北京大学物理学院－2016，11，22

超快激光光谱方法的发展及其在天然及人工光合体系中的应用研究

中国科学院物理研究所

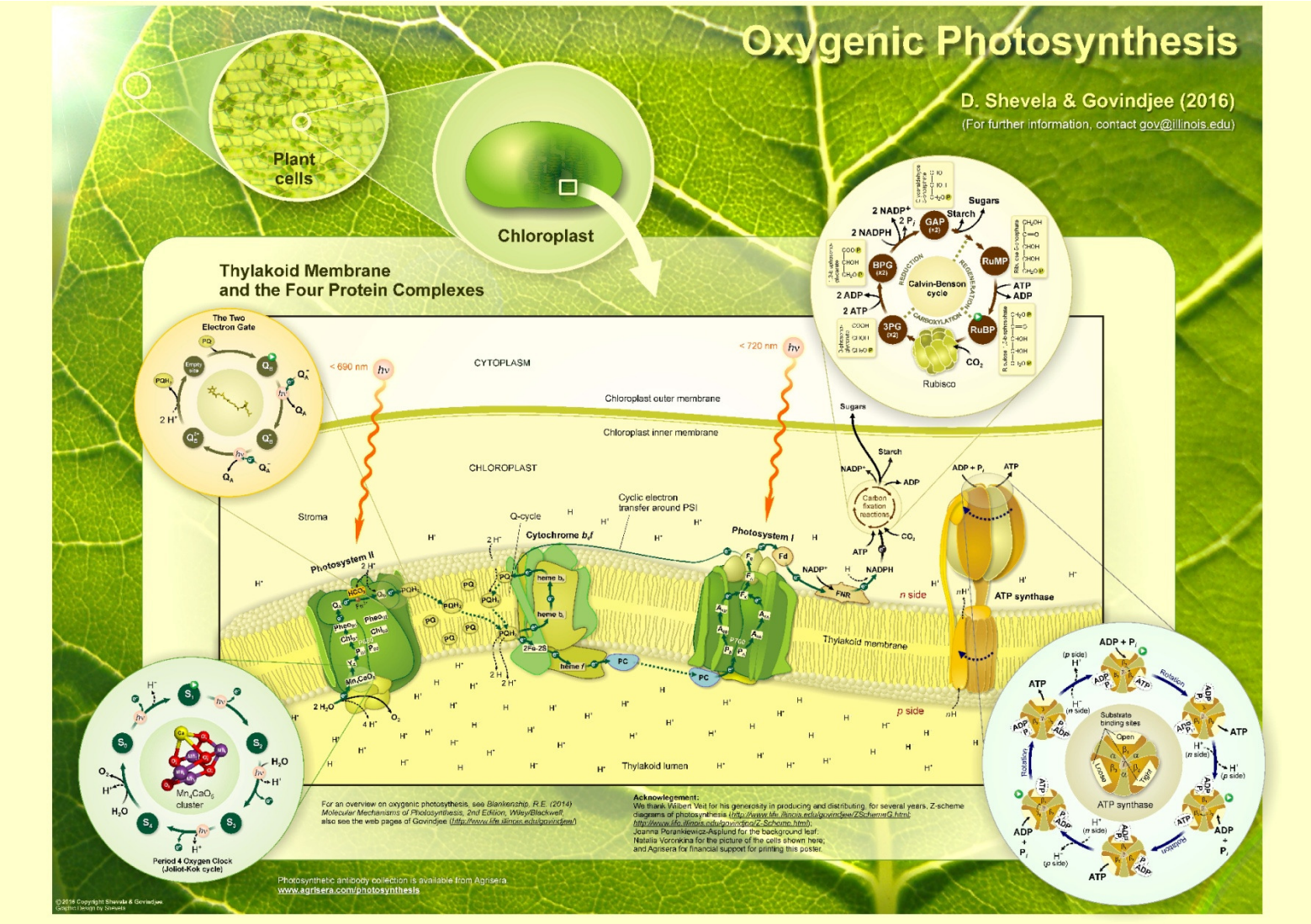
软物质院重点实验室

翁羽翔

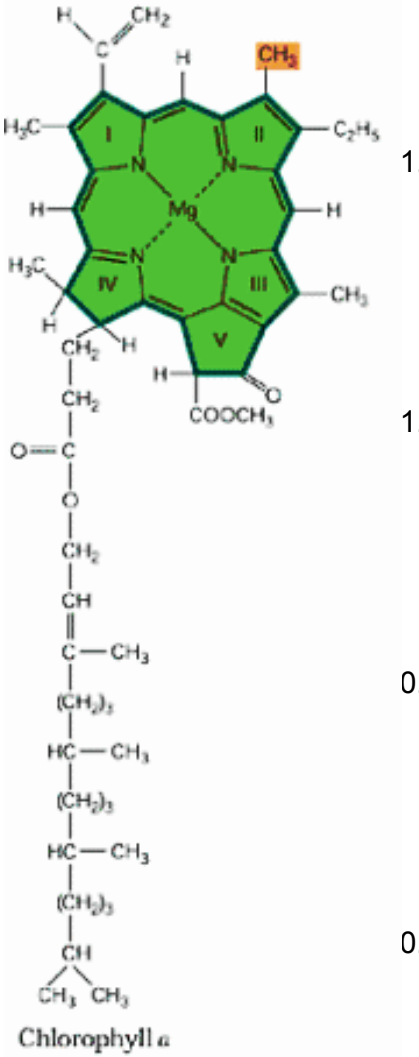
http://sm06.iphy.ac.cn

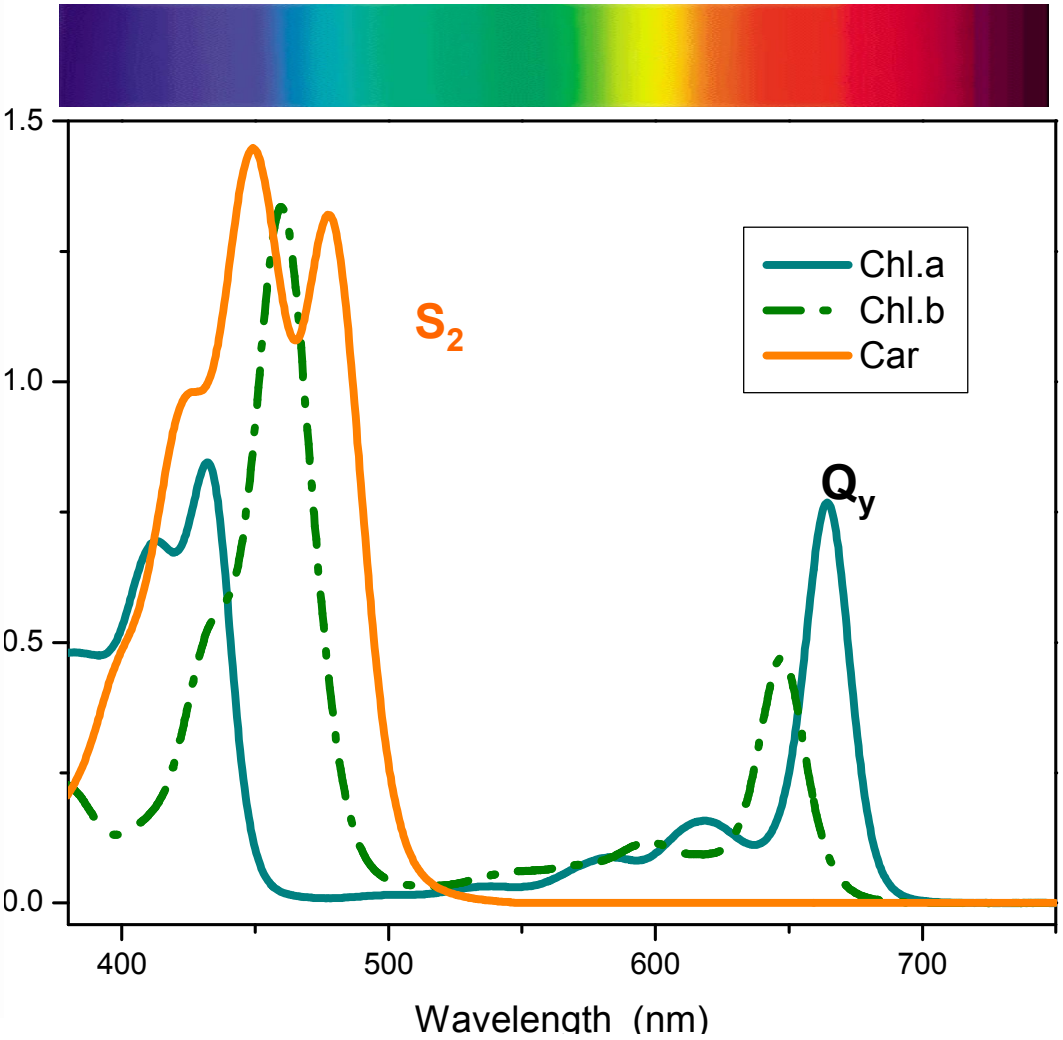
yxweng@aphy.iphy.ac.cn

光合作用


Oxygenic Photosynthesis
D. Shevela & Govindjee (2016)
(For further information, contact gov@illinois.edu)
Plant cells
Chloroplast
Thylakoid Membrane and the Four Protein Complexes
The Two Electron Gate
< 690 nm
< 720 nm
CYTOPLASM
Chloroplast outer membrane
Chloroplast inner membrane
CHLOROPLAST
Stroma
Thylakoid lumen
Thylakoid membrane
Photosystem II
Photosystem I
Cytochrome b6f
Q-cycle
Cyclic electron transfer around PSI
ATP synthase
n side
p side
Sugars
Starch
Calvin-Benson cycle
Rubisco
Carbon fixation reactions
Period 4 Oxygen Clock (Joliot-Kok cycle)
Mn4CaO5 cluster
Substrate binding sites
Open
Loose
Tight
rotation
Photosynthetic antibody collection is available from Agrisera
www.agrisera.com/photosynthesis

光合作用色素分子



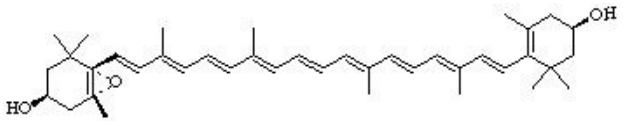


Herbert van Amerongen

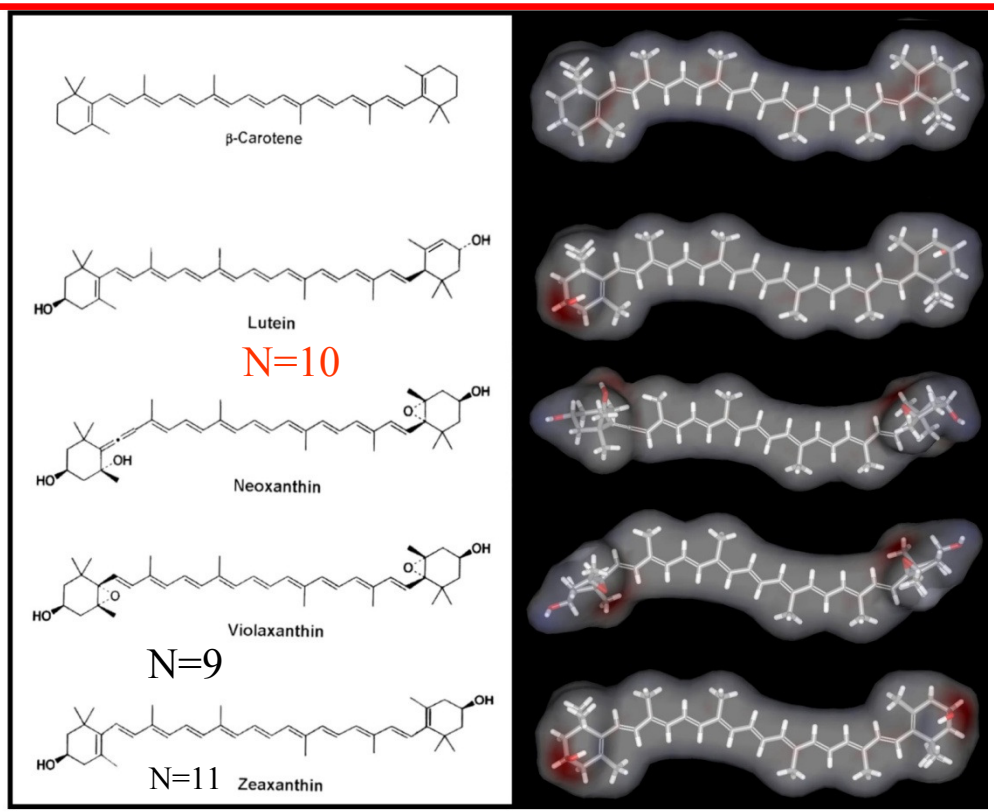
Laboratory of Biophysics Wageningen

类胡萝卜素分子 Carotenoids

Lutein 叶黄素
Neoxanthin 新叶黄素
Violaxanthin 紫黄素，堇菜黄素
Zeaxanthin 玉米黄素
Xanthin　花黄素
Xanthophyll 叶黄素, 胡萝卜醇
Antheraxanthin 环氧玉米黄质

