Lecture on
Solar cells (SCs)

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March 02, 2022

Introduction

Renewable capacity growth between 2019 and 2024 by technology

Renewable power capacity is set to expand by 50% between 2019 and 2024, led by solar PV
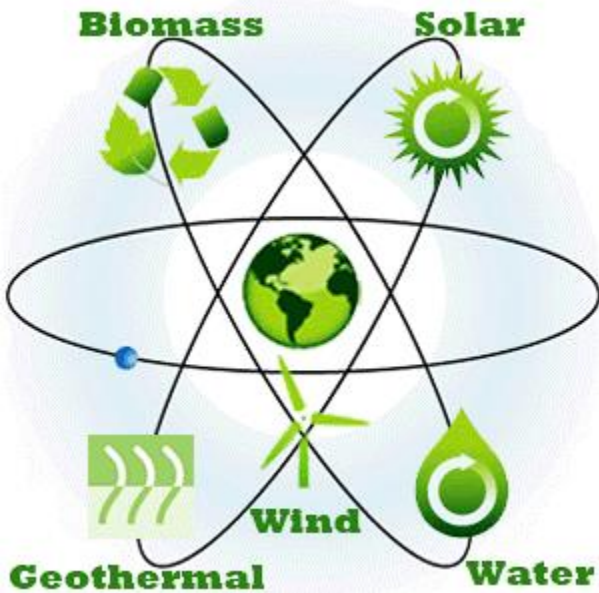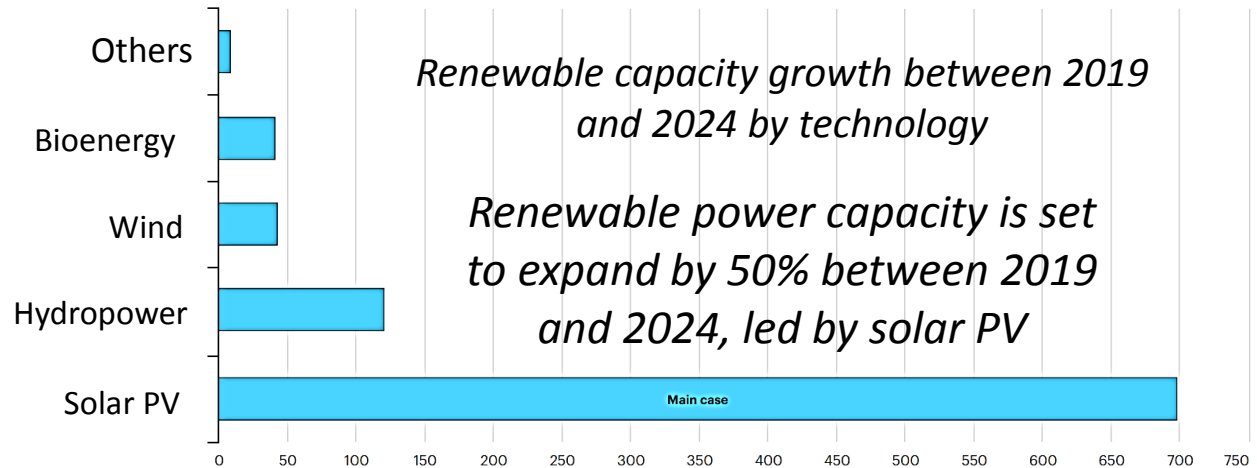
Various types of solar cells technologies

Solar cells: discovery

25 April 1954, Bell Labs (Daryl Chapin, Calvin Fuller and Gerald Pearson)

Progress in efficiency of SCs

https://www.nrel.gov/pv/cell-efficiency.html

4
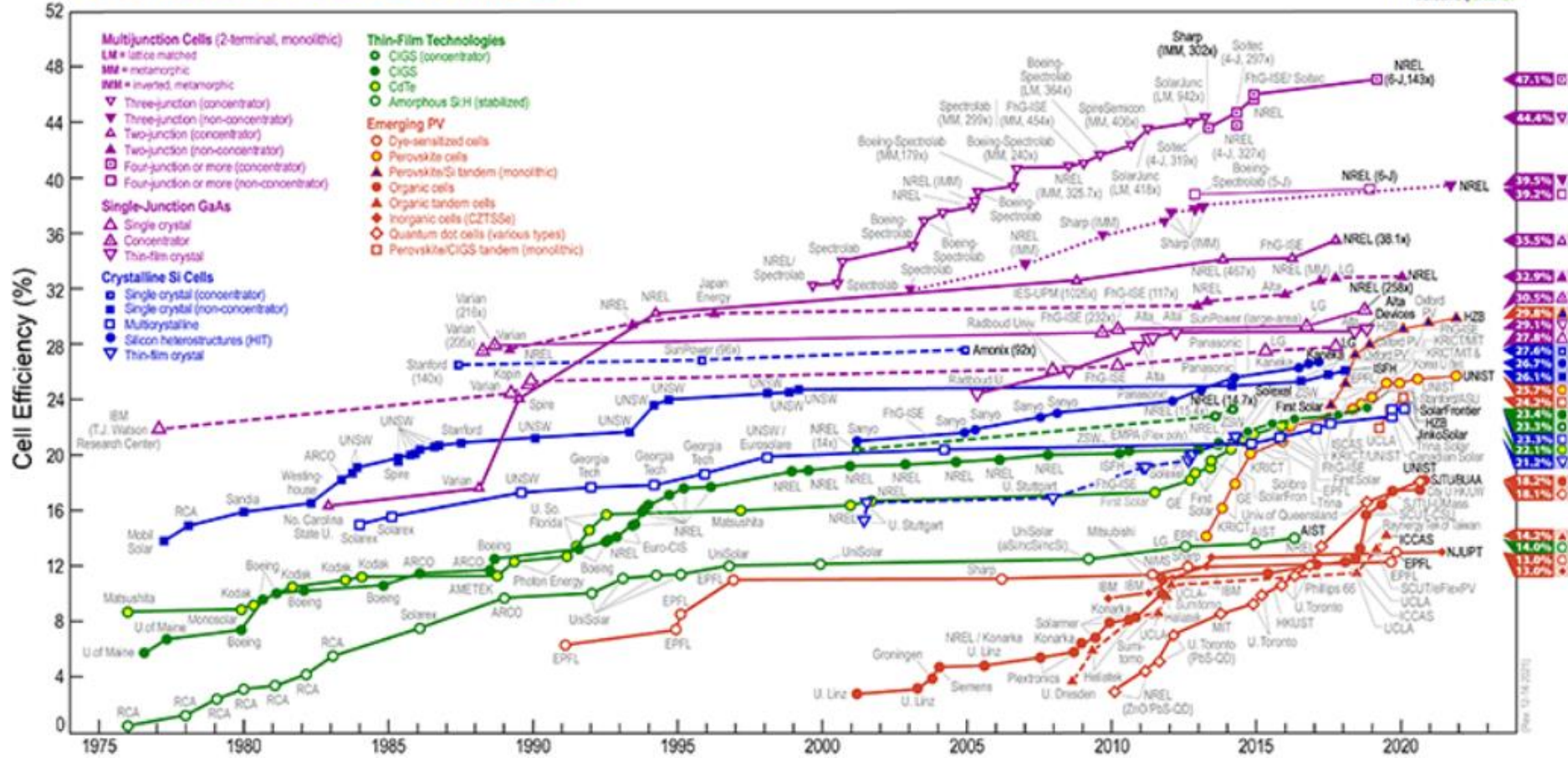
Inorganic and hybrid SCs

Intrinsic and doped silicon
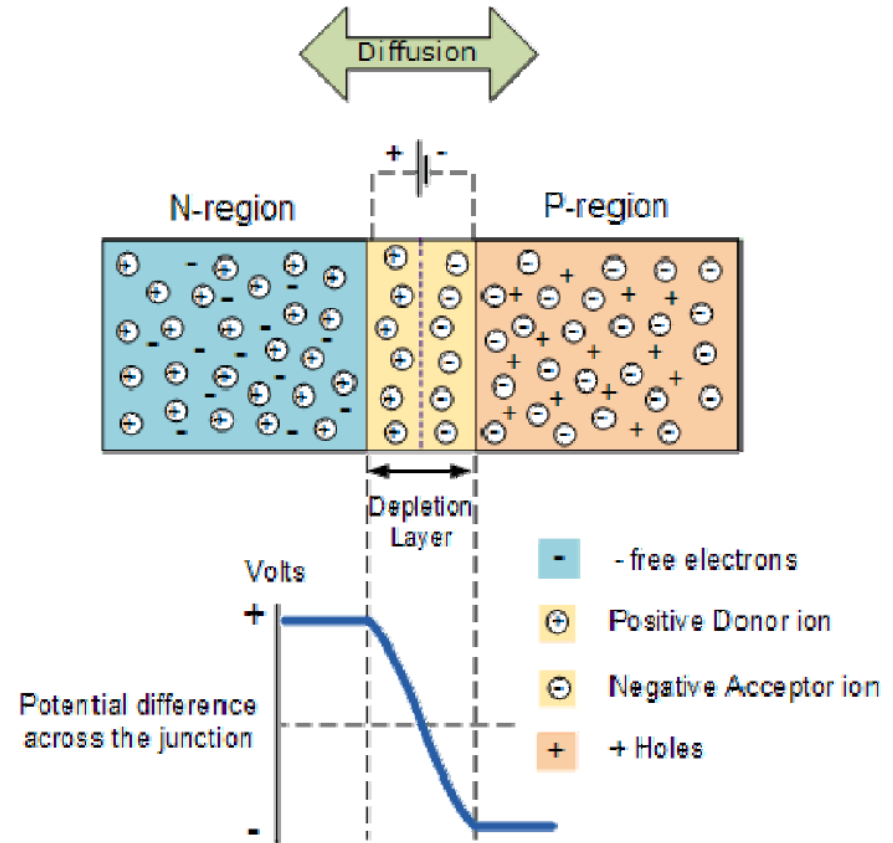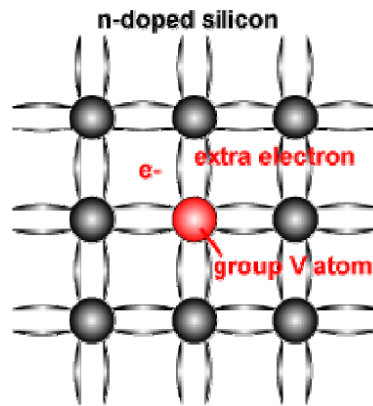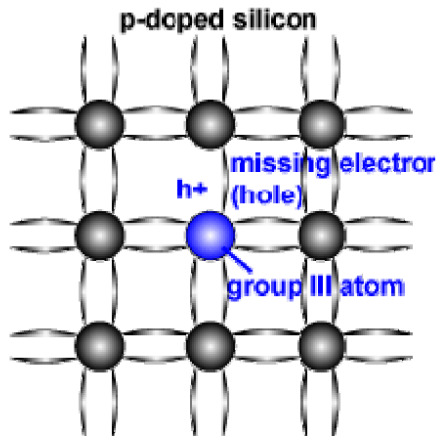
Silicon modifications
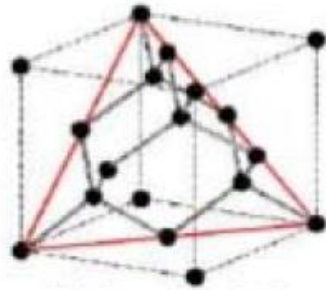
Unit cell of Si
a=0.5431 nm
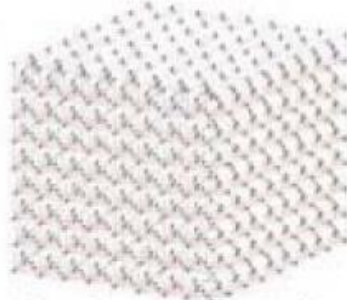
Single Crystal Si
(completely ordered)
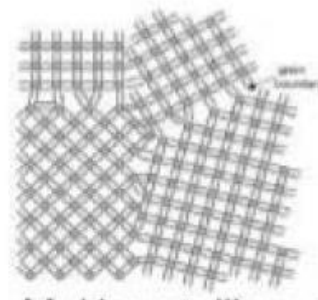
Multicrystalline or
poly Si (grains of
different orientations)
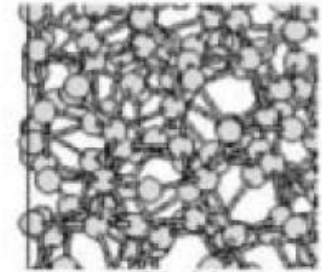
a-Si: H
(very short range order
in <1 nm regime)

