1 分子レベルから見た有機材料のナノスケール世界

Martin Vacha

Department of Materials Science and Engineering
Tokyo Institute of Technology

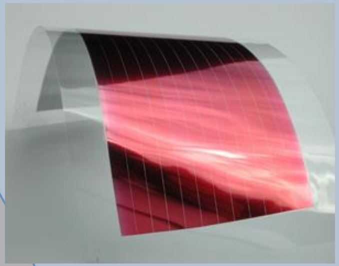
vacha.m.aa@m.titech.ac.jp

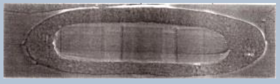
有機材料とは

有機物質は炭素や水素を中心とする比較的小数の種類の元素から構成されているが、その物性は無限と言ってよいほど多様。

構造材料

機能材料・デバイス





有機材料とは

有機物質は炭素や水素を中心とする比較的小数の種類の元素から構成されているが、その物性は無限と言ってよいほど多様。

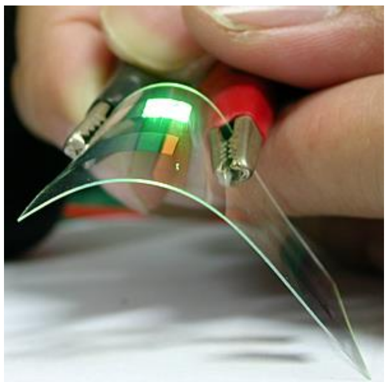
5” AMOLED

1980’s: 5” crt display

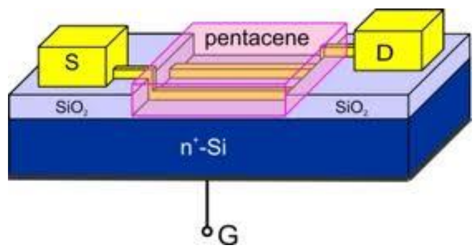
5” LCD

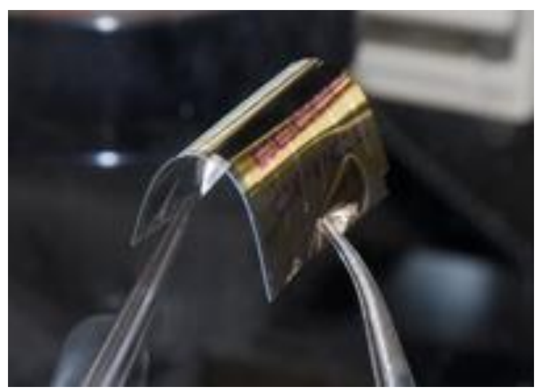
有機半導体

OLED

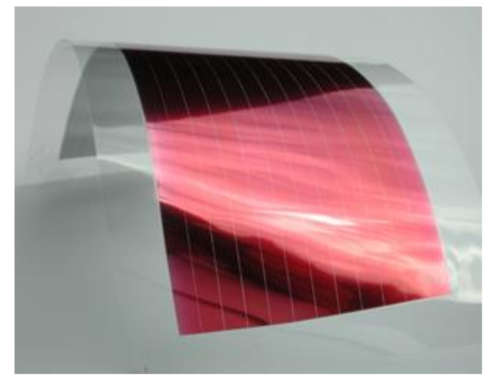


OFET

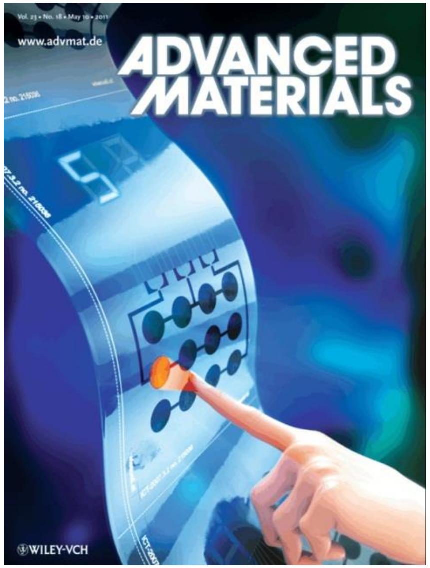




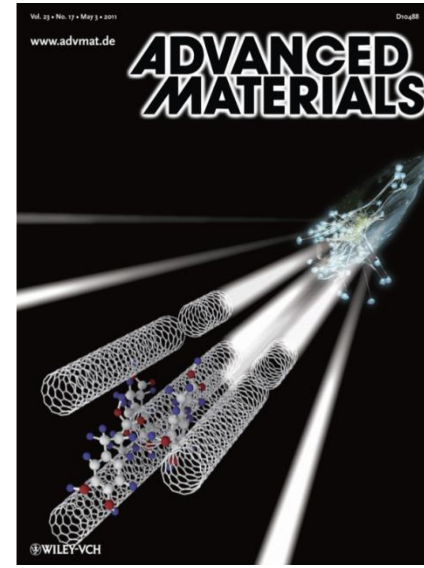
SOLAR CELLS



有機材料研究の位置づけ



学術雑誌Advanced
Materialsに
1ヶ月に
出る材料研究報告
（論文）



有機材料
64%

無機材料
28%

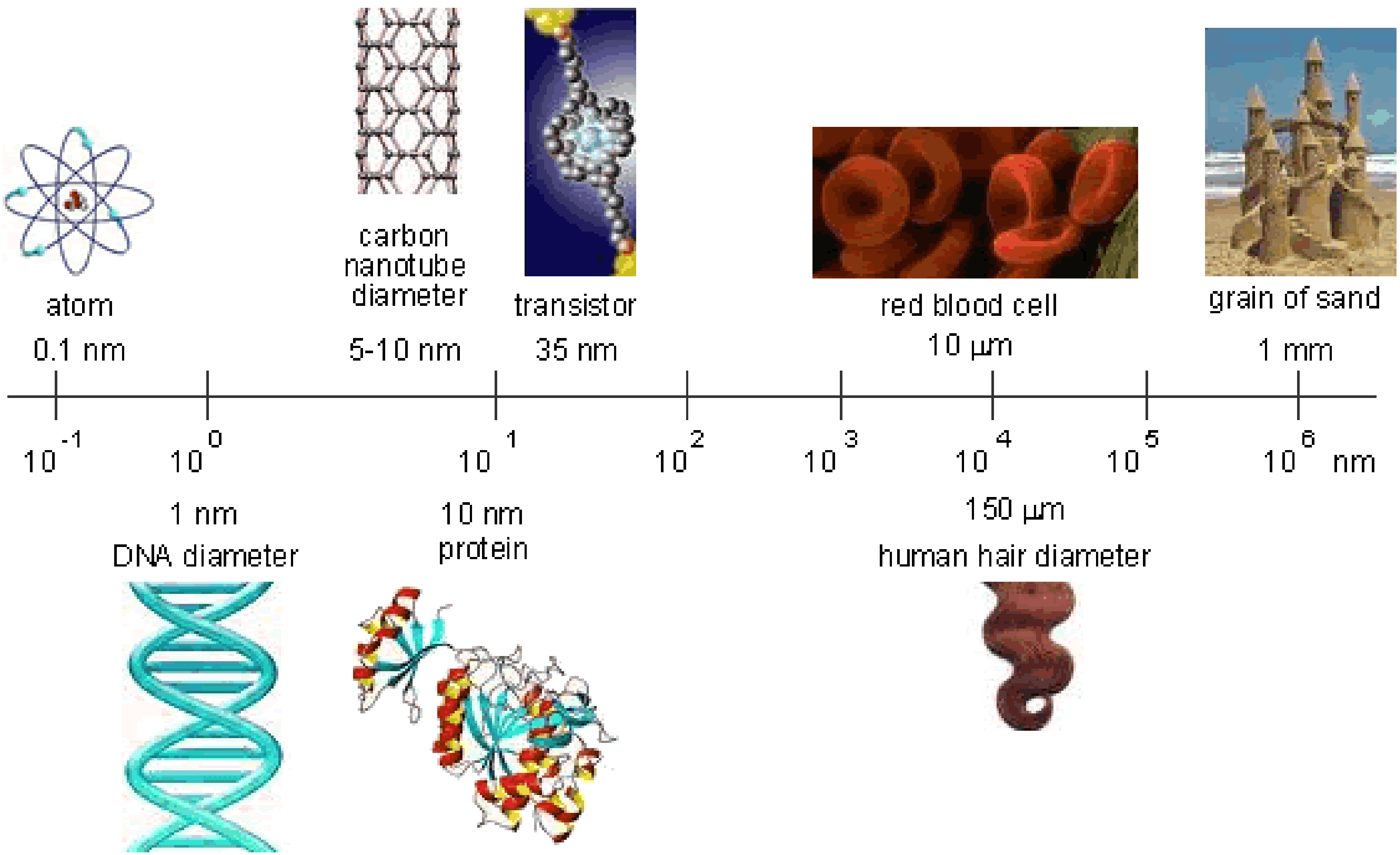
金属材料
8%

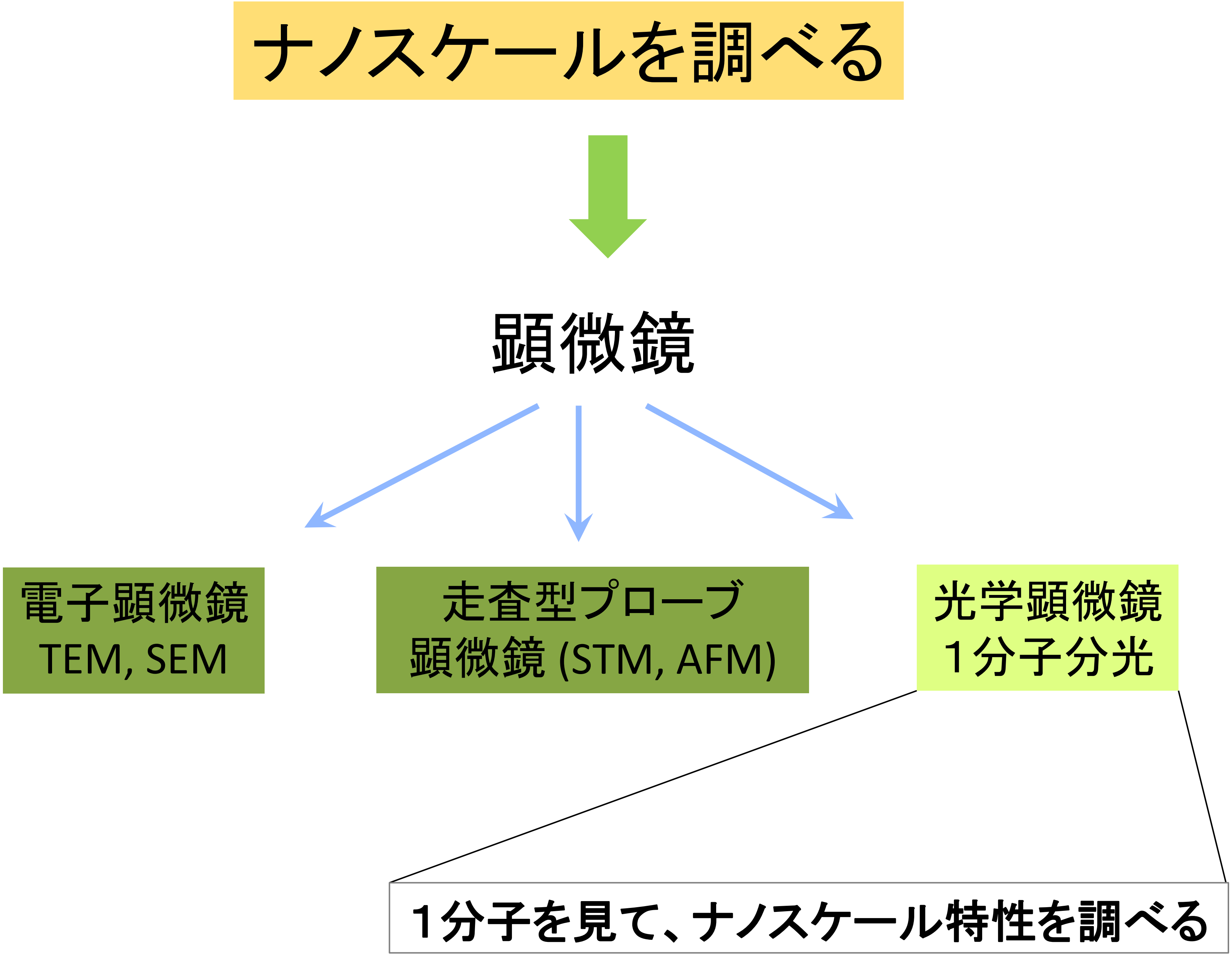
１分子レベルから見た有機材料のナノスケール世界

ナノスケールとは？

1 nanometer (nm) = 10^{-9} m

C-C　結合～0.15 nm




ナノスケールを調べる
顕微鏡
電子顕微鏡
TEM, SEM
走査型プローブ
顕微鏡 (STM, AFM)
光学顕微鏡
1分子分光
1分子を見て、ナノスケール特性を調べる

1分子が見えるか

Light as an electromagnetic wave

Maxwell's equations

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

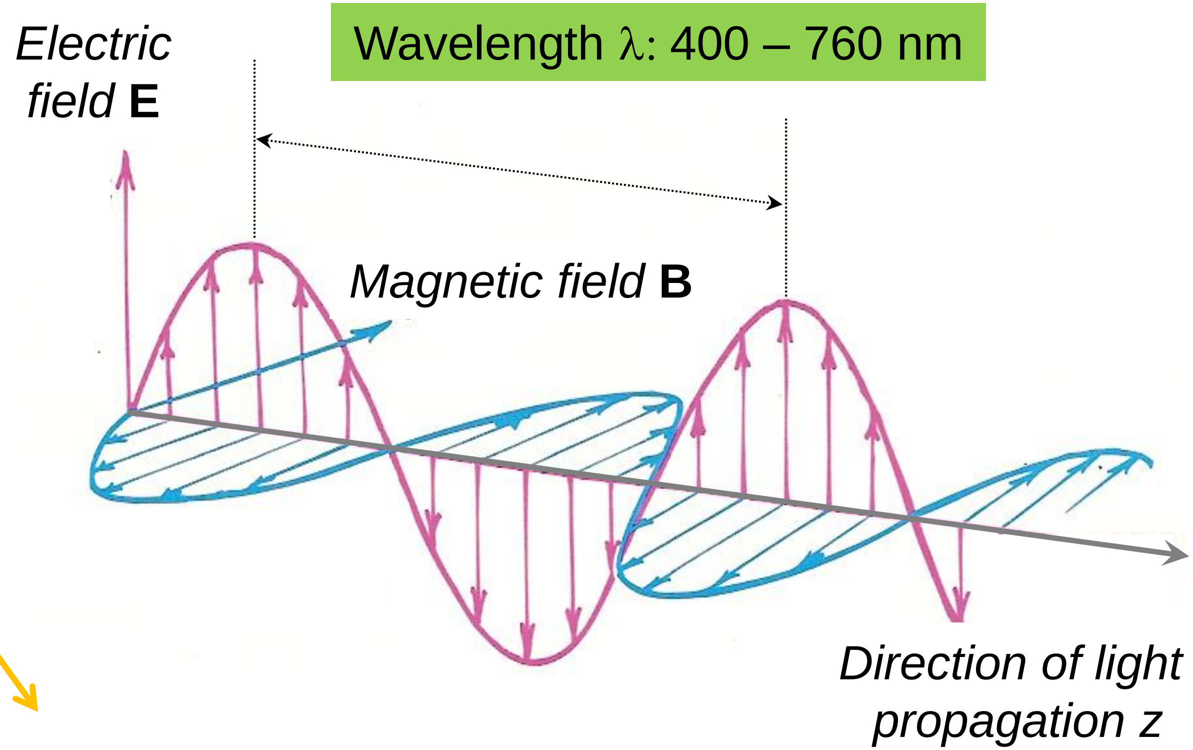
$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$

$$\nabla \cdot \mathbf{B} = 0$$

Wave equation

$$\nabla^2 \mathbf{E} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}$$

$$c = 1/\sqrt{\mu_0 \varepsilon_0}$$



Light is TRANSVERSE electromagnetic wave

$$E = E_0 \cos(kz - \omega t)$$

$\omega = 2\pi\nu = 2\pi/\tau$ angular frequency

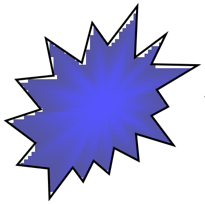
$k = \frac{2\pi}{\lambda}$ propagation number

E_0 amplitude

Can we see molecules?

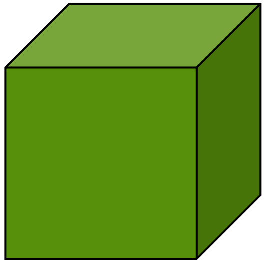
What does it mean <u>SEEING</u> things?