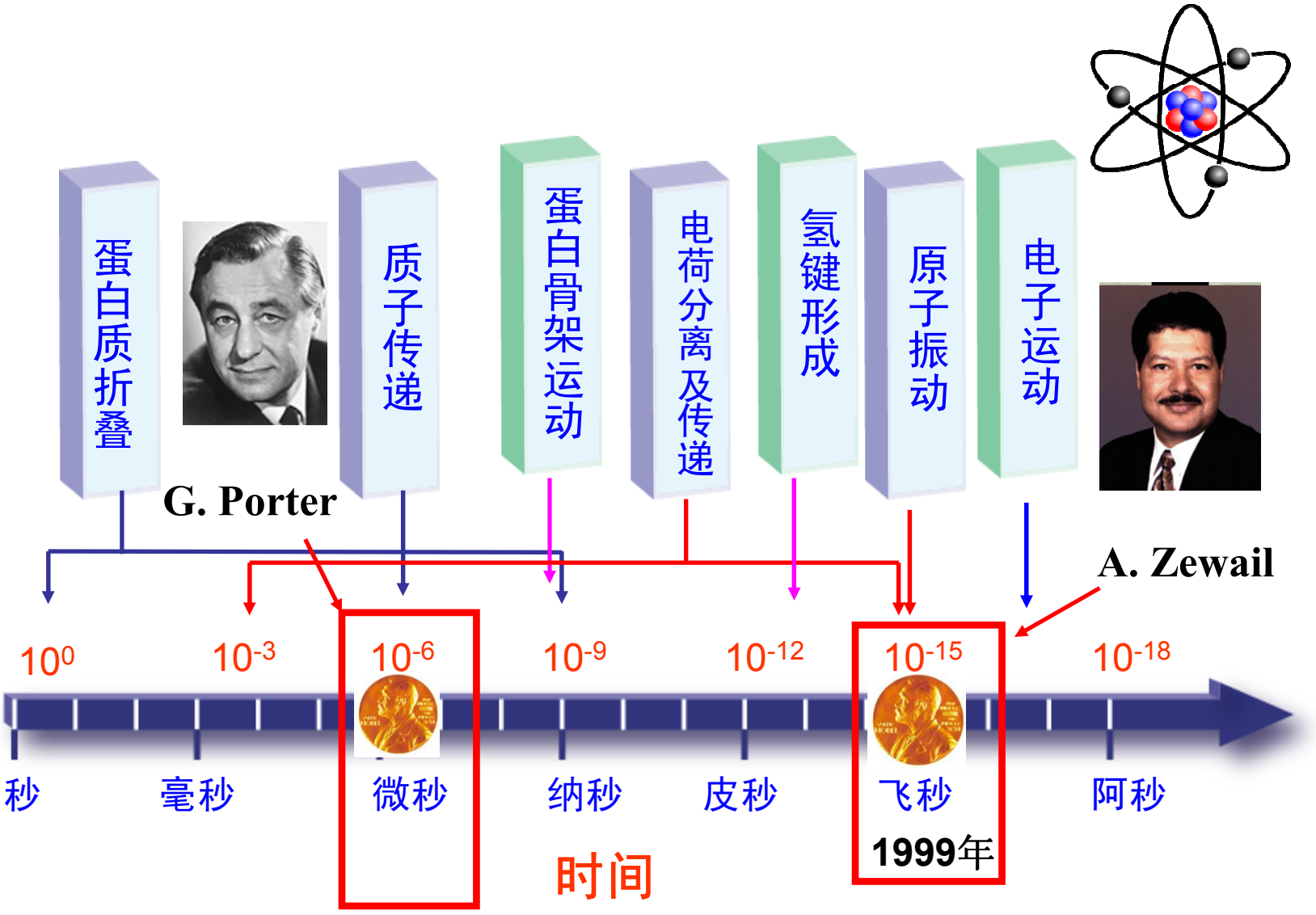


Lumen 腔
Stroma 基质



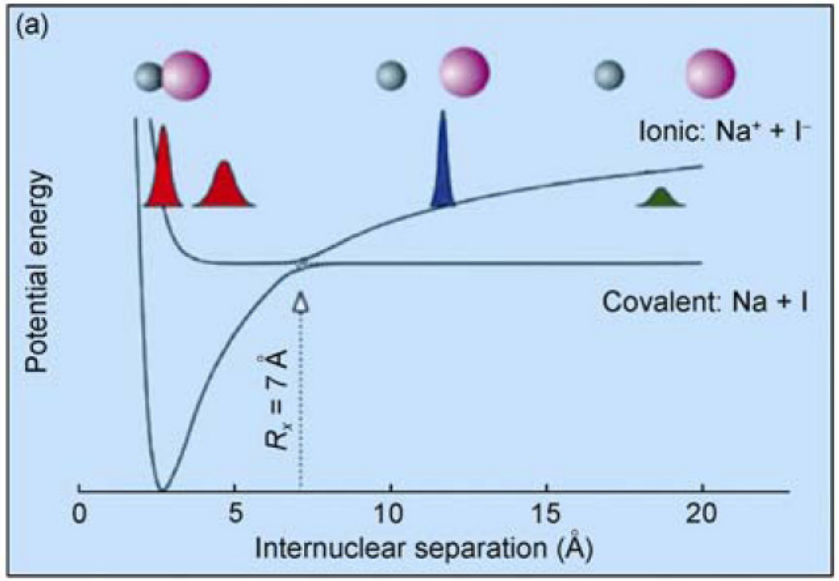
The group of xanthophylls includes lutein, zeaxanthin, , violaxanthin, and α - and β - cryptoxanthin

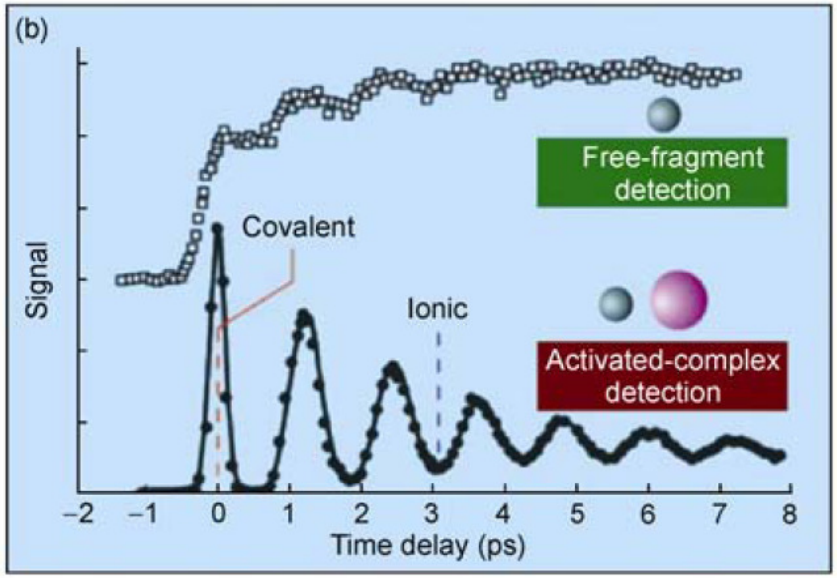
光　研究　物理　学


蛋白质折叠
质子传递
蛋白骨架运动
电荷分离及传递
氢键形成
原子振动
电子运动
G. Porter
A. Zewail
10^{0}
10^{-3}
10^{-6}
10^{-9}
10^{-12}
10^{-15}
10^{-18}
秒
毫秒
微秒
纳秒
皮秒
飞秒
阿秒
时间
1999年

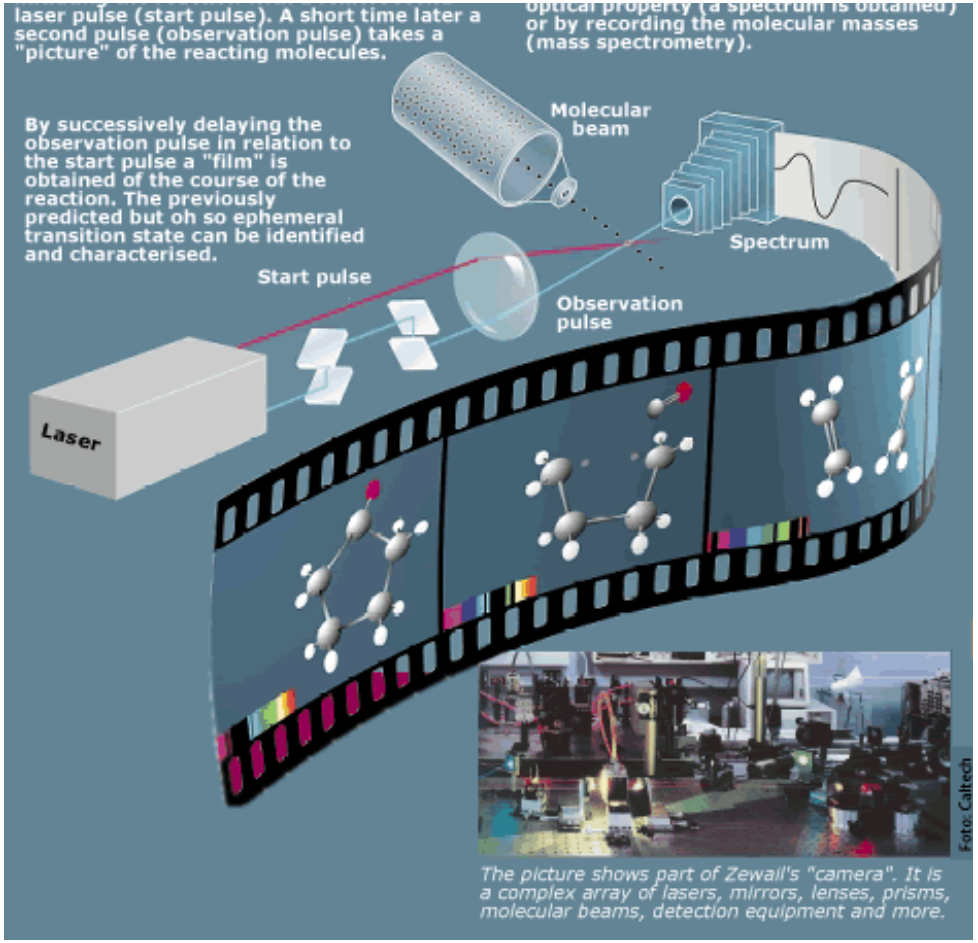
Zewail组应用超快光谱对化学键断裂过程的实时观测

2016,8,2逝世



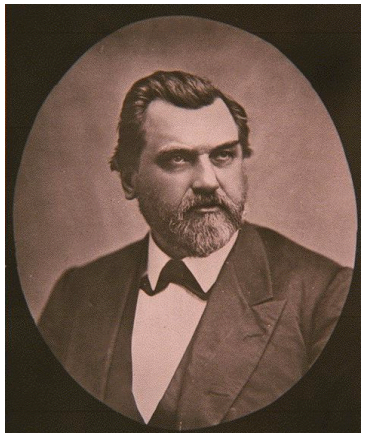


Zewail:　学　　实时

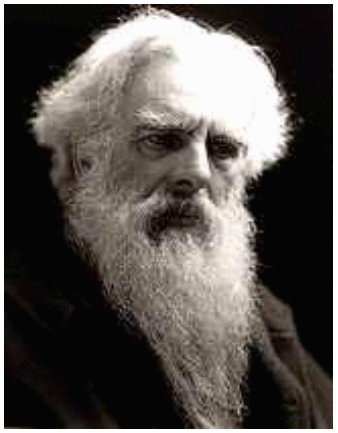

laser pulse (start pulse). A short time later a second pulse (observation pulse) takes a "picture" of the reacting molecules.
or by recording the molecular masses (mass spectrometry).
By successively delaying the observation pulse in relation to the start pulse a "film" is obtained of the course of the reaction. The previously predicted but oh so ephemeral transition state can be identified and characterised.
Molecular beam
Spectrum
Start pulse
Observation pulse
Laser
Foto: Caltech
The picture shows part of Zewail's "camera". It is a complex array of lasers, mirrors, lenses, prisms, molecular beams, detection equipment and more.

