中国科学技术大学
University of Science and Technology of China

有机高分子固体概述

徐航勋

Email: *hxu@ustc.edu.cn* Website: *http://staff.ustc.edu.cn/~hxu*

合肥微尺度物质科学国家研究中心
中国科学院软物质化学重点实验室
中国科学技术大学高分子科学与工程系

授课时间与考核方式

授课时间：

这门课每周1次课，周五下午6/7节课，授课时间大约是8~10周左右

成绩及考核方式：

每人作一次ppt，综述有机高分子固体相关文献，讲10分钟

闭卷考试，时间90分钟

授课内容

- 绪论、概论、历史
- 导电高分子
- 高分子半导体
- 二维高分子固体
- 有机晶体 (导体和超导体)
- 有机固体中的能量传递

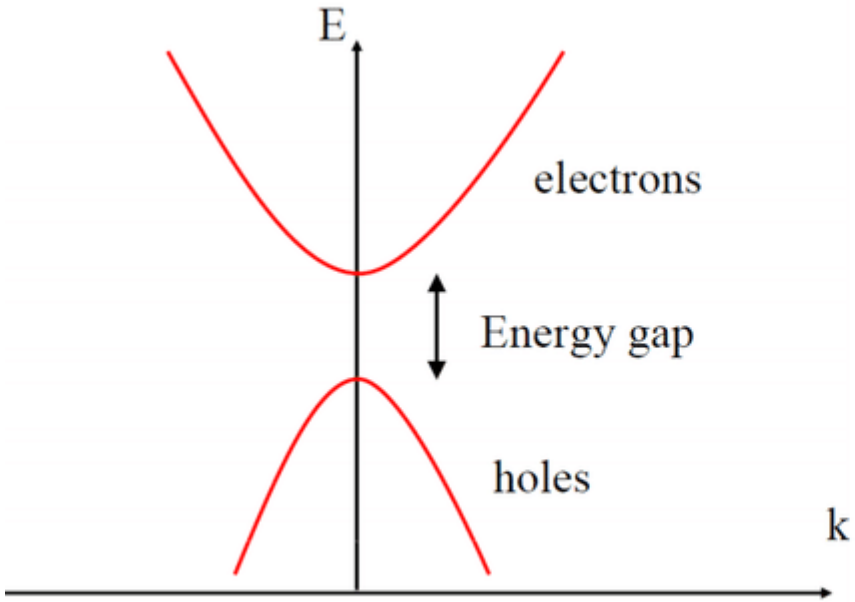
几个概念

激子 exciton

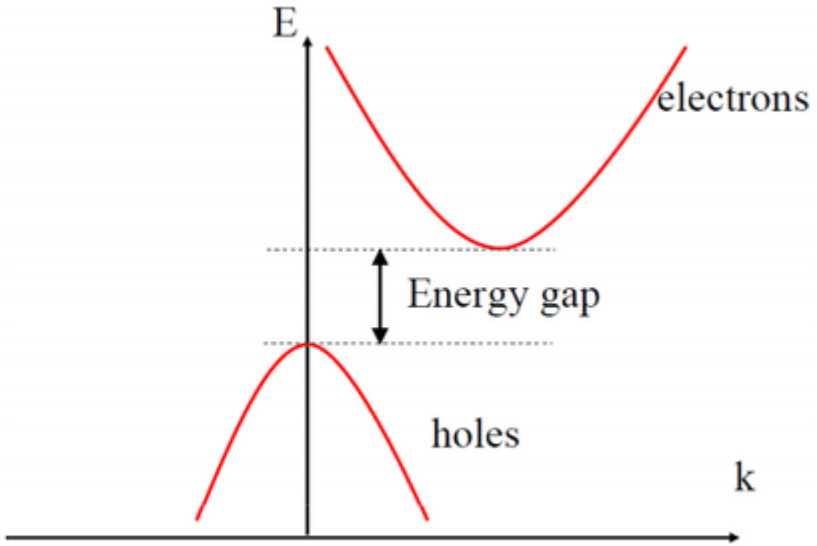
极化子 polaron

声子 phonon

孤子 soliton

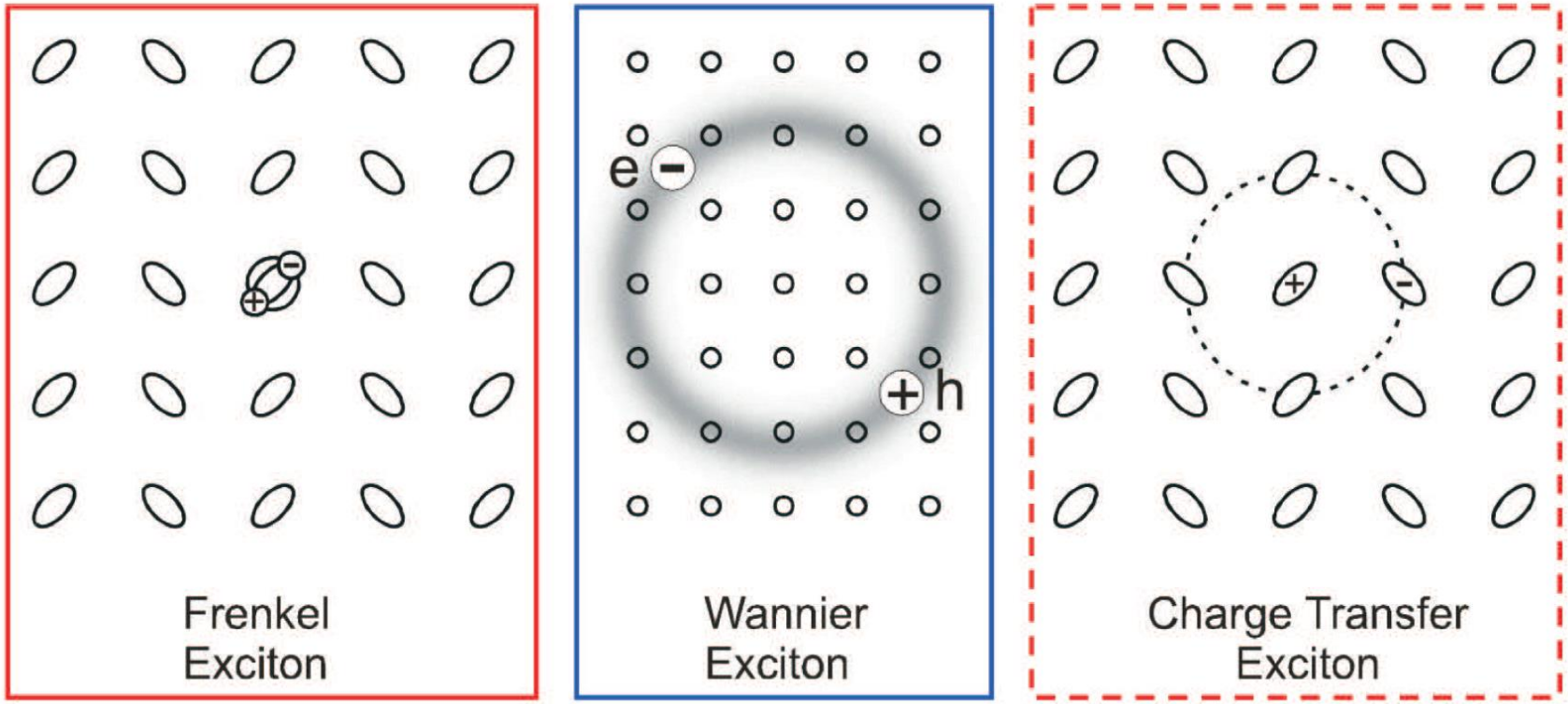


Direct bandgap semiconductors



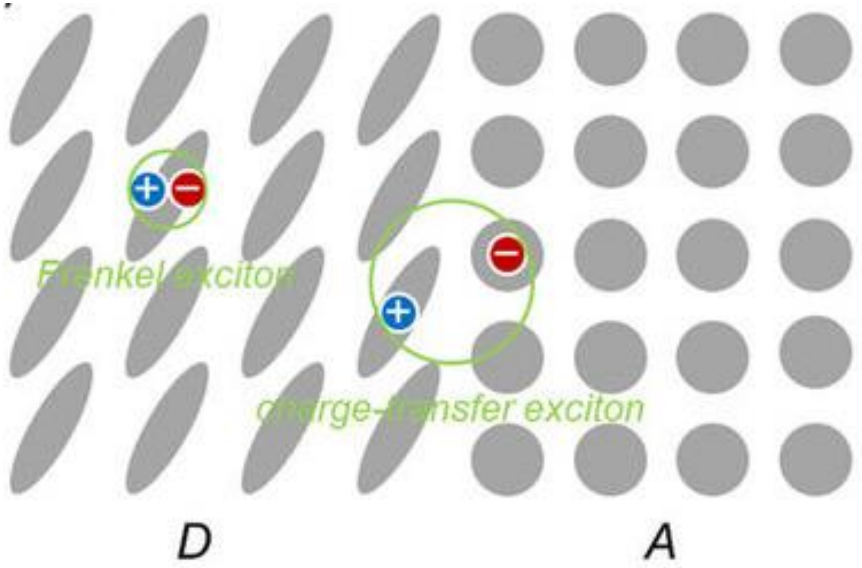
Indirect bandgap semiconductors

