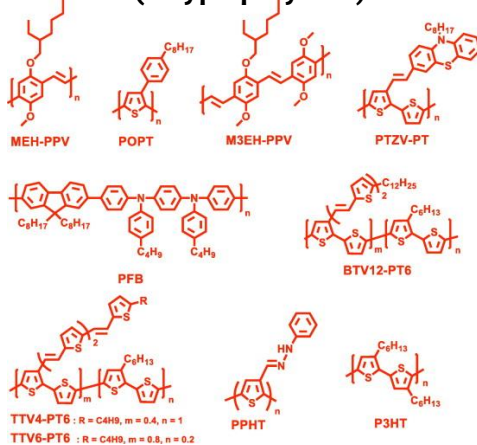
1. New Regeneration Energy
2. Fine dust
3. Global warming
4. Carbon Dioxide Reduction

Eco-friendly solar energy

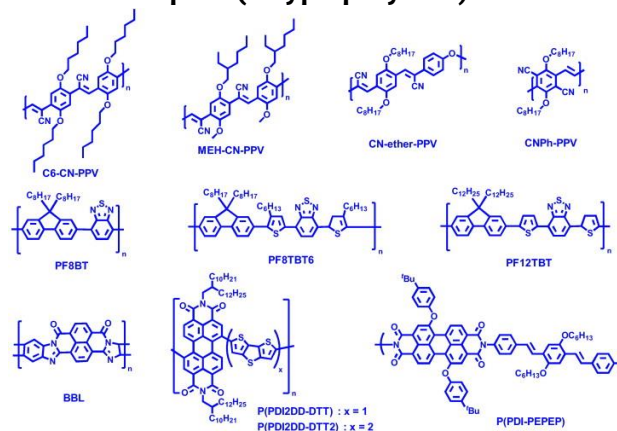
Best Research-Cell Efficiencies



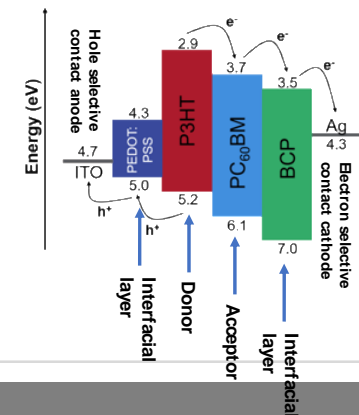
Electron donor (P-type polymer)



Electron acceptor (n-type polymer)

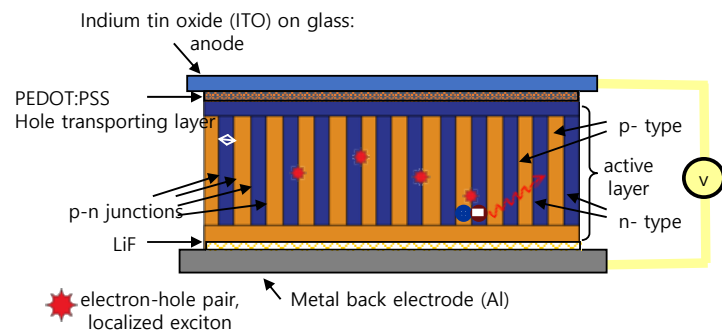


- Well matched energy level
- Wide optical absorption to match the solar spectrum



Polymer solar cells

How can we achieve very high efficiency in polymer solar cells?



Modified from Gunes et al., Chem. Rev. **2007**, 107, 1324-1338

For efficient active layer materials

- **molecular scale**
- : efficient **charge transport (crystallinity)**
- **nanoscale**
- : exciton diffusion length (~ 10 nm)
- to facilitate **charge separation** to reduce recombination
- **colloidal scale**
- : optimal structures for **transport of both electrons and holes**

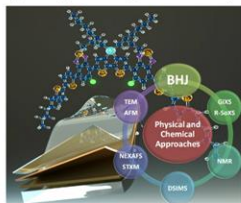
CHEMICAL
REVIEWS

Review
pubs.acs.org/CR

Bulk Heterojunction Solar Cells: Morphology and Performance Relationships

Ye Huang,^{†,‡} Edward J. Kramer,^{*,§,§} Alan J. Heeger,^{*,||} and Guillermo C. Bazan^{*,†}

[†]Center for Polymers and Organic Solids, Department of Chemistry & Biochemistry, [§]Department of Materials, [§]Department of Chemical Engineering, and ^{||}Department of Physics, University of California, Santa Barbara, California 93106, United States



1. INTRODUCTION

With the hope of solving the present energy crisis and associated environmental issues, much research has been focused on solar cells that can harvest energy directly from sunlight to enable sustainable and green energy technology. Organic photovoltaic thin films offer considerable promise for meeting some of these needs.¹ Their potential for low-cost and fast roll-to-roll production as well as their light weight and fabrication on flexible substrates could give them major advantages over traditional inorganic solar cells.