Confirming the existence or non-existence of objects	*Recognizing the shape, pattern, size of objects*

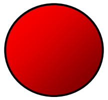


YES
(there is something)

NO
(there is nothing)



LARGE CUBE



SMALL SPHERE

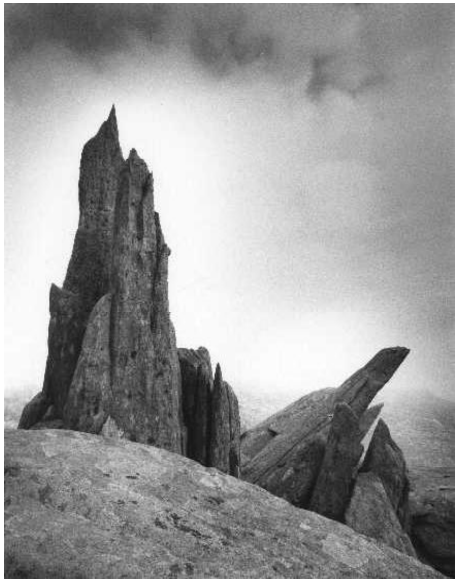
Why we see things – confirming the existence of objects

Light must **interact** with matter

ABSORPTION

REFLECTION

EMISSION



SCATTERING

Why we see things – confirming the existence of objects

SCATTERING

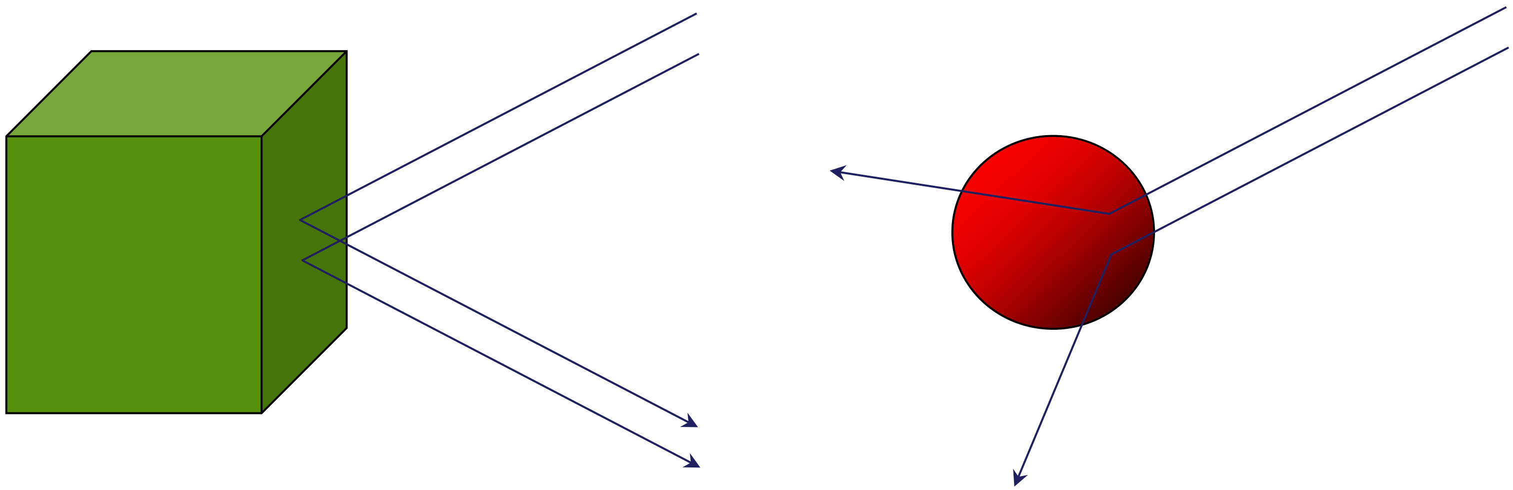
EMISSION

REFLECTION

ABSORPTION

Why we see things – recognizing shape, size of objects

Interaction of light with **different parts** of an object must be **different**



As a result, we see differences in color (wavelength), intensity (amplitude) or phase of light waves.

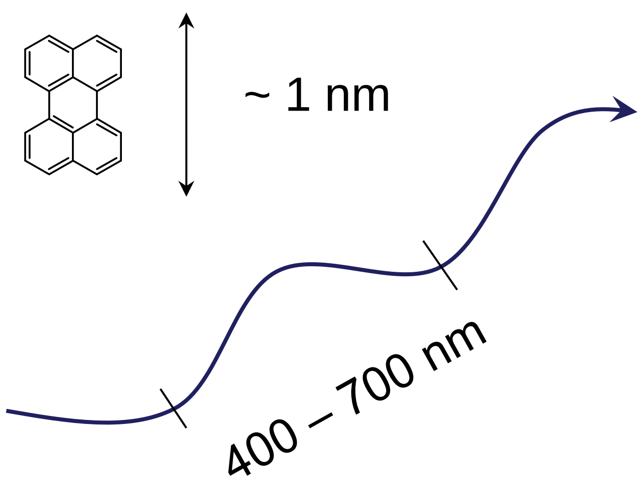
Objects must be larger than the wavelength of light

Can we see molecules?

Can we see **shape** of a molecule?

NO

Typical organic molecule is **too small** compared to the wavelength of light



Can we see **the existence** of a molecule?

MAYBE

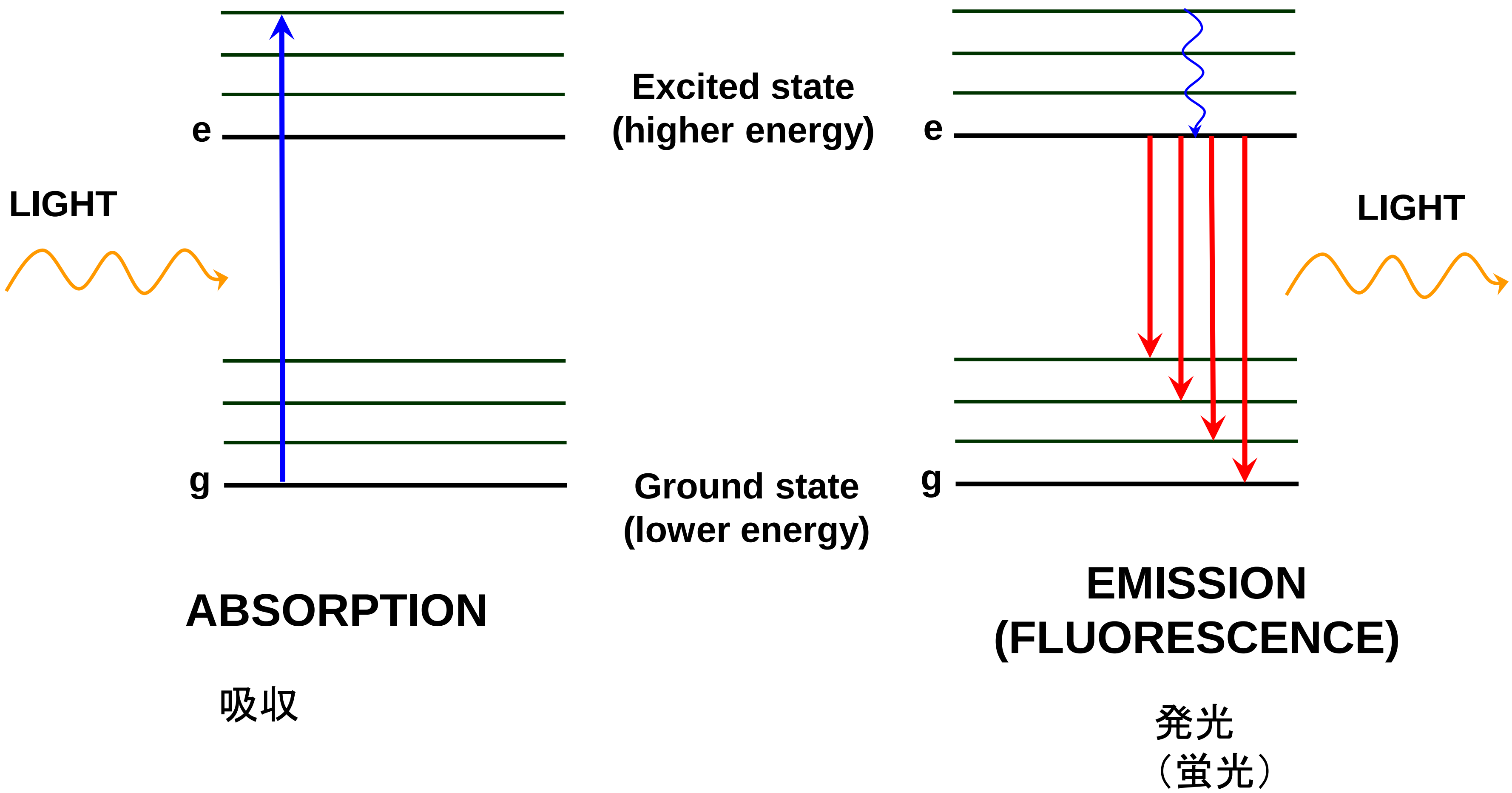
Molecules **interact with light**

We could use the interaction of a molecule with light to detect its presence or absence.

Interaction of light with molecules – absorption and emission

ENERGY STATES OF VALENCE MOLECULAR ELECTRONS

吸収および発光

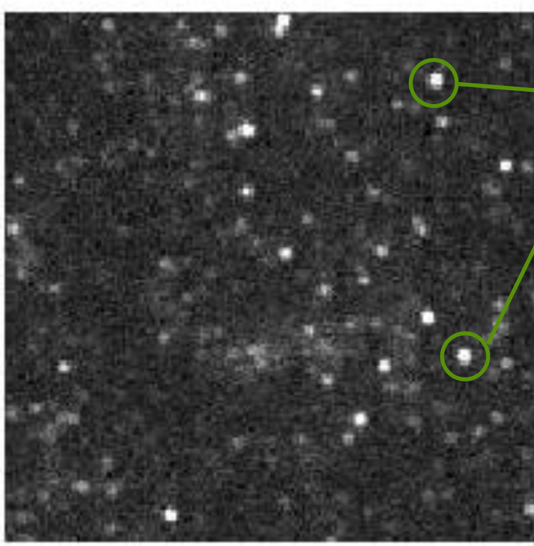


Observing light emitted by single molecules

Repeated absorption and emission of light by molecules with:

- high absorption cross-section
- high luminescence quantum yield
- high photostability

fluorescence microscope

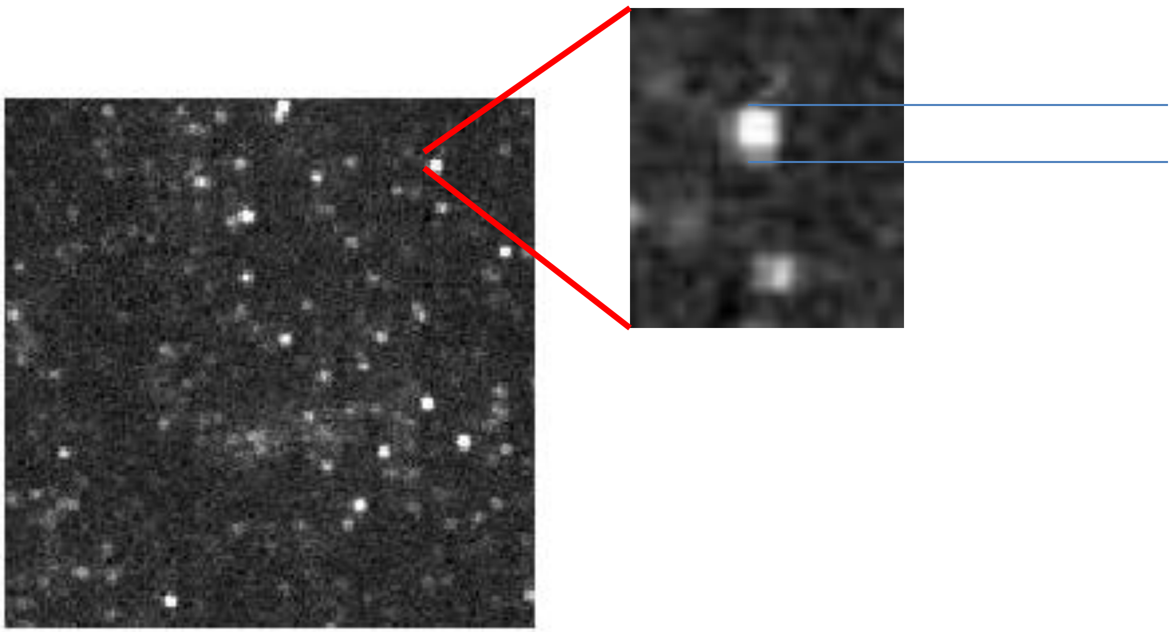


Fluorescence of individual molecules

Observing light emitted by single molecules

Repeated absorption and emission of light by molecules with:

- high absorption cross-section
- high luminescence quantum yield
- high photostability



not size of molecule
‘size’ of light

回折限界

MOLECULES UNDER MICROSCOPE

BASICS OF LIGHT

光について

Light is an electromagnetic wave　電磁波としての光

Maxwell's equations

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}$$

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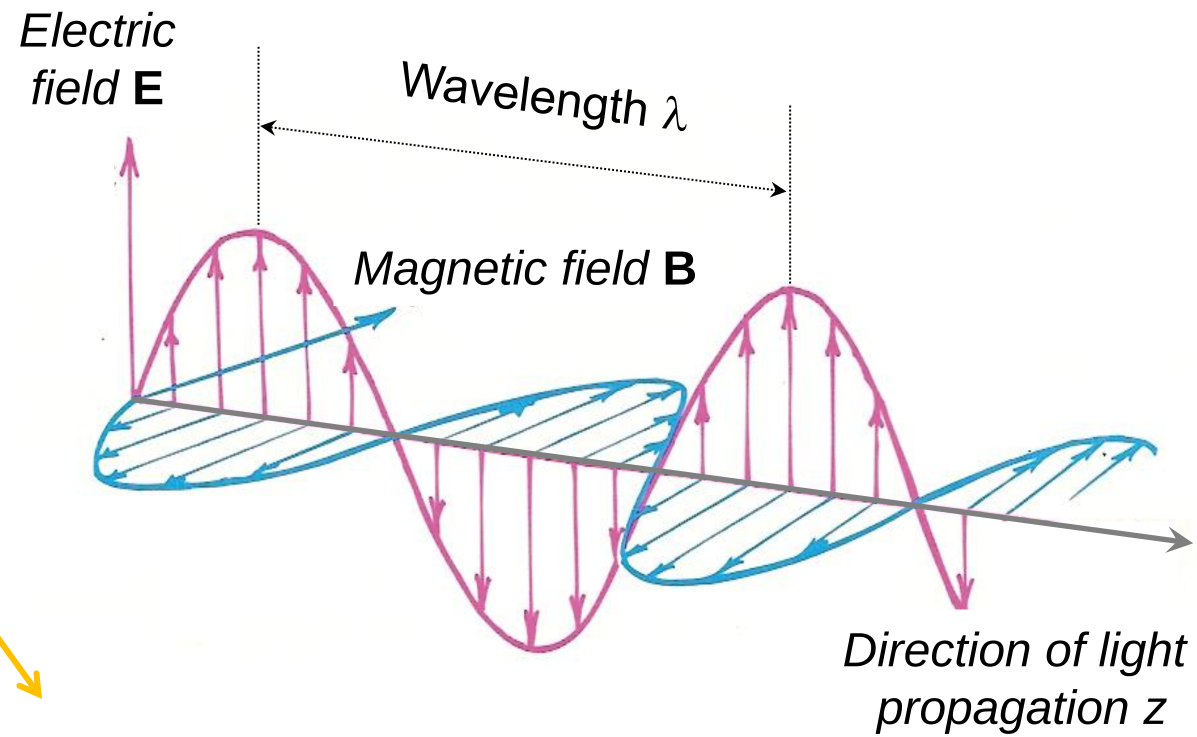


Light is TRANSVERSE electromagnetic wave

$$E = E_0 \cos(kz - \omega t)$$

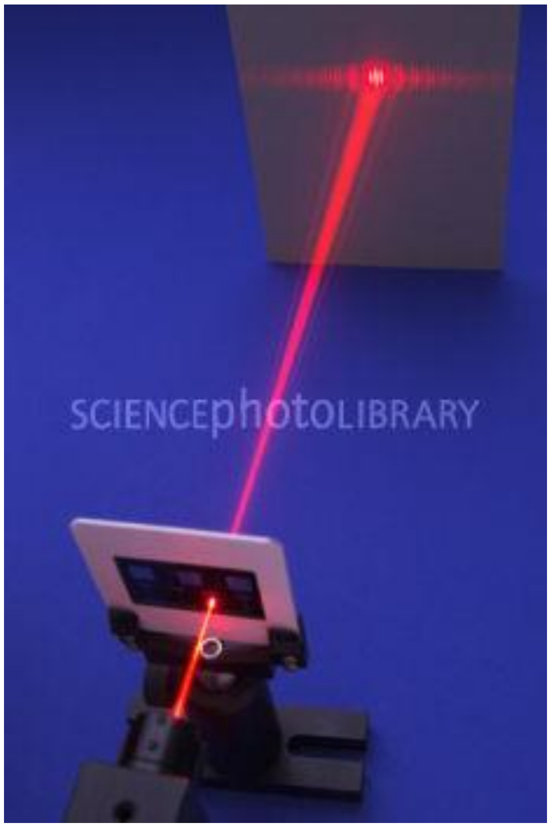
$\omega = 2\pi\nu = 2\pi/\tau$　angular frequency