	Symbol	Grain Size	Mobility (cm^2 V/sec)	Eg (eV)	Common Growth Techniques
Single crystal	sc-Si	Completely ordered	~10^3	1.1	Czochralski (CZ) or float zone (FZ)
Multicrystalline Polycrystalline	mc-Si pc-Si	μm-mm	Mid 10-10^3	1.1	Cast, ribbon, Chemical-vapor deposition (CVD)
Microcrystalline nanocrystalline	μc-Si nc-Si	<1μm <5 nm	Mid 10	1.1 1.1-1.7	CVD, sputtering
Amorphous	a-Si/ a-Si:H	Very short range order <1 nm	1-10	1.7-1.9	CVD

Behaves more like direct gap

Silicon modifications

Single crystal (c-Si)

- **High efficiency (> 25% of PCE)**
- **Long-term stability (> 25 years)**

- **High costs**
- **High total embodied energy (required to produce)**

Polycrystalline (pc-Si)

- **Still high efficiency – 21.3%**
- **Module efficiencies 14-16%**
- **Cheaper and easier to produce**
- **Long-term stability (> 25 years)**

- **Not as efficient as c-Si cells**
- **Still expensive**
- **High total embodied energy**
- **Non-uniform visual appearance**

Amorphous (a-Si)

- **a-Si has a direct bandgap**
- **Lower total embodied energy**
- **Cheaper and easier to produce**

Glass
Transparent conducting oxide
aSi p-layer
aSi i-layer
aSi n-layer
Back contact
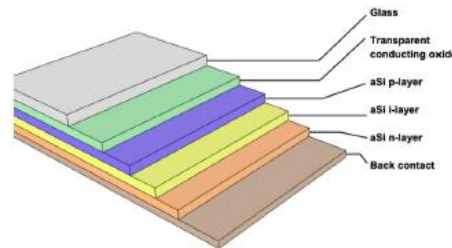
- **Low PCE of 10.2%**
- **Low stability**
- **Production was abandoned**

Metal chalcogenides

Cu(In,Ga)Se$_2$ (CIGS)
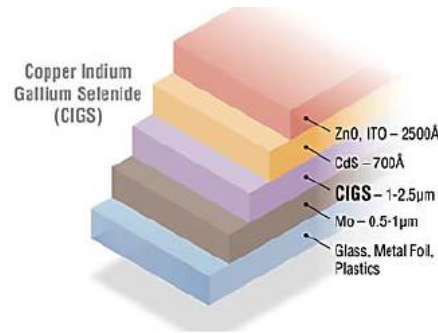
- **High efficiency (> 21%)**
- **Easy thin-film production technology**

- **Complex material composition (chalcogen loss)**
- **Low abundance of In**
- **Toxicity of Cd (if used) and Se**

Thin film CdTe
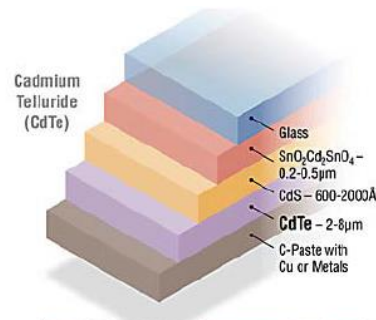
- **High efficiency (≈ 20 %)**
- **Easy thin-film production technology**
- **The lowest cost per watt of energy**

- **Low abundance of Te**
- **Toxicity of Cd**

Quantum dots
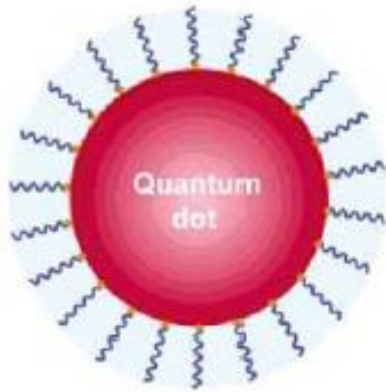
Optical properties are controlled by the size of the "dot"
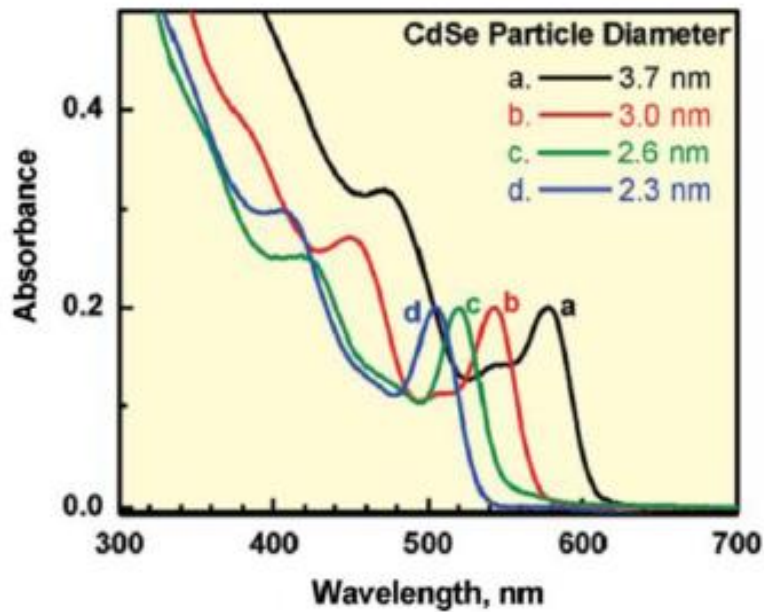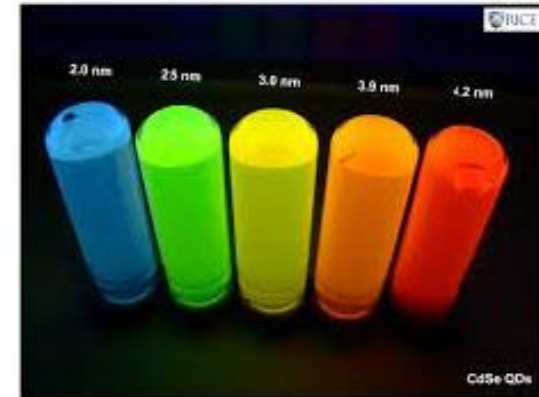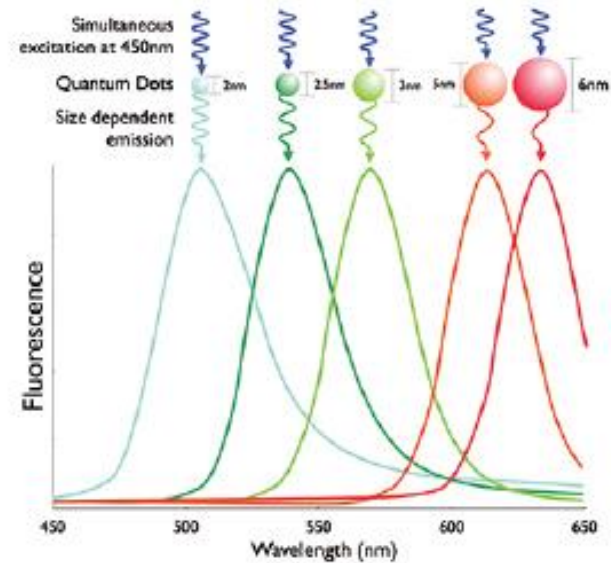
Quantum dots + conjugated polymers

P3HT

MEH-PPV

AFPO-3

PCPDTBT
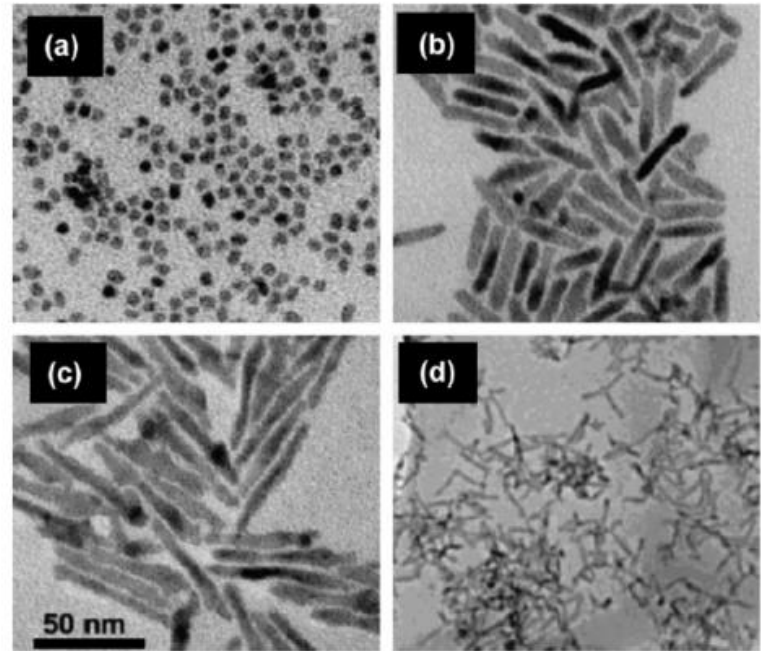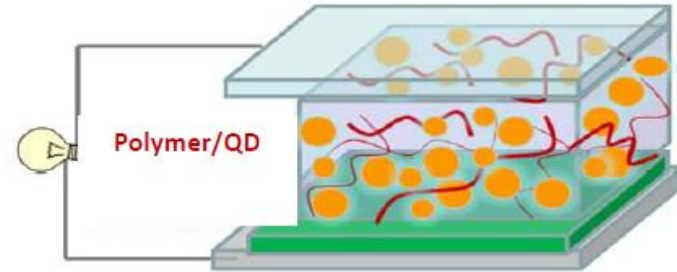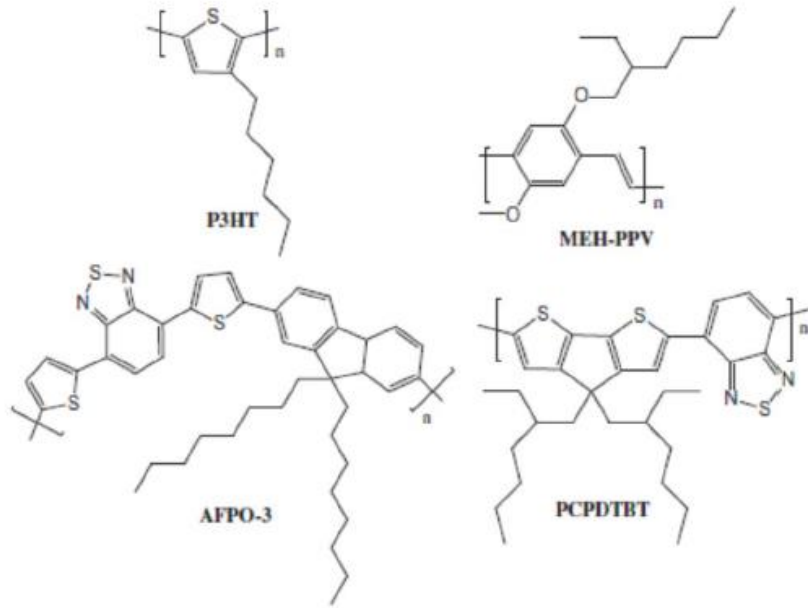
Polymer/QD

Table 1
Photoconversion efficiencies of bulk heterojunction devices composed of CdSe nanocrystals and various hole conducting polymers.

Nanocrystals	Polymers	Eff. (%)	References
CdSe dots	P3HT	1.8	Olson et al. (2010)
CdSe dots	P3HT	2.0	Zhou et al. (2010)
CdSe dots	P3HT	2.6	Sun and Greenham (2006)
CdSe tetrapods	APFO-3	2.4	Wang et al. (2006)
CdSe tetrapods	PCPDTBT	3.1	Dayal et al. (2010b)

(a) (b) (c) (d)   50 nm

S. Emin et al. / Solar Energy 85 (2011) 1264–1282

Organic SCs

Progress in efficiency of OSCs

7.4%
2010,
L. Yu
PTB7
FA

10.8%-11.7%
2014-2016,
H. Yan
PffBT4T
FA

14.2%
2018,
J. Hou
PDTB-EF-T
NFA

18%
2020,
L. Ding
D18
NFA

20%
?