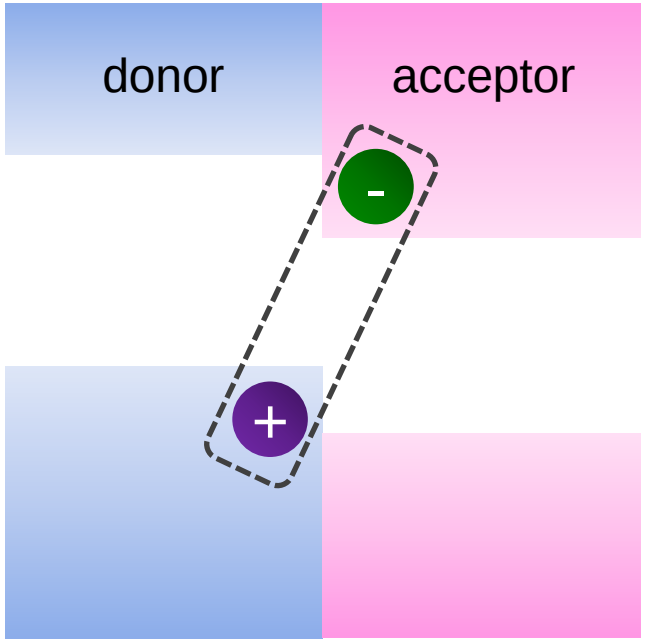
Excitons in Different Materials



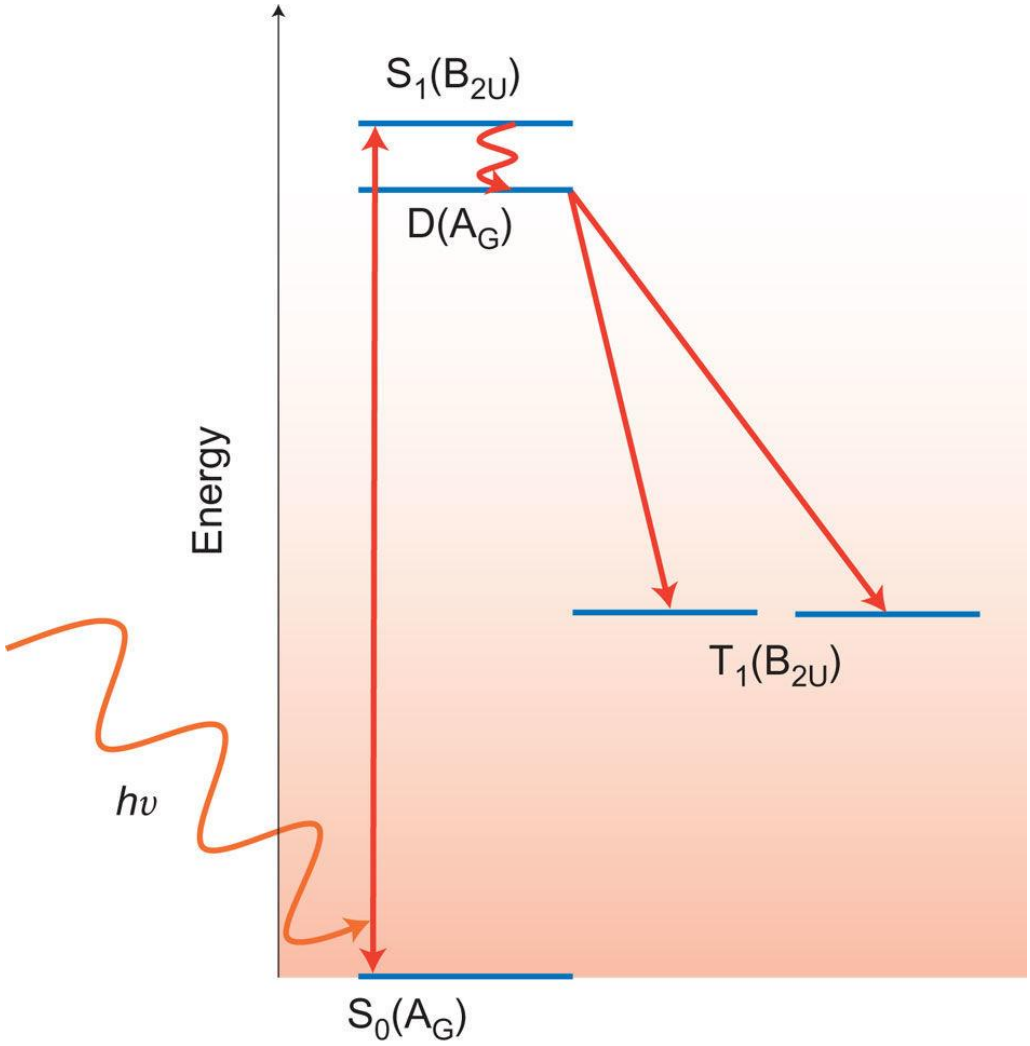
~1 eV
~1 nm

~10 meV
~10 nm


Frenkel exciton
charge-transfer exciton
D
A

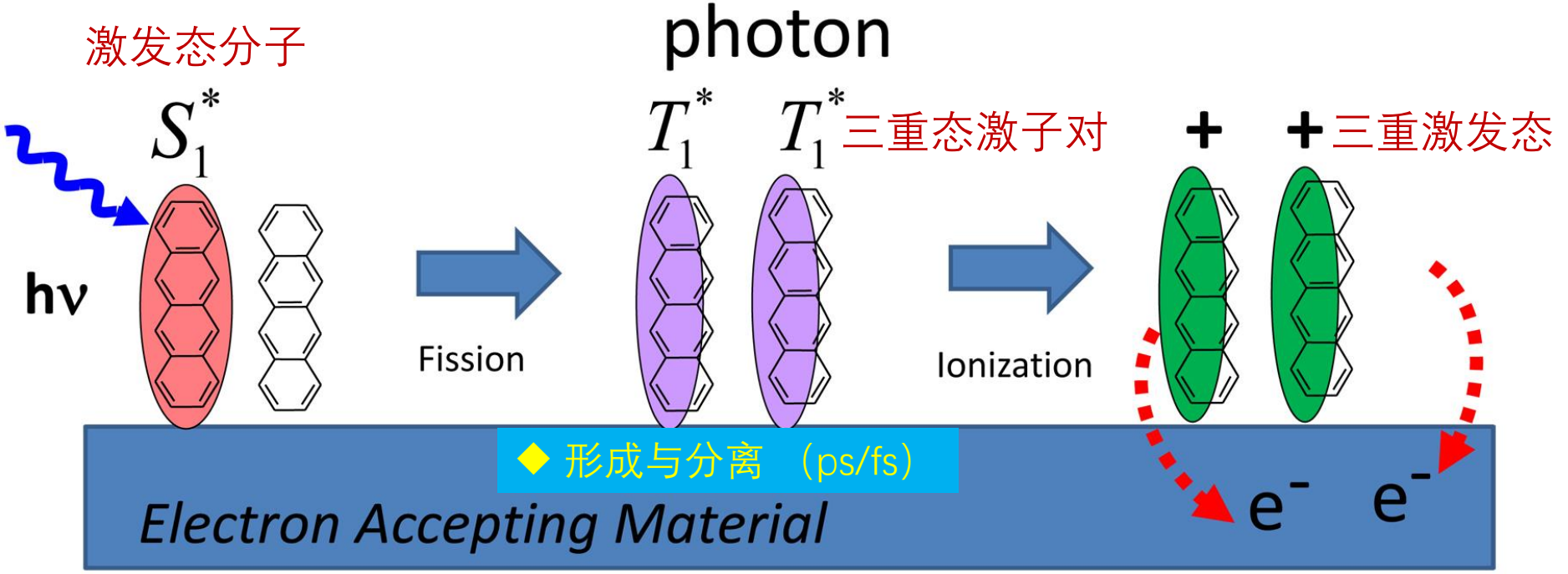

donor
acceptor
-
+

Singlet Fission

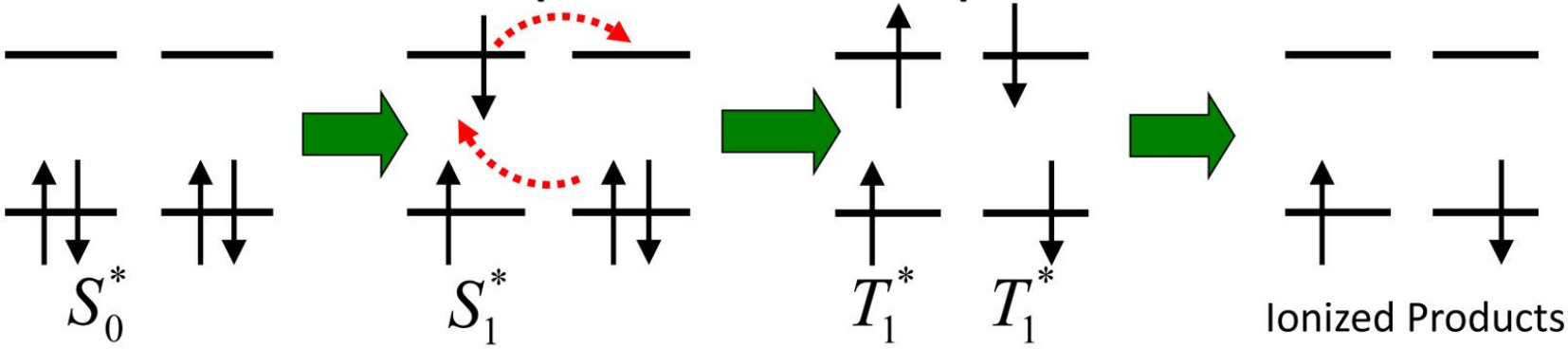


单线态裂分（Singlet Fission, SF）是指当一个有机半导体分子吸收一个光子产生单线态激子（singlet exciton）后，通过一个自旋允许的裂分过程形成两个三线态激子（triplet exciton），即吸收一个光子后可以产生两个三线态激子 (提出于1965年).

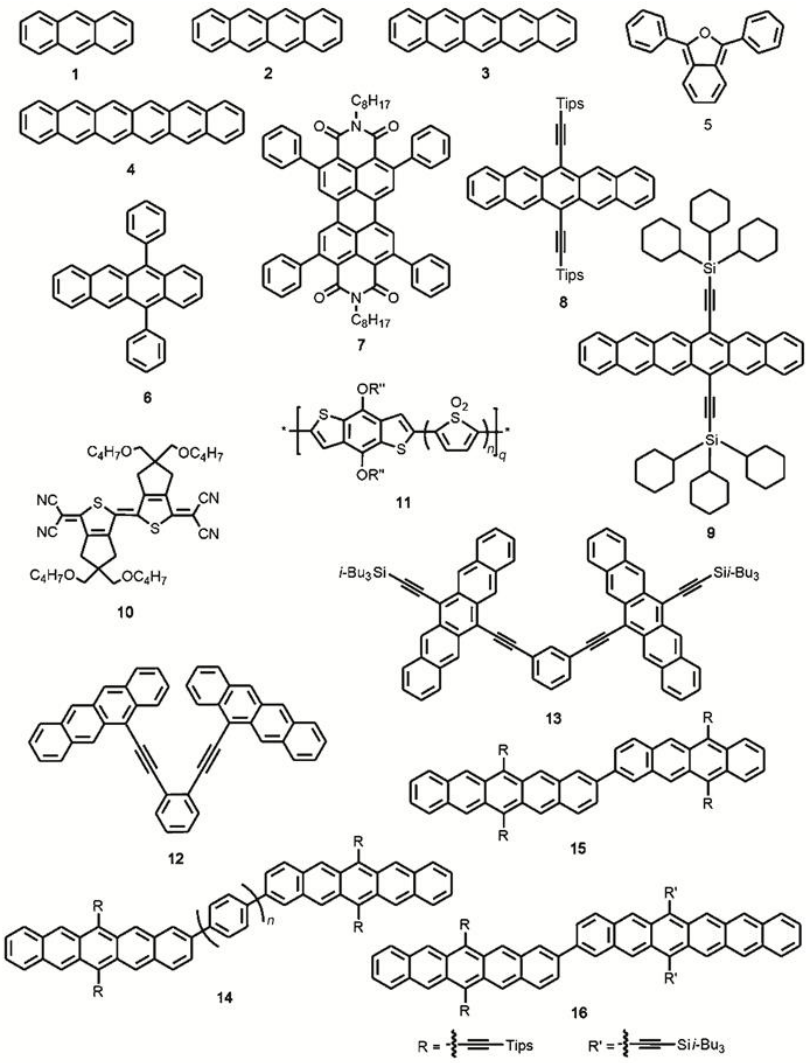
Singlet Fission: 2 excitons for the price of 1 photon



Harvest 2 electron-hole pairs for 1 absorbed photon in a solar cell.