光　　时间

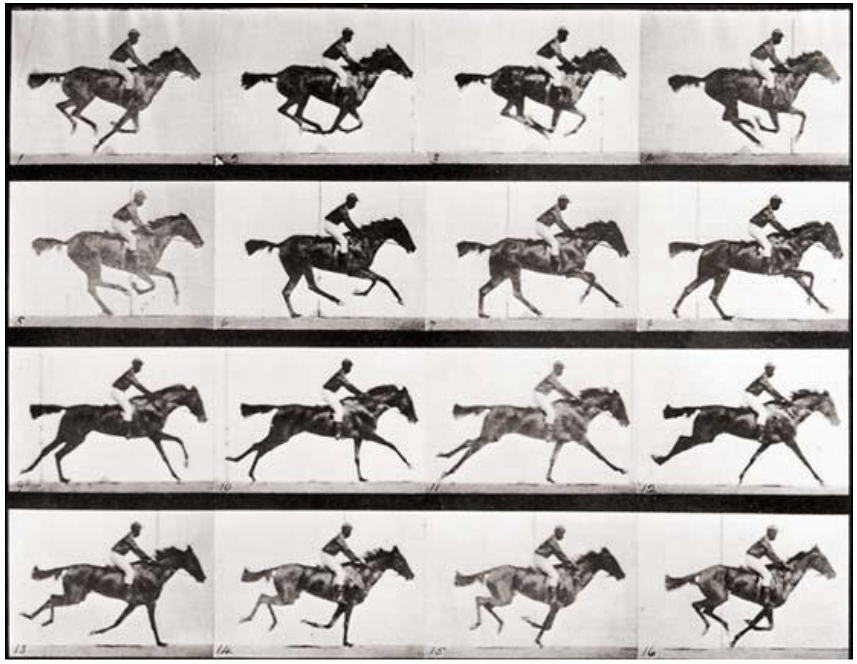
赌：马飞奔的时候四腿是否同时离地？



Leland Stanford

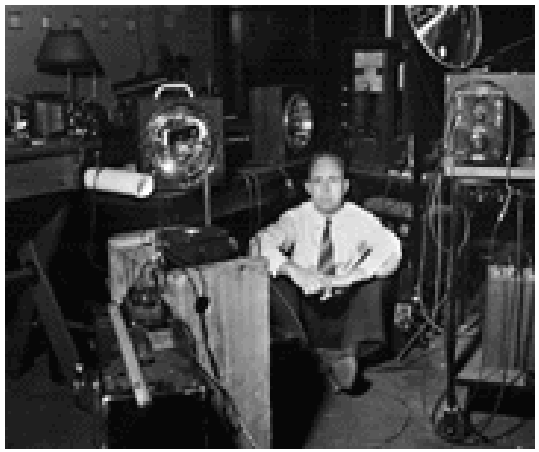


Eadweard Muybridge



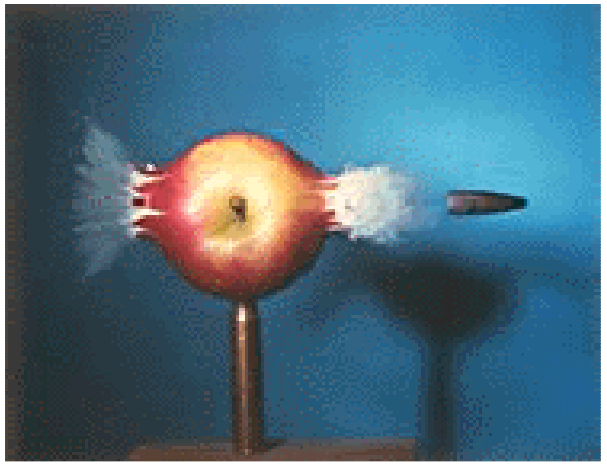
The “Galloping Horse” Controversy
Palo Alto, CA 1872

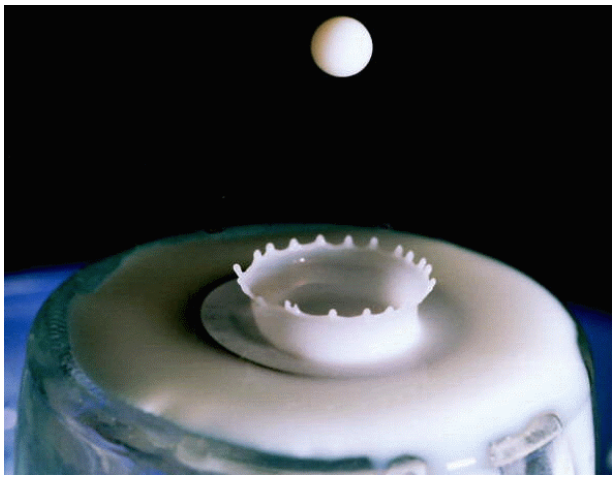
Time resolution:
1/60th of a second



Harold Edgerton
MIT, 1942

"How to Make Apple sauce at MIT"
1964

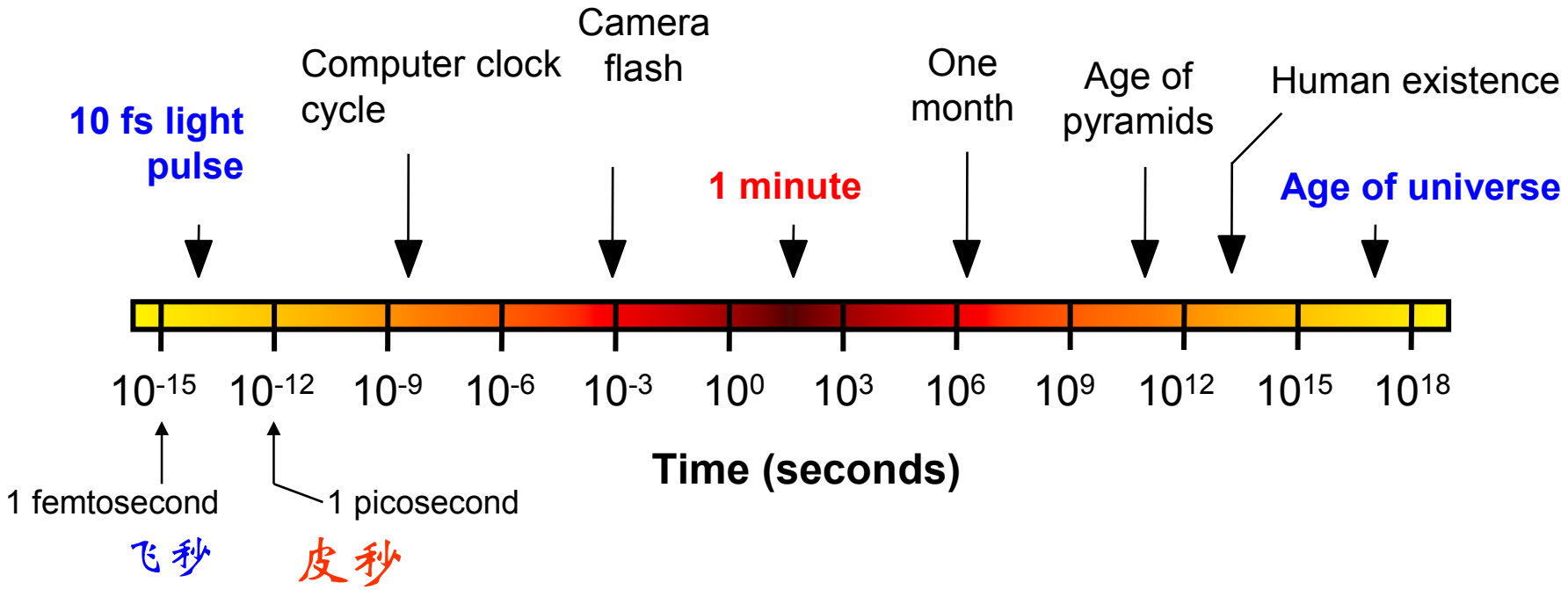




"Splash on a Glass"
Junior High School student
1996

时间分辨率：数微秒

时间


10 fs light pulse
Computer clock cycle
Camera flash
1 minute
One month
Age of pyramids
Human existence
Age of universe
10-15
10-12
10-9
10-6
10-3
100
103
106
109
1012
1015
1018
Time (seconds)
1 femtosecond
飞秒
1 picosecond
皮秒