5.5%
2007,
G.Bazan
PCPDTBT
FA

3.5%
2003,
N. Sariciftci
P3HT
FA

3%
1995,
A. Heeger
MDMO-PPV
FA

1%
1986,
C.Tang
CuPc, PV

PCPDTBT

PffBT4T

D18

MDMO-PPV

P3HT

PTB7

PDTB-EF-T

13
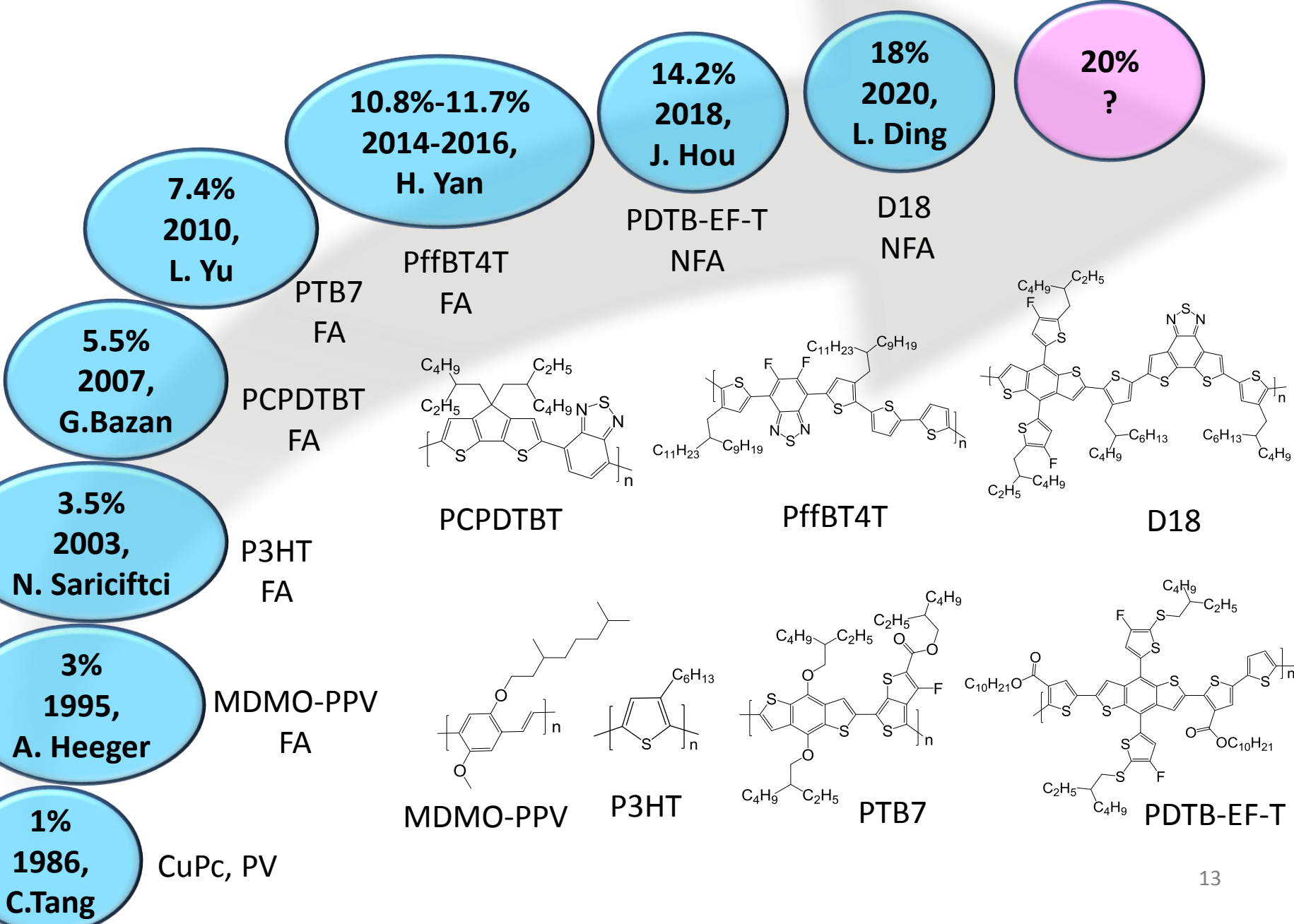
Advantages of organic solar cells

- ## Processability (roll-to-roll production)

Feasibility of industrial fabrication of solar cells using R2R compatible techniques (slot-die coating, spray-coating, inkjet printing etc.)

- ## Flexibility

The flexible printed solar cells are available in different sizes and shapes. The devices can be stretchable
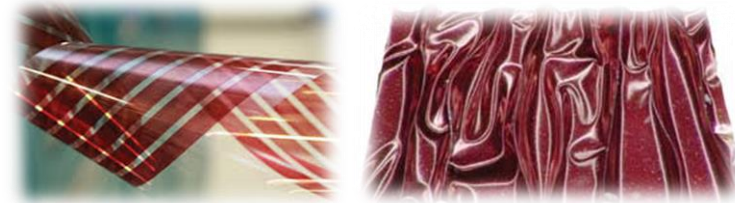
- ## Color-tunable devices

Organic solar cells are available in different colors and can be semitransparent that is important for BIPV

- ## Low cost and environment-friendly materials

Operating principle of OSCs

Channel I

LUMO

hv

D

HOMO

LUMO

hv

A

HOMO

Channel II

hv

Anode

hv

D

A

Cathode

Exciton generation & Exciton diffusion

Anode

D

A

Cathode

Generation of free charge carriers

Anode

D

A

Cathode

Charge transport to the electrodes
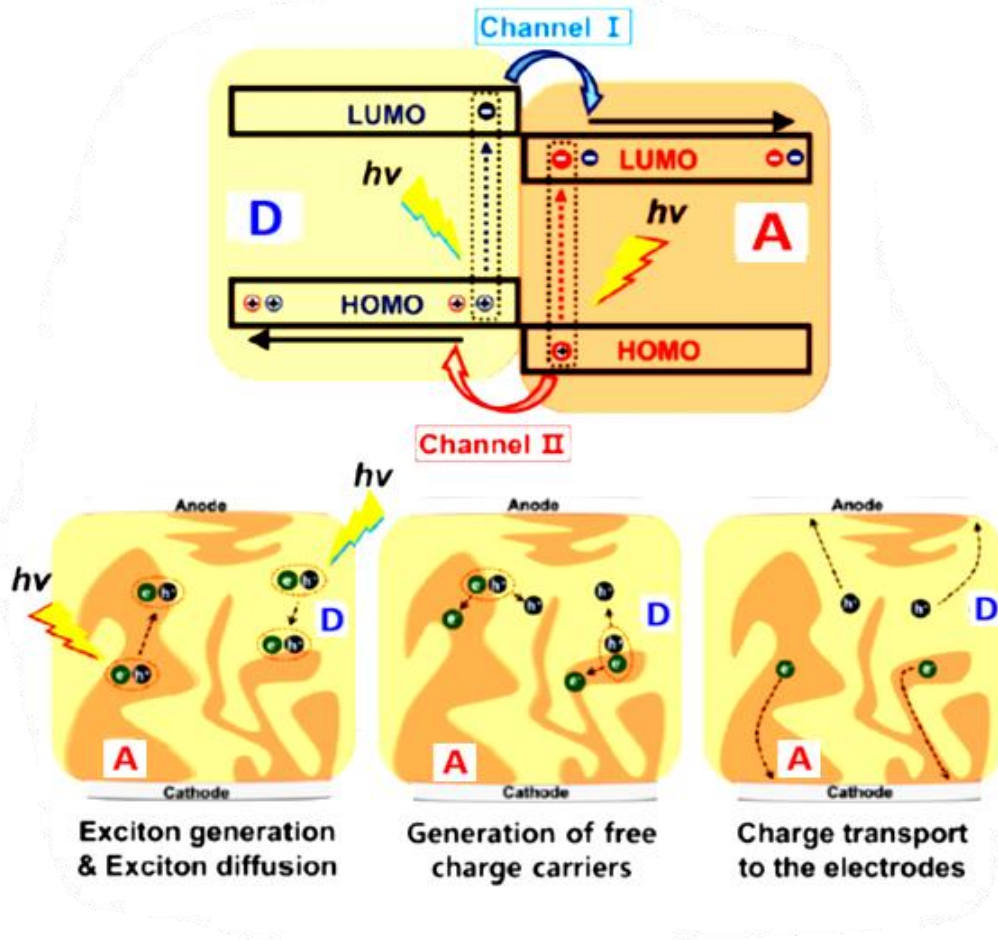
D - donor material
A - acceptor material

Structure of OSCs

Top electrode	Metals: Al, Ag, Au
ETL	ETL – electron transporting (hole blocking) layer
Active layer	p-type (donor) and n-type (acceptor) molecules
HTL	HTL – hole transporting (electron blocking) layer
Bottom electrode	Transparent conductive oxides (ITO, FTO)
Substrate	Substrate: glass, plastics (PET, PEN)

[70]PCBM
n-type

N2200
n-type

P3HT (p-type)

PCDTBT (p-type)

ITIC
n-type

BDT-T3 (p-type)
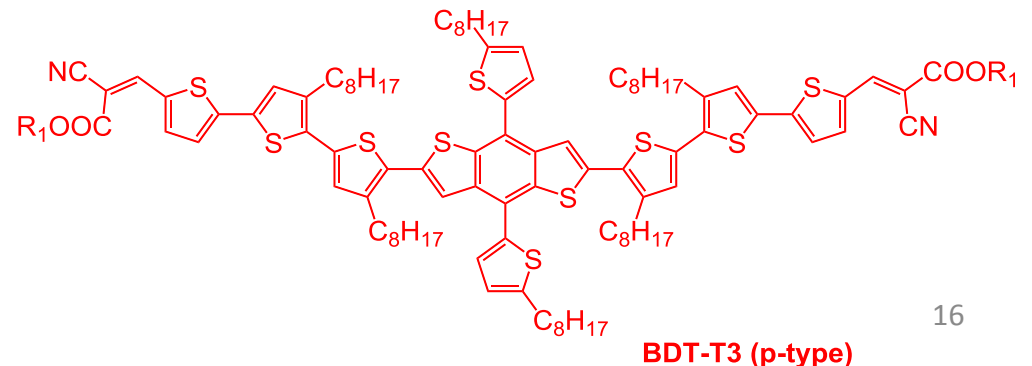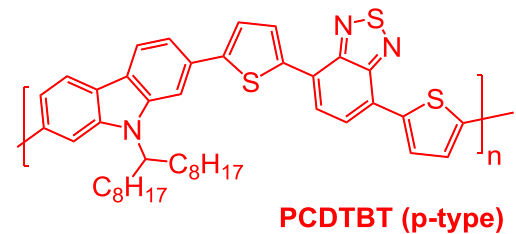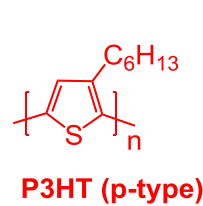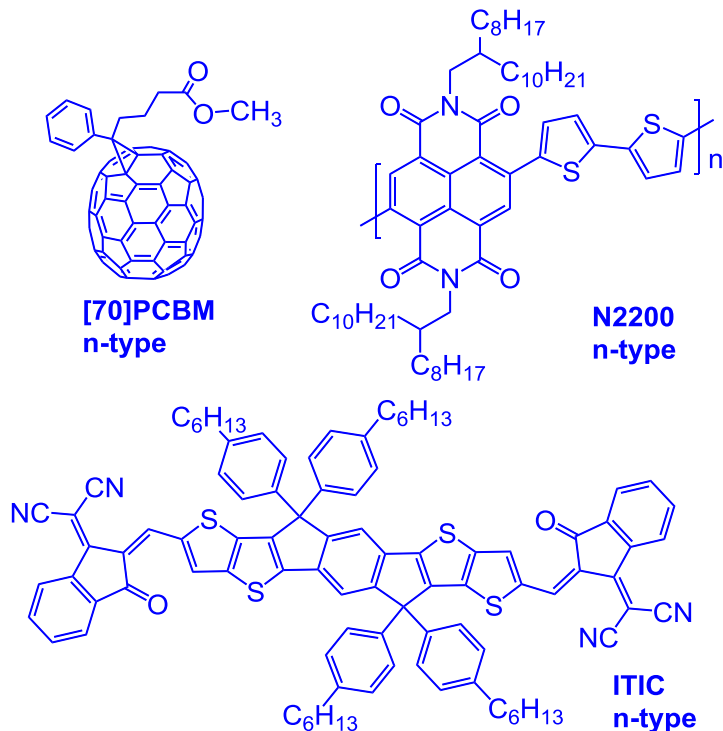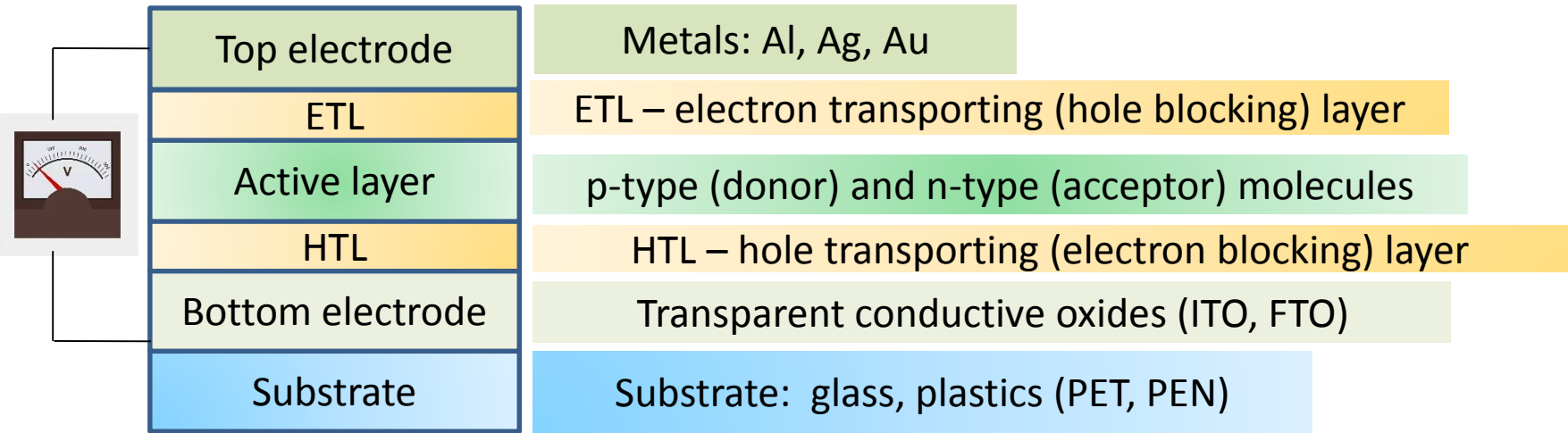
Planar structure of OSCs

| Top electrode (Au/Ag) |
| Acceptor (PV) |
| Donor (CuPc) |
| Bottom electrode (Sn-doped In_2O_3) |
| Substrate (glass) |