The discovery of ultrafast charge transfer opened the field of

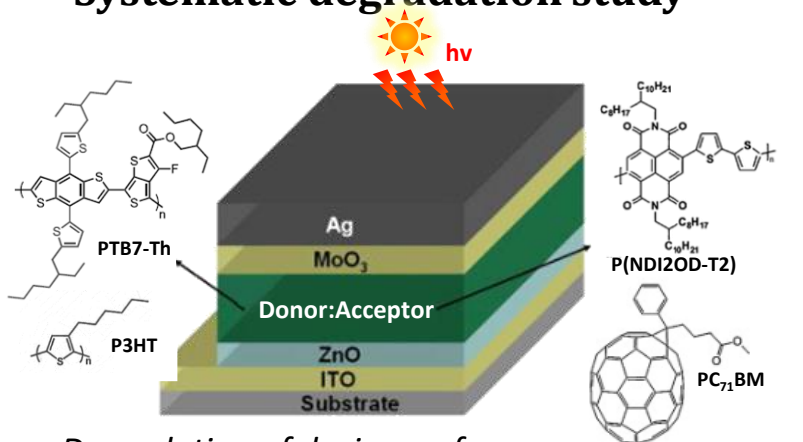
-**Chemical modification**

: HOMO and LUMO levels, Absorbed band range

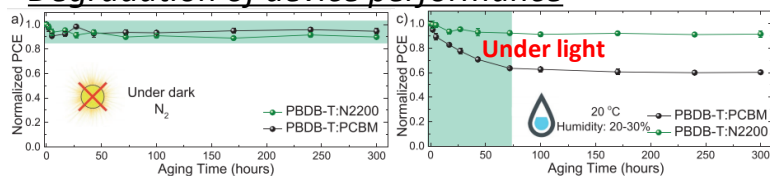
-**Physical method** (processing condition)

- : Solvent (single or multiple)
- : Additives
- : Rate of solvent evaporation
- : Thermal annealing
- : Kinetics of ordering

Systematic degradation study

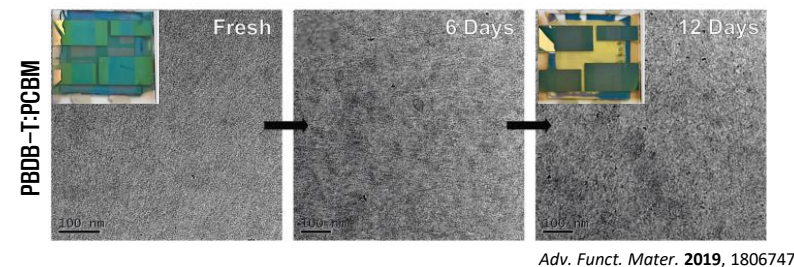


Degradation of device performance



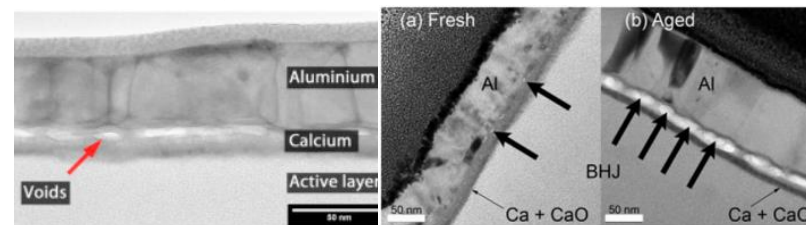
Adv. Funct. Mater. 2019, 1806747

2. Phase separation of active layer materials



Adv. Funct. Mater. 2019, 1806747

3. Oxidation of metal electrode

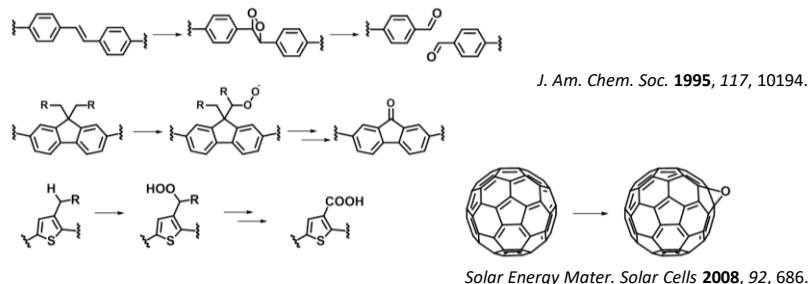


Sol. Energy Mater. Sol. Cells 2013, 110, 36.