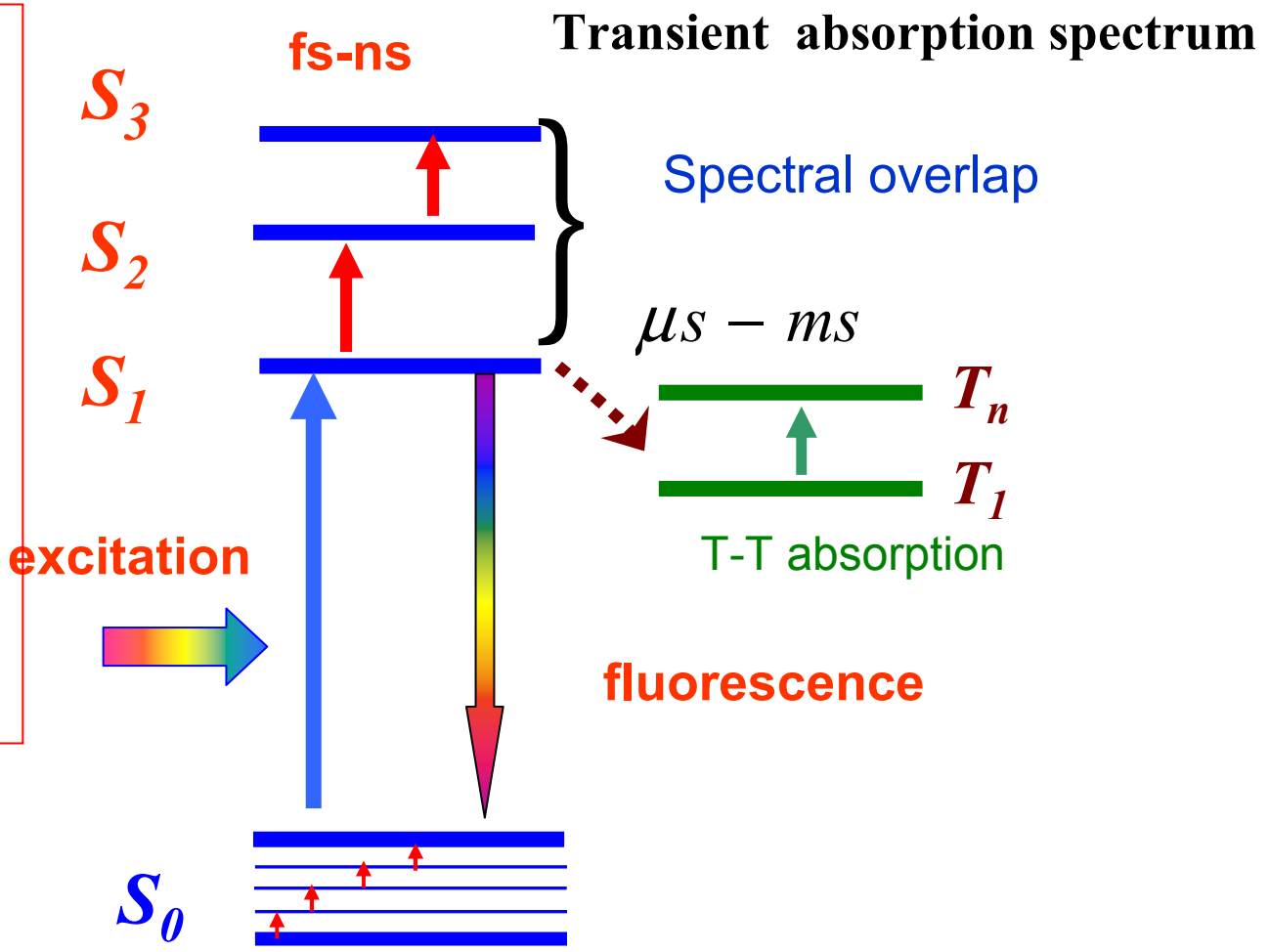
超快时间分辨瞬态荧光光谱与瞬态吸收光谱

光光

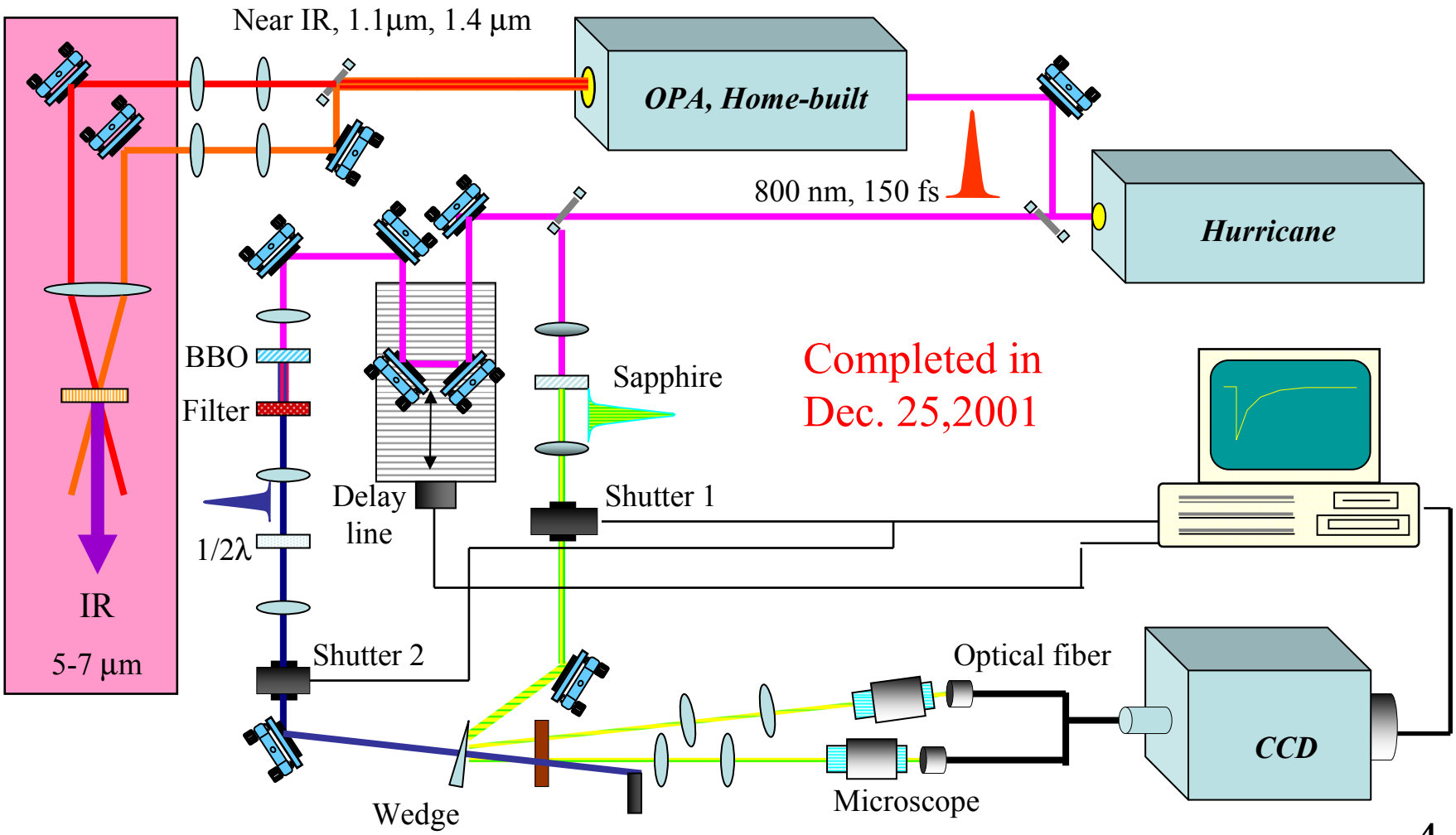
Methods for detecting the excited states

(1) Time-resolved transient absorption

(2) Time-resolved fluorescence



飞秒　　光


Near IR, 1.1μm, 1.4 μm
OPA, Home-built
800 nm, 150 fs
Hurricane
BBO
Filter
1/2λ
IR
5-7 μm
Delay
line
Sapphire
Shutter 1
Shutter 2
Completed in
Dec. 25,2001
Optical fiber
CCD
Microscope
Wedge