PV (n-type)

CuPc (p-type)
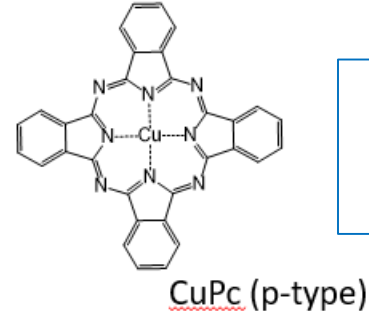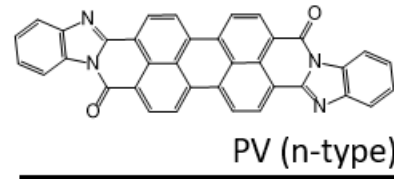
p-type and n-type semiconductors are sequentially stacked on top of each other

C.W. Tang, Appl/ Phys. Lett. 1986, 48, 183

- Exciton lifetimes of organic semiconductors are short (diffusion length ~ 5-20 nm)

- Only excitons created within the distance of 5-20 nm from the heterojunction interface contribute to the current generation

- Loss of absorbed photons results in low quantum efficiency and power conversion efficiency

Bulk heterojunction OSCs

Donor MEH-PPV : **Acceptor [60]PCBM**
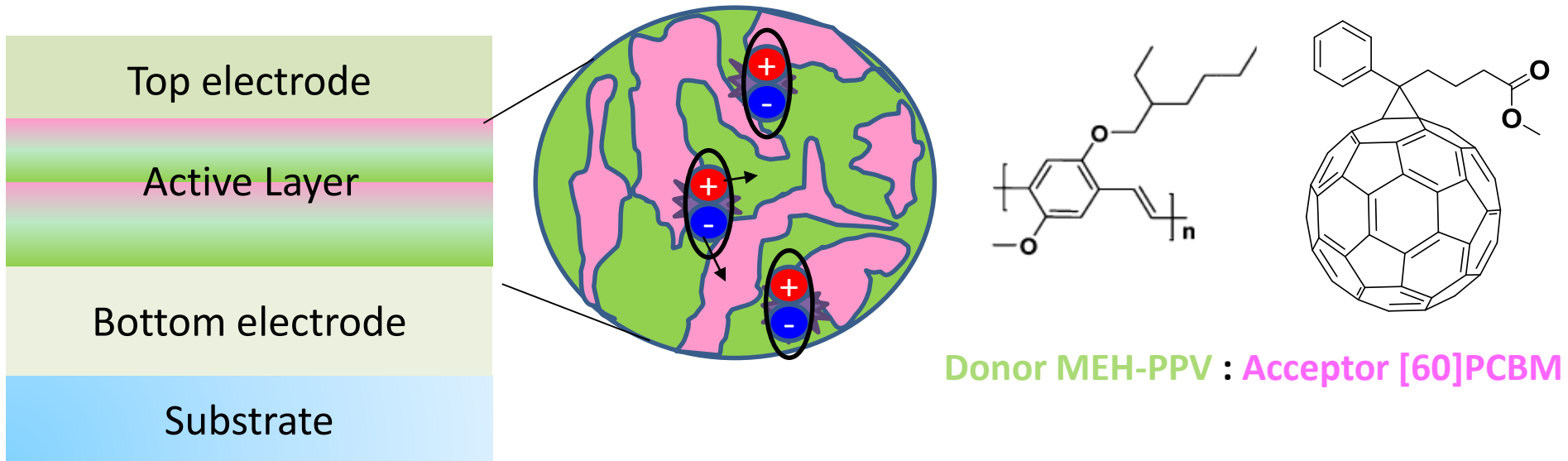
- **Donor** and **acceptor** materials are mixed together to form a bicontinuous interpenetrating network

- Increased interfacial area between donor and acceptor leads to the efficient exciton dissociation and increasing of PCE
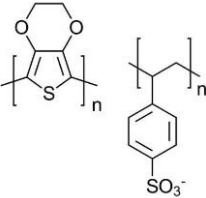
Planar structure of OSCs

Standard configuration

| Cathode |
| Electron transport layer |
| Active layer |
| Hole transport layer |
| Anode |

ITO - anode

polarity of charge collection is reversed
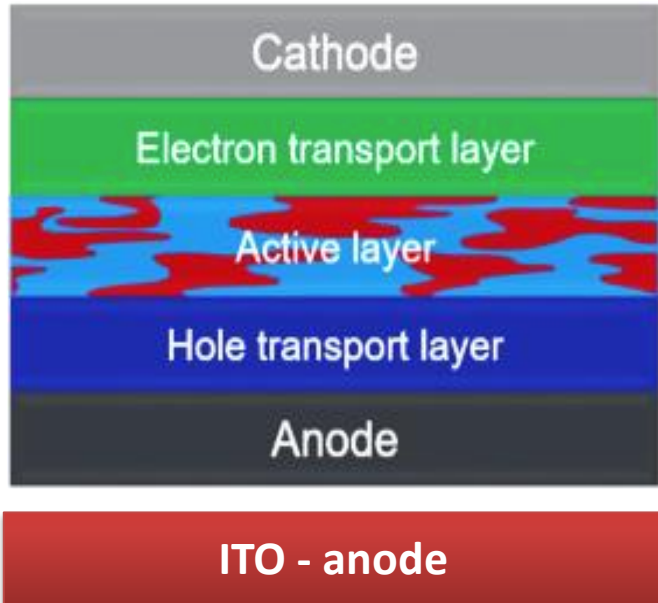
Inverted configuration

| Anode |
| Hole transport layer |
| Active layer |
| Electron transport layer |
| Cathode |

ITO - cathode
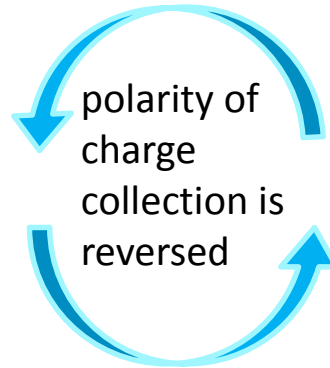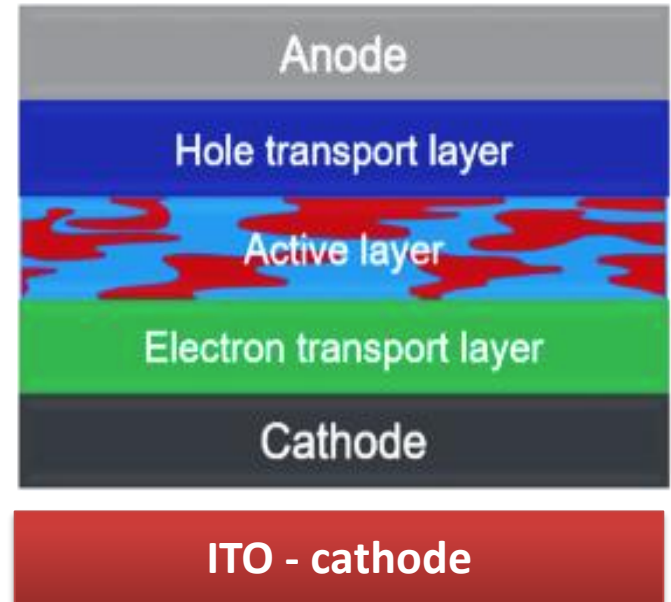
- **Cathode:** low work-function metals (Ca, Mg)
- **ETL:** some fullerene derivatives
- **Anode:** high work-function transparent conducting metal oxide ITO, FTO

- **HTL:** PEDOT:PSS , graphene oxide

- **Cathode:** ITO, FTO

- **ETL:** ZnO, TiO_x, Cs_2CO_3, CsF

- **Anode:** high work-function metals (Ag, Au)

- **HTL:** V_2O_5, MoO_3, WO_3, NiO

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Main parameters of SCs
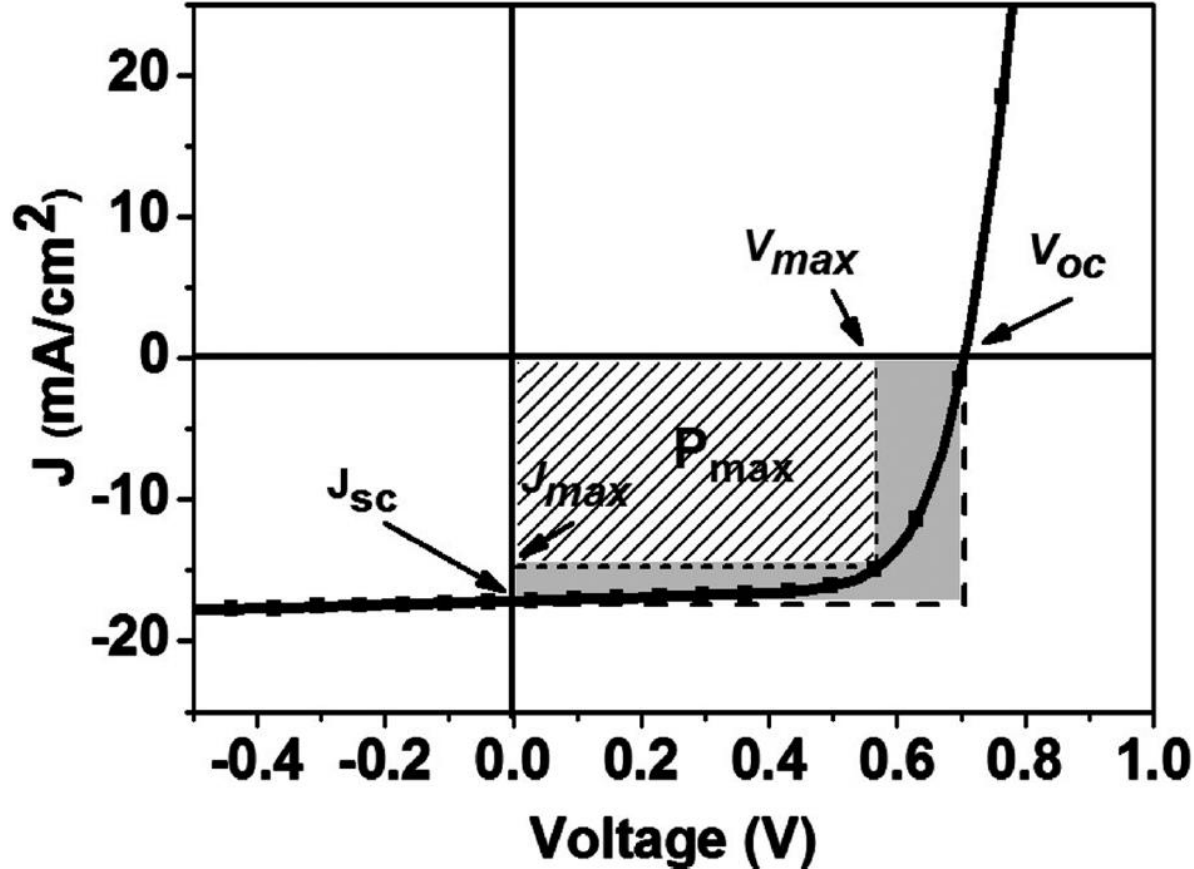
$$PCE = \frac{(V_{OC} \times J_{SC} \times FF)}{P_{in}}$$

$$FF = \frac{(V_{max} \times J_{max})}{(V_{OC} \times J_{SC})}$$

L. Yu et al., Chem. Rev. 2015, 115, 12666−12731

V_{OC} - open circuit voltage, J_{SC} - short circuit current density

FF -   fill factor, PCE – power conversion efficiency

J_{max} and V_{max} are the current density and voltage at the maximum power point (P_{max})