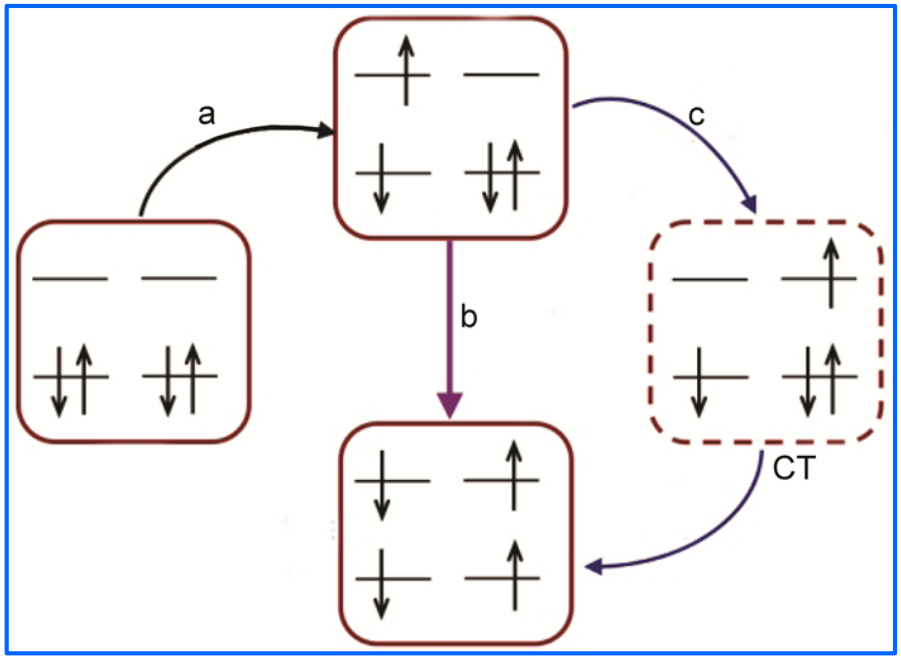


化学结构



- 基态为闭壳结构的交替型碳氢化合物
- 基态为开壳结构的双自由基型分子

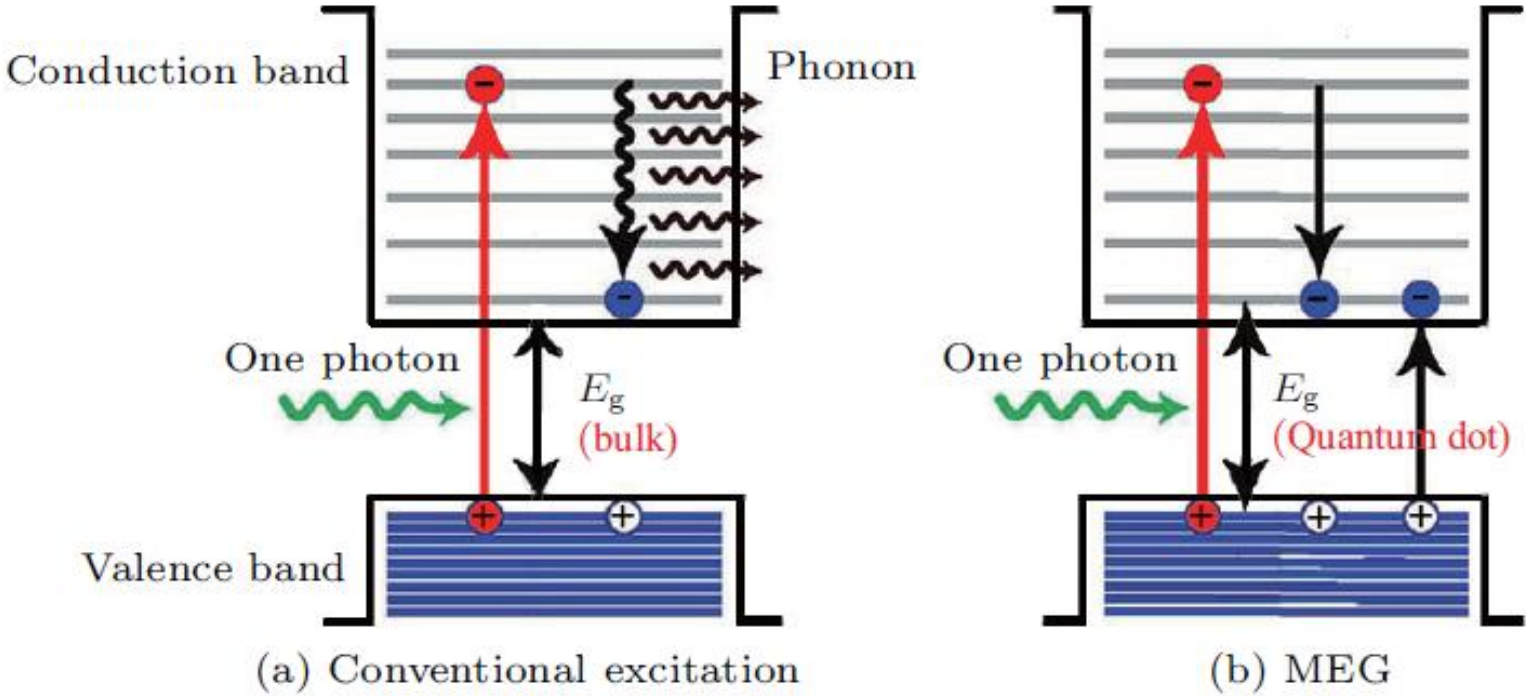
激子裂分过程



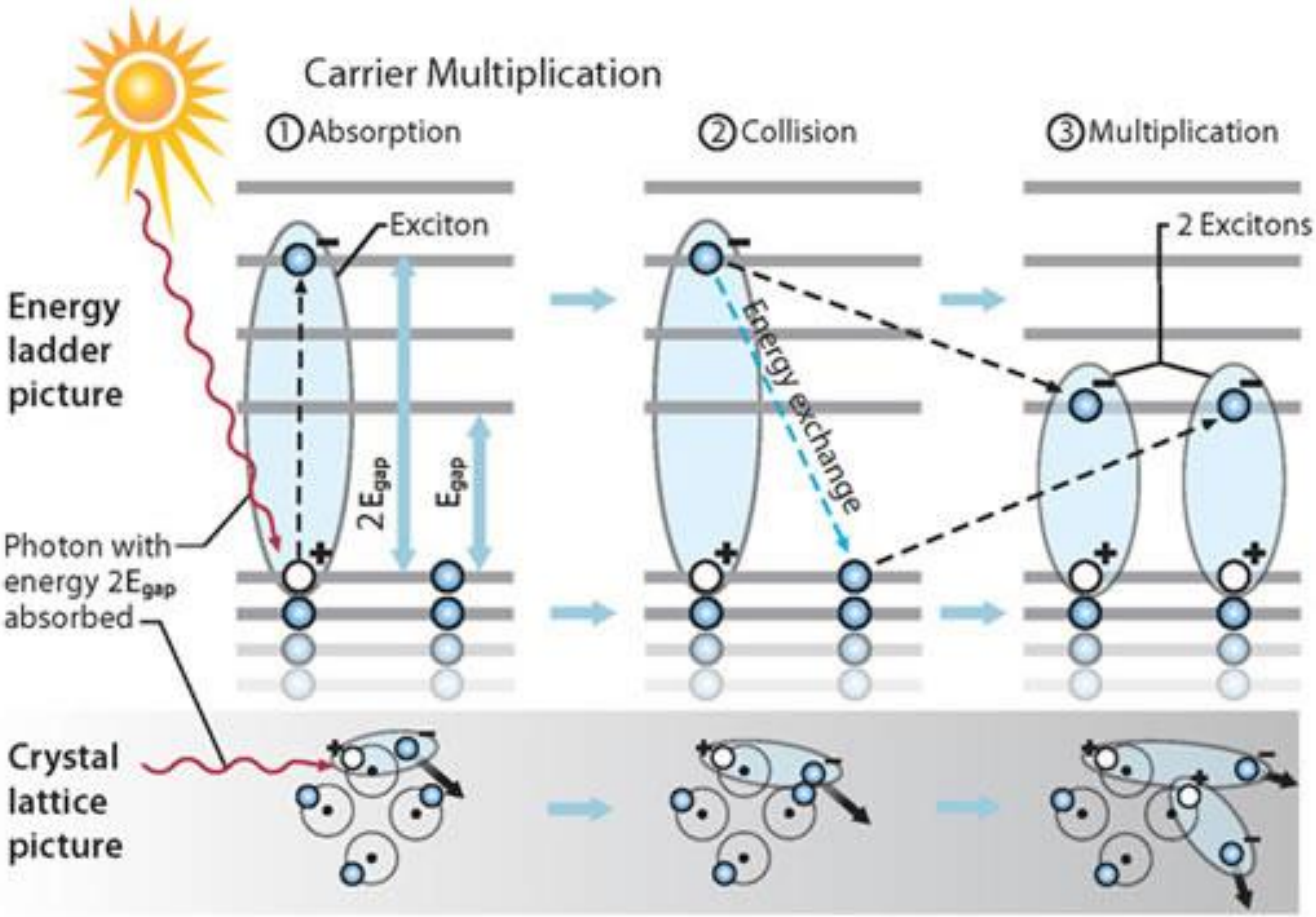
能量要求?

$$E(S_1),\ E(T_2) \geq 2E(T_1)$$

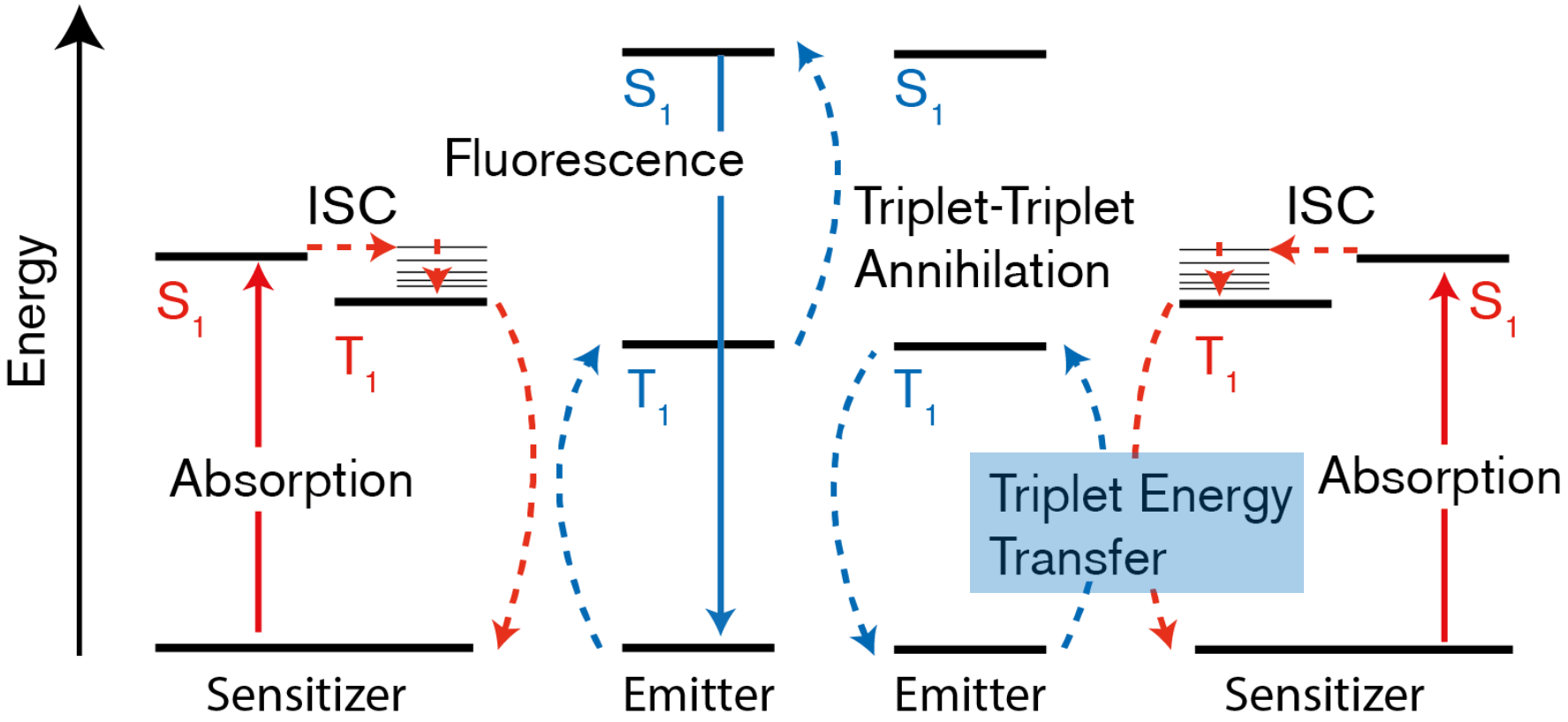
Multi Exciton Generation (MEG) 多重激子效应



Multi Exciton Generation (MEG) 多重激子效应

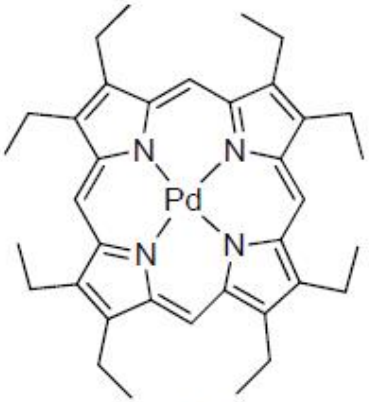


三重态-三重态湮灭上转换
(Triplet-triplet annihilation upconversion，简称TTA上转换)