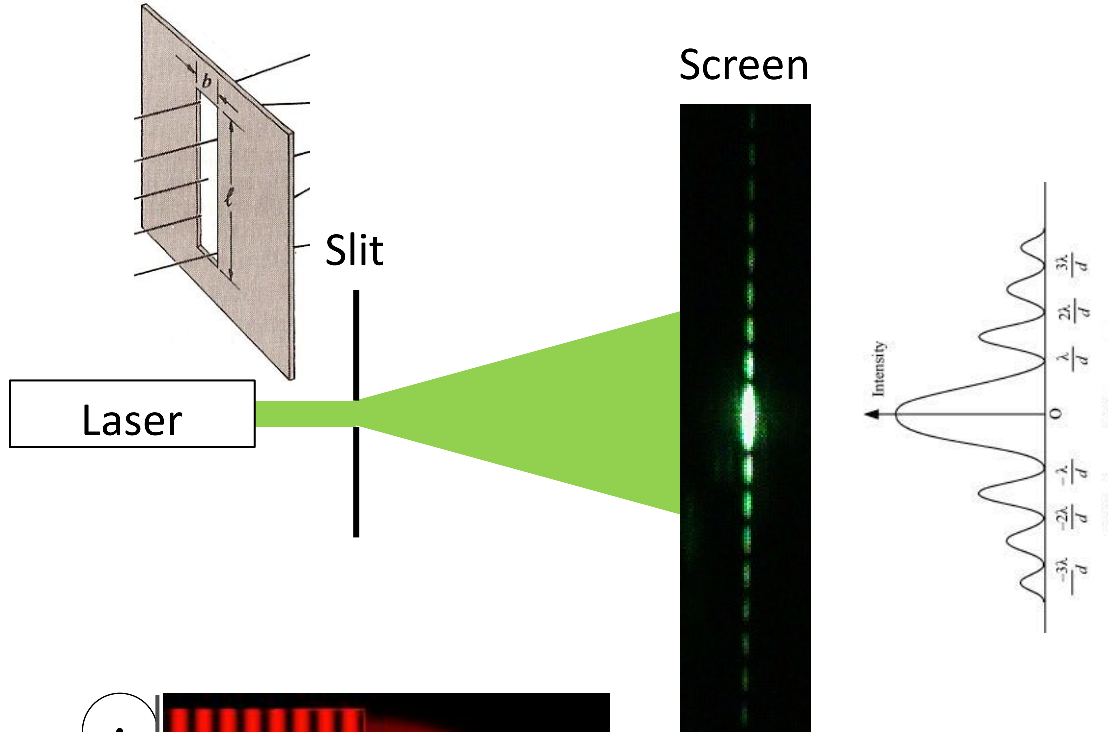
$k = \frac{2\pi}{\lambda}$　propagation number

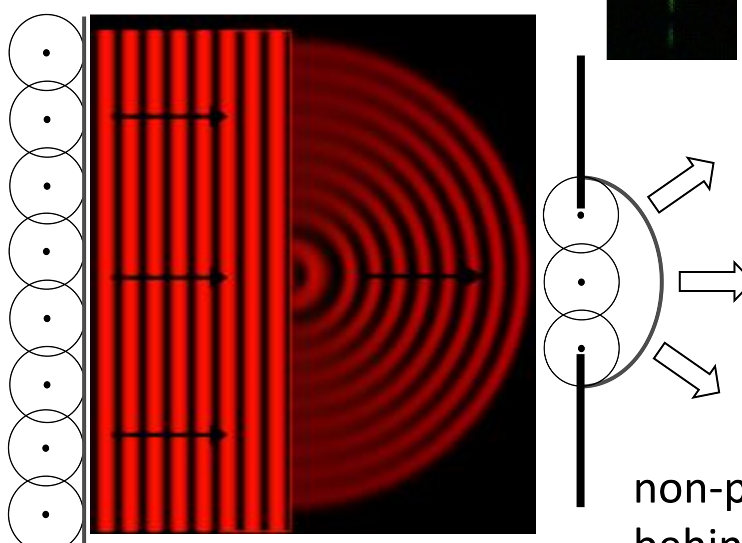
E_0　amplitude

Diffraction of light　光の回折

diffraction from a slit



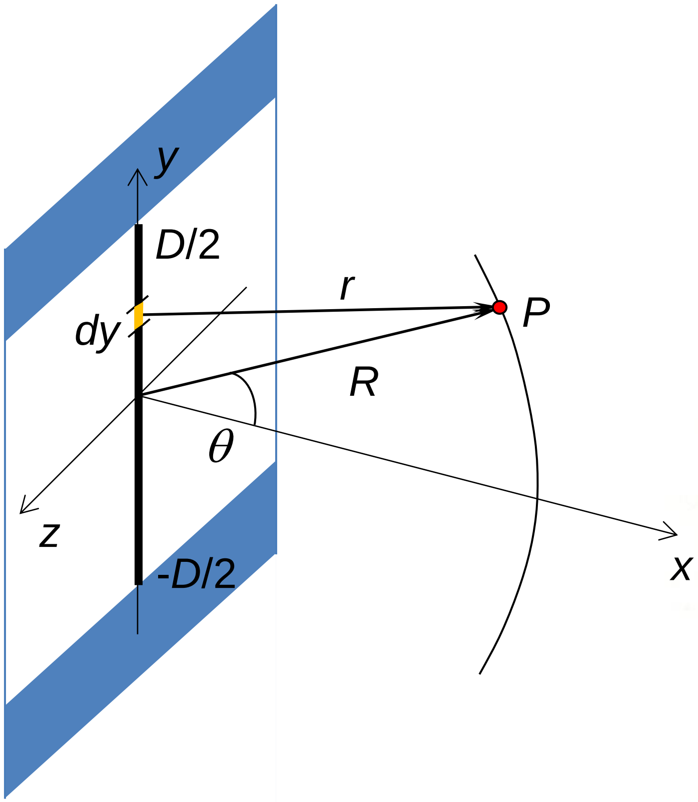


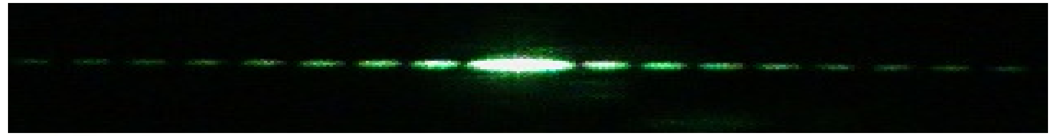


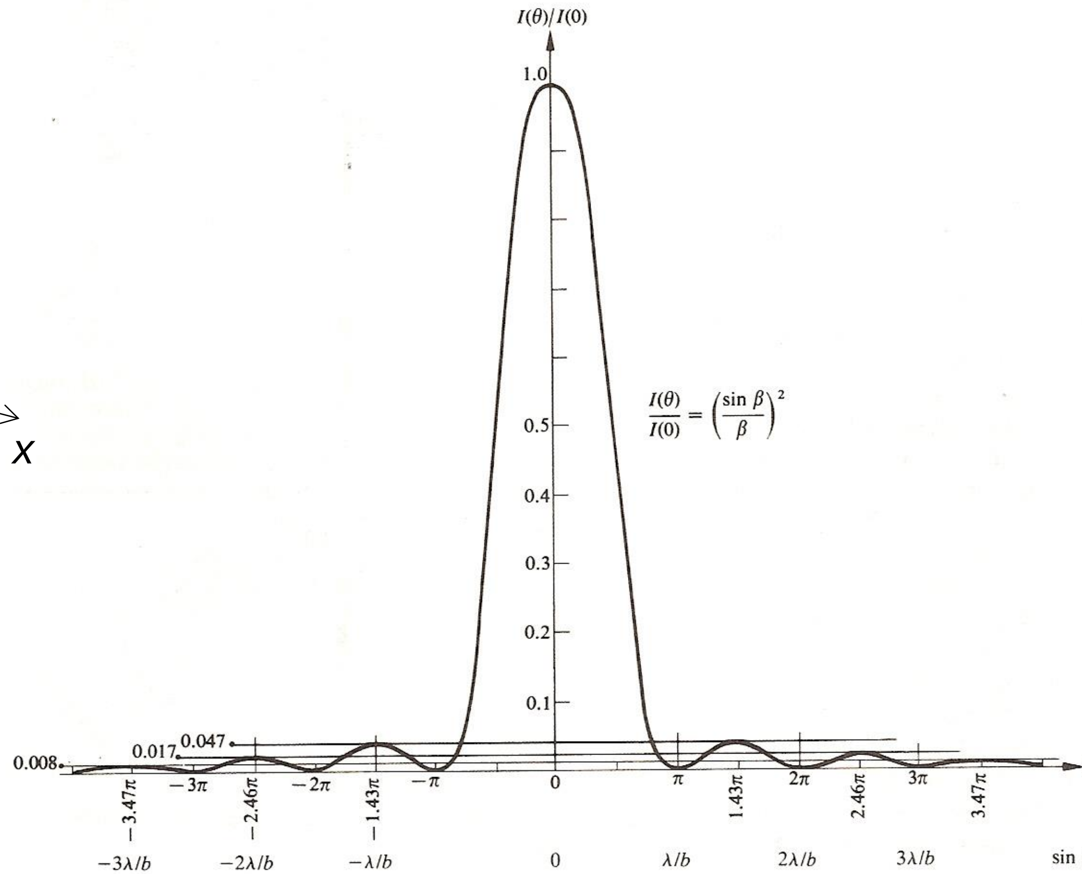
non-planar wave
behind an object

planar freely propagating wave

Diffraction of light　光の回折



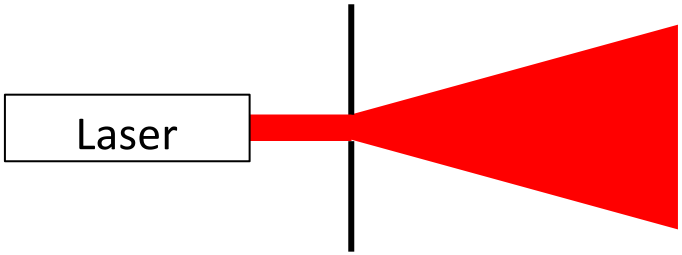




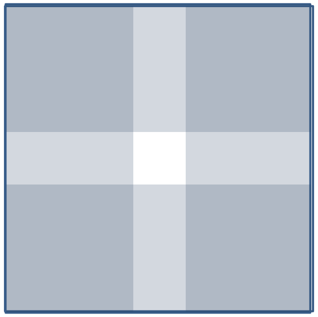
Fraunhofer diffraction

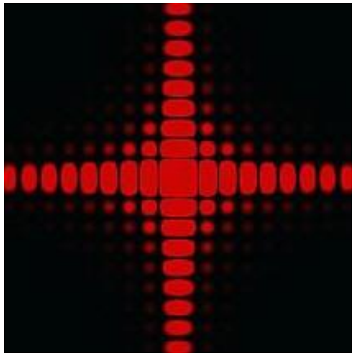
$$I(\theta) = \frac{1}{2}\left(\frac{\varepsilon_L D}{R}\right)^2 \left(\frac{\sin\beta}{\beta}\right)^2 = I(0)\left(\frac{\sin\beta}{\beta}\right)^2$$

Diffraction of light　光の回折

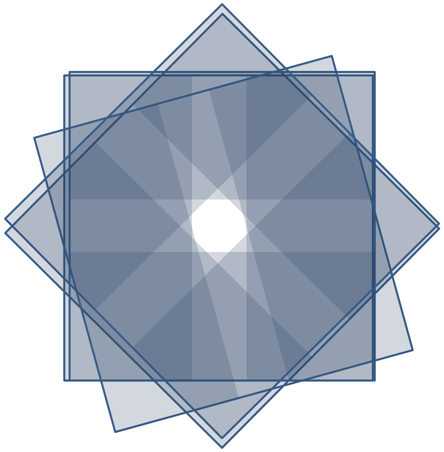


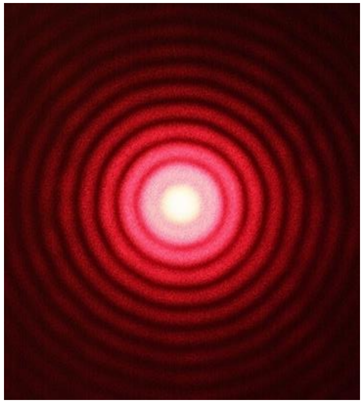
Rectangular opening





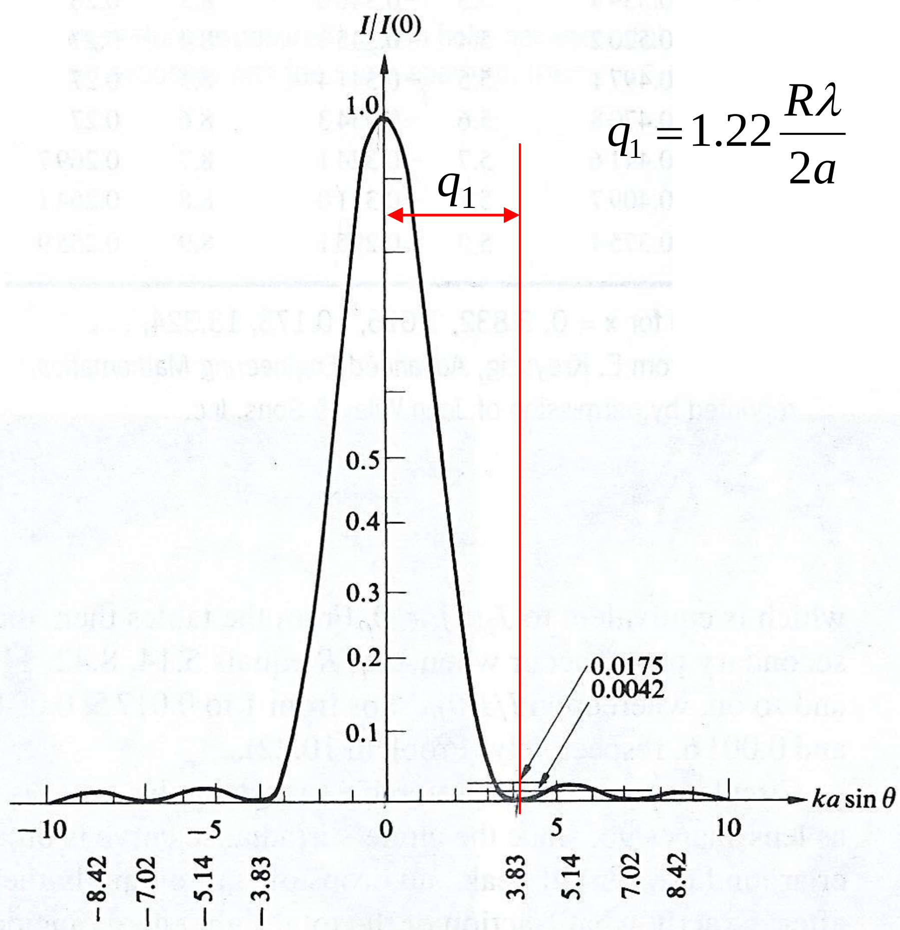
Circular aperture
(pinhole)



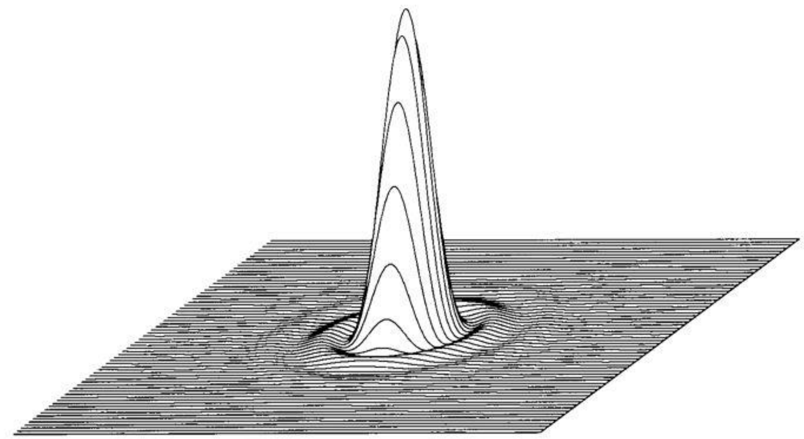


Diffraction of light　光の回折

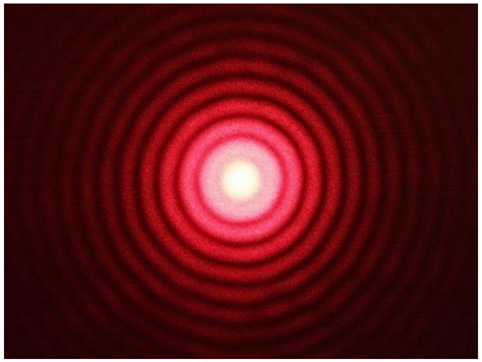
$$I(\theta) = I(0)\left[\frac{2J_1(ka\sin\theta)}{ka\sin\theta}\right]^2$$



$$q_1 = 1.22\frac{R\lambda}{2a}$$

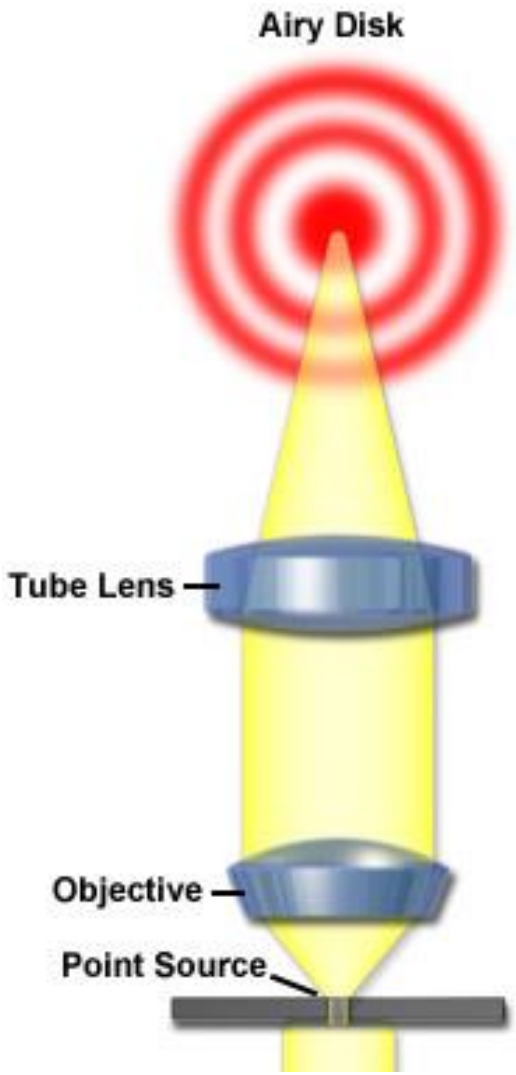


Airy disk



Optical resolution in microscopes　顕微鏡の光学分解能

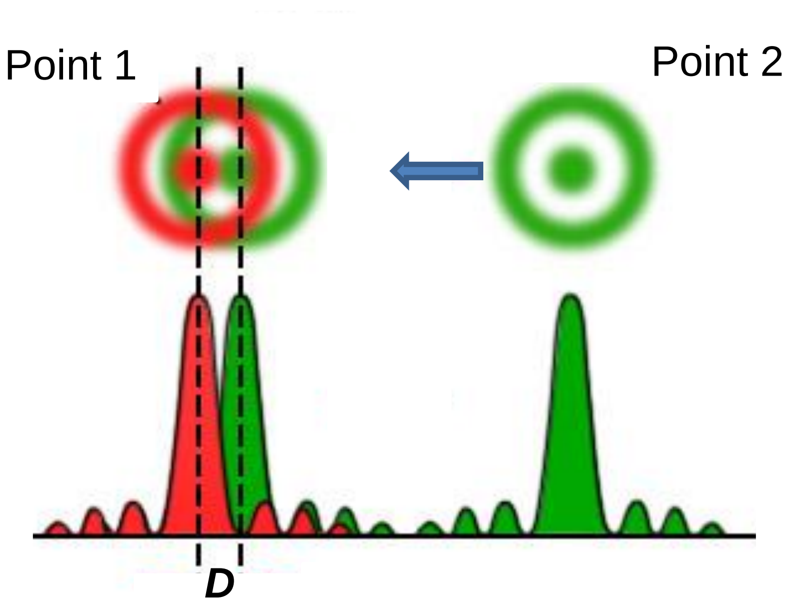
Imaging involves diffraction on optical elements in the system, e.g. microscope