P_{in} -   the incident light power

Open circuit voltage (V_{oc})
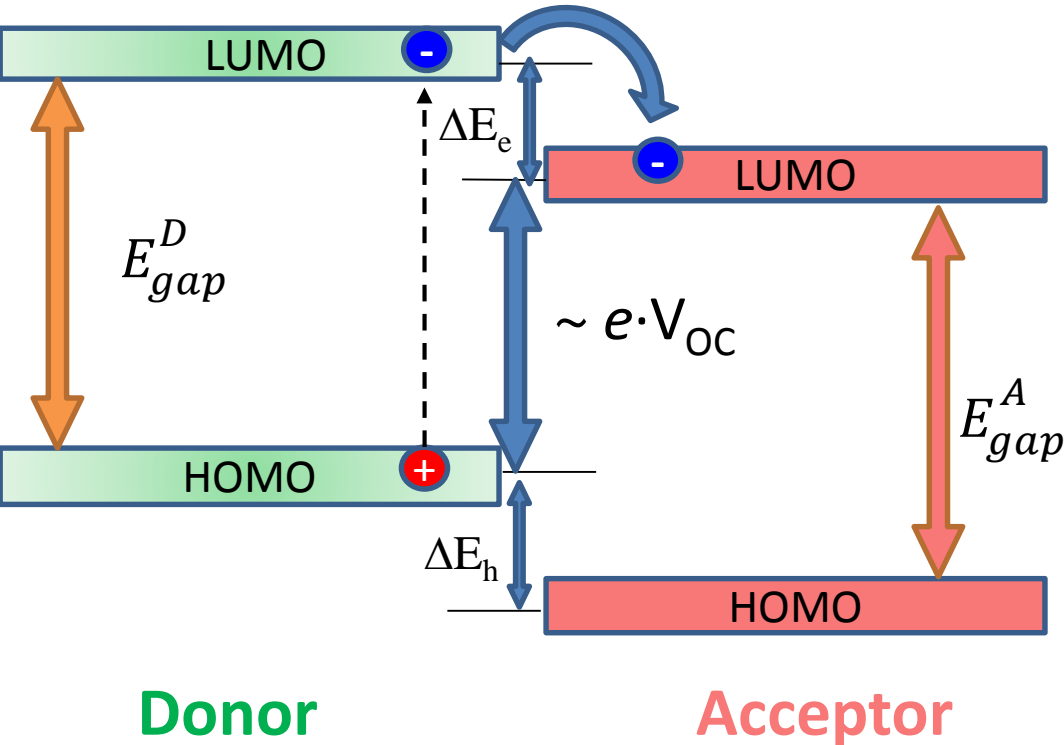
The maximal achievable V_{OC} in organic solar cells is proportional to the energy offset between the HOMO energy of the donor material and the LUMO energy of the acceptor

Donor   Acceptor

- ΔE_h and ΔE_e – "driving force" for efficient exciton splitting and charge separation (>0.3 eV)

- For fullerene-polymer system, ΔE_e should be ≈ 0.3 eV

- For non-fullerene-polymer, ΔE_e can be ≈ 0.05 eV

Open circuit voltage (V_{oc})
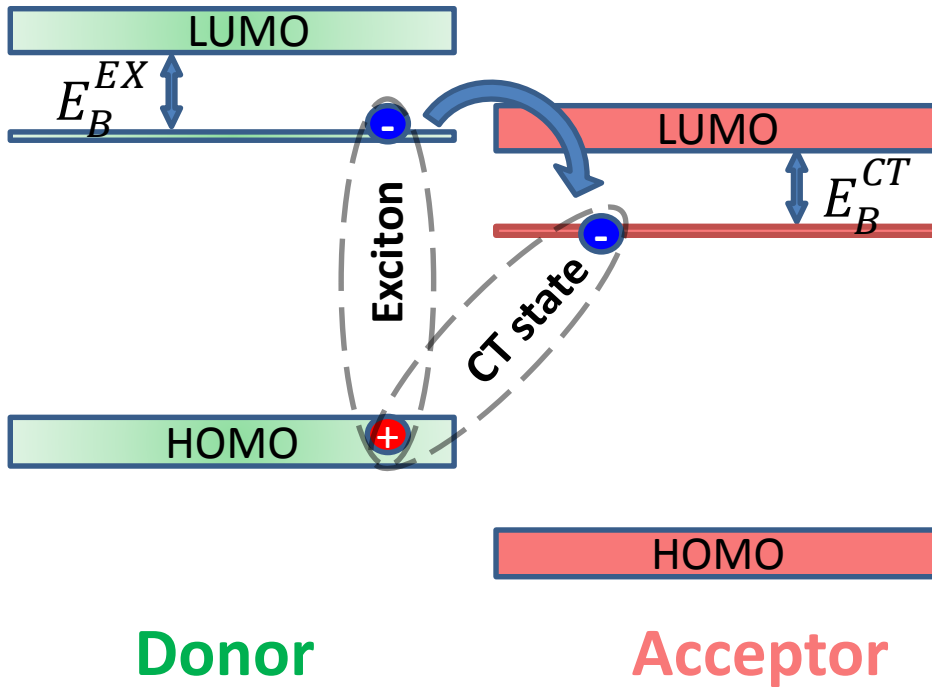
Donor   **Acceptor**

The Coulombically bound electron–hole state at the donor/acceptor interface is known as charge-transfer (CT) state

E_B^{CT} - binding energy of CT state

E_B^{EX} - singlet exciton binding energy

q - the elementary charge

E_g^{CT} - a band gap of the charge transfer (CT) state

$$V_{OC}(exp) \approx E_g^{CT}/q - 0.43, V$$

Open circuit voltage (V_{oc})

$$V_{oc} = \frac{E_{CT}}{q} + \frac{kT}{q}\ln\left(\frac{J_{sc}h^3c^2}{fq2\pi(E_{CT}-\lambda)}\right) + \frac{kT}{q}\ln(EQE_{EL}).$$

Radiationless decay

E_{CT} – energy of the CT state,

~[HOMO(D)-LUMO(A)]

f – CT absorption strength,

~ density of DA pairs;
~ DA coupling

$EQE_{EL} \sim 10^{-6}$

Empirical formula:

$qV_{OC} = E_{CT} - 0.6\ eV$

Open circuit voltage (V_{oc})

Short current density (J_{SC})
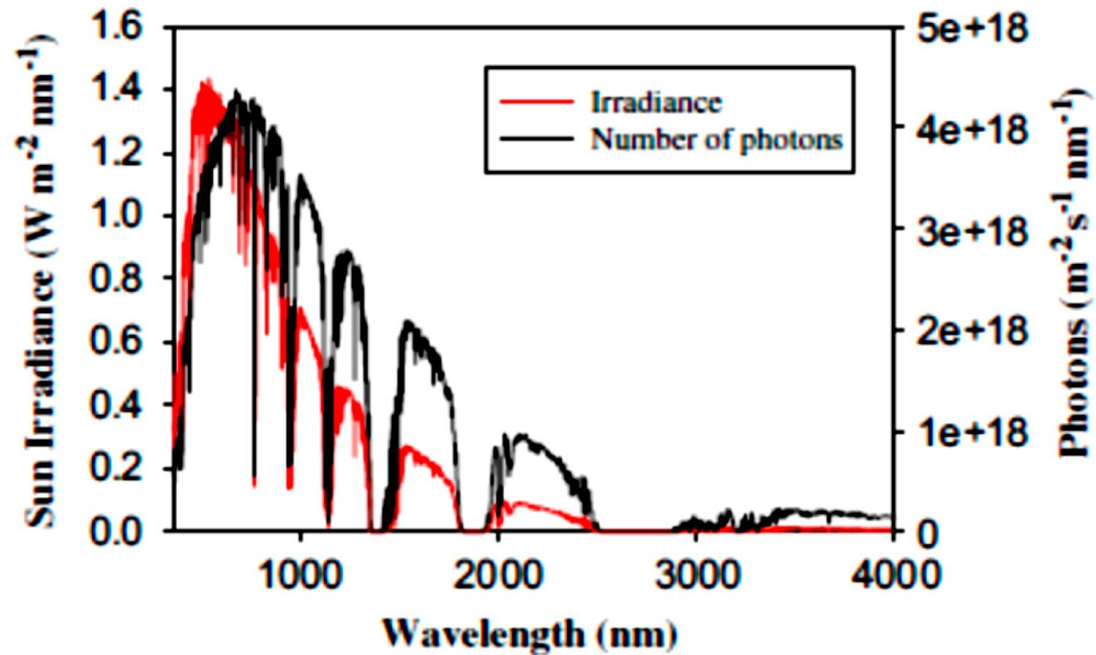
Sun irradiance (red) and number of photons (black) as a function of wavelength

The maximal achievable J_{SC} in organic solar cells depends on number of photons absorbed in active layer of organic solar cell

Short current density (J_{SC})
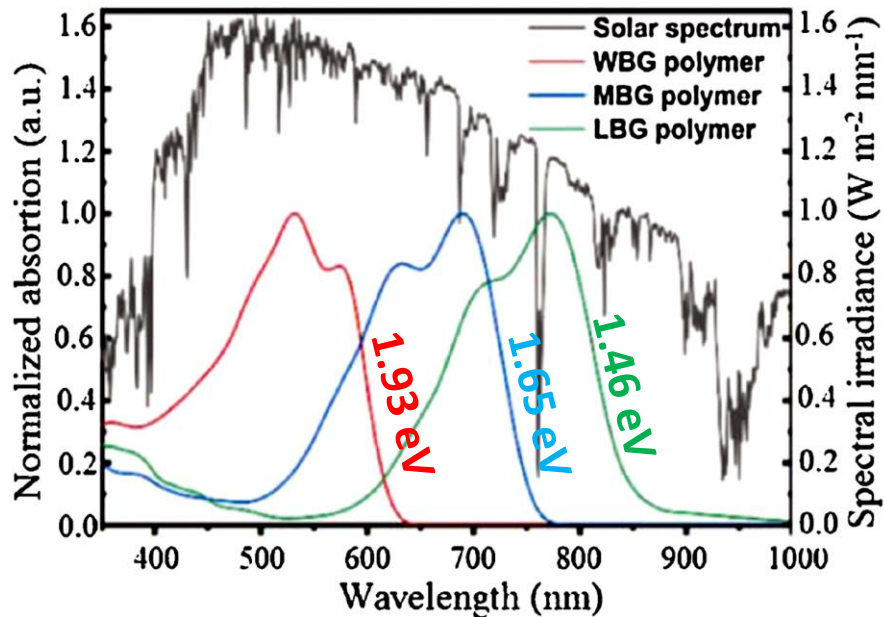
$$E_g = h\upsilon = \frac{hc}{\lambda_{edge}} \approx 1241/\lambda_{edge}$$

- To efficiently harvest solar energy, the absorption spectra of OSCs should have a large overlap with the solar spectrum

- Low bandgap polymers with broad absorption spectrum are required to maximize the J_{SC} in OSCs

L. Yu et al., Chem. Rev. 2015, 115, 12666−12731

Short current density (J_{sc})