Chem. Phys. Lett. 2015, 640, 201.

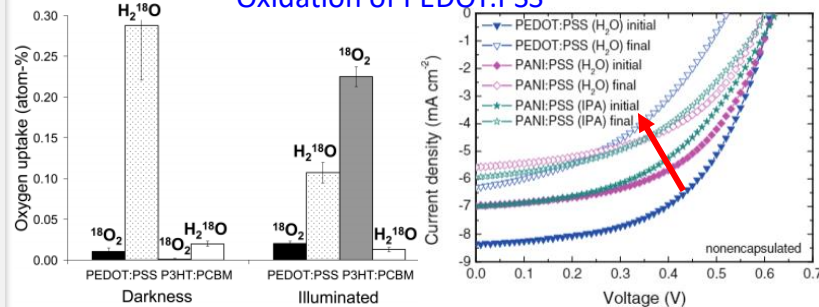
1. Photo-oxidation of active layer materials

Under light in the presence of oxygen



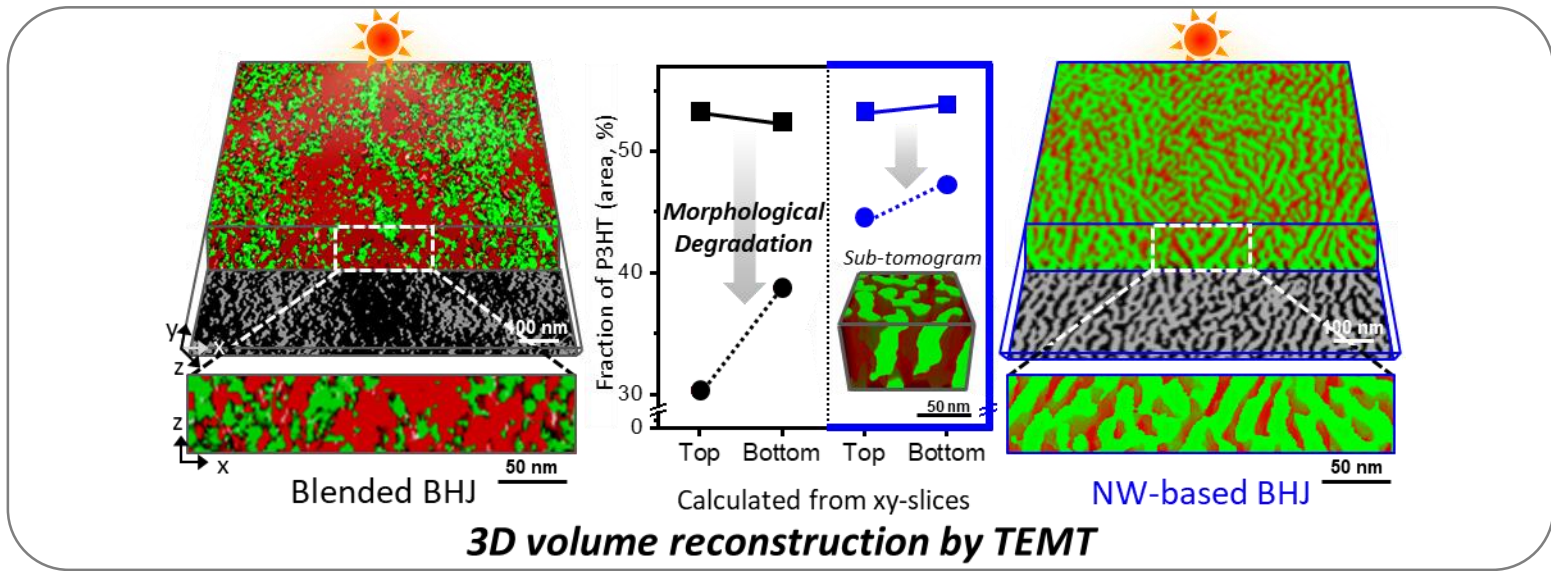
4. Degradation of buffer layer

Oxidation of PEDOT:PSS



J. AM. CHEM. SOC. 2010, 132, 16883

Adv. Energy Mater., 2011, 21, 2705.



- 3D analysis of active layer morphologies revealed by 3D TEM