飞秒　　光光　研究

150 fs Laser

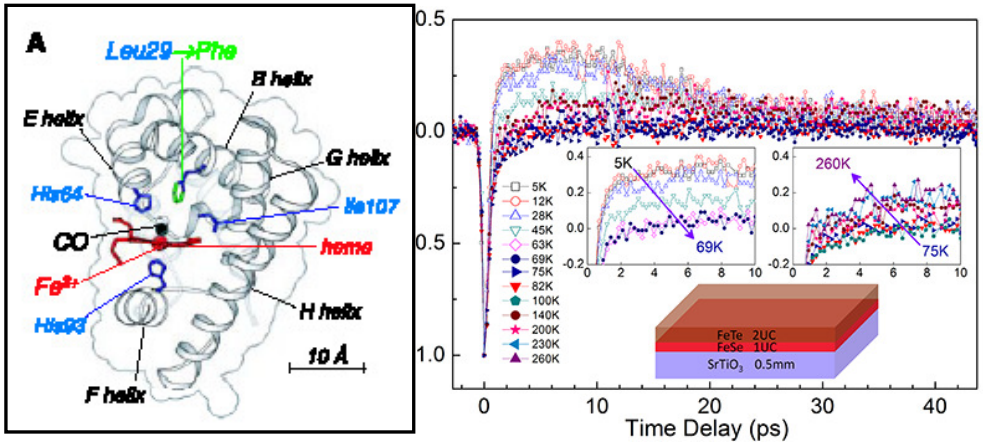
研究

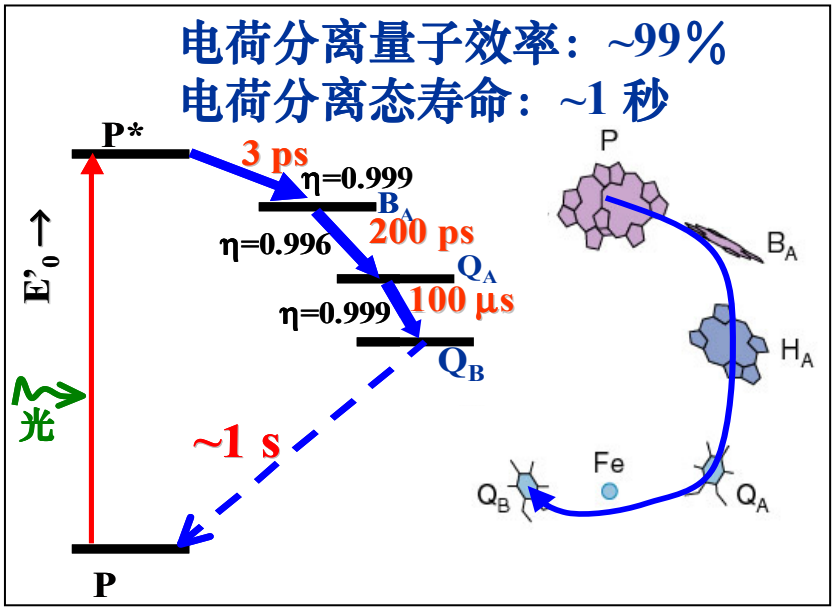
飞秒生物：光合作用原初能量传递及电荷分离过程； 蛋白质动态结构

飞秒物理：超导机制，自旋电子学

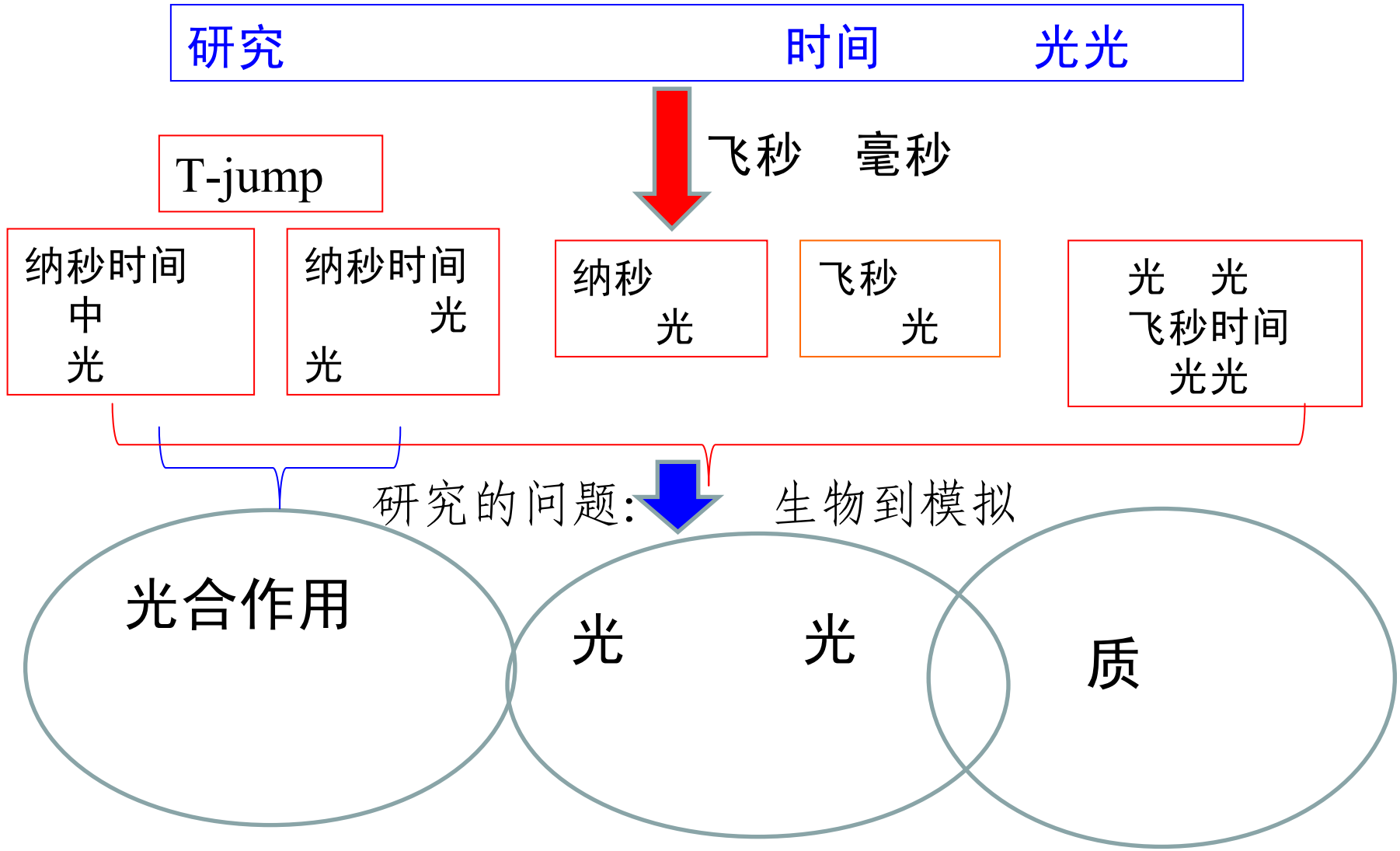
飞秒化学：化学反应，界面过程

飞秒材料：光伏材料，光催化材料





时间　　光　　研究　　物理　　学
物　　科学研究



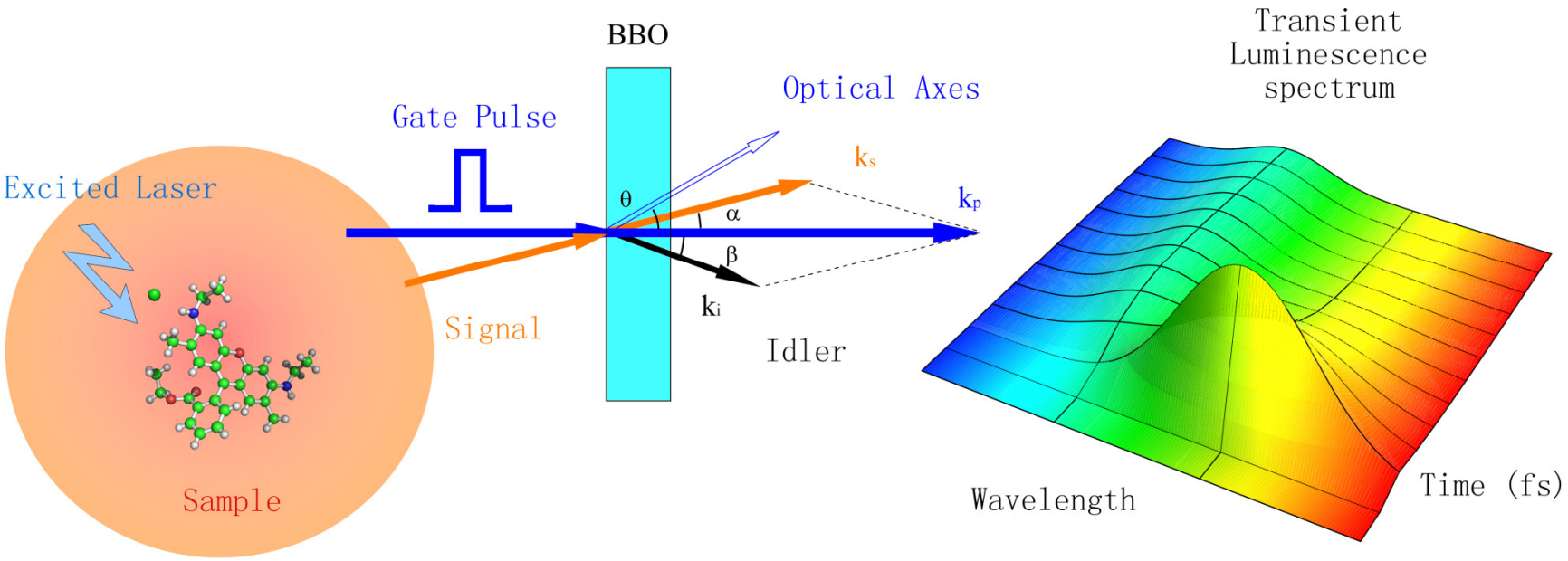
用

光　　光　　光　　飞秒时间　　光
光

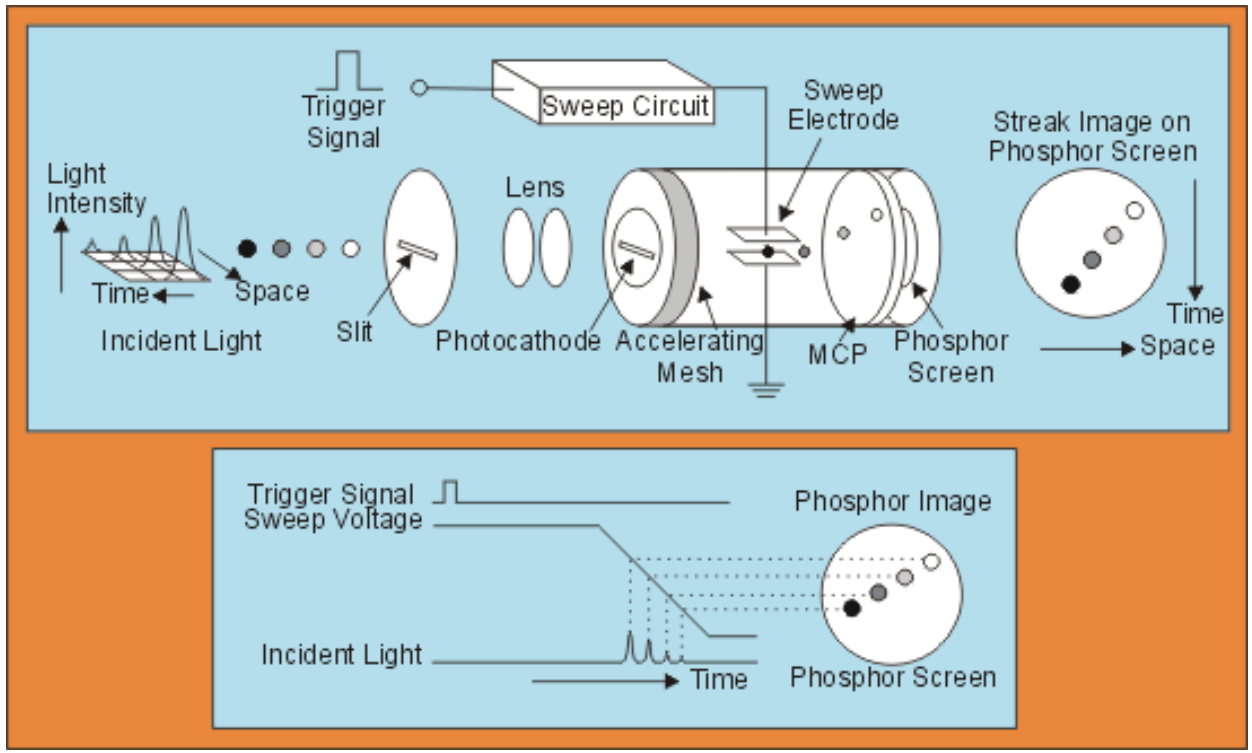
飞秒时间　　中　　光

时间　　中　　—　　光

(1)　光　　光　　光　　飞秒时间
光光　　用

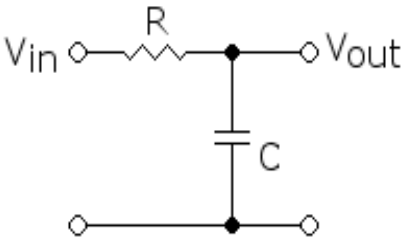


超快时间分辨荧光光谱商用设备：条纹相机工作原理



光电子的空间偏折

Hamamatsu, Japan



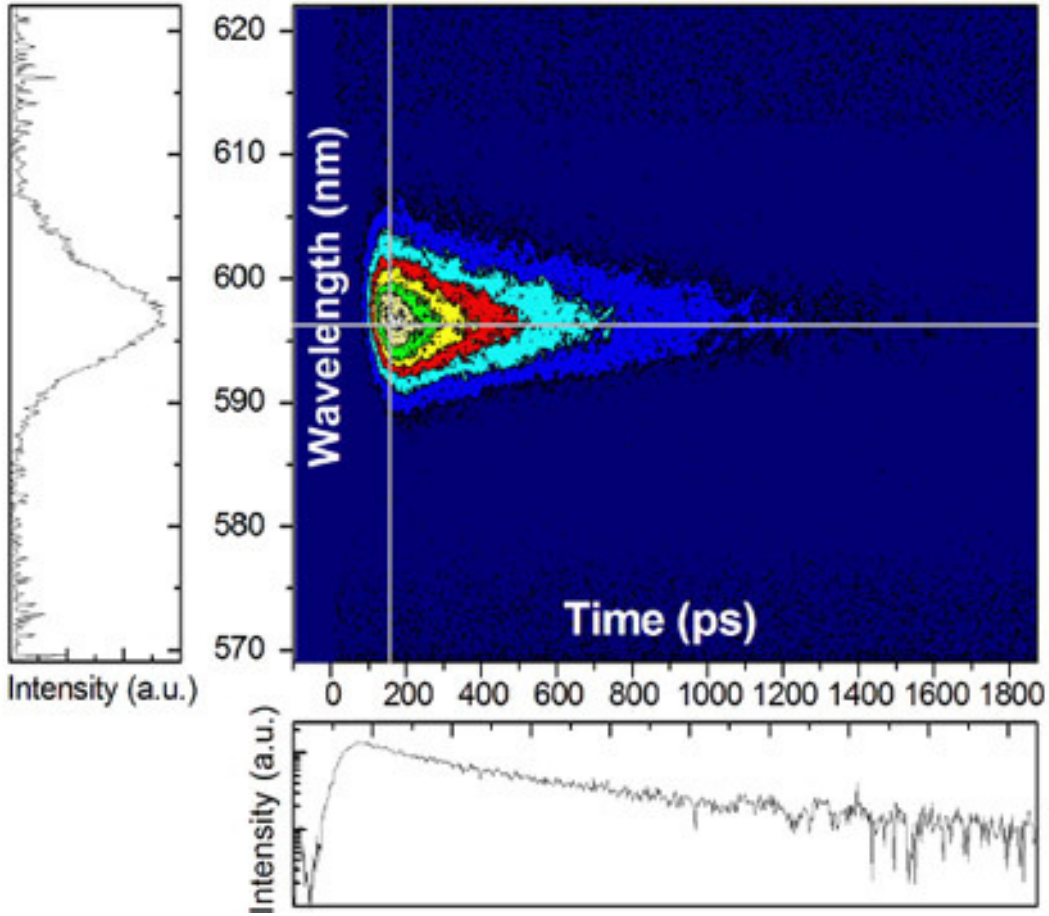
$$\tau = RC$$

Advantages: Broad band spectrum, large temporal region

Very high photon to electron gain (10^8)

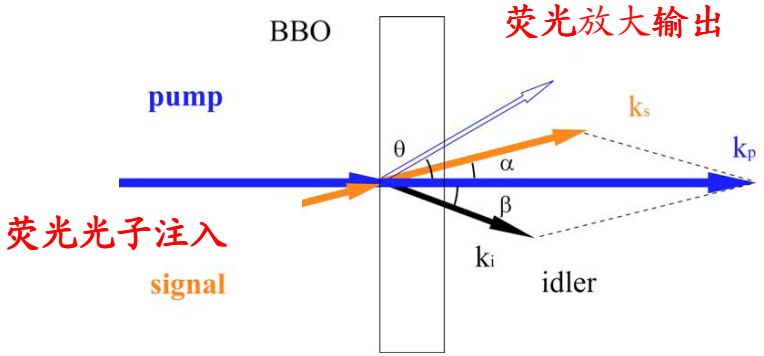
时间分辨率约 1 ps

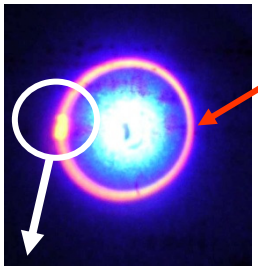
时间　　光　实


620
610
600
590
580
570
Wavelength (nm)
Time (ps)
0
200
400
600
800
1000
1200
1400
1600
1800
Intensity (a.u.)
Intensity (a.u.)

光　　光　　光　　飞秒时间　　光光

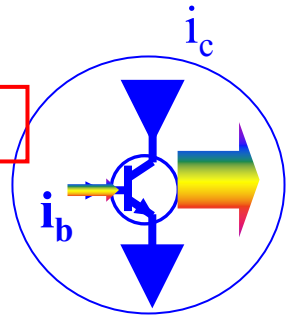
传统光测量方法（条纹相机）：光子→电子→电子学放大: 时间分辨极限 1-2ps
我们的方法: 光子→光子放大:　　时间分辨率：小于1飞秒





荧光被放大10^6倍!

量子噪声



BBO 晶体光学放大

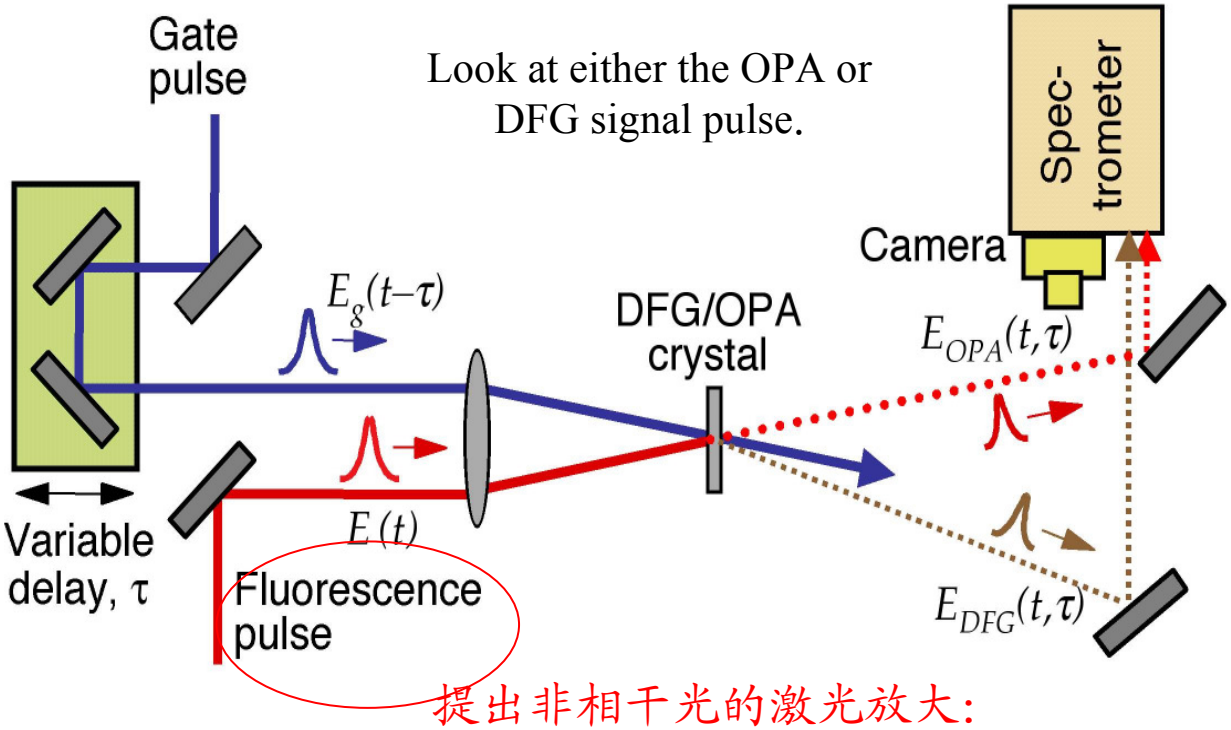
超短光脉冲门采样

(1) Chen; et al., *APL.* 2006, *89* , 061127 ;
(2) Han; et al., *JOSA B* 2007, *24*, 1633-1638;
(3) Han; et al., *APL* 2008, *92* , 032102.
(4) Han; et al., *APL* 2008, *92*, 151109.
(5) Weng.; et al., *JOSA B* 2008, *25*, 1627-1631.
(6) Chen.; et al., *JOSA B* 2009, *26* ,1627-1634;
(7) Chen; et al., *Chin. J. Chem. Phys.* 2011, *24*, 253-255;
(9) Chen; et al., *Photosynthesis Res.* 2012, *111*, 81-86;
(10) Dang; et al., *Rev. Scientific Instr.* 2013, *84* (7) 073105
(11) Liao; et al., *J. Mater. Chem. C* 2014, *2* (15), 2773-2778;
(12) Mao; et al., d. *Rev. Scientific Instr.* 2015, *86*,123113.