$h\nu$

LUMO

ΔE_e

LUMO

E^D_{gap}

$\sim e \cdot V_{OC}$

HOMO

ΔE_h

HOMO

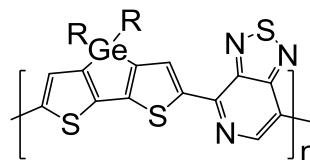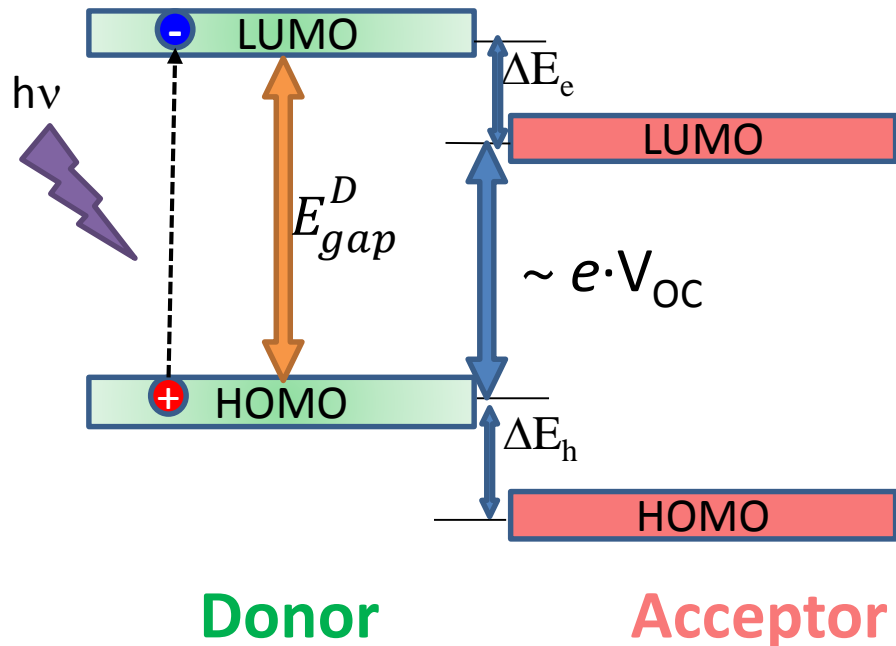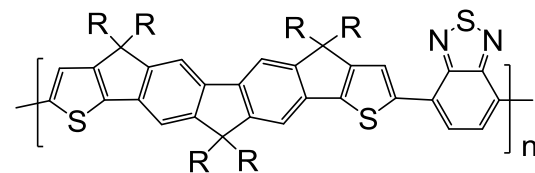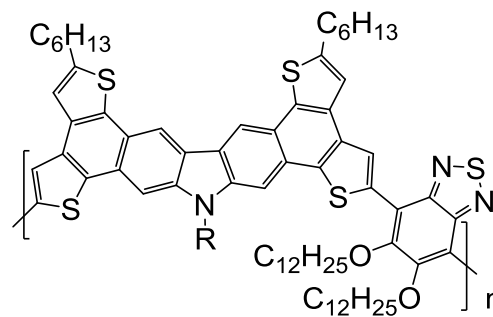**Donor**   **Acceptor**

P1: X=Ge, R=2-ethylhexyl   **P2:** R=C_8H_{17}

P3:R=2-ethylhexyl

	E_g, eV	J_{SC}, mA/cm²	HOMO, eV	V_{OC}, mV
P1	1.3	17.6	-4.9	590
P2	1.7	12.6	-5.3	830
P3	1.9	9.3	-5.4	910

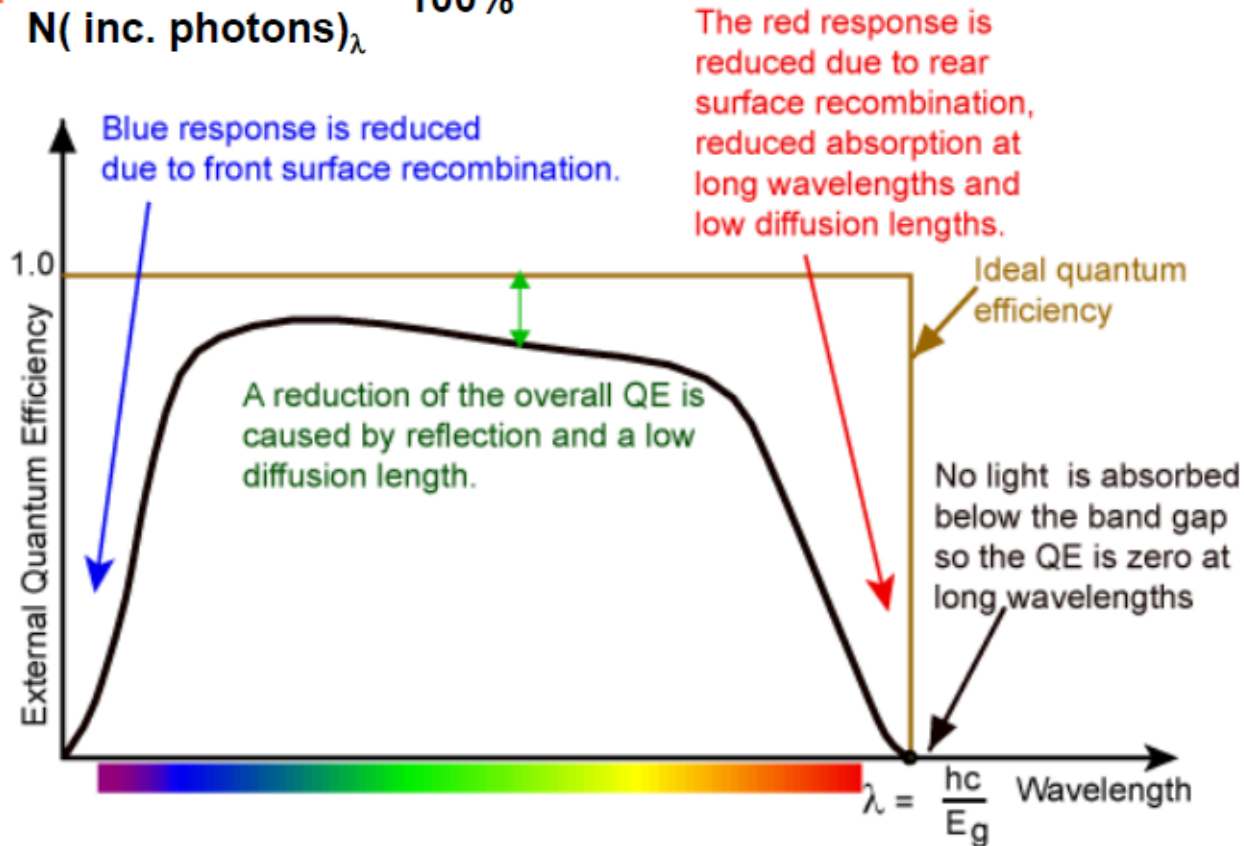Increase in J_{SC} in OSCs compromises V_{OC}, so an optimal balance needs to be found

Z. Fei et al., J. Mater. Chem., 2011, 21, 16257–16263;

C.-Y. Chang et al., Adv. Mater. 2012, 24, 549–553;

*Z. Li et al., Macromolecules 2014, 47, 21, 7407-7415;*

Quantum efficiency

$$EQE_\lambda = IPCE_\lambda = \frac{N(col.\ electr.)_\lambda}{N(inc.\ photons)_\lambda} \cdot 100\%$$

Blue response is reduced due to front surface recombination.

The red response is reduced due to rear surface recombination, reduced absorption at long wavelengths and low diffusion lengths.

Ideal quantum efficiency

A reduction of the overall QE is caused by reflection and a low diffusion length.

No light is absorbed below the band gap so the QE is zero at long wavelengths

1.0

External Quantum Efficiency

$\lambda = \dfrac{hc}{E_g}$ Wavelength

The quantum efficiency of a silicon solar cell.

Quantum efficiency is usually not measured much below 350 nm as the power from the AM1.5 spectrum contained in such low wavelengths is low.

Fill factor (FF)

(b)
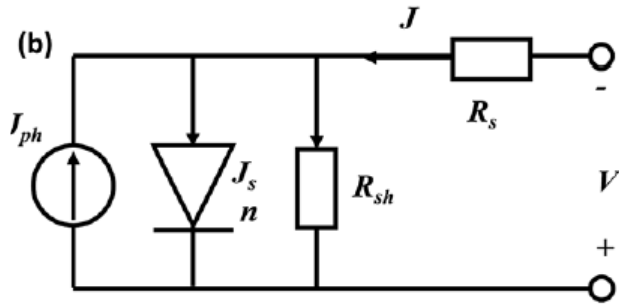
$$FF_0 = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1}$$

$v_{oc} = qV_{OC}/nkT$, normalized open circuit voltage

n - ideality factor of diode (typically 1.5–2.0 for OSCs)

q - the elementary charge

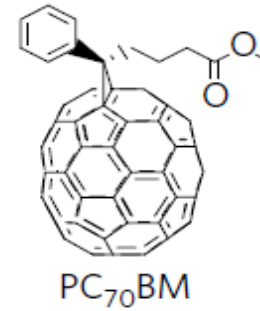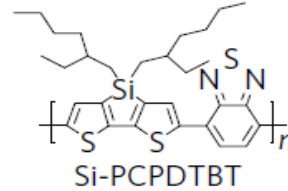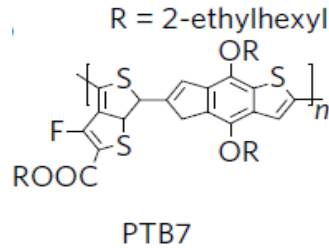k - the Boltzmann constant

$$FF_s = FF_0(1 - r_s)$$

$$FF_{sh} = FF_0\left[1 - \frac{(v_{oc} + 0.7)}{v_{oc}} \frac{FF_0}{r_{sh}}\right]$$

FF_0 - calculated from eqn

$r_s = R_s J_{SC}/V_{OC}$, the normalized series resistance

$$FF_{s+sh} = FF_s\left[1 - \frac{(v_{oc} + 0.7)}{v_{oc}} \frac{FF_s}{r_{sh}}\right]$$

From a semiconductor theory point of view, reaching high FF requires a small series resistance (R_s) and a large shunt resistance (R_{sh})

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W.-F. Su et al., J. Mater. Chem. A, 2016, 4, 5784–5801; X. Guo et al., Nature Photon. 2013, 7, 825–833

Fill factor: role of photoactive layer morphology

R = 2-ethylhexyl

PTB7

Si-PCPDTBT

$PC_{70}BM$

TEM images of **PTB7 : Si-PCPDTBT : PC$_{70}$BM** blends

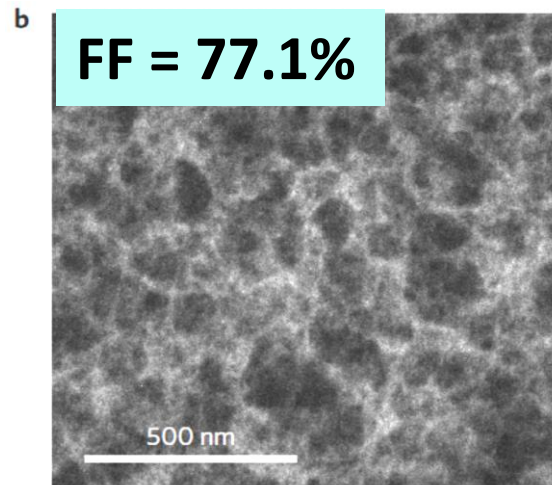**1 : 0 : 1.5**   **0.85 : 0.15 : 1.5**   **0.75 : 0.25 : 1.5**

Domain size

10-20 nm → 200 nm
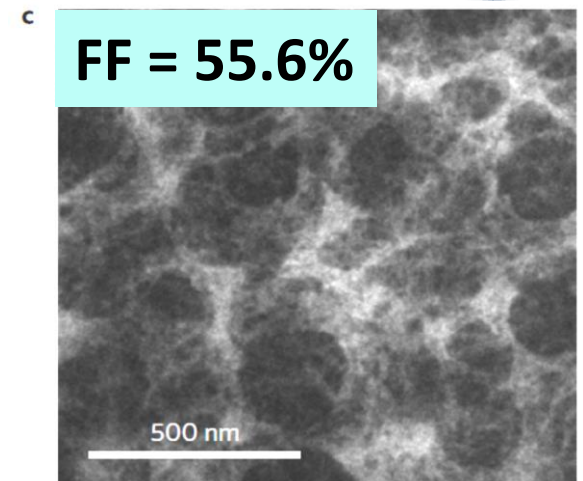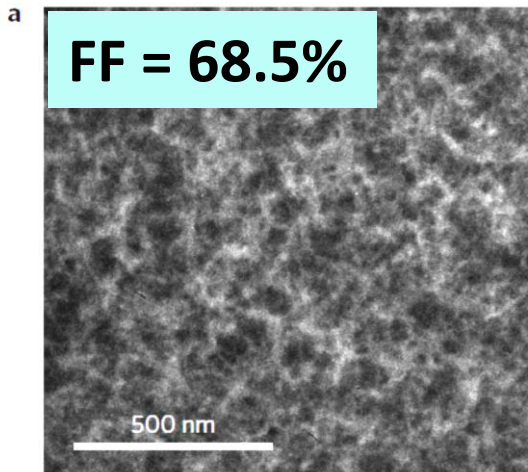
FF = 68.5%   FF = 77.1%   FF = 55.6%