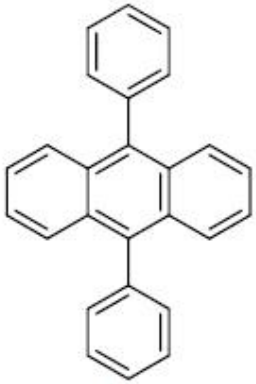


遵循Dexter机制，发生能量传递和湮灭的分子需要其碰撞半径内才能完成

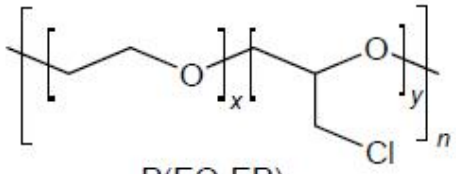
三重态-三重态湮灭上转换



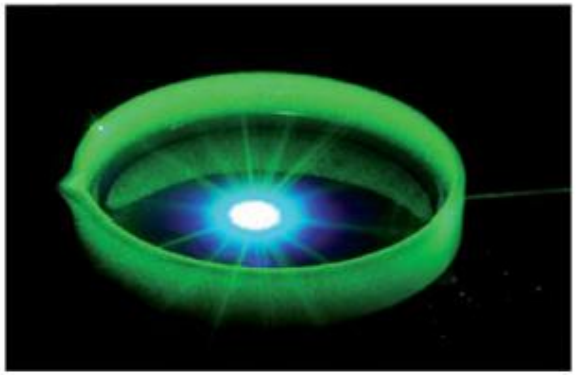
S-1

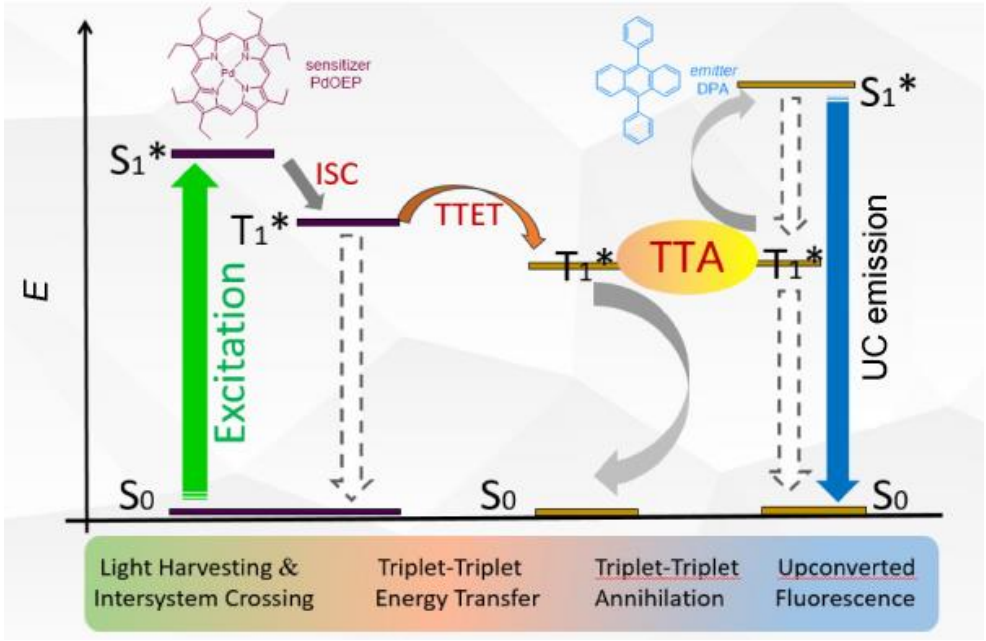


A-1



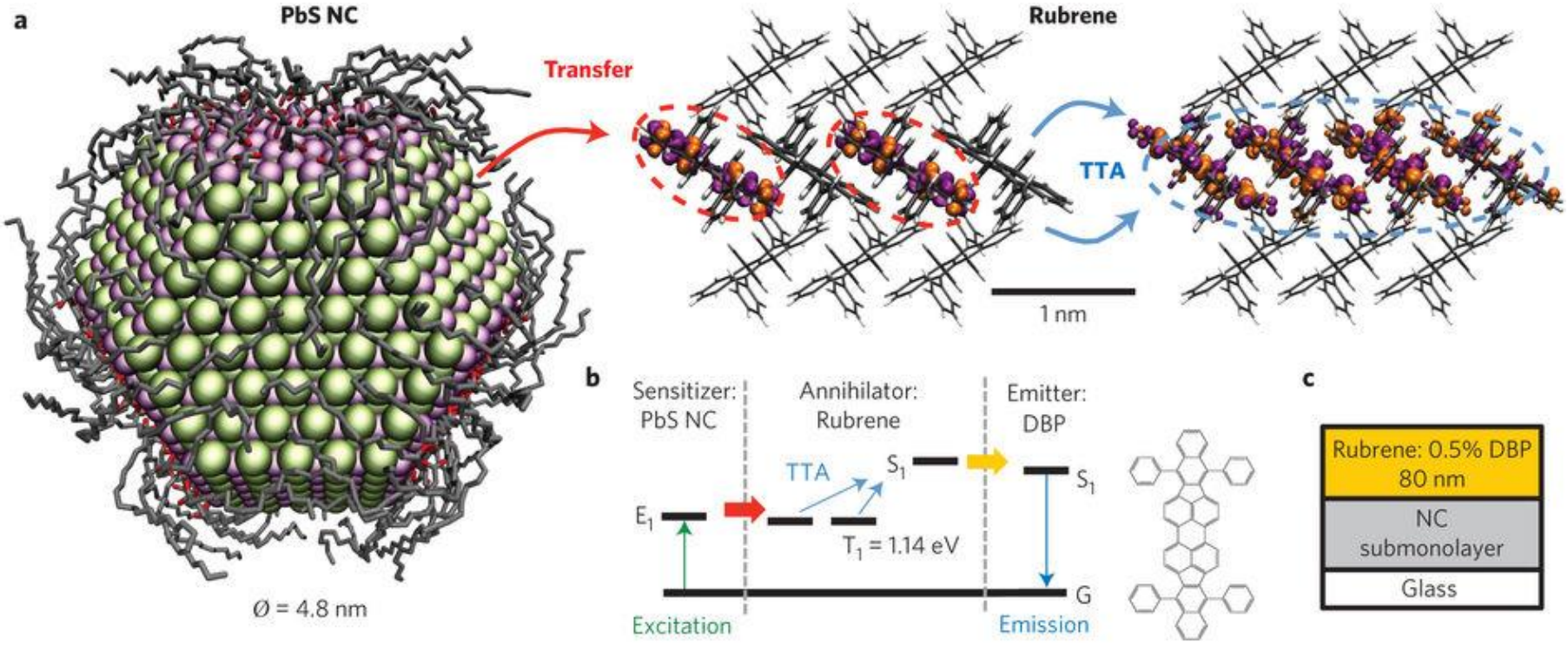
P(EO-EP)