Microscopic image of point source is Airy disk

Criteria for distinguishing two point sources

Airy disks

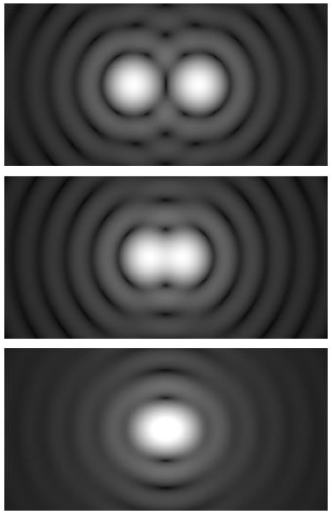


Distance ***D*** at which maximum of Point 2 disk falls into first minimum of Point 1 disk - **Rayleigh criterion**

$$D = 0.61\frac{\lambda}{NA}$$

D – resolution of microscope

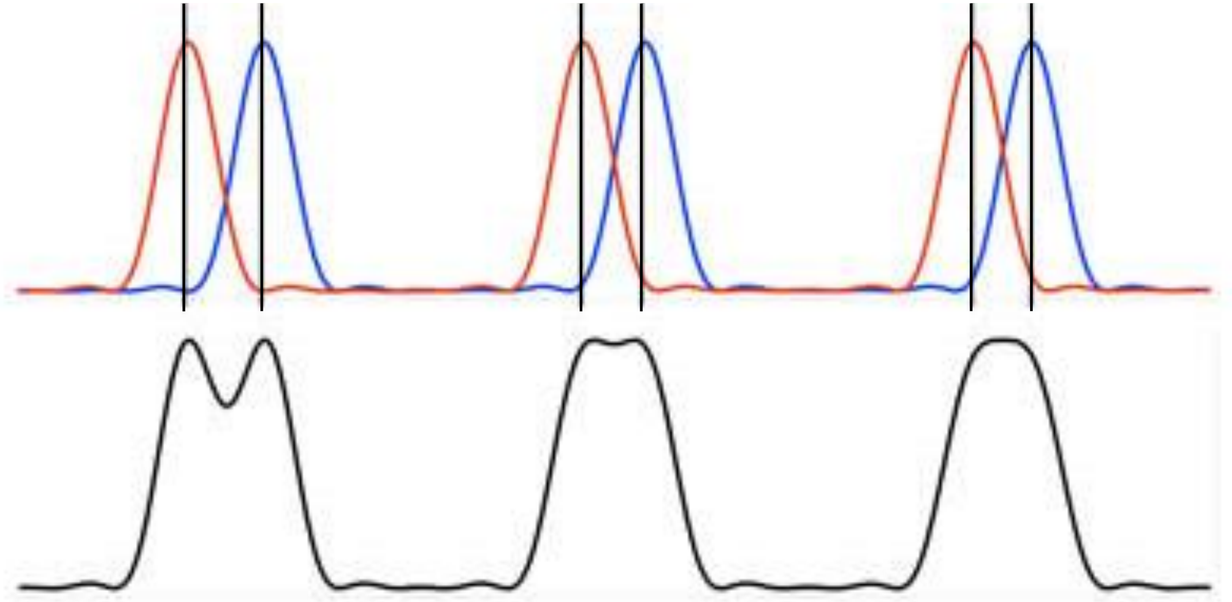
Optical resolution in microscopes　顕微鏡の光学分解能



Other criteria for distinguishing two point sources

For λ = 500 nm
NA = 1.4

218 nm　　179 nm　　168 nm



Rayleigh limit	Abbe limit	Sparrow limit
$D = 0.61\frac{\lambda}{NA}$	$D = 0.5\frac{\lambda}{NA}$	$D = 0.47\frac{\lambda}{NA}$

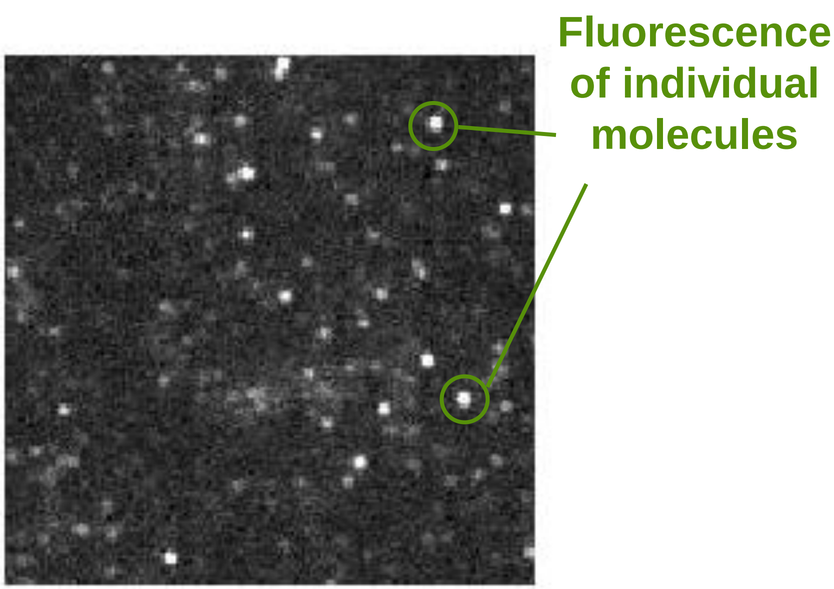
D – resolution of microscope

Observing light emitted by single molecules

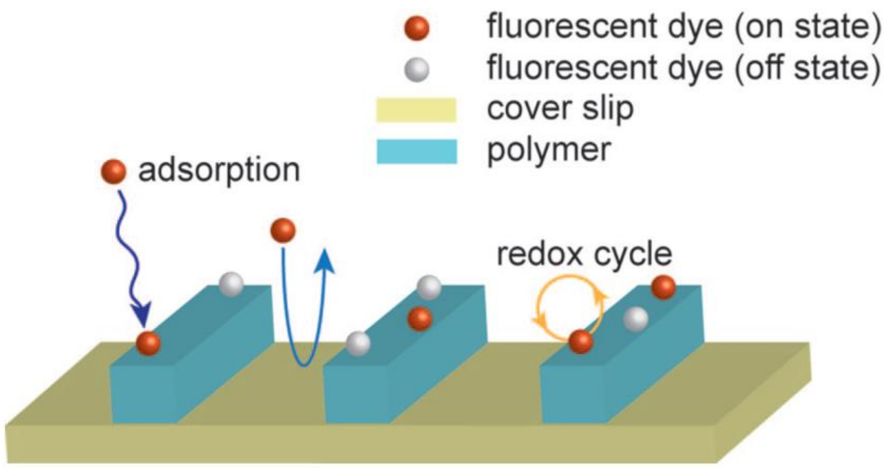
Repeated absorption and emission of light by molecules with:

- high absorption cross-section
- high luminescence quantum yield
- high photostability

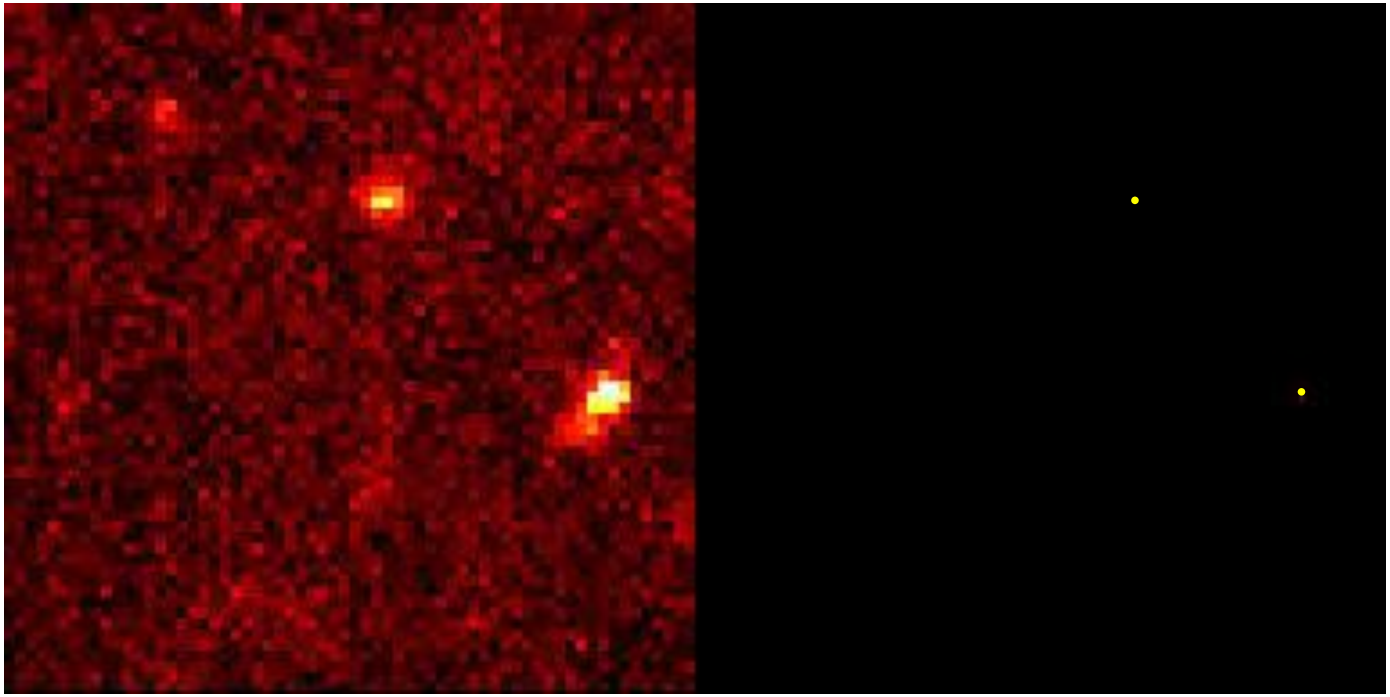
fluorescence microscope



Super-resolution fluorescence microscopy

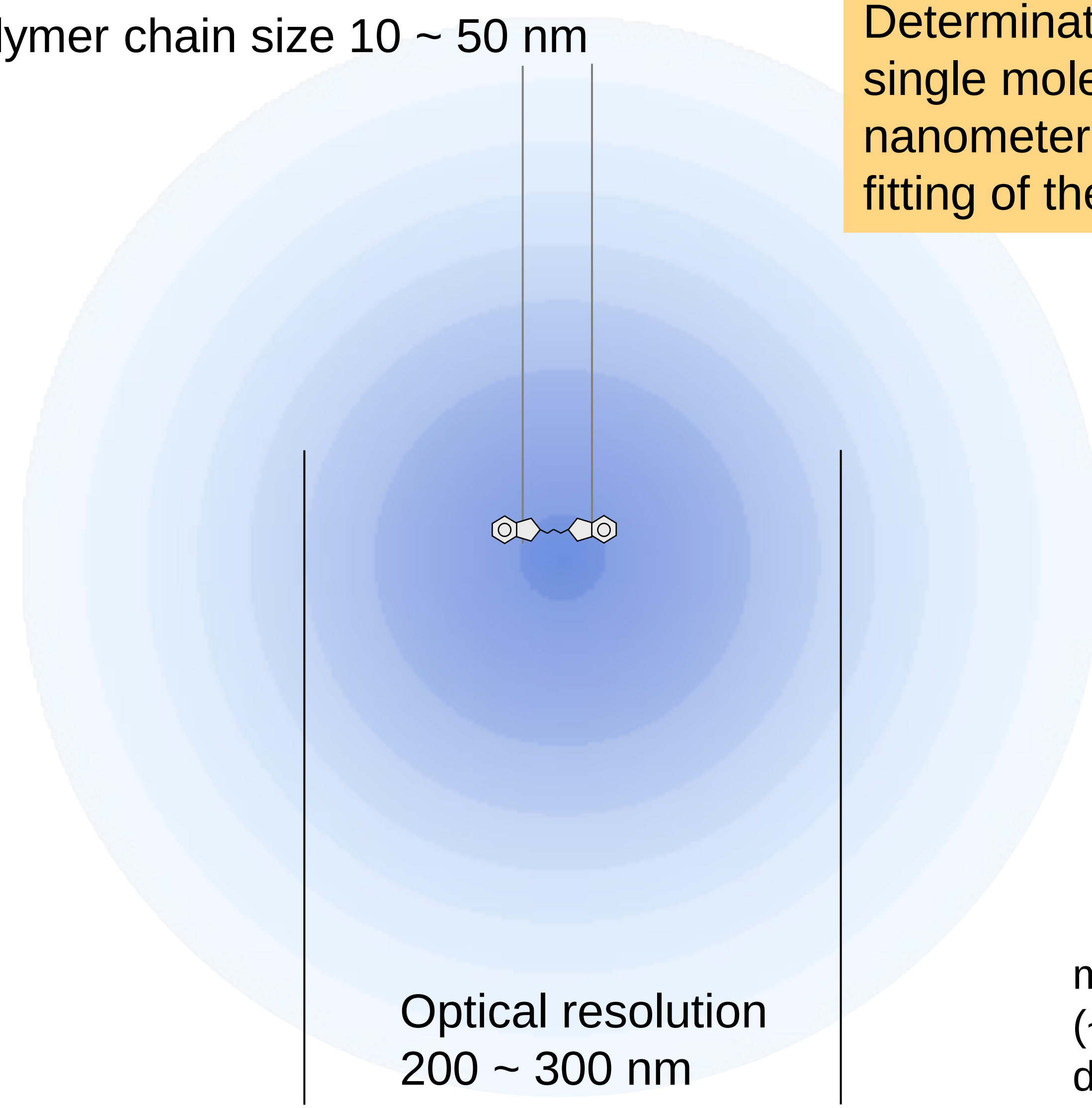


Y. Yabiku et al., AIP ADVANCES **3**, 102128 (2013



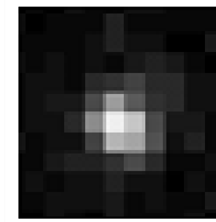
Super-resolution fluorescence microscopy

molecular size ~ 1 nm
polymer chain size 10 ~ 50 nm

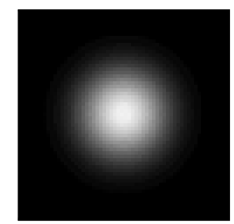


Super-resolution localization: Determination of the position of single molecule or nanoparticle with nanometer accuracy by **2D** Gaussian fitting of the emission profile

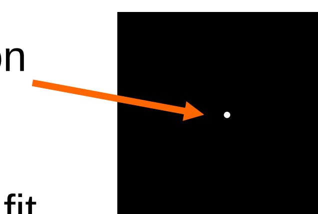
single molecule fluorescence CCD image



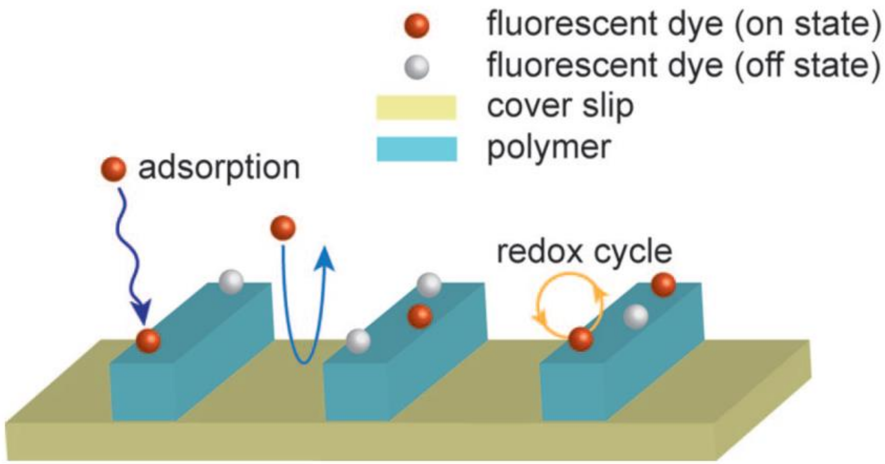
2D Gaussian fitting



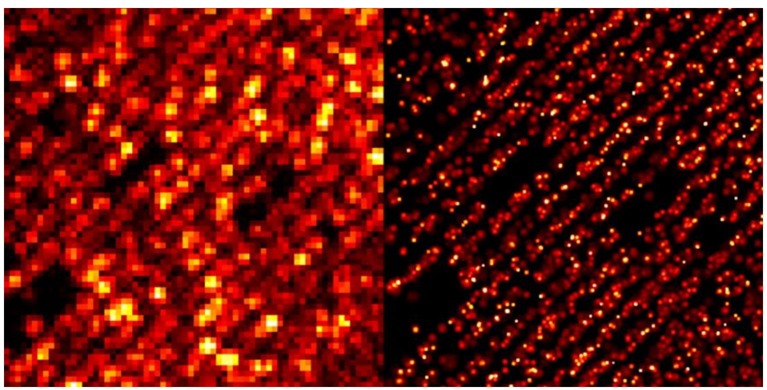
molecular position (~ 1-2 nm) determined from the center of the fit