500 nm   500 nm   500 nm

N. Gasparini et al., Nat. Energy, 2016 ,1, 16118

Power conversion efficiency
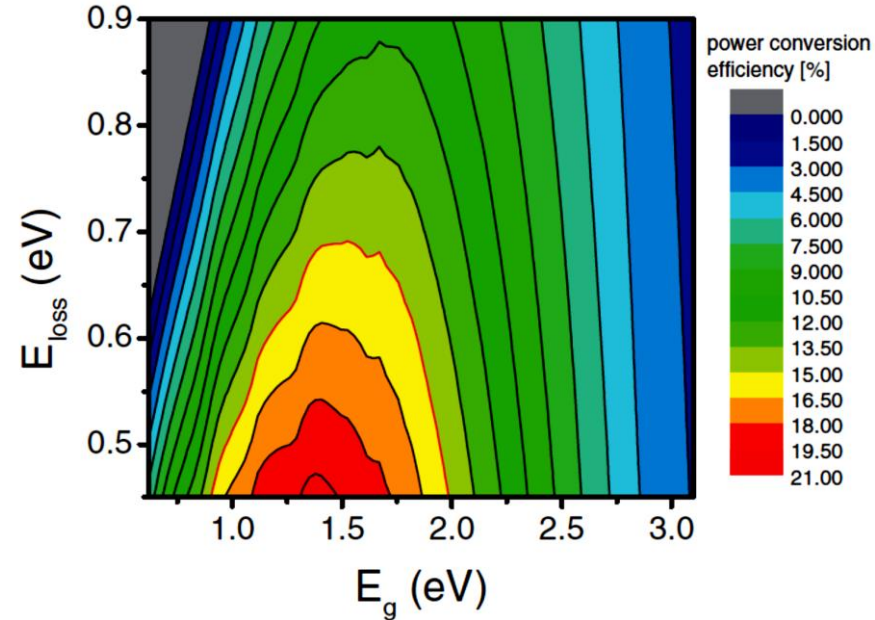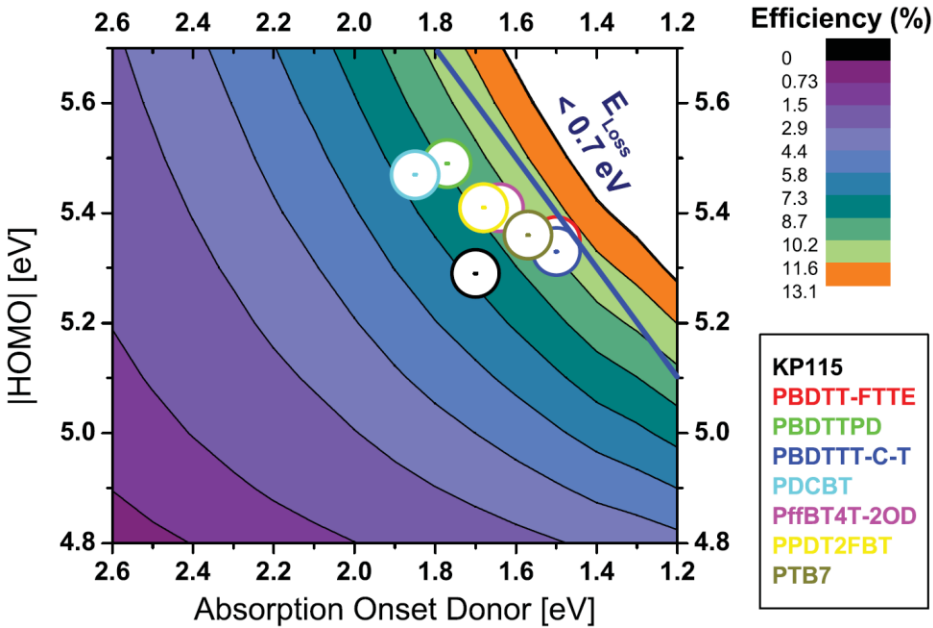
Assumptions:

V_{OC} losses = 0.7 eV ($E_{loss} = E_g - eV_{OC}$)
EQE = 70%, FF = 70%

PCE = 12-13%:

E_g = 1.2÷1.7 eV
HOMO= -5.7 ÷ -5.3 eV

Assumptions:

EQE = 80%, FF = 80%

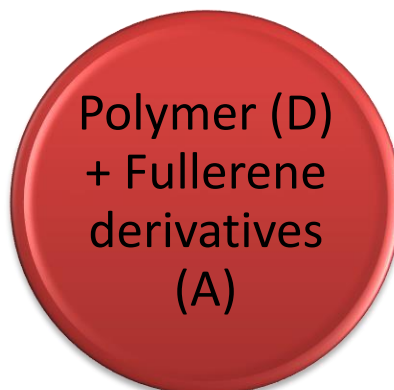**PCE = 12-13%:**

E_g = 0.75÷2.1 eV
E_{loss} = 0.75 eV
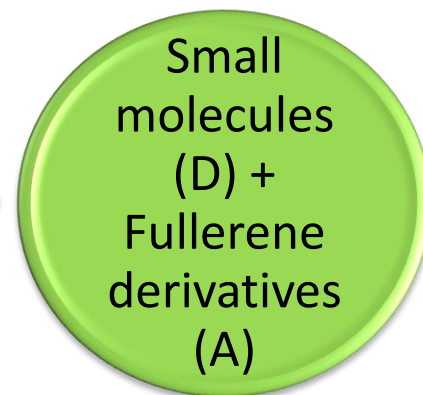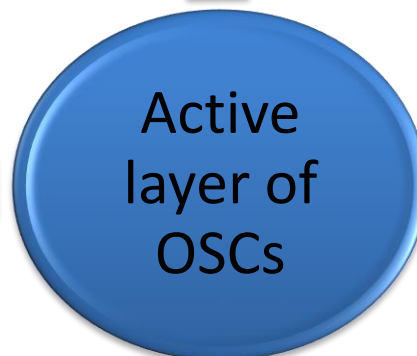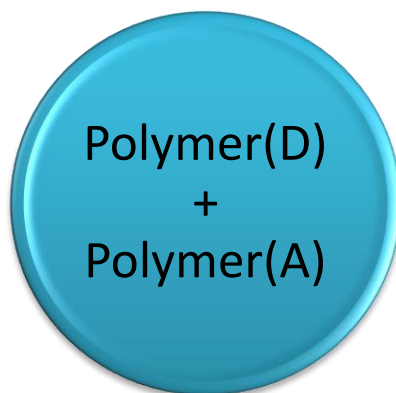
PCE >15%:

E_g = 1.0÷1.9 eV
E_{loss} < 0.60 eV

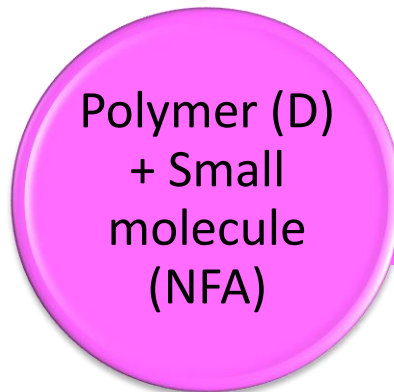$$PCE = \frac{(V_{OC} \times J_{SC} \times FF)}{P_{in}}$$

Materials for OSCs

PCE = 11.7 %

Polymer (D) + Fullerene derivatives (A)

PCE = 11.3 %

Polymer(D) + Polymer(A)

Active layer of OSCs

Small molecules (D) + Fullerene derivatives (A)
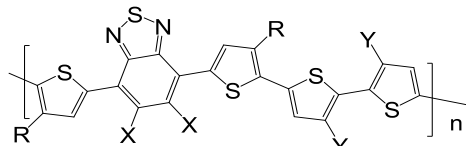
PCE = 11.0 %
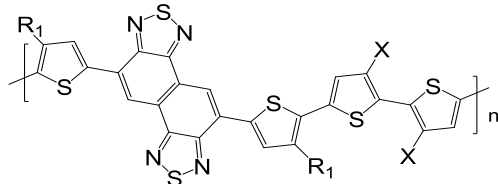
Polymer (D) + Small molecule (NFA)

PCE = 18.0 %

Most promising systems "Polymer (D) + Fullerene derivative (FA)"

P1: R=2-octyldodecyl, X=F, Y= H,
P2: R_1=2-octyldodecyl, X=H, Y=F
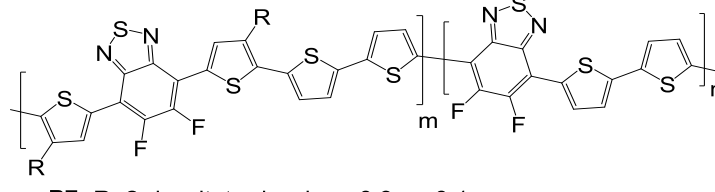**P3:** R_1=2-nonyltridecyl, X=F, Y=H

P4: R_1=2-octyldodecyl, X=F
P5: R_1=2-decyltetradecyl, X=H
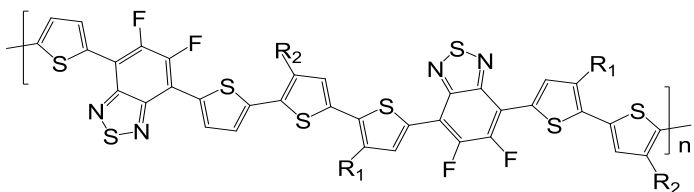
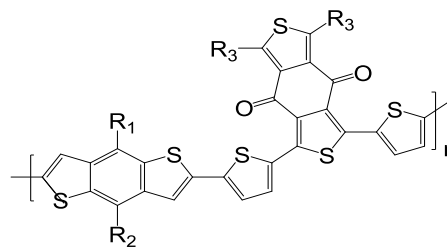**P6:** R_1=2-hexyldecyl, R_2=2-hexylnonyl

P7: R=2-decyltetradecyl, m=0.9, n=0.1
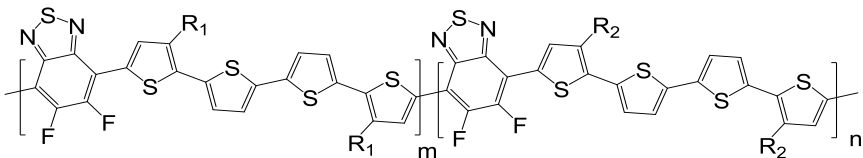
P8: m=0.75, n=0.25
R_1=(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)pentyl
R_2=2-decyltetradecyl

P9:R_1=R_2=5-(2-ethylhexylthio)thiophen-2-yl,
R_3=2-butyloctyl
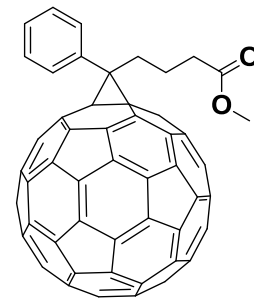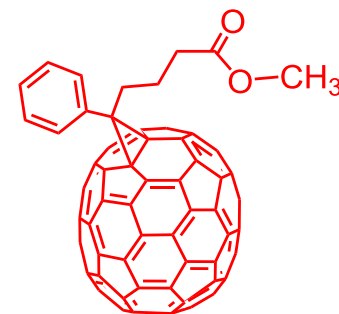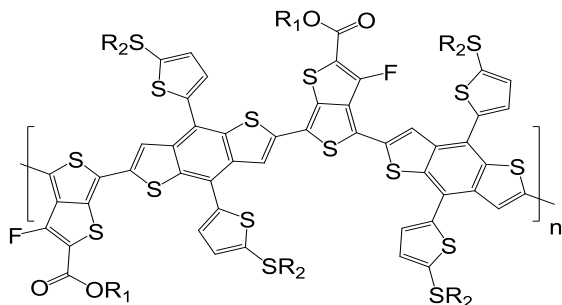
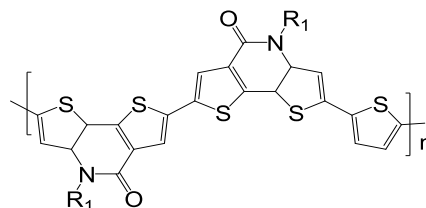**P10:** R_1=2-ethylhexyl, R_2=n-octyl

P11: R_1=2-octyldodecyl

[60]PCBM

[70]PCBM
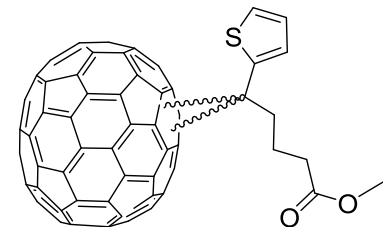
TCBM

Most conjugated polymers comprise "strong acceptor" benzothiadiazole units, "strong donor" thiophene units and their fluorinated counterparts