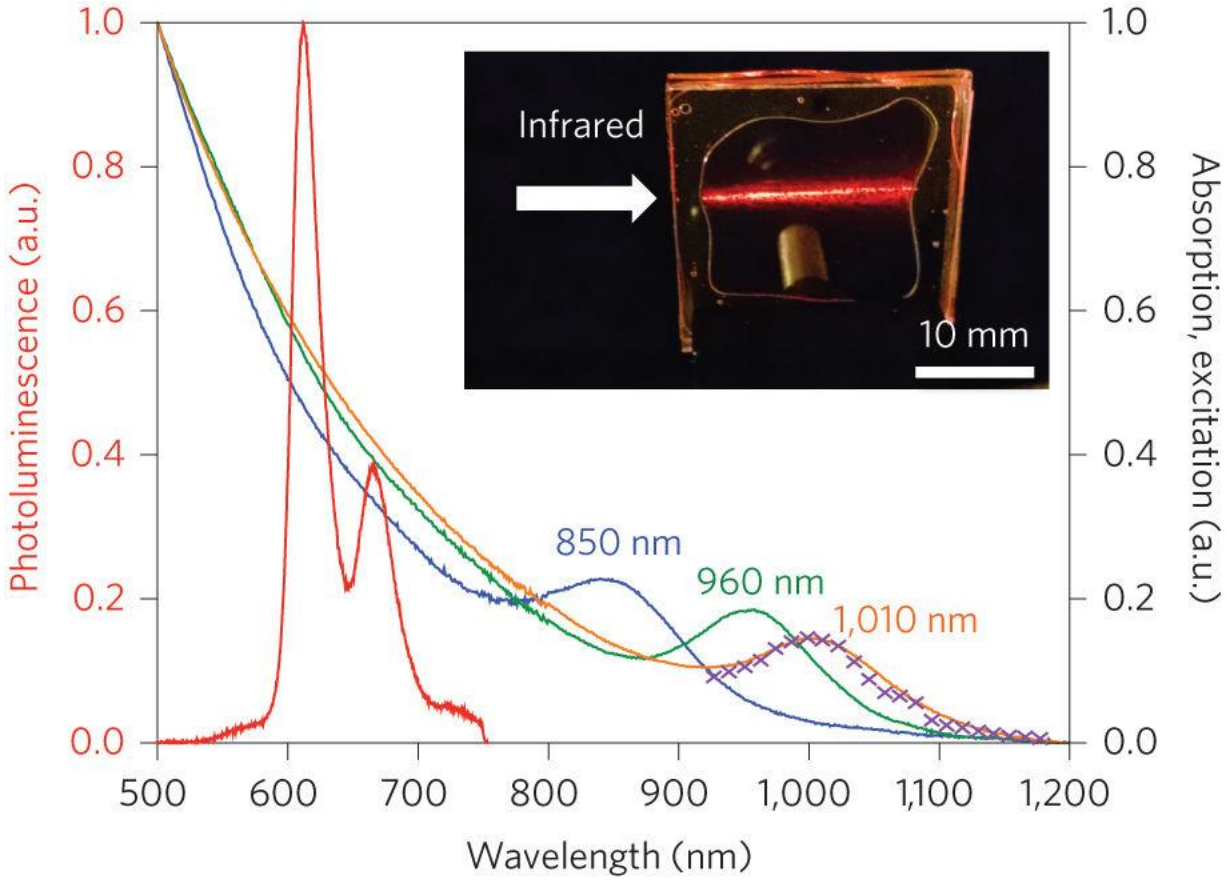


基于TTA 上转换的三重态光敏剂和能量受体之间的Jablonski图及能量传递过程

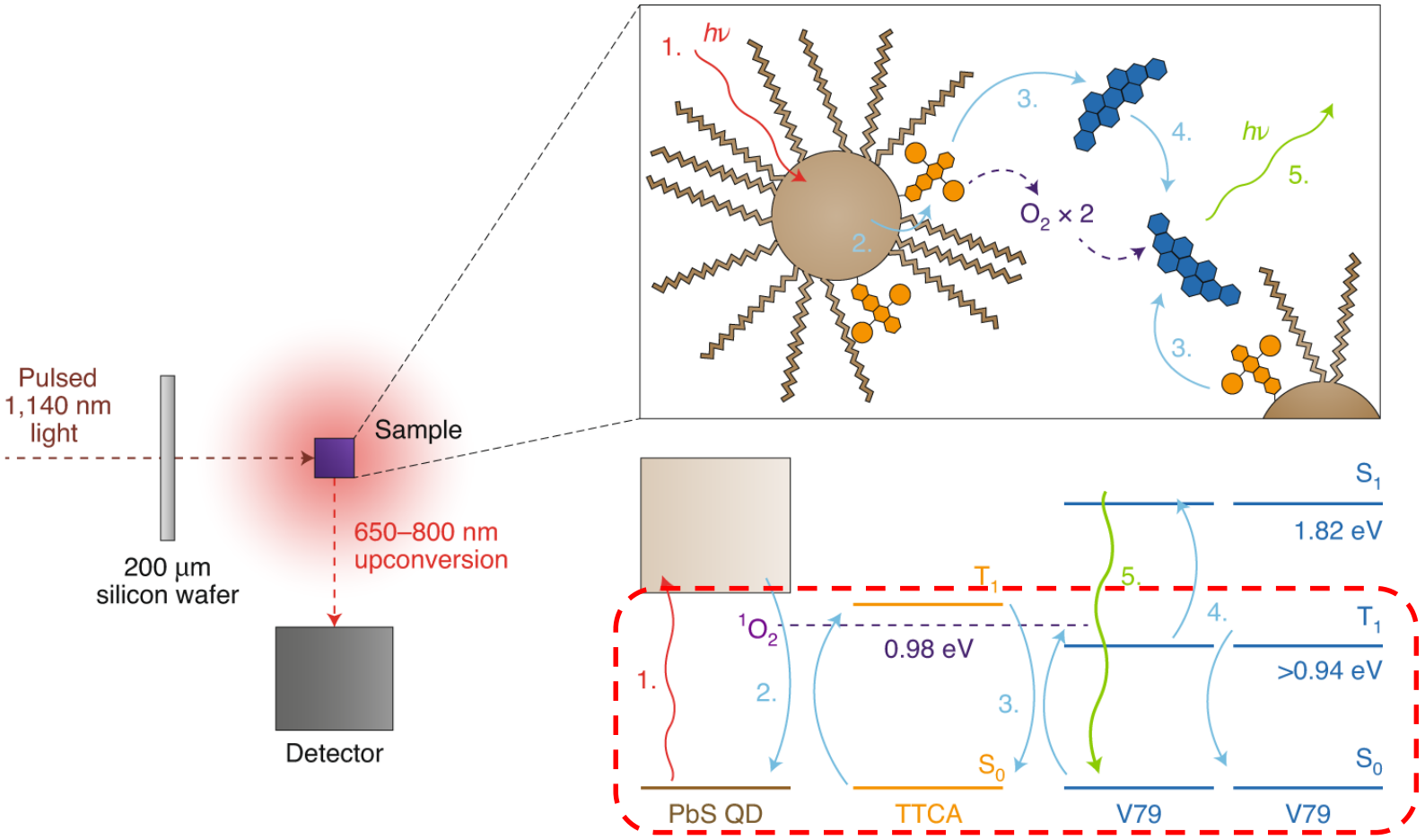
有机功能固体材料研究---上转换



有机功能固体材料研究---上转换

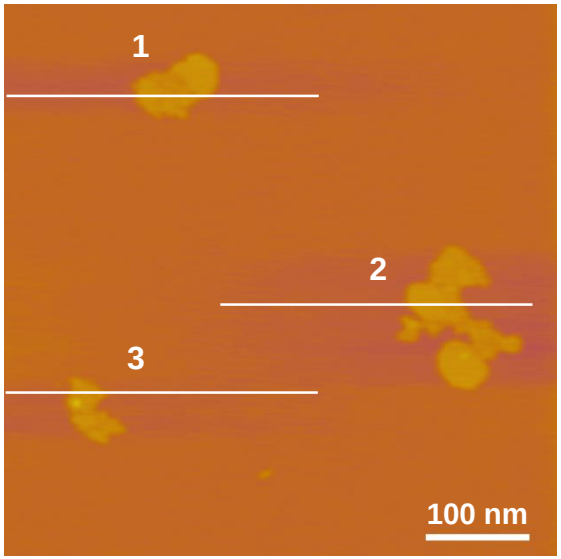


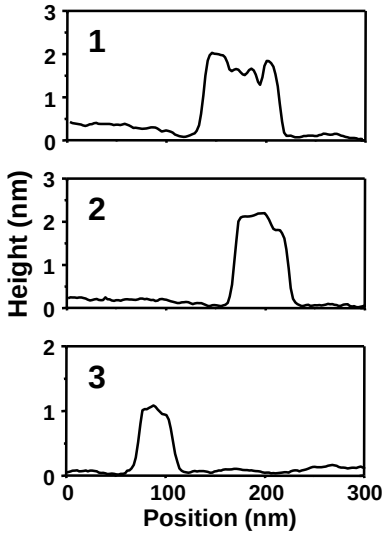
有机功能固体材料研究---上转换

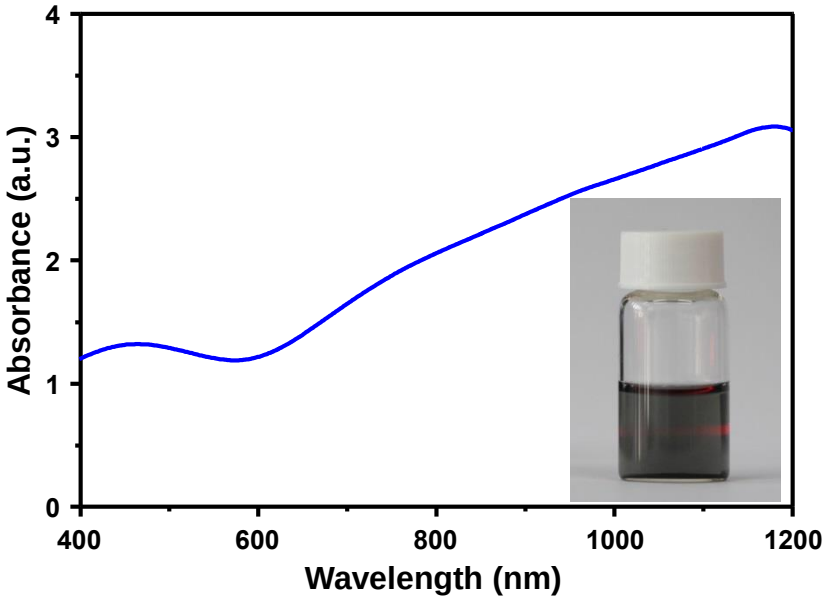


能级调控

二维聚吡咯纳米片


1
2
3
100 nm


1
2
3
Height (nm)
Position (nm)
0
100
200
300

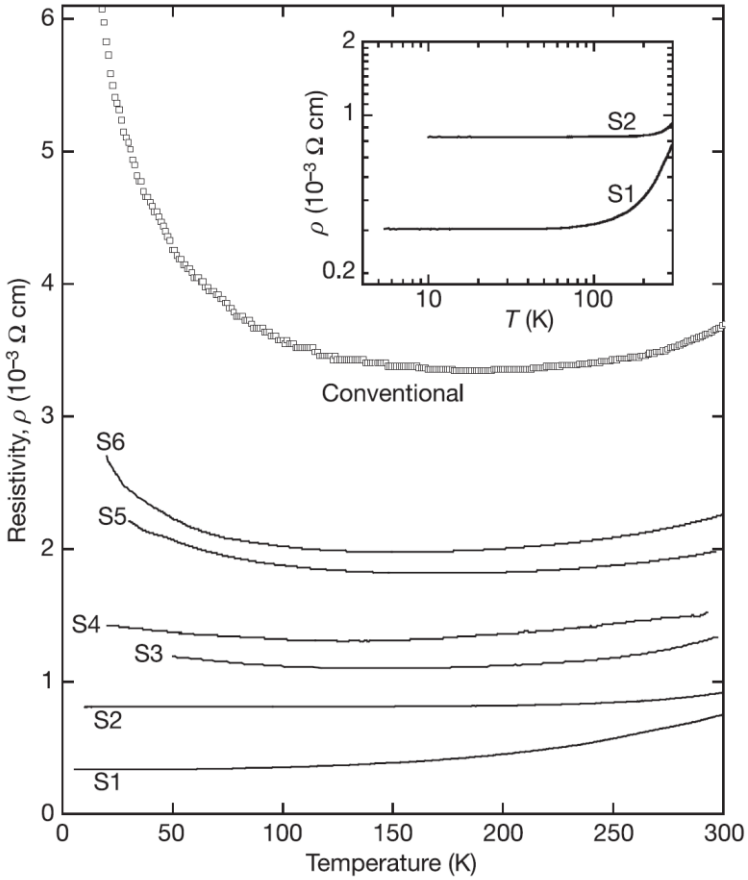

Absorbance (a.u.)
Wavelength (nm)
400
600
800
1000
1200

Vol 441|4 May 2006|doi:10.1038/nature04705 nature

LETTERS

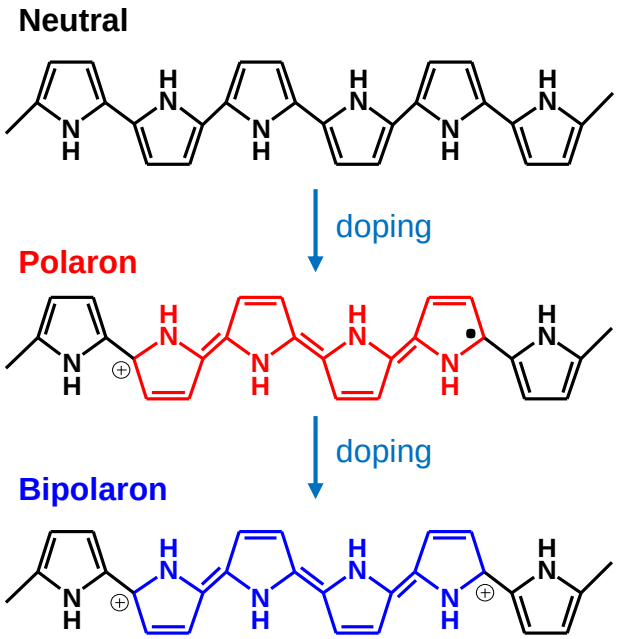
Metallic transport in polyaniline

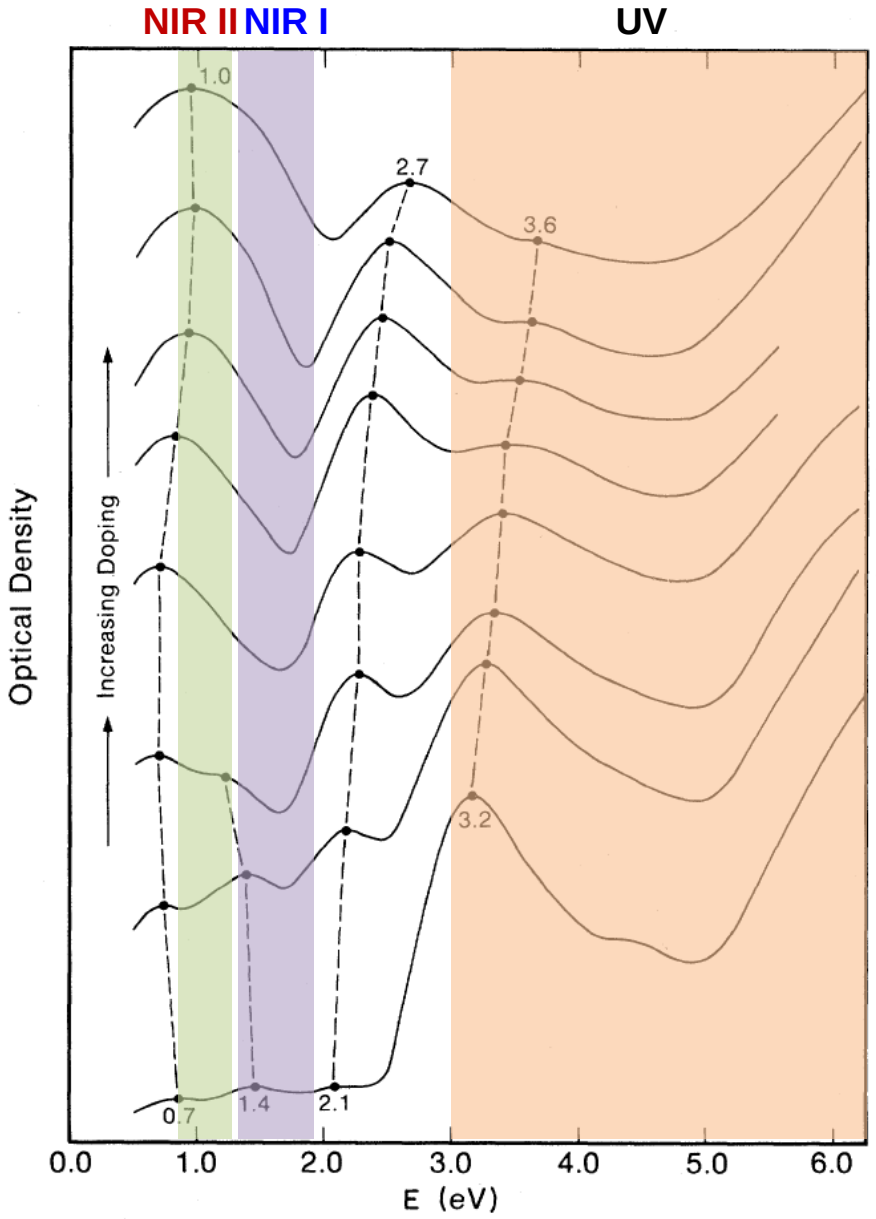
Kwanghee Lee[1,2]*, Shinuk Cho[1], Sung Heum Park[1], A. J. Heeger[2], Chan-Woo Lee[3] & Suck-Hyun Lee[3]*