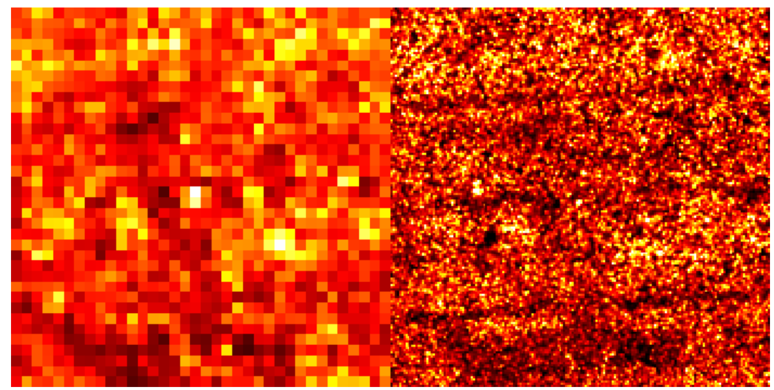


Super-resolution fluorescence microscopy

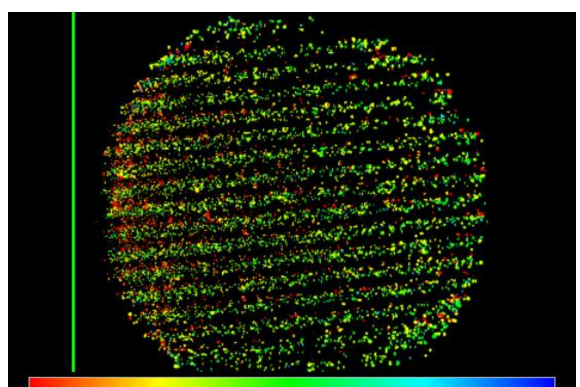


Y. Yabiku et al., AIP ADVANCES **3**, 102128 (2013





3D super-resolution image



Super-resolution fluorescence microscopy

The Nobel Prize in Chemistry 2014
Eric Betzig, Stefan W. Hell, William E. Moerner

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The Nobel Prize in Chemistry 2014

Photo: Matt Staley/HHMI

Eric Betzig

Prize share: 1/3

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Stefan W. Hell

Prize share: 1/3

Photo: K. Lowder via Wikimedia Commons, CC-BY-SA-3.0

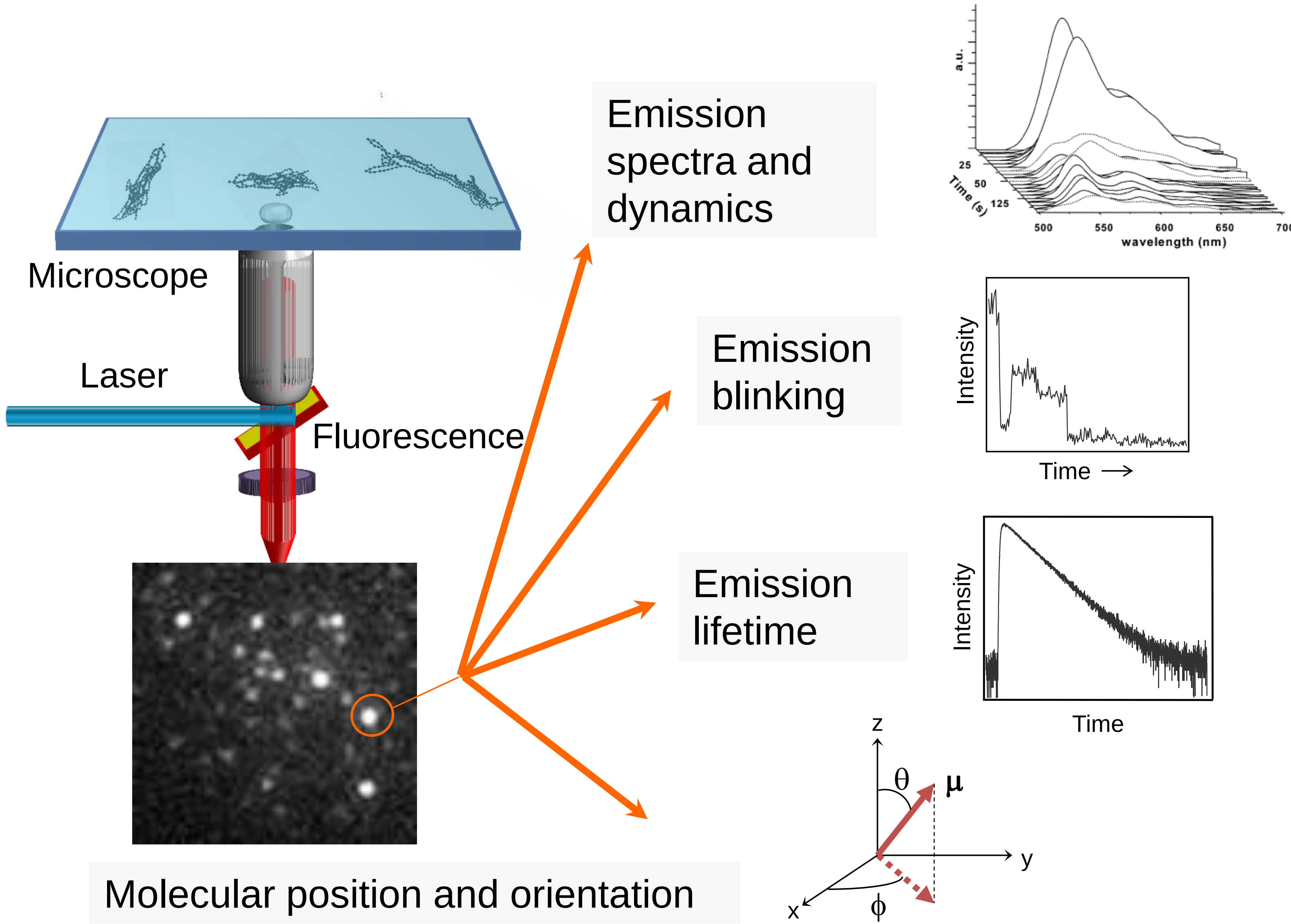
William E. Moerner

Prize share: 1/3

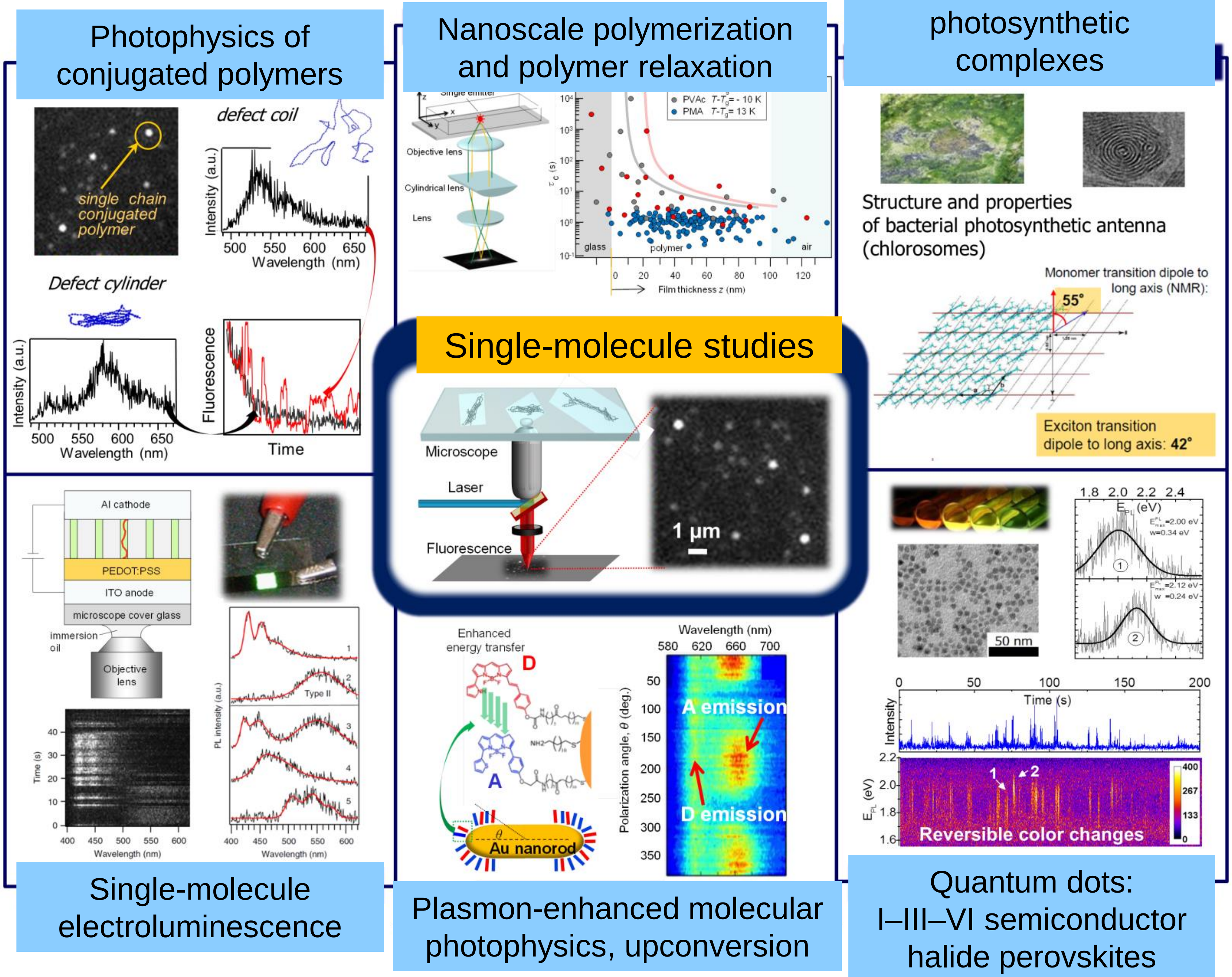
The Nobel Prize in Chemistry 2014 was awarded jointly to Eric Betzig, Stefan W. Hell and William E. Moerner *"for the development of super-resolved fluorescence microscopy".*

NANOSCALE PROPERTIES OF ORGANIC MATERIALS OBSERVED BY SINGLE MOLECULE SPECTROSCOPY

Principle of single-molecule spectroscopy　単一分子分光の原理



現在の主な研究テーマ:



Photophysics of conjugated polymers
single chain conjugated polymer
defect coil
Defect cylinder
Intensity (a.u.)
Wavelength (nm)
Fluorescence
Time
Nanoscale polymerization and polymer relaxation
Objective lens
Cylindrical lens
Lens
PVAc
PMA
glass
polymer
air
Film thickness z (nm)
Natural and artificial photosynthetic complexes
Structure and properties of bacterial photosynthetic antenna (chlorosomes)
Monomer transition dipole to long axis (NMR):
55°
Exciton transition dipole to long axis: 42°
Single-molecule studies
Microscope
Laser
Fluorescence
1 µm
Al cathode
PEDOT:PSS
ITO anode
microscope cover glass
immersion oil
Objective lens
Time (s)
Wavelength (nm)
PL intensity (a.u.)
Type II
Enhanced energy transfer
D
A
Au nanorod
Wavelength (nm)
Polarization angle, θ (deg.)
A emission
D emission
50 nm
Time (s)
Intensity
Reversible color changes
Single-molecule electroluminescence
Plasmon-enhanced molecular photophysics, upconversion
Quantum dots:
I–III–VI semiconductor
halide perovskites

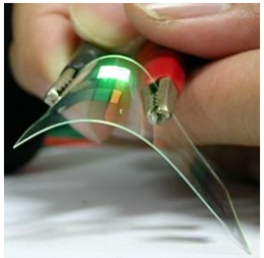
NANOSCALE PROPERTIES OF CONJUGATED POLYMERS

Conjugated polymers – why are they important?

共役系高分子

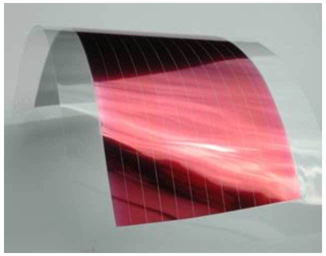
optoelectronic properties → **semiconductors**

mechanical properties, processing → **plastics**

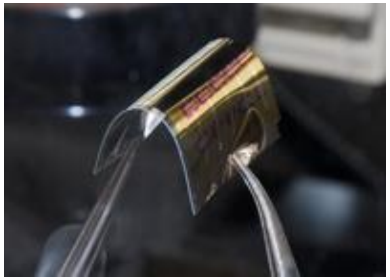


OLED

Applications in: - organic light-emitting diodes
- photovoltaic cells
- organic transistors



photovoltaics

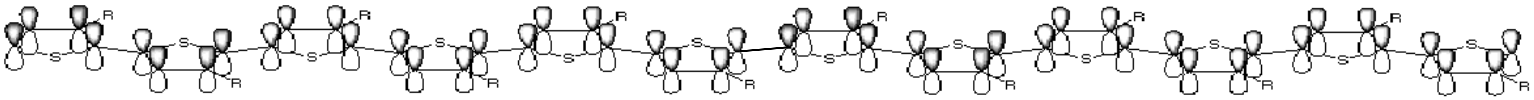


OFET

photophysical properties important in these applications

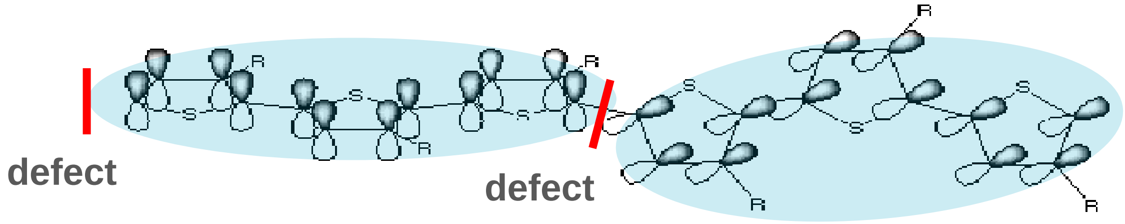
Conjugated polymers – basic photophysics

Polymer chain: ~100 – 1000 monomer units



π-electrons NOT delocalized over the whole chain

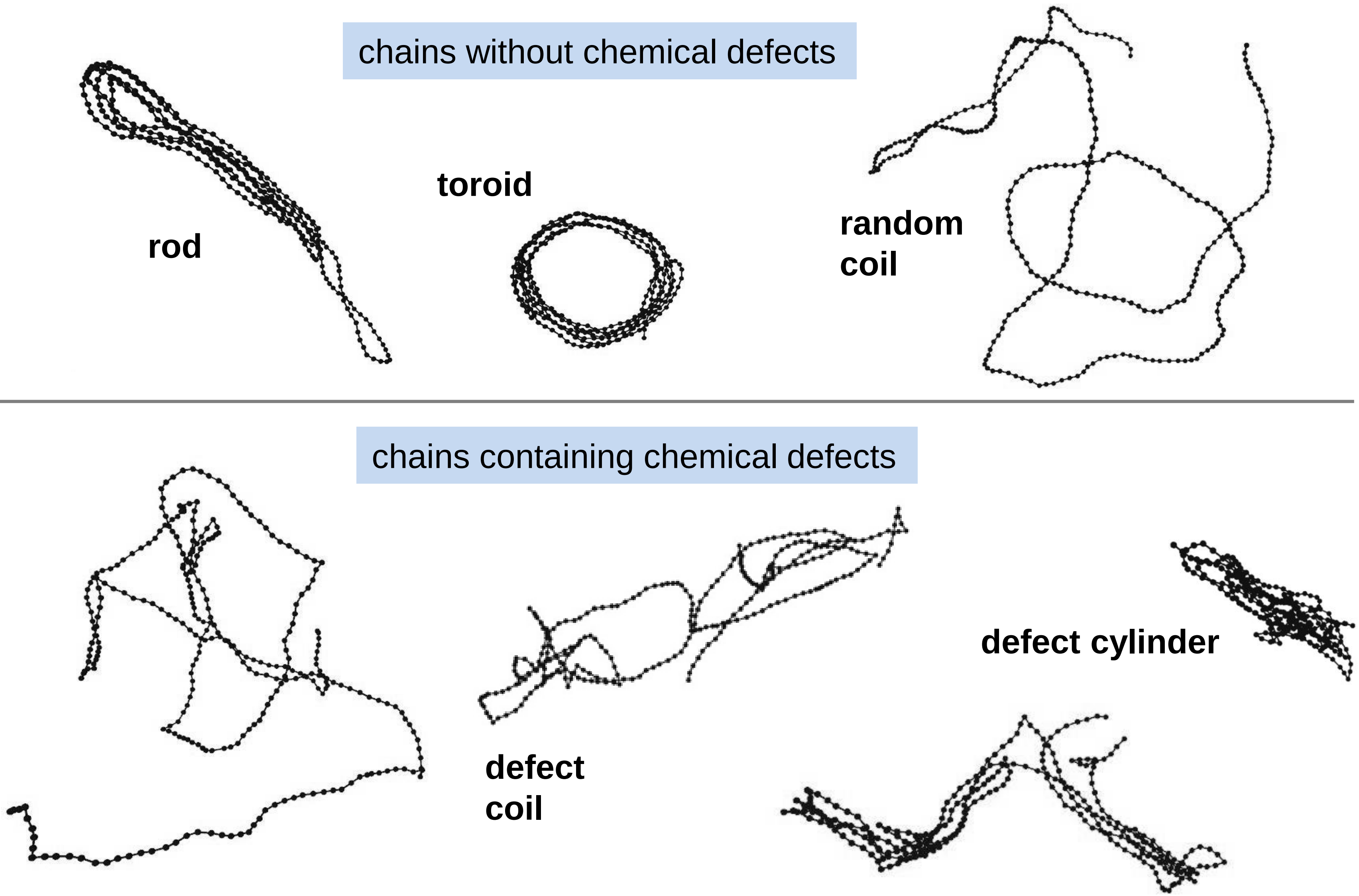
Topological or chemical defects – localization of excitation of a few monomers