Most promising systems "Polymer (D) + Small molecule (NFA)"
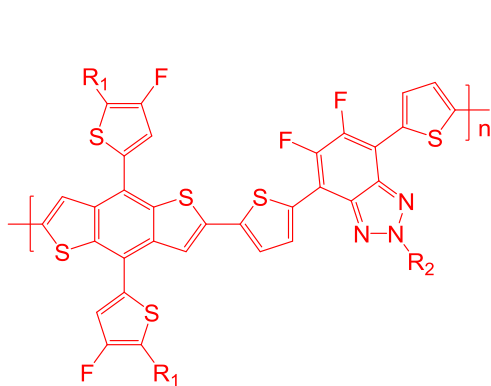
P12: R_1= 2-ethylhexyl, R_2=2-hexyldecyl
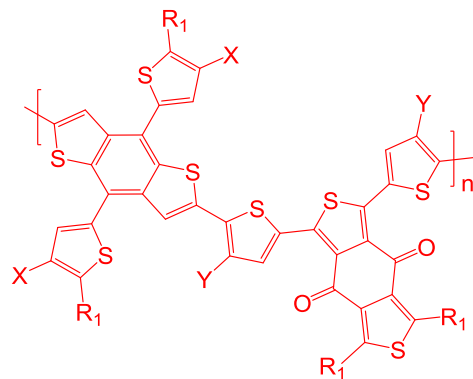
P13: R_1= 2-ethylhexyl, X=H, Y=F
P14: R_1= 2-ethylhexyl, X=F, Y=H
P15: R_1= 2-ethylhexyl, X=Cl, Y=H

ID-M: R= 4-hexylphenyl
C8-ITIC: R= n-octyl

IT-4F: R= 4-hexylphenyl
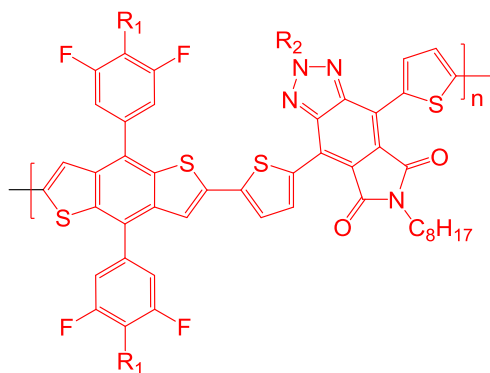
P15: R_1= 2-ethylhexyl, R_2= 3-ethylheptyl
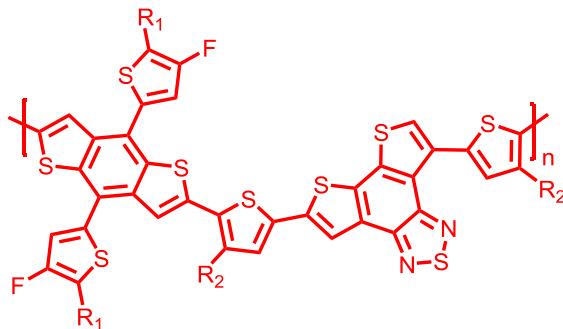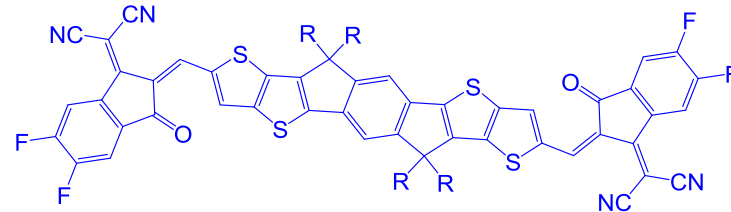
P17: R_1= 2-ethylhexyl, R_2= 2-butyloctul
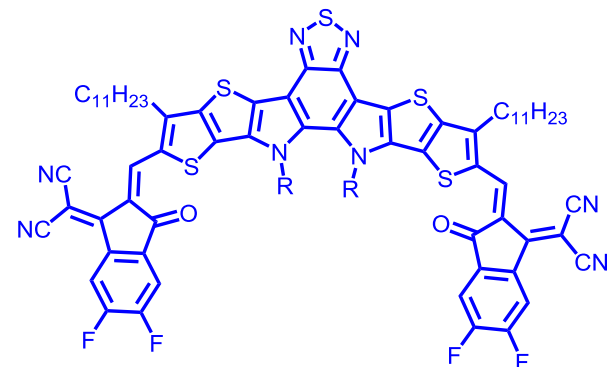
Y6: R= 2-ethylhexyl, X=F
BTP-4Cl: R= 2-ethylhexyl, X=Cl

Conjugated polymers comprise "weak donor" blocks and "weak acceptor" blocks
Acceptor components are fused-ring heterocyclic compounds with planar structure

Upscaling of OSCs

$ca.$ 50-200 cm^2

$ca.$ 10-25 cm^2

$ca.$ 1 cm^2

$ca.$ 2-5 mm^2

18-16%

15-12%

10-4%

7-3%
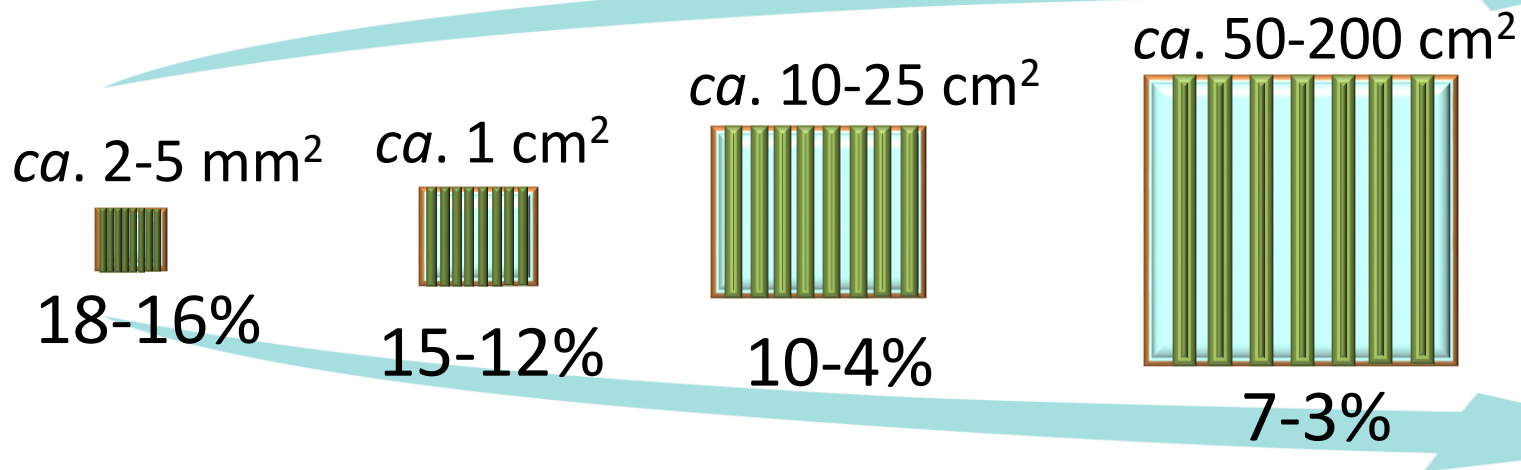
Towards flexible devices
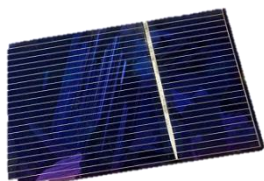
5.3% in rigid module (35 cm^2)

7.7% in rigid module (7.5 cm^2)

16.7% in rigid cell (4.0 mm^2)

4.2% in flexible module (35 cm^2)

5.6% in flexible module (7.5 cm^2)

14.06% in flexible cell (4.0 mm^2)

Q. Liu, *Science Bulletin,* ***2020,*** *DOI: 10.1016/j.scib.2020.01.001;* B. Fan et al., *Sci. China. Chem.* **2019**, 62, 746 ; *Y. Han et al., Adv. Sci.* ***2019***, *6, 1901490; B. Fan et al., ACS Energy Lett.* **2019**, 4, 10, 2466-2472; K. M. Huang et al., *Sol. RRL* **2019**, 3, 1900071; Lucer et al., *Energy Environ. Sci.*, **2016,** 9, 89-94; N. Li et al., *Adv. Energy Mater.* **2014**, 1400084; T Yan et a., *Adv.Mater.,* **2019**, 31, 1902210

Thickness-insensitive photovoltaic materials

20%-40% of the incident photon flux is wasted → J_{SC} limited

AL thickness ~100 nm

J_{SC}=19.52 mA cm^{-2}

FF =78%

PCE =13.5%

electrode
AL ~100 nm
ITO
Glass

→

electrode
AL ~500 nm
ITO
Glass
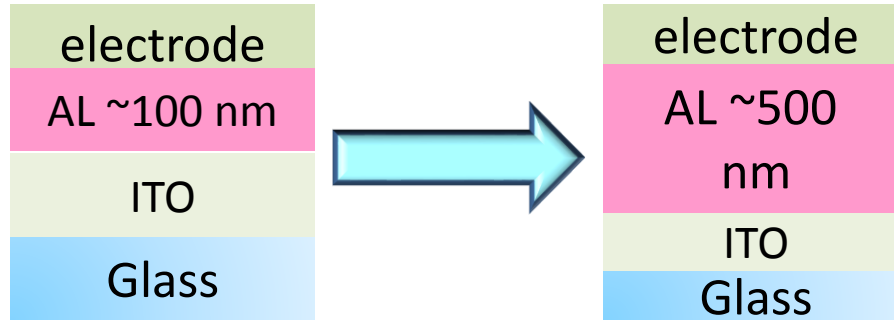
The increased probability of charge recombination → *FF* limited

AL thickness ~500 nm

J_{SC}= 19.78 mA cm^{-2}

FF =53%

PCE =9.03%

OSCs performance with thick photoactive layer – promising candidates for scalable fabrication

System	Thickness, nm	V_{OC}, mV	J_{SC} mA cm^{-2}	FF, %	PCE, %	Ref.
PffBT4T-2DT/[70]PCBM	440	750	15.10	57.7	6.53	1
PM6/F–2Cl	600	879	19.61	58.0	10.05	2
NT812/[70]PCBM	1000	720	8.12	62.1	8.35	3
PNTT-H/[70]PCBM	1050	750	19.90	59.6	9.00	4

[1] X. Zhu et al., *Chem. Mater.* **2016**, *28*, 943; [2] Y. Zhang et al., *Adv. Energy Mater.* **2019**, 9, 1902688; [3] Y. Jin et al., *Adv.Mater.***2016**, 28, 9811–9818;[4] Y. Jin et al., *Adv. Energy Mater.* **2017**, 1700944.

Stability of OSCs
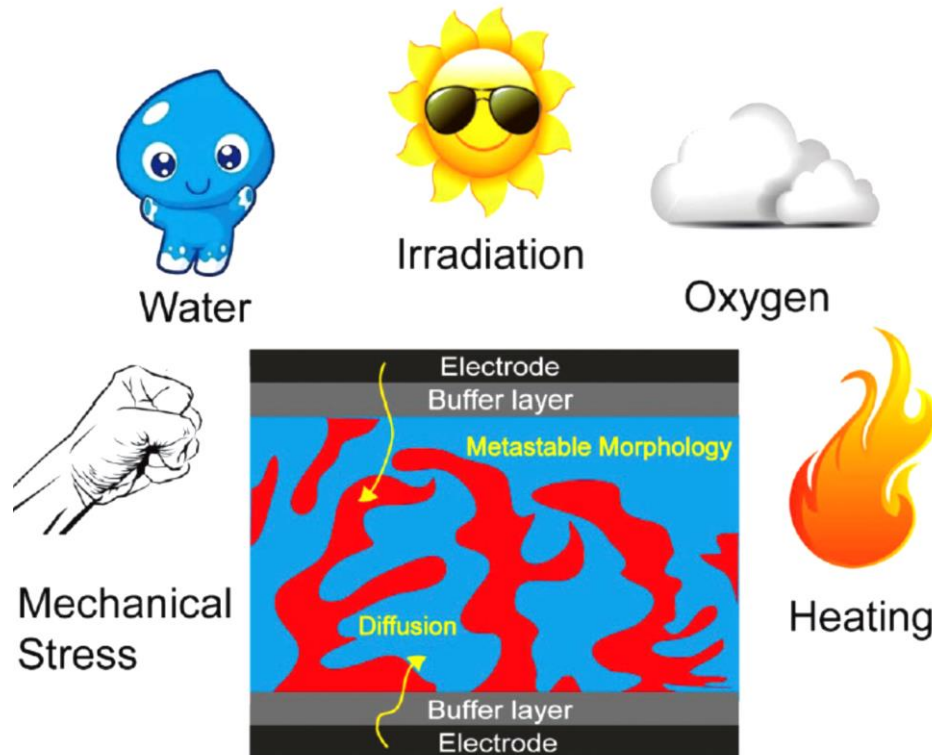
✓ Photochemical destruction of active layer materials

✓ Morphological destruction of active layer (aggregation, materials migration, etc.)

✓ Destruction of electrodes