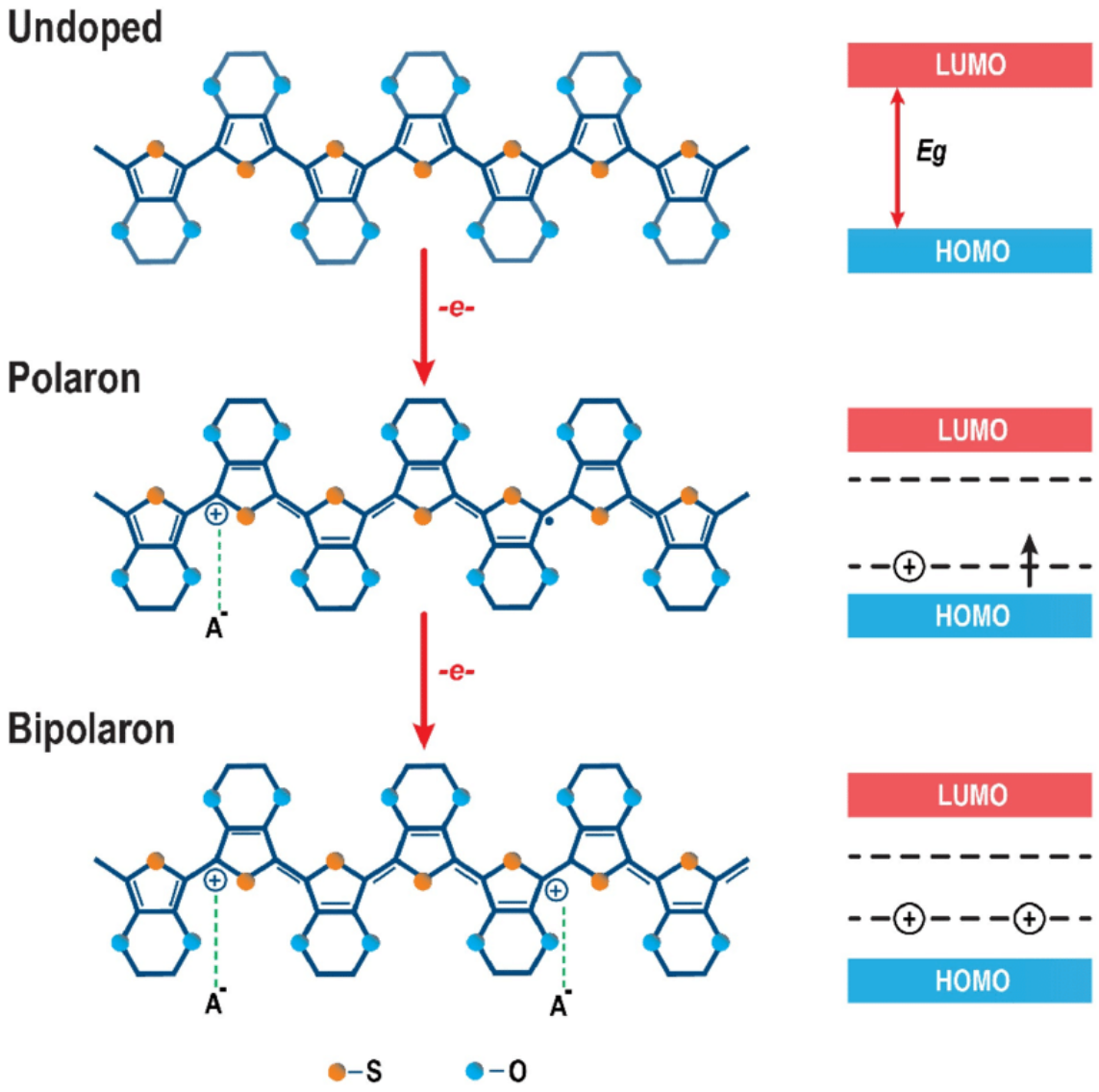
For more highly conducting samples (S5 → S1), the resistivity minimum weakens and shifts down to lower temperature and eventually disappears in the S1 and S2 samples

二维聚吡咯纳米片

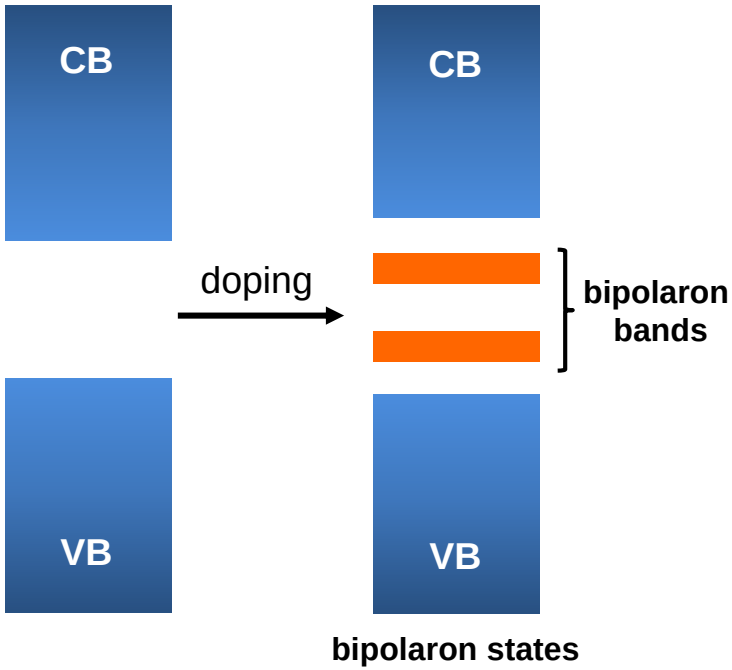

Neutral
doping
Polaron
doping
Bipolaron

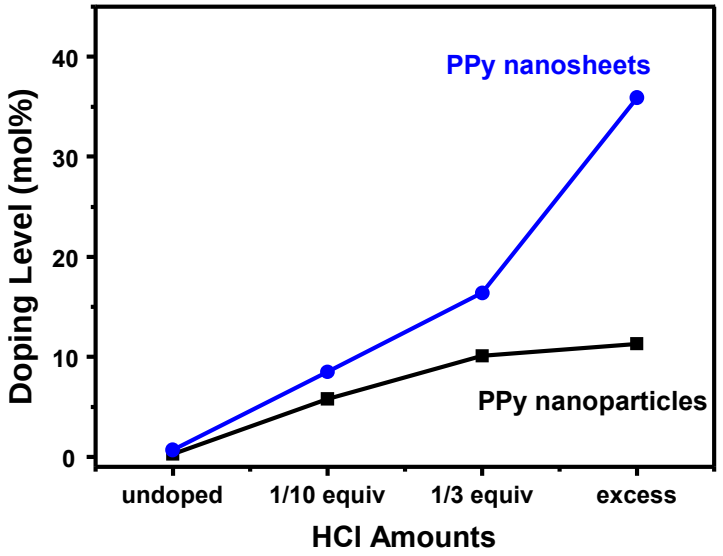

NIR II
NIR I
UV
Optical Density
Increasing Doping
1.0
2.7
3.6
3.2
0.7
1.4
2.1
0.0
1.0
2.0
3.0
4.0
5.0
6.0
E (eV)

极化子概念在导电高分子里相当普遍



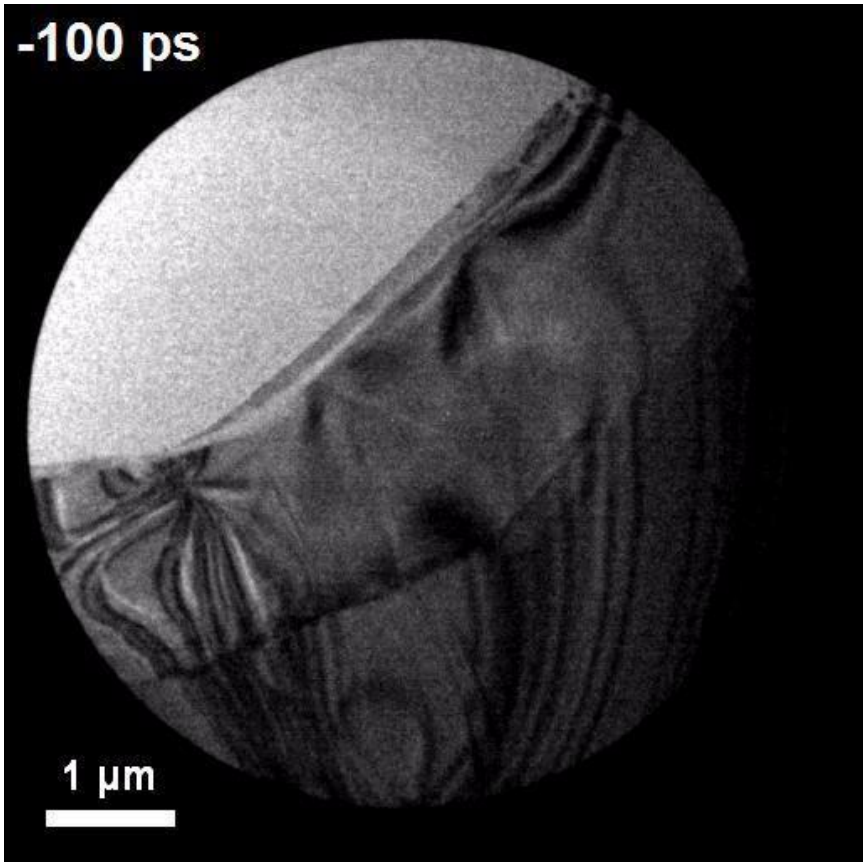
二维聚吡咯纳米片


CB
CB
doping
bipolaron
bands
VB
VB
bipolaron states


PPy nanosheets
PPy nanoparticles
Doping Level (mol%)
40
30
20
10
0
undoped
1/10 equiv
1/3 equiv
excess
HCl Amounts