2003年张景园教授等首次提出用OPA光放大测量荧光

Optical Express， 11（6）601-609， 2003

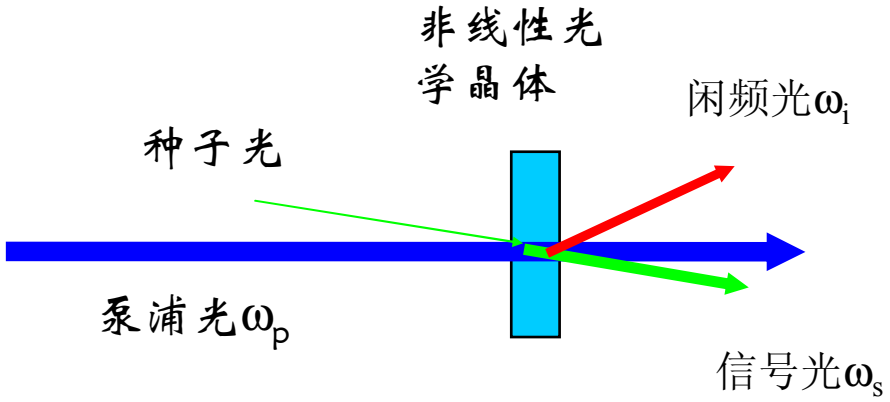
种子光的能量为阿焦量级

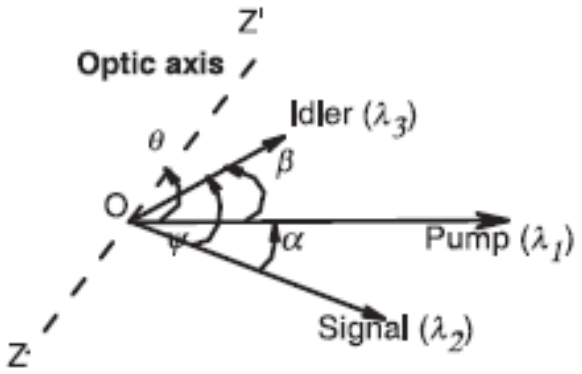


提出非相干光的激光放大：

荧光 → 激光

非共线光参量放大（Nonecolinear Optical Parametric Amplifier,NOPA）：光-光放大原理简图





参量放大过程中能量守恒，动量守恒

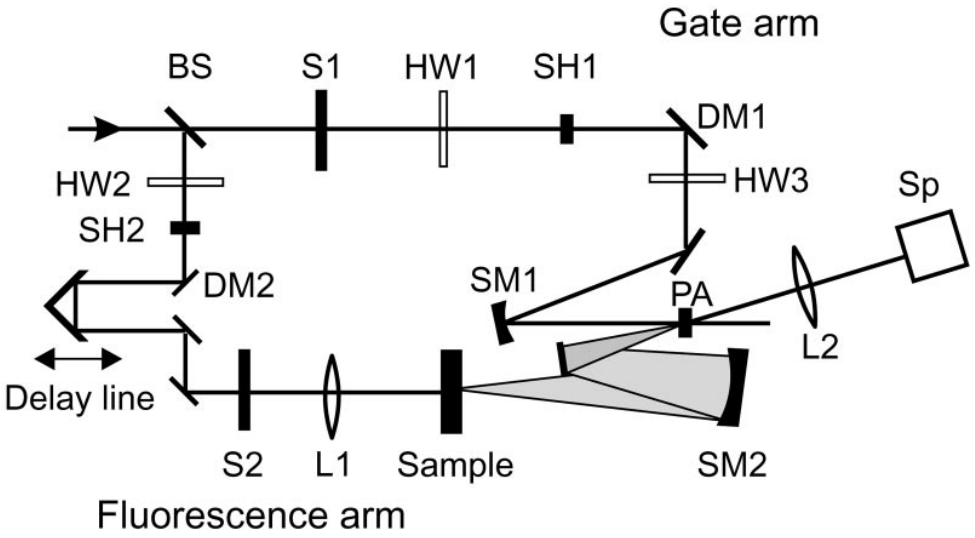
$$\omega_p = \omega_s + \omega_i \qquad \vec{k}_p = \vec{k}_s + \vec{k}_i$$

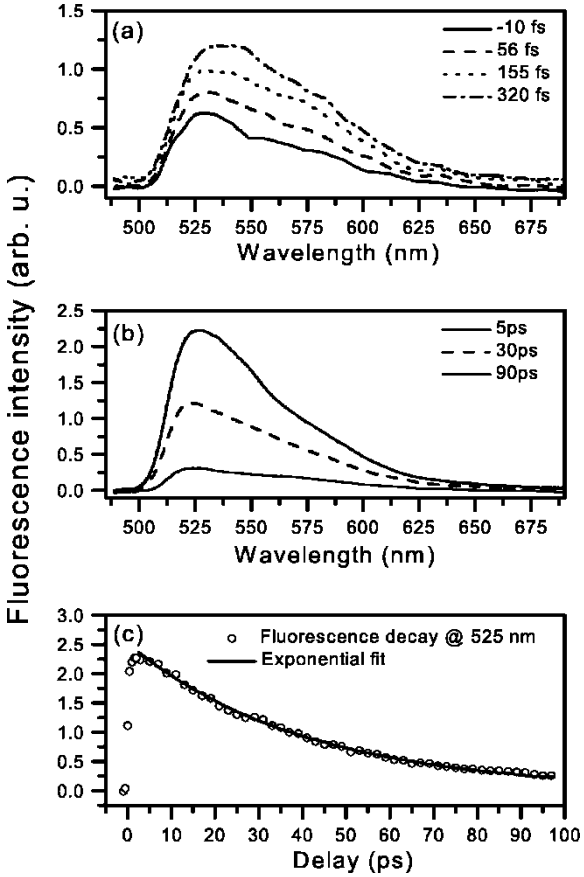
群速度匹配：　$v_s = v_p \cos\alpha$

2005年波兰科学家首先在荧光飞秒OPA放大实验中完成了非相干光子OPA放大的原理性实验

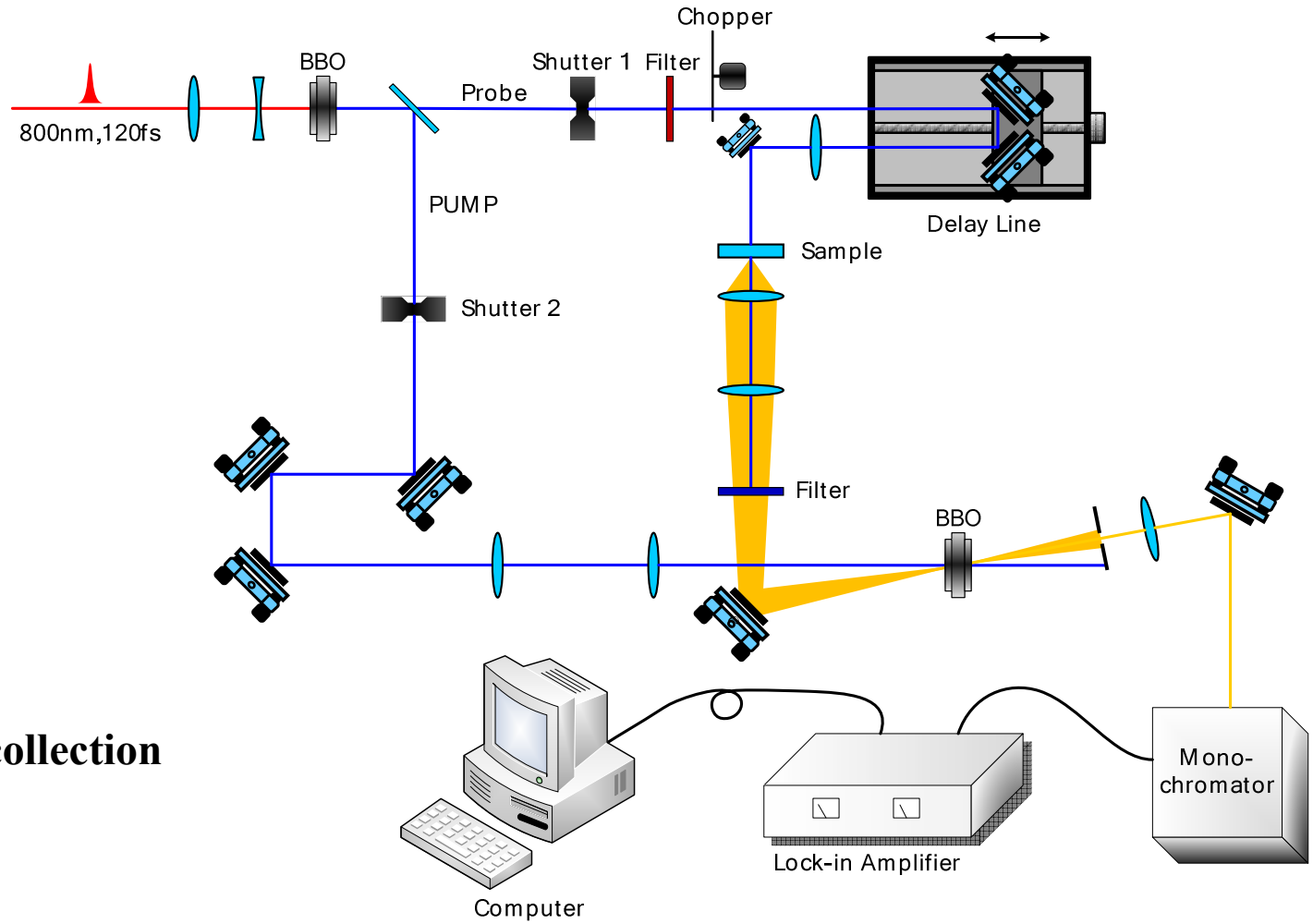
Fita, P.; Stepanenko, Y.; Radzewicz, C

Femtosecond transient fluorescence spectrometer based on parametric amplification, Appl. Phys. Lett. 2005, 86, 021909