CONJUGATED SEGMENTS

Conjugated segments

Conjugated segments are determined by chain conformation



Conjugated segments – optical properties and interactions

CONJUGATED SEGMENTS form **CHROMOPHORES** – basic entities interacting with light

***Optical properties** of conjugated polymers:*

- number of conjugated segments (10 – 100)
- length (5 – 15 monomers) and length distribution of conjugated segments
- inter-segment interactions

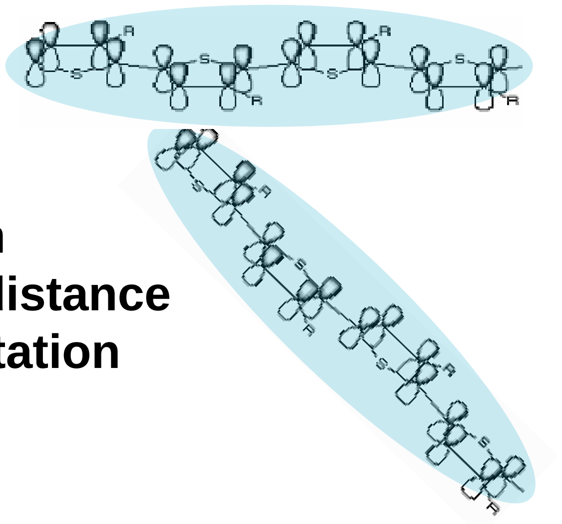
INTERACTIONS

intra-chain and inter-chain

- excited energy transfer
- photoinduced charge transfer
- formation of excimers and aggregates
- radiative polaron-pair recombination
- T-T annihilation

depend on segment **distance** and **orientation**

chain CONFORMATION

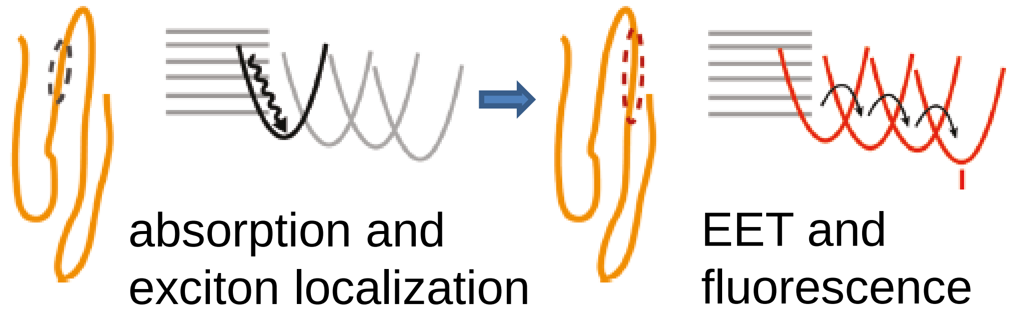


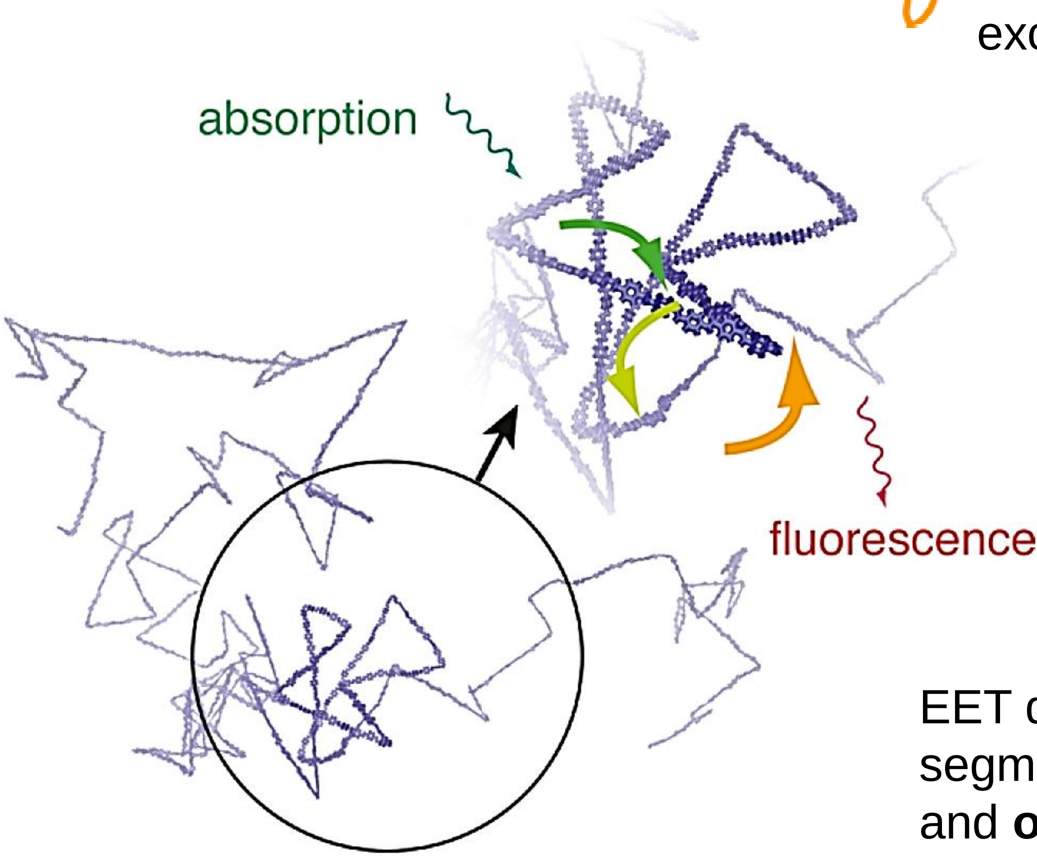
Conjugated segments – optical properties and interactions

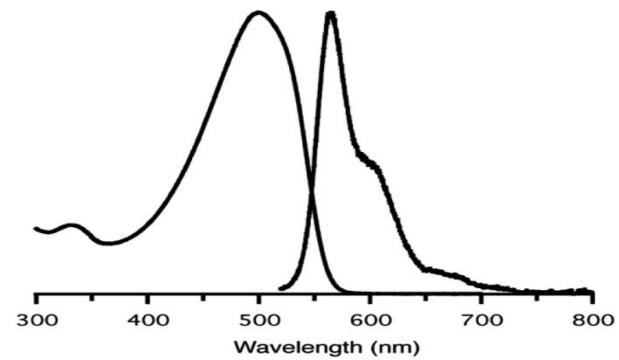
INTERACTIONS

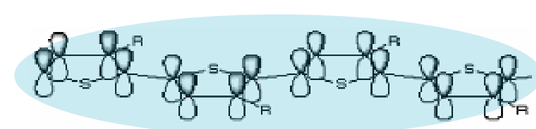
intra-chain and inter-chain

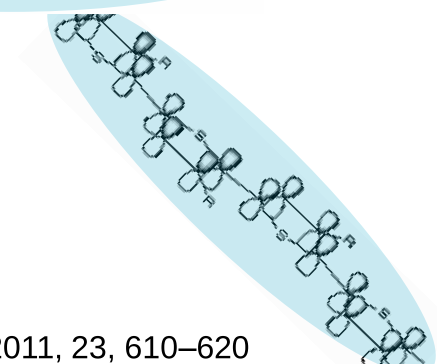
- **excited energy transfer EET**











EET depends on segment **distance** and **orientation**

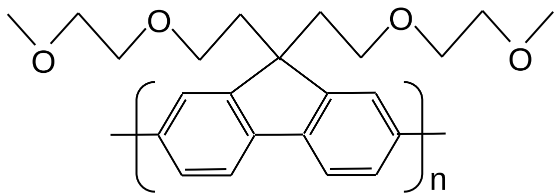
Efficient interchain, inefficient intrachain EET

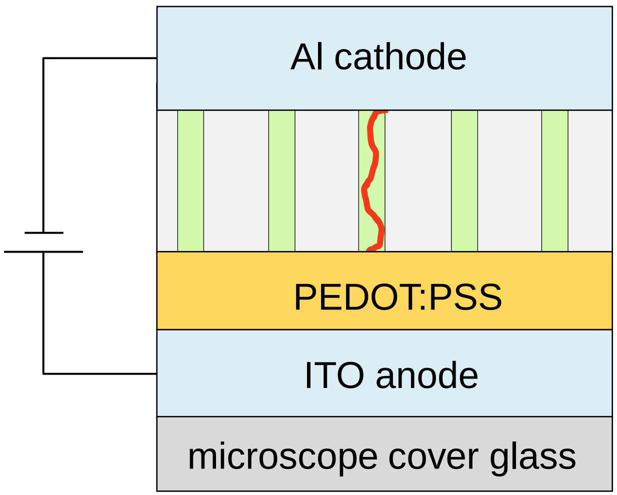
Chem. Mater. 2011, 23, 610–620

SINGLE-MOLECULE ELECTROLUMINESCENCE

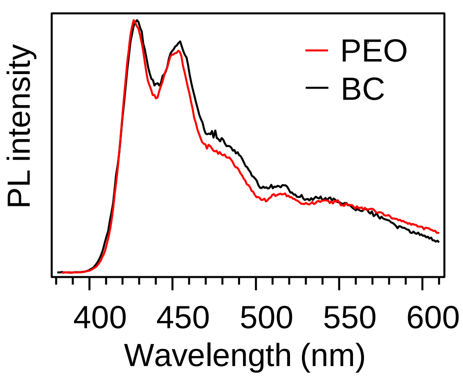
Single-molecule electroluminescence II. Conjugated polymers

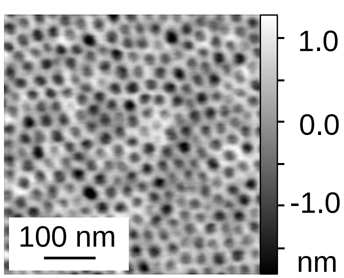
BDOH-PF



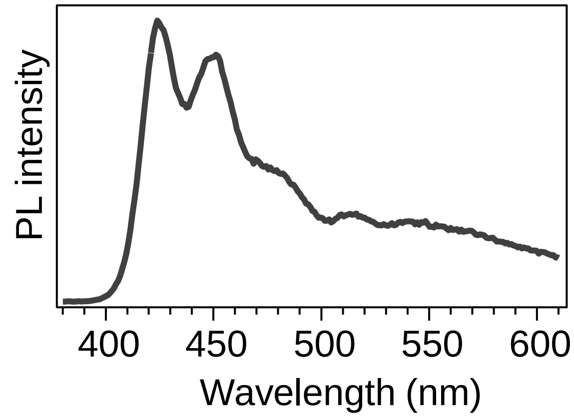


OLED device

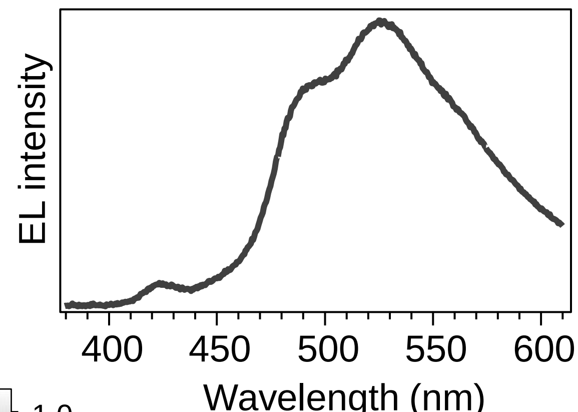




photoluminescence

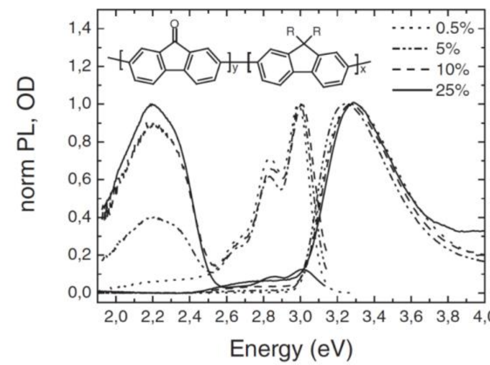


electroluminescence



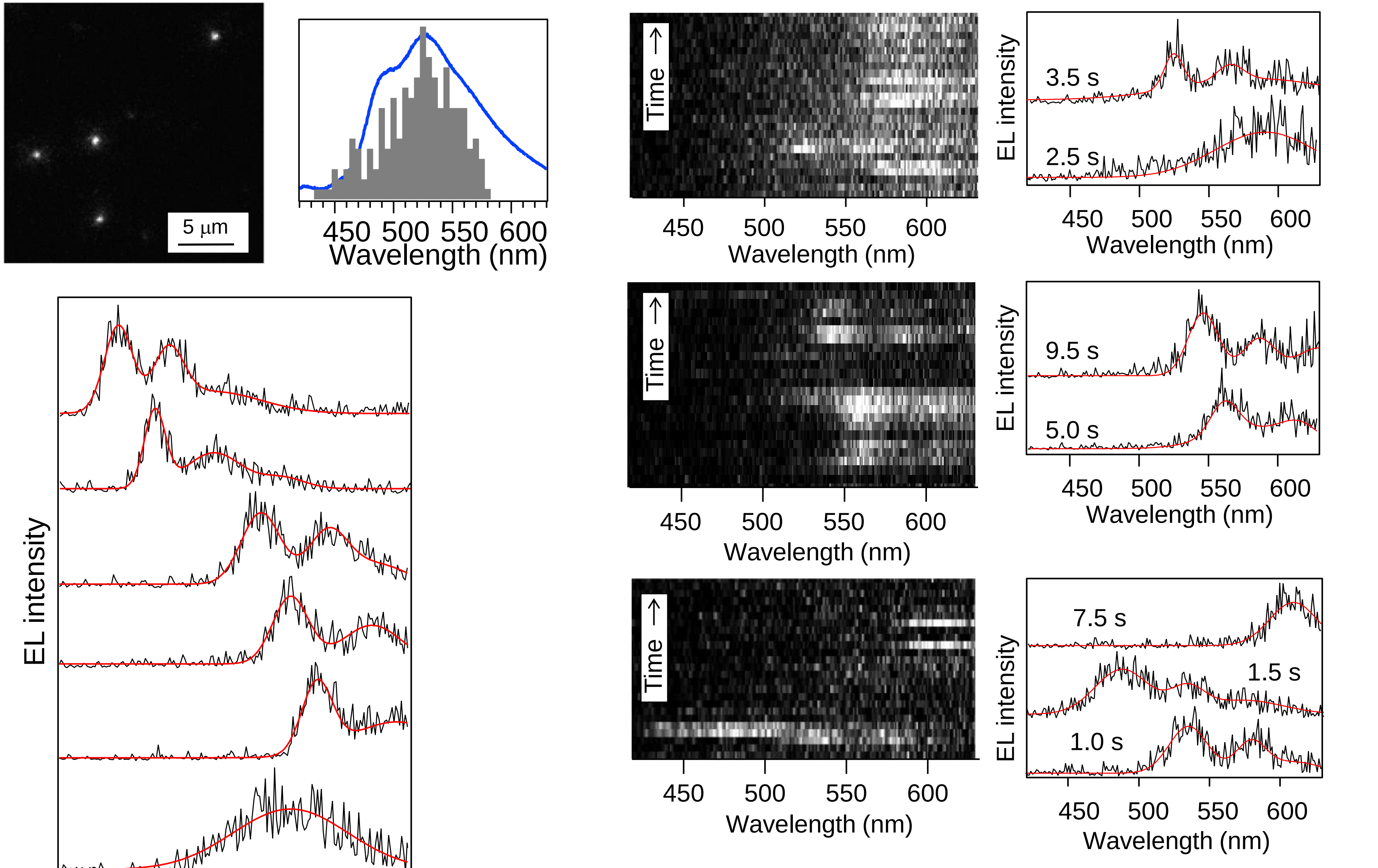
Proposed origins of the green band:

- fluorenone defects
- excimer fluorescence



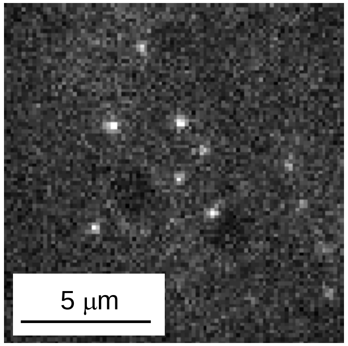
E. List et al., *Adv. Funct. Mater*. 13 (2003) 597

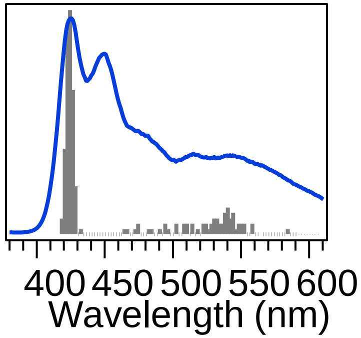
Single molecule electroluminescence

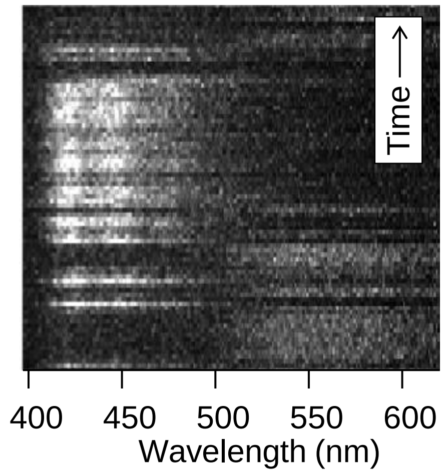


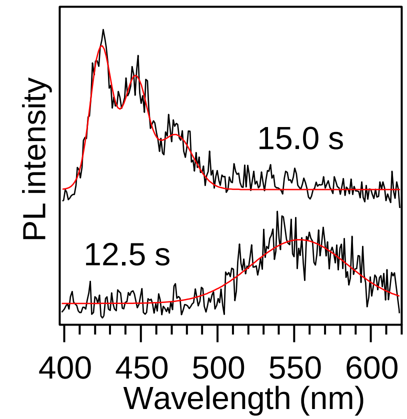
Large distribution of EL spectral position and shapes, large distribution of spectral jumps energies