Phonons

Femtosecond electron imaging of defect-modulated phonon dynamics



Propagating phonons in a WSe_2 flake

dynamics slowed by 5 x 10^9 times

Phonons in Polymers

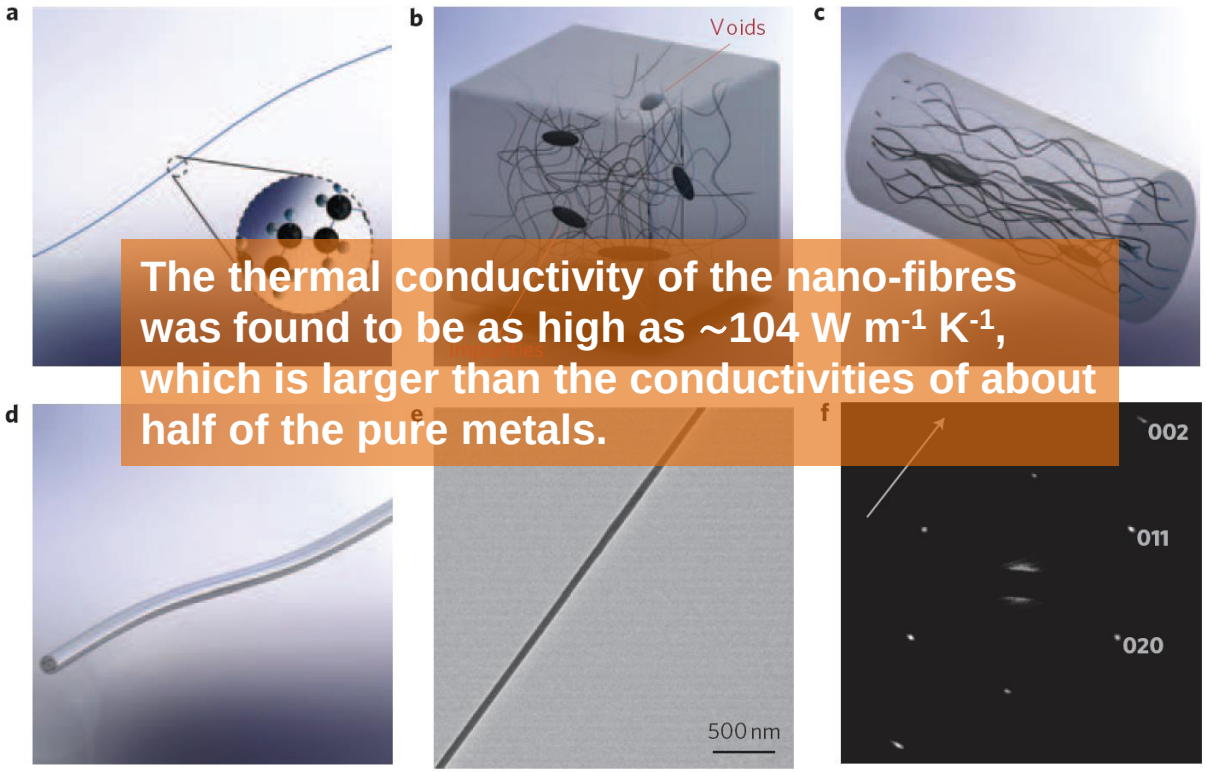
nature nanotechnology

LETTERS

PUBLISHED ONLINE: 7 MARCH 2010 | DOI: 10.1038/NNANO.2010.27

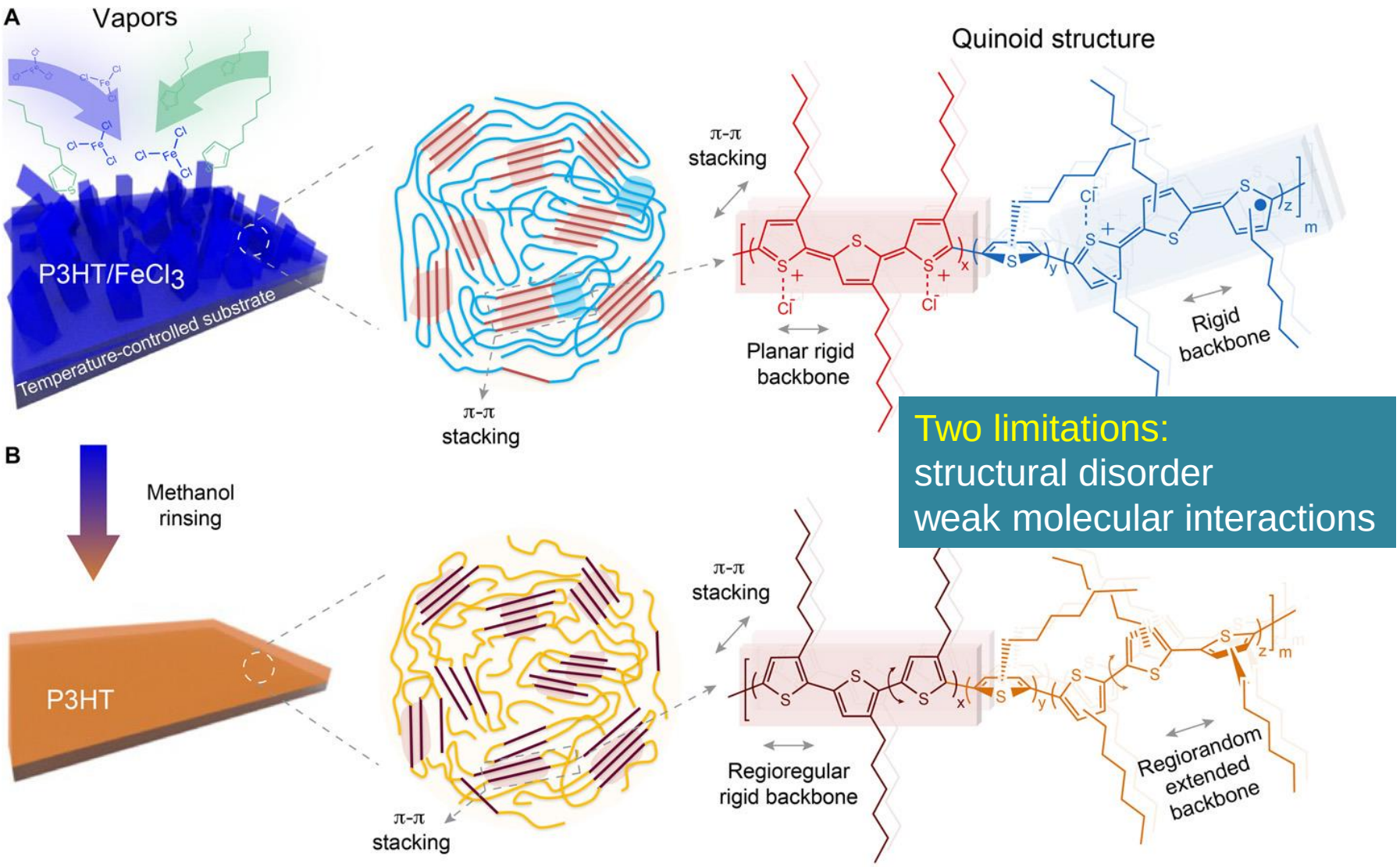
Polyethylene nanofibres with very high thermal conductivities

Sheng Shen[1], Asegun Henry[1], Jonathan Tong[1], Ruiting Zheng[1,2] and Gang Chen[1]*



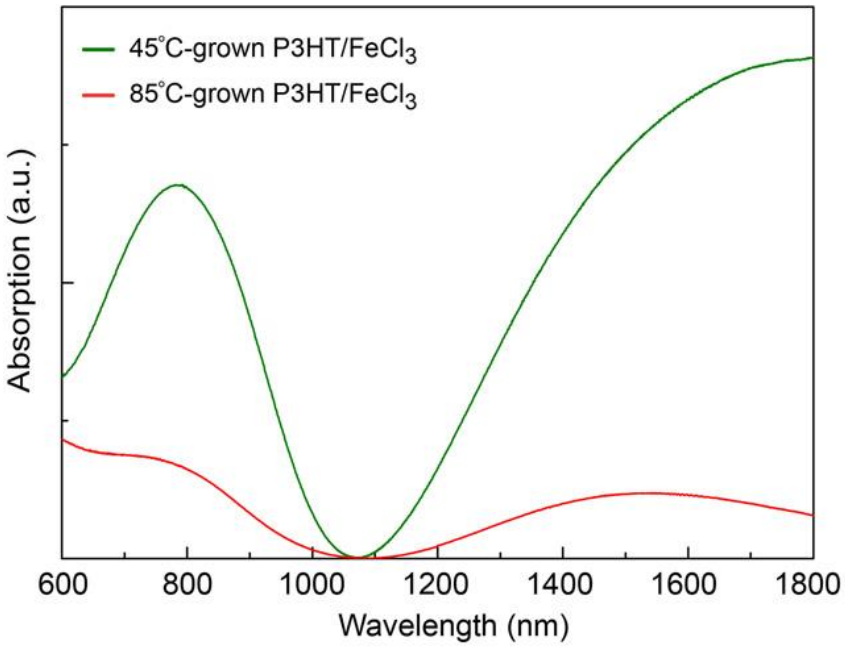
The thermal conductivity of the nano-fibres was found to be as high as ~104 W m^{-1} K^{-1}, which is larger than the conductivities of about half of the pure metals.

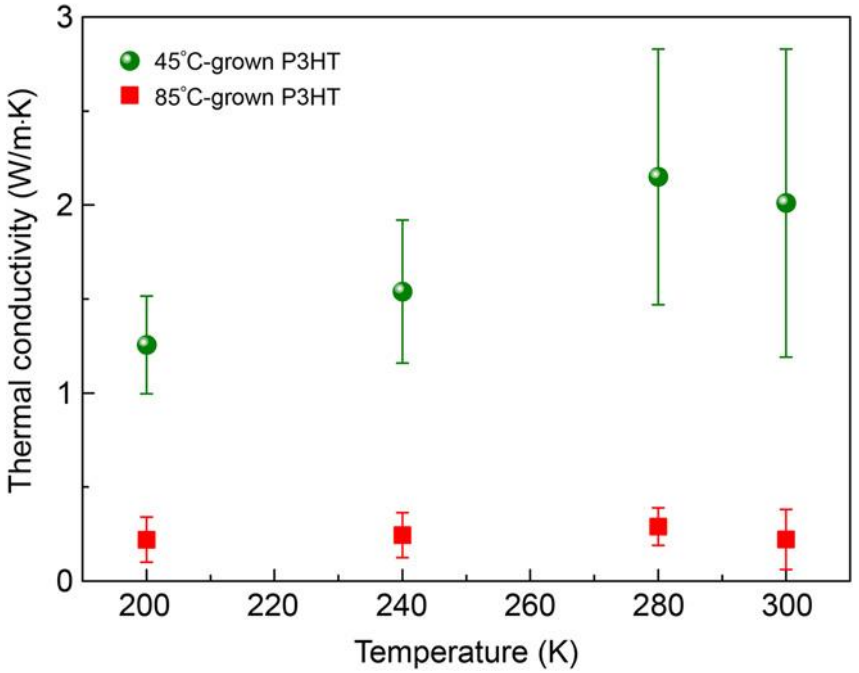
Phonons in Polymers



Two limitations:
structural disorder
weak molecular interactions

Phonons in Polymers





control both intermolecular and intramolecular structures at the molecular level during polymerization.

conjugated carbon-carbon double bonds along the extended polymer chains and the strong π-π stacking interactions between chains.