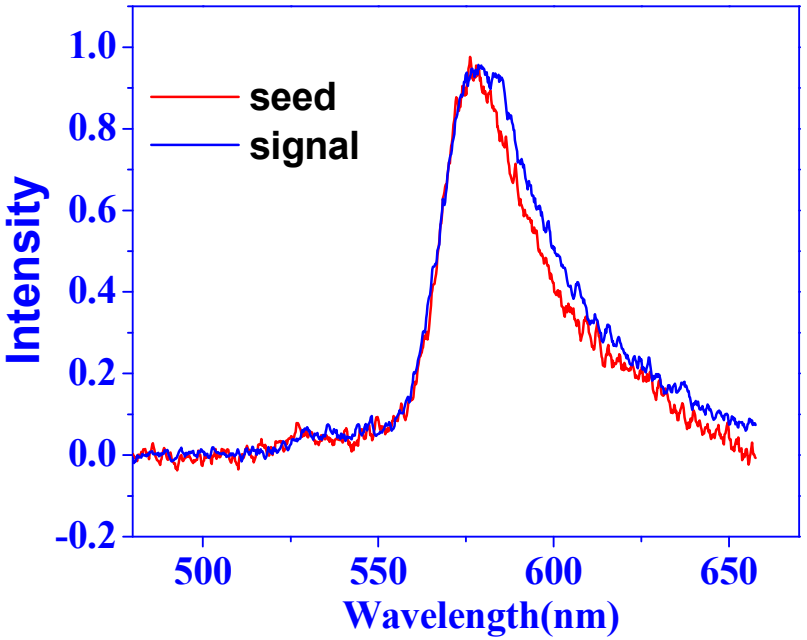
研究　实　　光光　　光光　　光



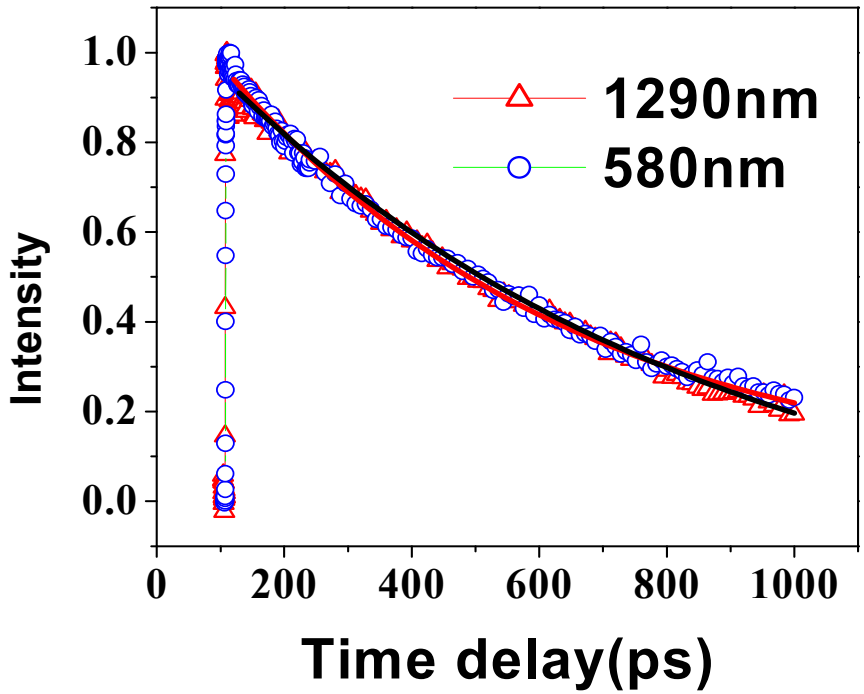
Forward collection

2006年我们研究组首次报道了近红外光的飞秒OPA上频变换荧光放大实验

Rhodamine 6G



诺丹明6G的稳态荧光光谱（实线）和在2ps测得到瞬态荧光光谱（虚线）

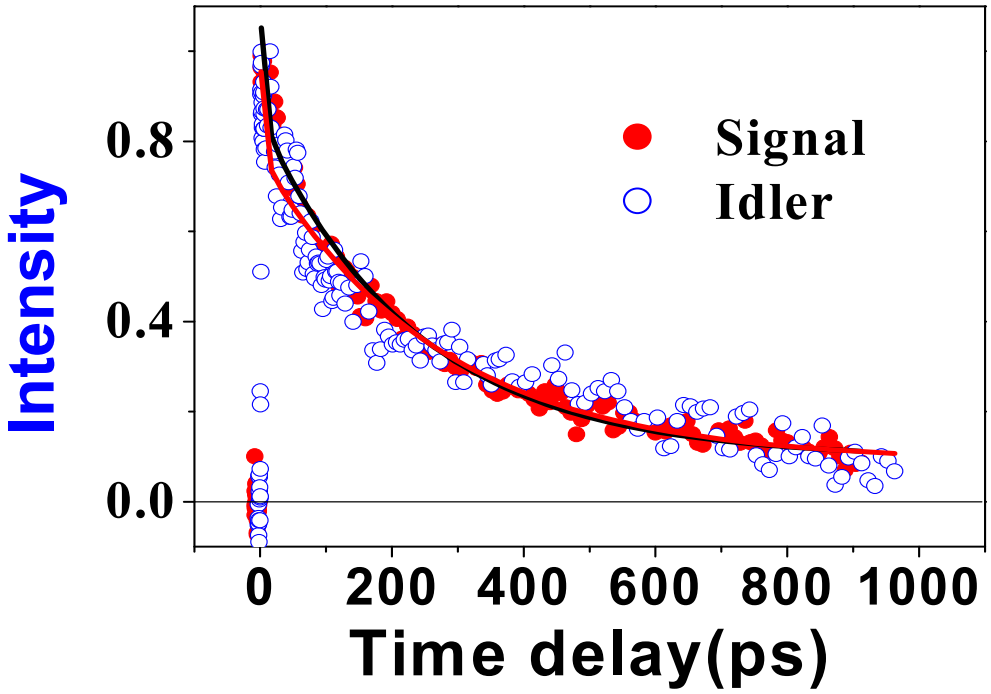


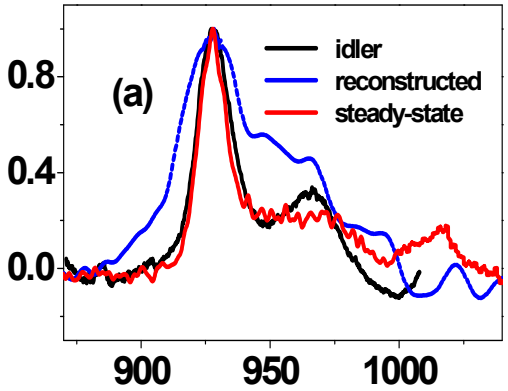
诺丹明6G的荧光经参量放大后的信号光和闲频光的动力学曲线

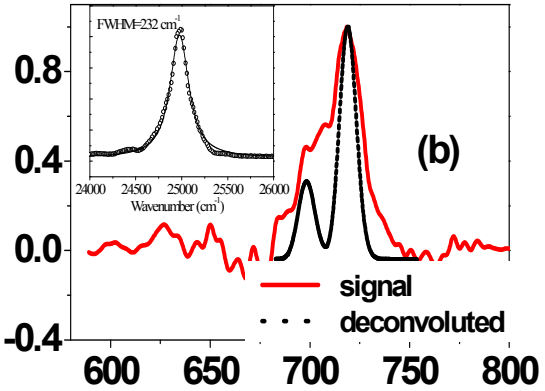
IR140　近红外荧光的上频变换测量

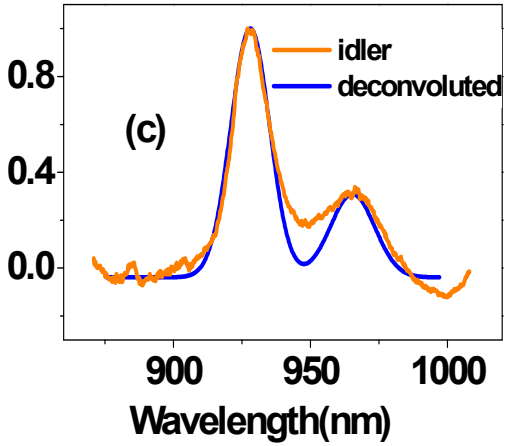
Appl. Phys. Lett. 2006, 89,061127,
Virtual Journal of Ultrafast Science, Sept. 2006

红外变到可见



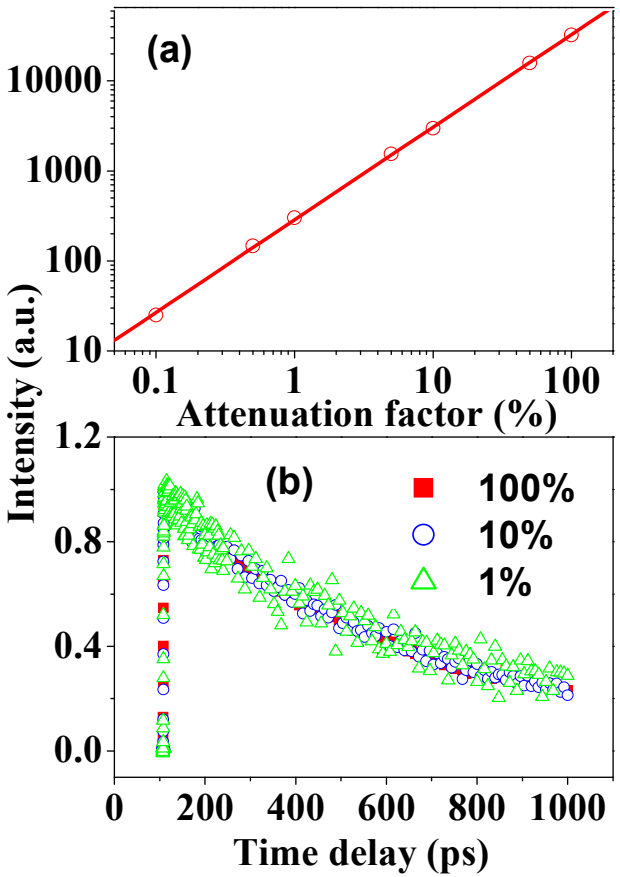




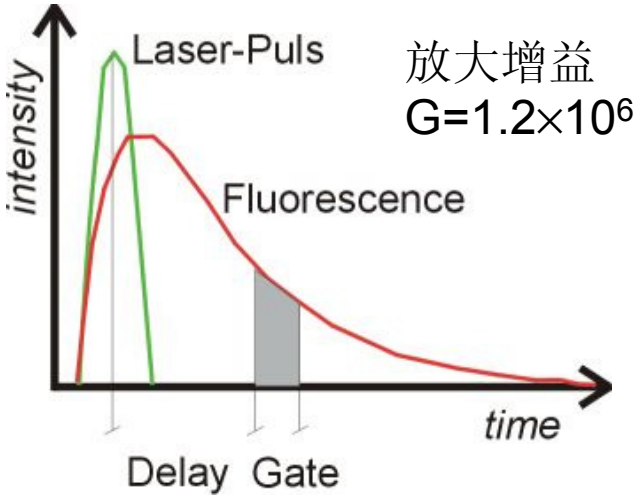


光　光

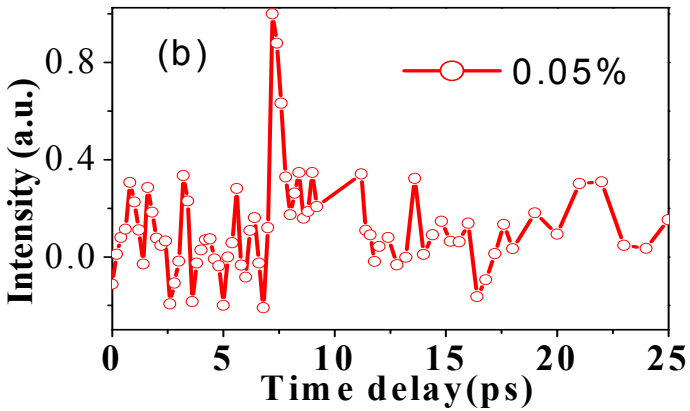
J. Opt. Soc. Am. B 2007, 24(7), 1633-1638



参量荧光放大为线性增益



放大增益
$G=1.2\times10^6$



在580 nm处相当于15个光子

测量极限的再确定：与波兰科学家开展的学术争鸣

挑战方

Comment on "Ultrasensitive femtosecond time-resolved fluorescence spectroscopy for relaxation processes by using parametric amplification"

Piotr Fita[1,*] and Czeslaw Radzewicz[1,2]

[1]Institute of Experimental Physics, University of Warsaw, 00-681 Warsaw, Poland
[2]Institute of Physical Chemistry, Polish Academy of Sciences, 01-224, Warsaw, Poland
*Corresponding author: fita@fuw.edu.pl

Received November 2, 2007; revised March 27, 2008; accepted March 28, 2008;
posted July 24, 2008 (Doc. ID 89271); published September 12, 2008

A recent paper [J. Opt. Soc. Am. B 24, 1633 (2007)] reports the gain and sensitivity of a time-resolved fluorescence spectrometer based on parametric amplification. We question the claimed detection limit and explanation for the unusual temporal shape of the measured signal at very low levels of fluorescence. We provide an alternative explanation for the observations. Several other points are also clarified. © 2008 Optical Society of America

OCIS codes: 190.4410, 190.4970, 300.6280, 300.6500.

应战方

Determination of the detection limit for a noncollinear optical parametric amplification-gated femtosecond time-resolved fluorescence spectrometer—Reply to the Comment on "Ultrasensitive femtosecond time-resolved fluorescence spectroscopy for relaxation processes by using parametric amplification"

Yuxiang Weng,[1,*] Xiaofeng Han,[1] and Jingyuan Zhang[2]

[1]Laboratory of Soft Matter Physics, Institute of Physics, Chinese Academy of Sciences, and Beijing National Laboratory of Condensed Physics, Beijing 100080, China
[2]Department of Physics, Georgia Southern University, Statesboro, Georgia 30460, USA
*Corresponding author: yxweng@aphy.iphy.ac.cn

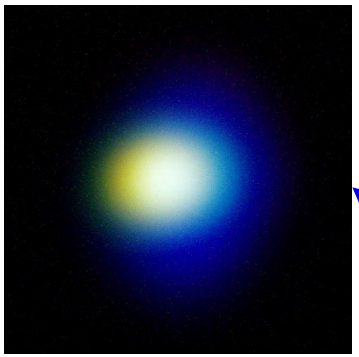
Received April 22, 2008; revised August 5, 2008; accepted August 5, 2008;
posted August 7, 2008 (Doc. ID 95343); published September 12, 2008

A backward fluorescence collection method is employed in a noncollinear optical parametric amplification-gated femtosecond time-resolved fluorescence spectrometer to determine the detection limit of this recently developed technique. In this way the supercontinuum generation that interferes with the determination of the detection limit is completely excluded, and the achieved upper limit of the detectable photon number with the 150 fs gating pulse is approximately 19. © 2008 Optical Society of America

OCIS codes: 190.4410, 190.4970, 300.6280, 300.6500.