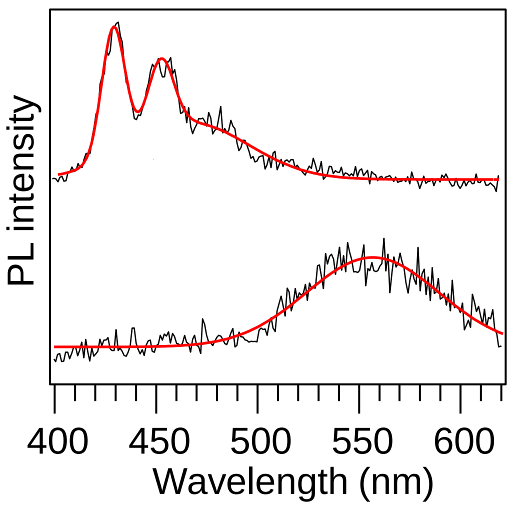
Single molecule photoluminescence

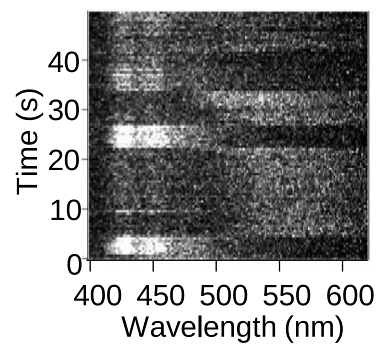


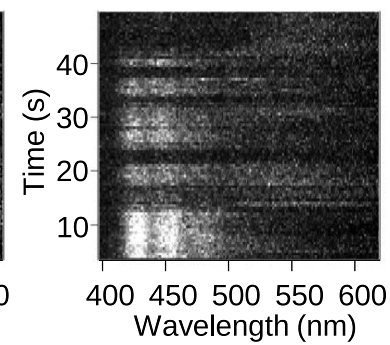


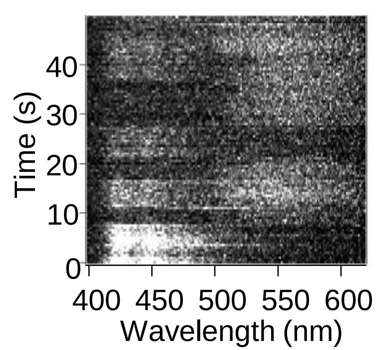


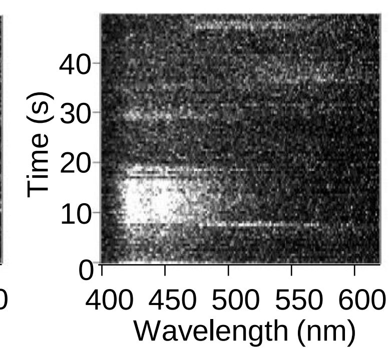








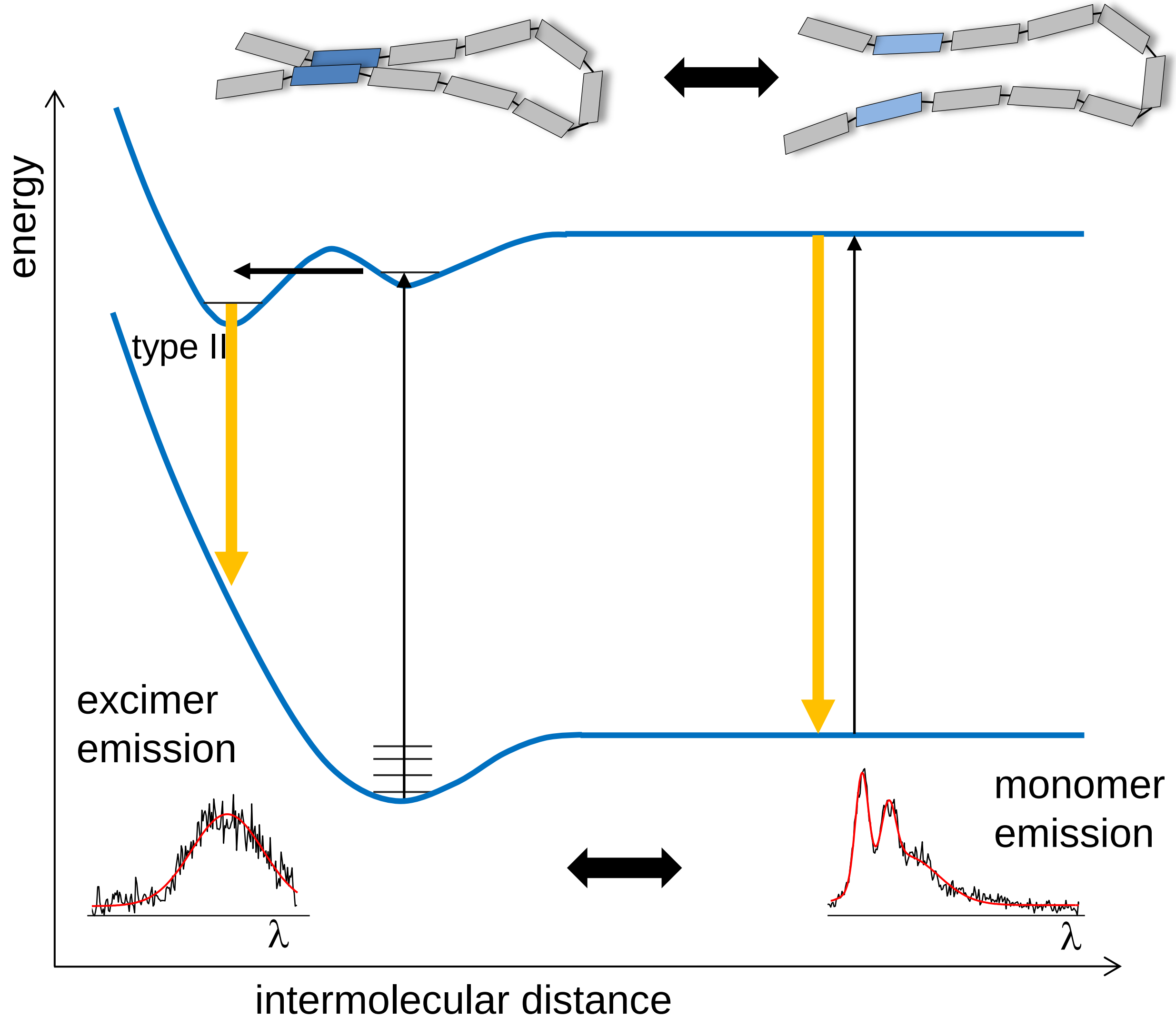




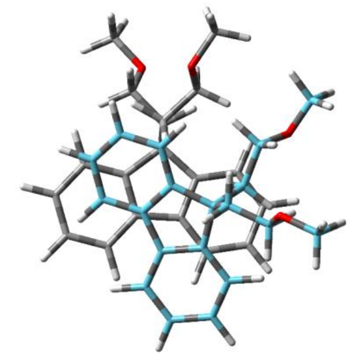
Two types of PL spectra, mainly two-state spectral jumps

Origin of the photoluminescence spectra

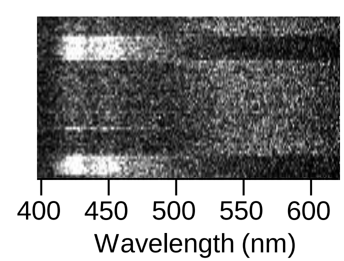
BDOH-PF conformation changes



neutral dimer



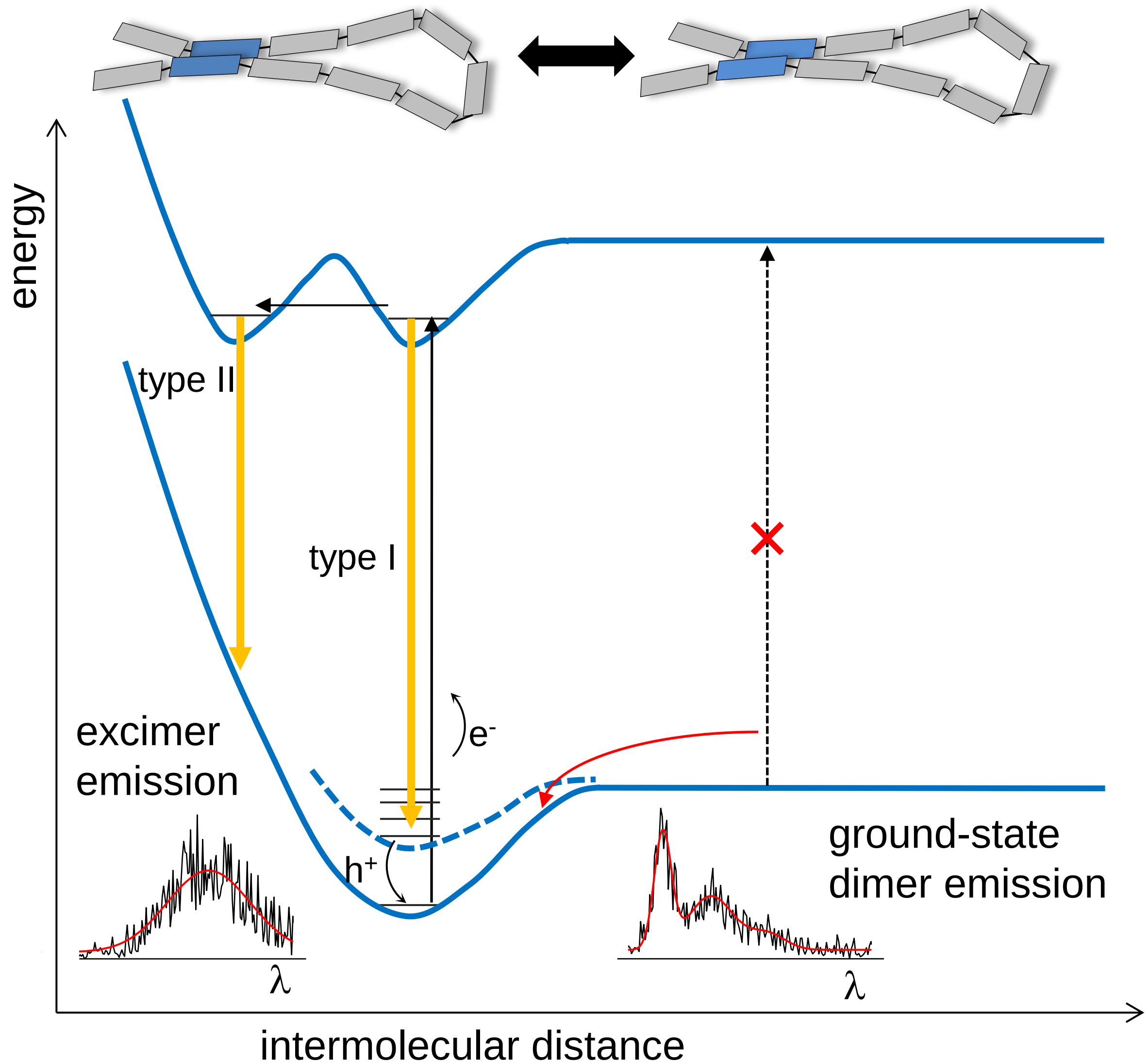
-49.6 kJ/mol



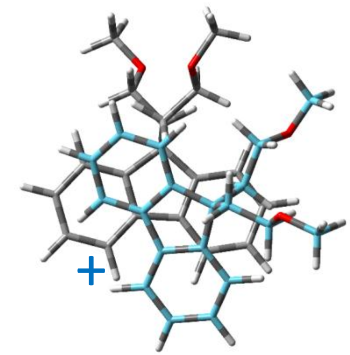
Nature Commun. 5 (2014) 4666

Origin of the electroluminescence spectra

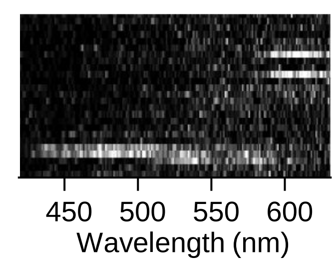
BDOH-PF conformation changes



mixed dimer



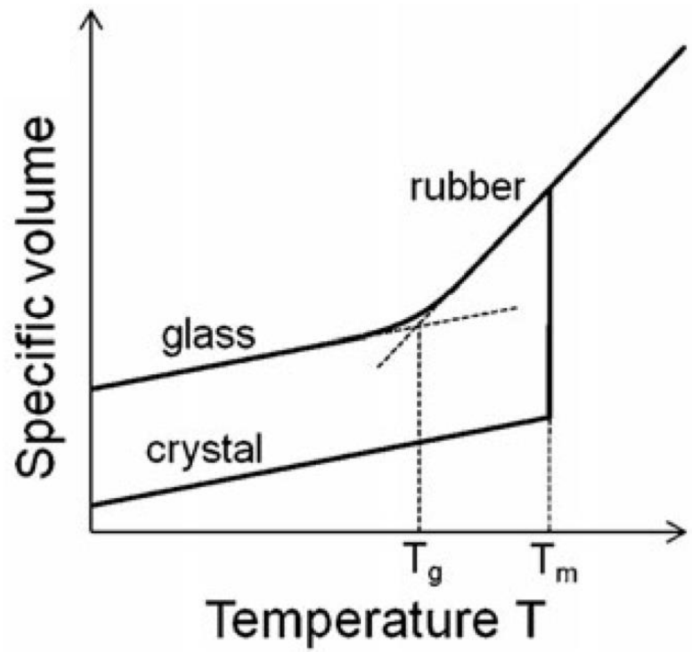
-101.5 kJ/mol



Nature Commun. 5 (2014) 4666

NANOSCALE PHYSICS OF POLYMER SOLIDS

Physics of polymer solids: Glass transition, chain relaxation



Physical properties near T_g originate from relaxation processes of polymer chains.

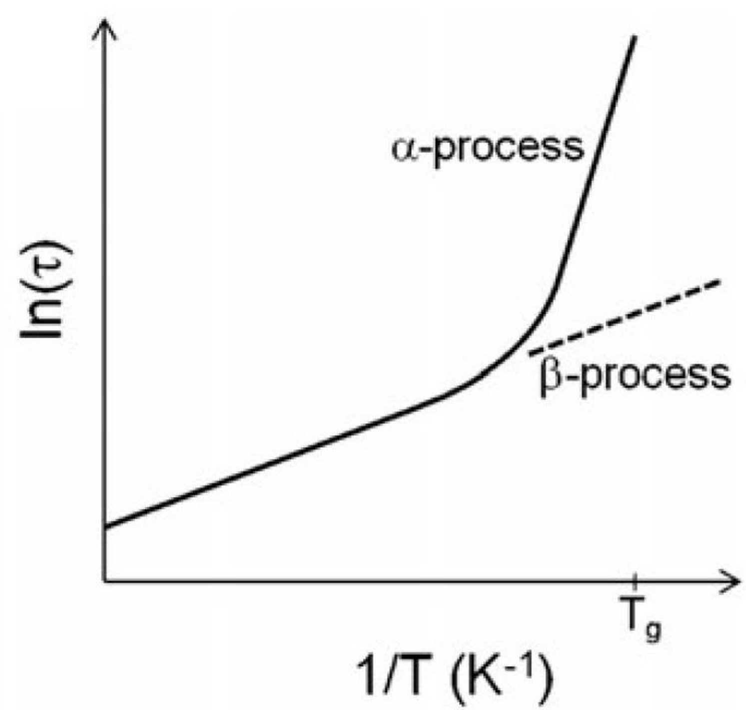
⇩

α-process (slowest) - relaxation due to *cooperative motions* of polymer chains (segments); non-exponential behavior

β, γ-processes – *local processes* (e.g., relaxation of sidechanis or sidegroups); Arhenius-like behavior