AIE:聚集诱导发光

GDCh Essays Angewandte International Edition Chemie

Check for updates

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International Edition: doi.org/10.1002/anie.202007525
German Edition: doi.org/10.1002/ange.202007525

Fluorescence

Aggregation-Induced Emission (AIE): A Historical Perspective

*Frank Würthner**

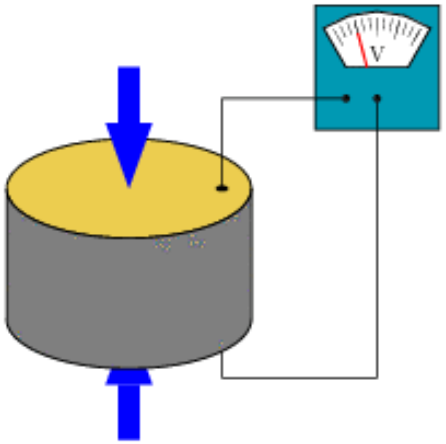
phenomena also attracted early attention. A nice example is provided by the work of Gerhard C. Schmidt, who began one of his early papers (from his habilitation thesis) in 1896 with the following statement (translated from German, for the original German text, see Ref. [11a]): "Already from old experiments it is known that many compounds fluoresce in some solvents but not in others, as well as that many salts fluoresce in the solid state whilst not doing so in the liquid state or in solution." He also concluded in one of his later papers in 1921 with the title "On the Luminescence of Solid Solutions" that many compounds fluoresce in solidified solutions but are quenched in the respective fluid solvents.[11b]

AIE:聚集诱导发光

In 1956, Oster and Nishijima reported on the relationship between fluorescence and internal rotation,[12a] and in 1971, Forster concluded that the diminished fluorescence of triphenylmethane dyes such as crystal violet in fluid solutions originates from the rotation of the phenyl groups and that the fluorescence of these dyes increases in more viscous solvents or in the solid state.[12b]
Accordingly, the RIM/RIR concept, which provides the mechanistic rationale for many AIE luminogens, might be attributed to these authors.

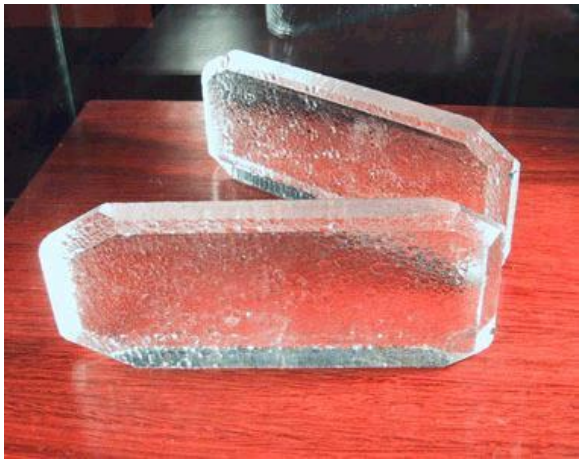
Whilst most of the AIE luminogens take advantage of intramolecular rigidification upon aggregation[1b] or binding of the fluorophore to a biomacromolecule,[16] but show essentially monomer-like emission, true aggregation-induced emission with a new fluorescence band that is due to intermolecular interactions was discovered in 1936 independently by Scheibe and Jelley.[17] These Scheibe or J-aggregates were first observed in aqueous solutions of pseudoisocyanine (PIC) 8 upon increasing the concentration, and later on observed for a large variety of other cyanine dyes (Figure 2).[18]

压电材料

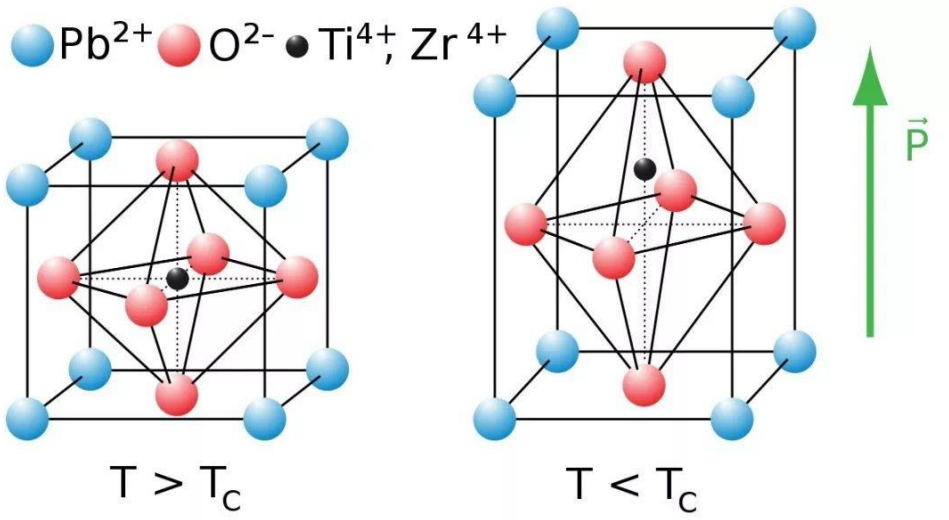


1880 年法国物理学家居里兄弟（Pierre and Paul-Jacques Curie）

受到压力作用时会在两端面间出现电压的晶体材料



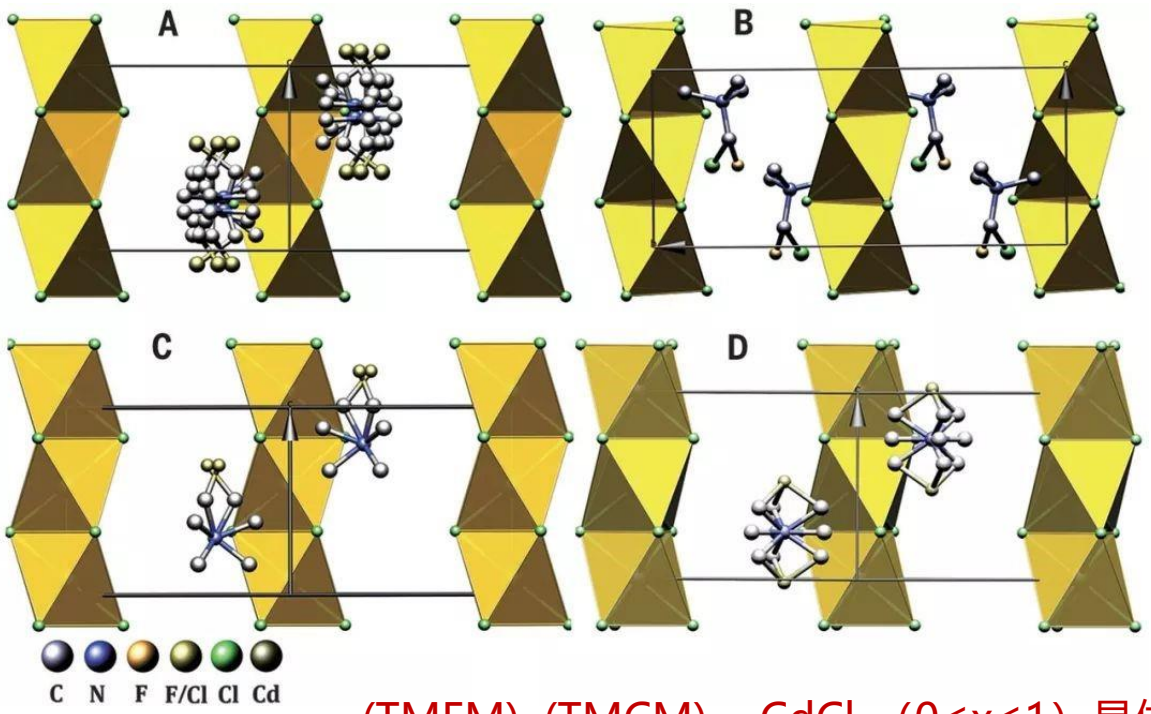
锆钛酸铅（PZT）、钛酸钡（BTO）



PIEZOELECTRICS

A molecular perovskite solid solution with piezoelectricity stronger than lead zirconate titanate

Wei-Qiang Liao[1]*, Dewei Zhao[1]*, Yuan-Yuan Tang[1]*, Yi Zhang[2]*, Peng-Fei Li[1], Ping-Ping Shi[2], Xiao-Gang Chen[2], Yu-Meng You[2], Ren-Gen Xiong[1,2]†



$(TMFM)_x(TMCM)_{1-x}CdCl_3$（0≤x≤1）晶体

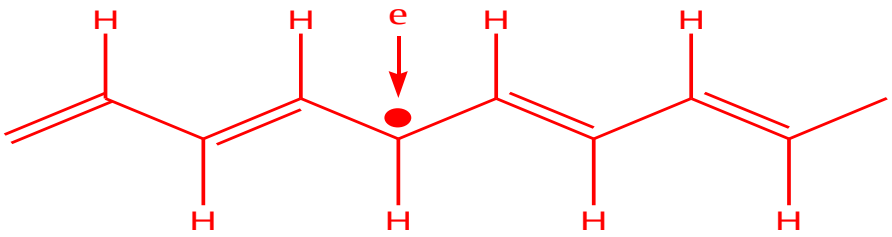
几个概念

化合物均是整比化合物?

非整比化合物普遍存在，是物质具有特异性能的本质原因

如：$YBa_2Cu_3O_{7-\delta}$陶瓷是一种超导体；

聚乙炔是导电高分子：



⇒ **缺陷化学：组成、结构缺陷, doping**

有机化合物的性能

物质的性能与分子的性能相关

分子的性能与分子的结构有关⇒分子设计与合成

聚集态的性能（材料的性能）

1）与分子的结构有关

2）与分子之间的作用力有关

3）与物质的结构有关

4）与物质的尺度有关⇒材料设计与制备

单晶（三维）、薄膜（二维）、纤维（一维）、纳米颗粒(0维)

有机材料理化性质与应用的对应关系

- 有机固态光化学反应 - 光信息储存
- 固态反应 - 化学传感器、记录
- 有机铁磁性 - 磁、磁光记录
- 液晶现象 - 电子显示
- 电光、非线性光学效应 - 倍频器、调制器、集成光学及光计算机

有机材料理化性质与应用的对应关系

- 有机超导性 - JOSEPHSON结、计算机

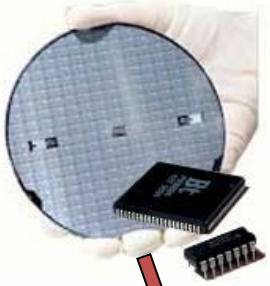
  逻辑门、强磁体、超导电机及电能输送、金属电导等特性

电子器件、塑料电池

- 有机光导和有机半导体 - 光记录及太阳能电池

- 压电、铁电现象 - 换能器、传感器

有机材料研究历史与背景



a-Si

poly-Si

Si

GaAs

0.1 | 1 | 10 | 100 | 1,000 | 10,000

Polymers:
Solution processing
Low performance

Small molecules:
Performance similar to a-Si
Vacuum dep.

Single crystals:
Study of intrinsic charge transport
Fragile, challenging integration

Crystalline carbon :
High mobility, 'robust'
High temp. growth, electr. heterogeneity