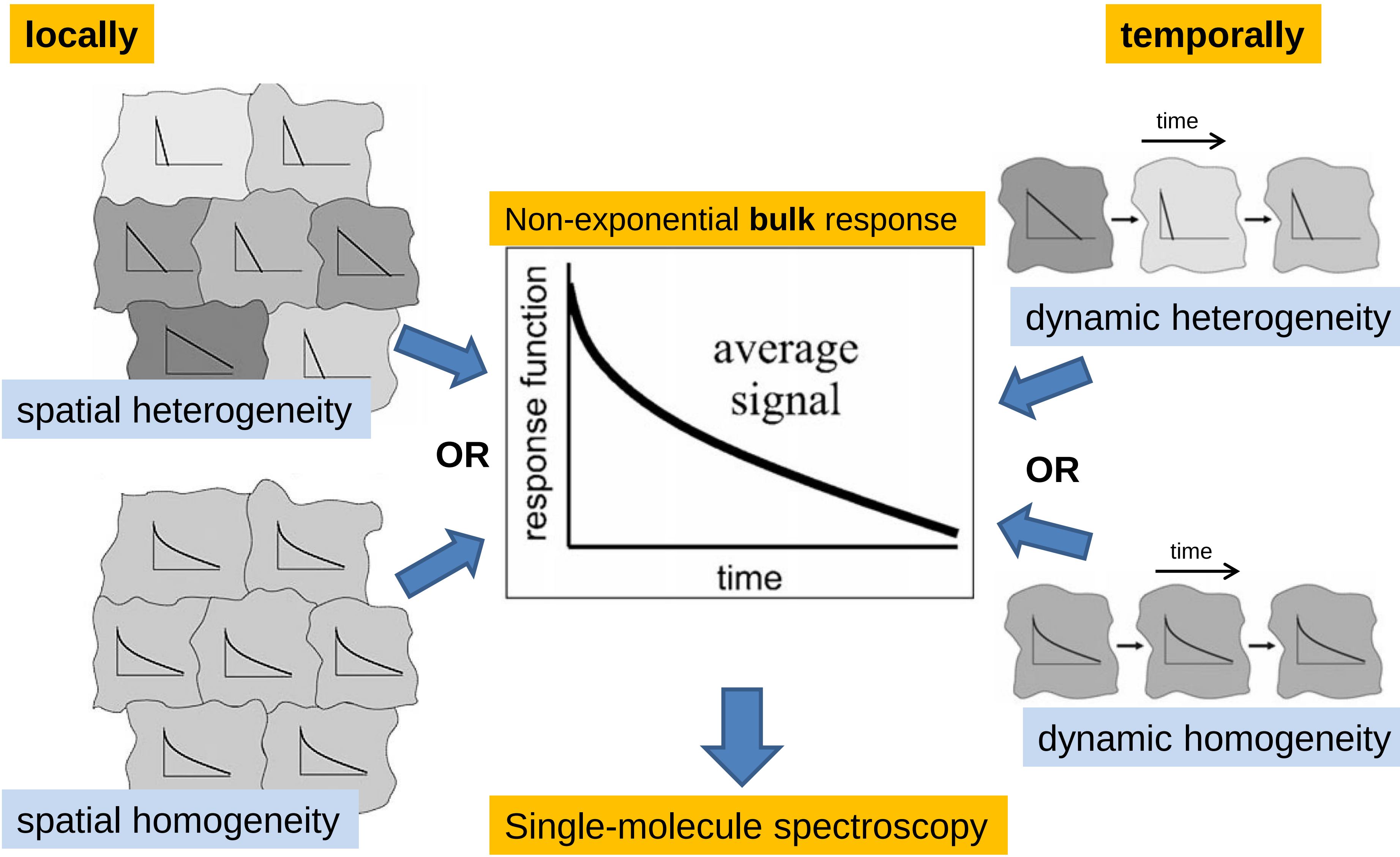
Glass transition

- polymers form a glassy state around a temperature T_g (glass transition temperature)
- physical properties, such as specific volume, expansion coefficient, heat capacity, viscosity, etc., change drastically at T_g
- T_g is measured mainly by heat capacity (DSC) or specific volume as function of temperature
- change of the properties occurs within a temperature range and depends on the cooling rate



Physics of polymer solids: Glass transition, chain relaxation

Non-exponential response in **bulk** physical properties of polymers to external perturbations, e.g. heating



Method

Macromolecules **1999**, *32*, 4474–4476

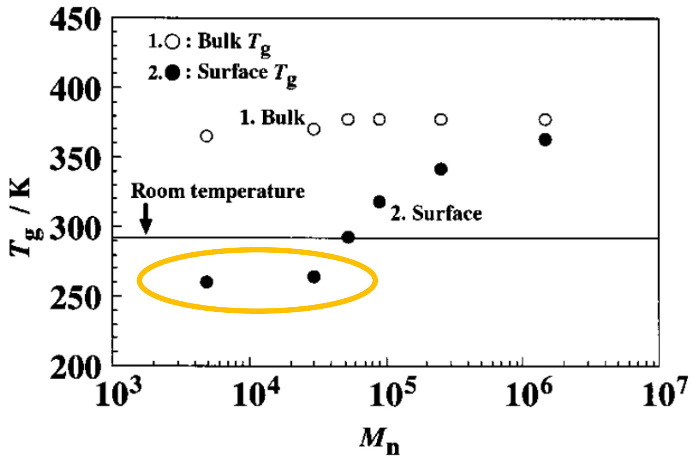
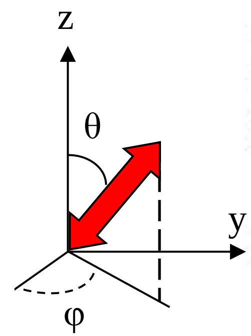
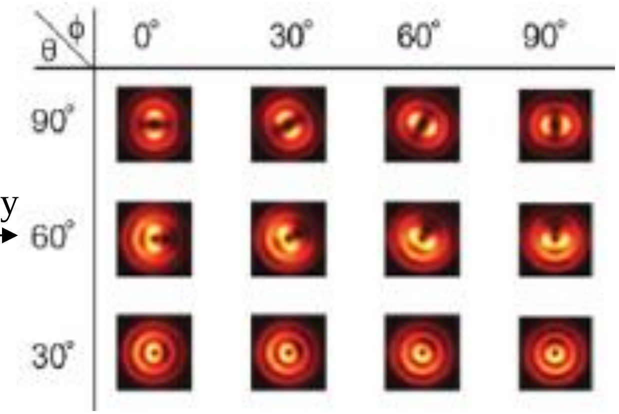
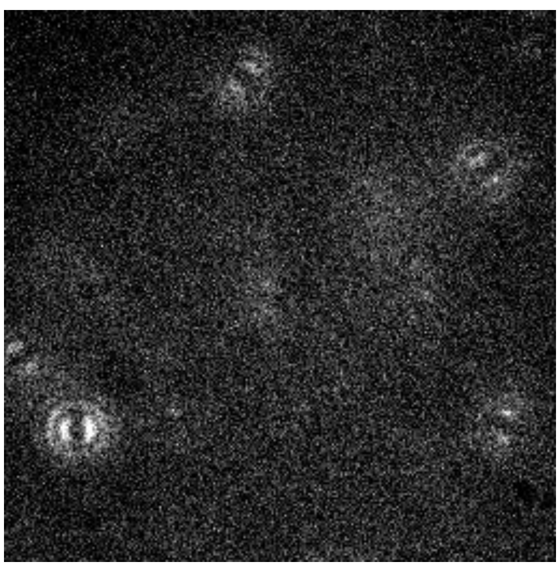


Figure 2. Molecular weight dependence of $T_{g,s}$ and $T_{g,b}$ for the monodisperse PS films.

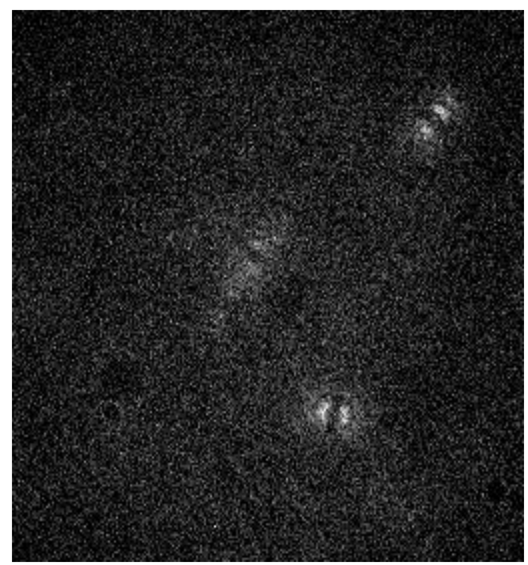






Styrene oligomer
M_w = 1,000
bulk T_g ~ 10 C

all molecules rotating



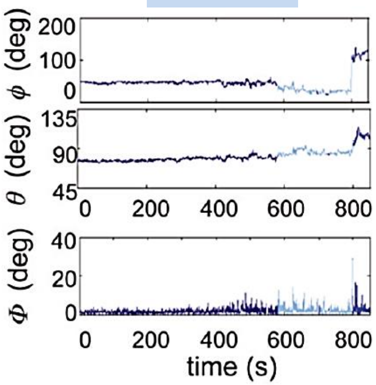
Low M_w PS
M_w = 10,000
bulk T_g ~ 90 C
surface T_g < R.T

80 nm film
– **14%** rotating
32 nm film
– **22%** rotating

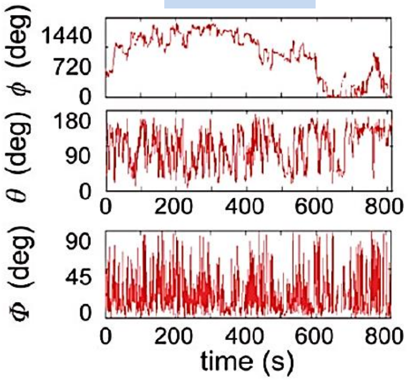
Heterogeneity of polymer dynamics near the Tg

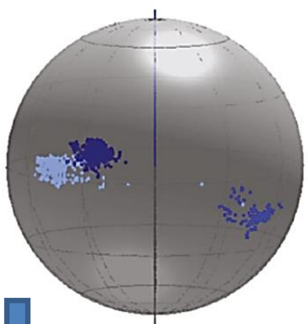
poly(n-butyl methacrylate) PnBMA; Tg = 296 K

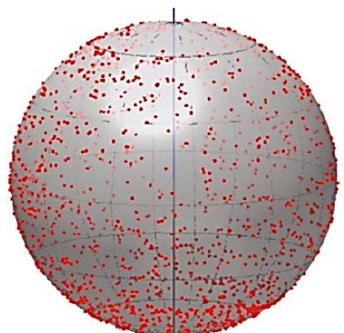
296 K



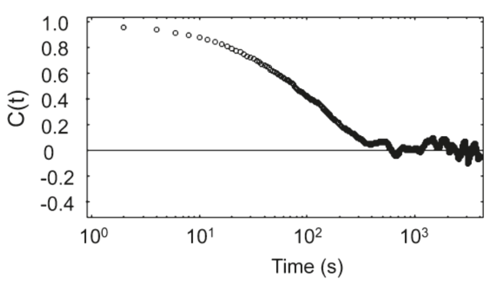
315 K







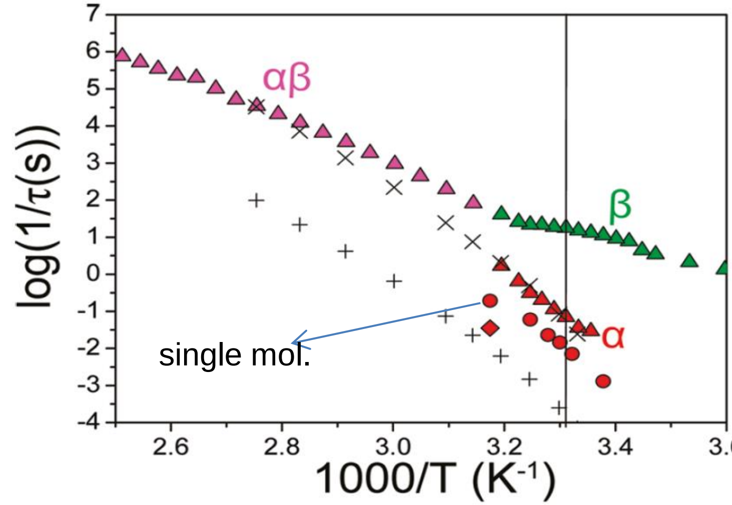
rotational diffusion behavior of PDI analyzed from defocused images

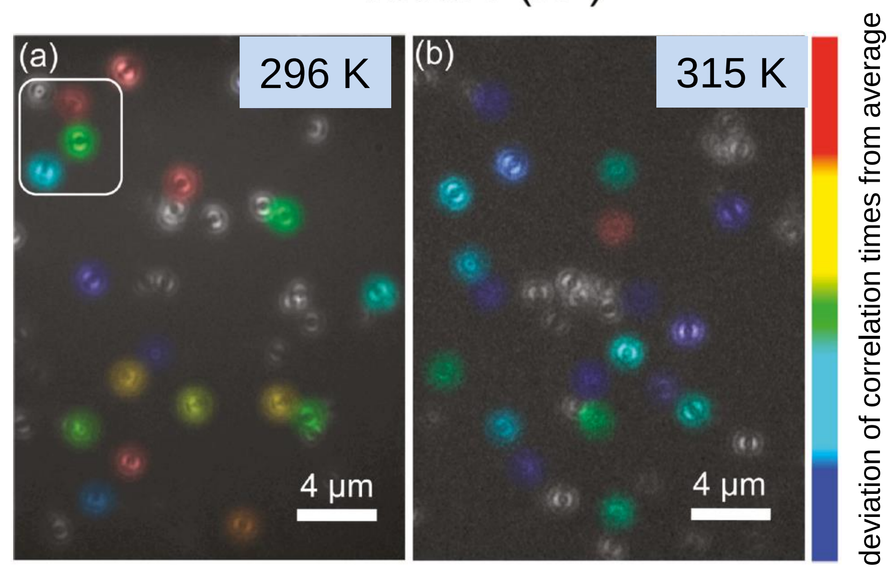


Autocorrelation function

Correlation time τ

Bulk and single-molecule relaxation times

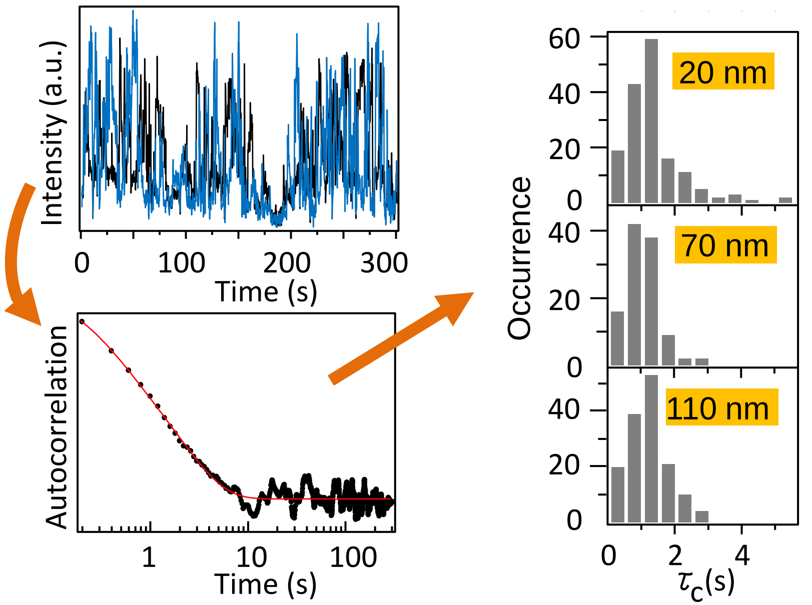




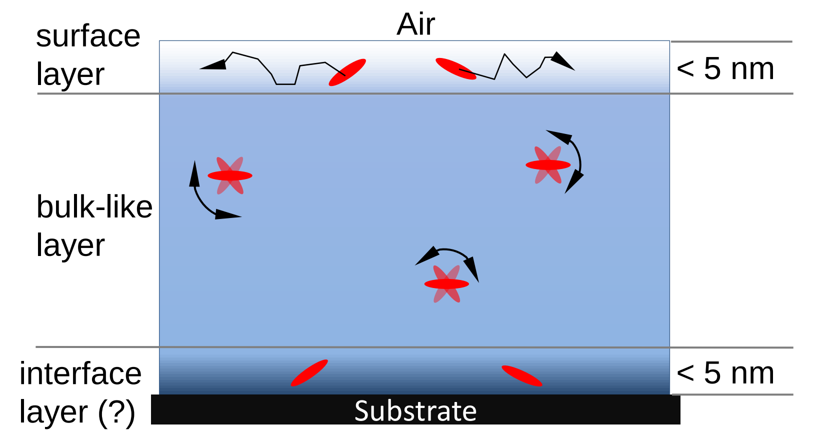
Spatial heterogeneity at different temperatures

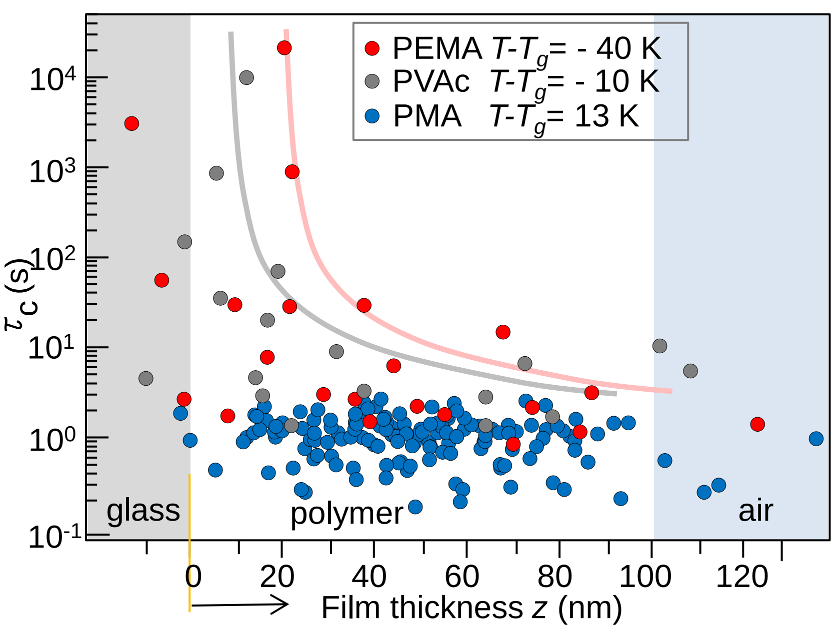
Macromolecules 2011, 44, 9703

Mapping of polymer dynamics across thin films



Thin poly(methacrylate) (PMA) films:
- no dependence of relaxation time on film thickness
- no dependence on position inside the film
- presence of thin surface mobile layer





Thin poly(ethyl methacrylate) (PEMA) and poly(vinyl acetate) (PVAc) films:
- relaxation time increases towards the substrate
- onset of the increase shifts with Tg
- effect of the interface is dominant over the effect of surface

ACS Macro Lett. 1 (2012) 784