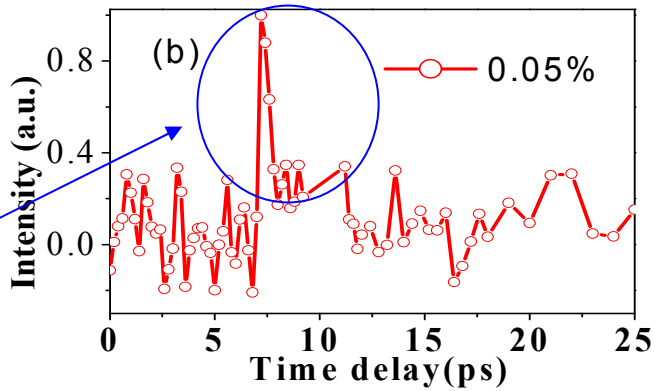
J. Optical Society America B, Vol 25, 2008

争论焦点： 荧光激发焦点产生白化光的干扰



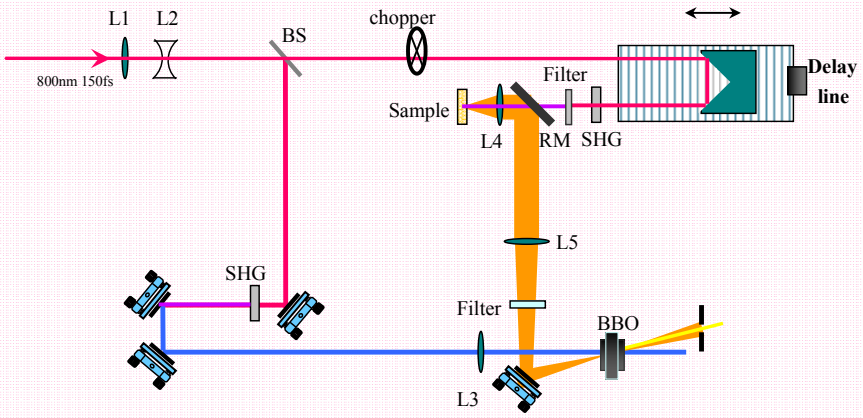
前向收集荧光

争论焦点

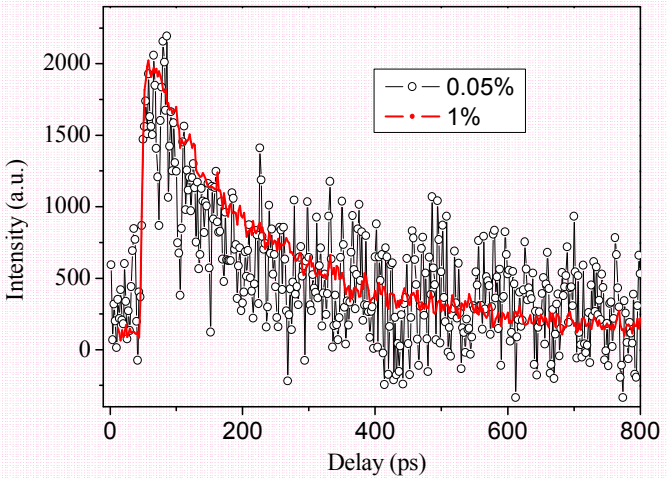


超连续白光：相干光

种子光衰减2000，极限15个光子



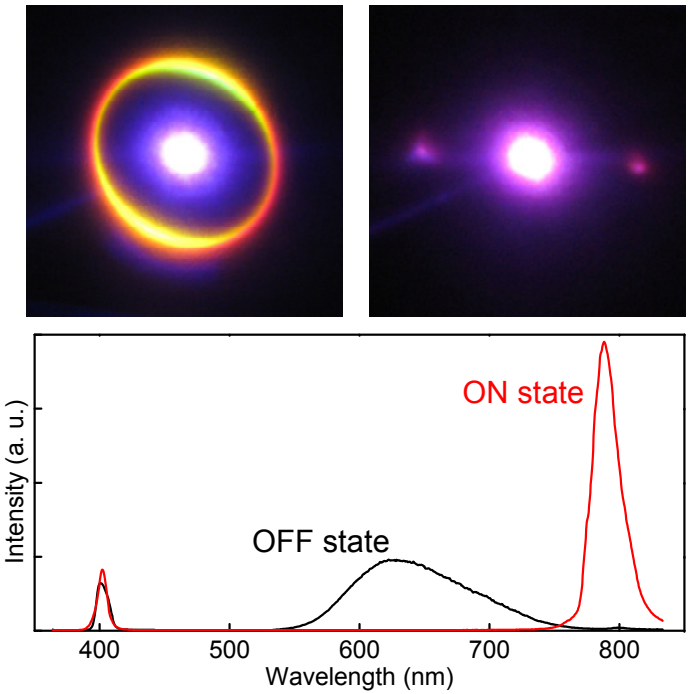
背 向收集荧光



种子光衰减2000, 极限<19个光子

单光子水平的光参量放大飞秒全光开关演示实验

合作方：赵继民，吴令安



Applied Physics Letters, 2008

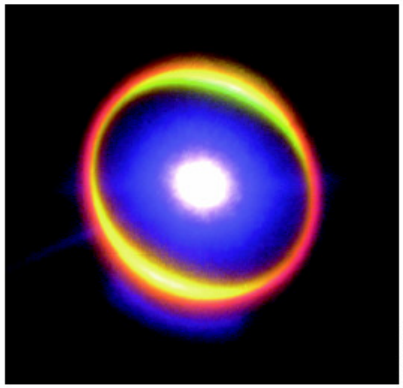
Nature Photonics，

Vol（2），331， 2008

中国学者在非线性光学四波混频光参量放大的基础上演示了全光开关

ALL-OPTICAL SWITCHING

Single-photon power



Appl. Phys. Lett. **92,** 151109 (2008)

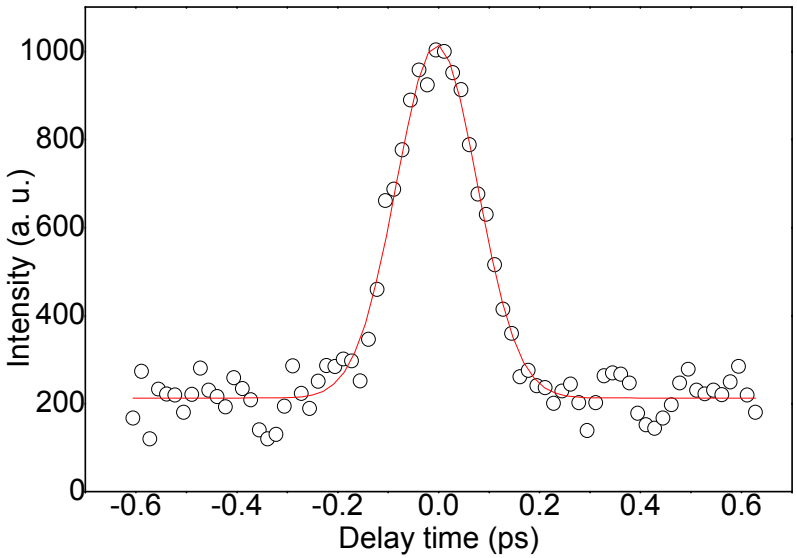
All-optical switching has the potential to offer ultrafast switching speeds that are not subject to conventional electronic limitations, and could help revolutionize communication and information processing. Researchers in China have now demonstrated an all-optical switch based on three-wave-mixing parametric amplification in a nonlinear crystal.

The idea underlying the scheme involves using a weak beam of light to turn a stronger beam of light on and off. This is essential for cascaded classical and quantum computation elements. Although the concept has already been demonstrated using four-wave mixing, Xiao-Feng Han and colleagues present an approach based on three-wave-mixing optical parametric amplification in a nonlinear crystal. Using a beta barium borate crystal as the core switching element, they show that a beam containing single photons (with an average of 0.75 photons per pulse) can be used to turn a beam containing up to 5.9×10^8 photons on and off. The switching can be performed within 400 fs. Analysis of the on/off states shows that they are well defined and that the switch has a broad bandwidth of 10 nm (or 5 THz).

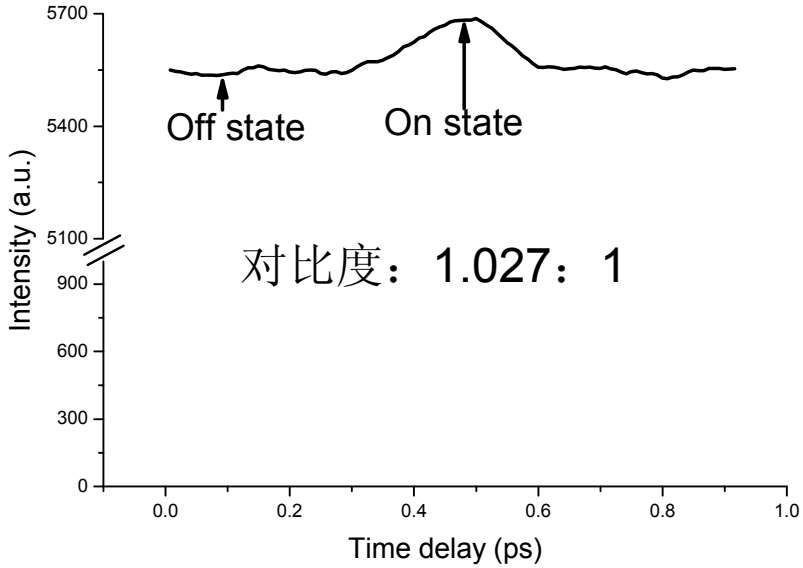
单光子水平的光子计数测定：0.75个光子

TABLE I. Probability of obtaining n photons in one pulse for an average photon number of μ.

μ	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
1	0.368	0.368	0.184	0.061	0.015	0.003	0.0005
0.75	0.472	0.354	0.133	0.033	0.006	0.0009	0.0001
0.4	0.670	0.268	0.054	0.007	0.0007	0.000057	0.0000038



斩波器斩种子光获得的信噪比



对比度：1.027：1

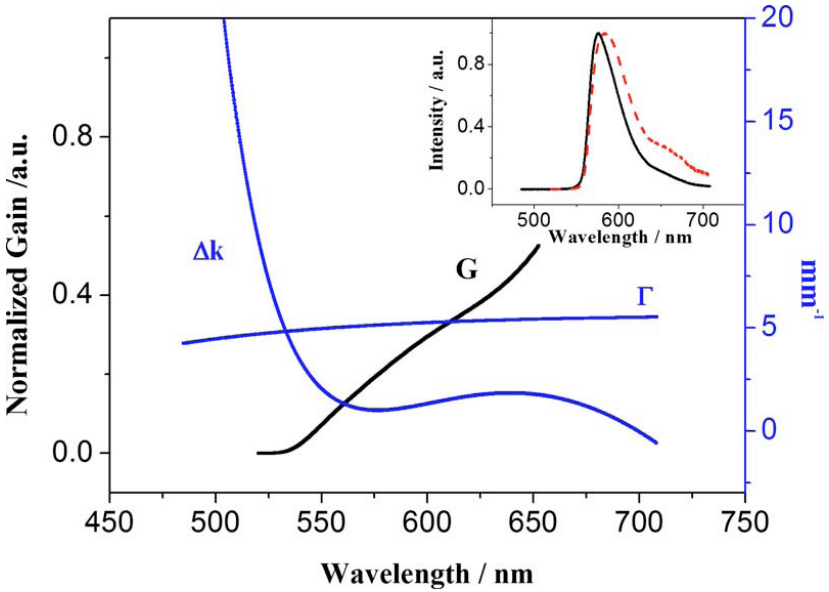
斩波器斩泵浦光获得的信噪比

依靠精确调整匹配角及入射角将极为困难

gain $G = 0.25 \exp\{2[\Gamma^2 - (\Delta k/2)^2]^{1/2} L\}$

parametric gain coefficient $\Gamma = 4\pi d_{\text{eff}}[I_p/(2\varepsilon_0 n_p n_s n_i c \lambda_s \lambda_i)]^{1/2}$

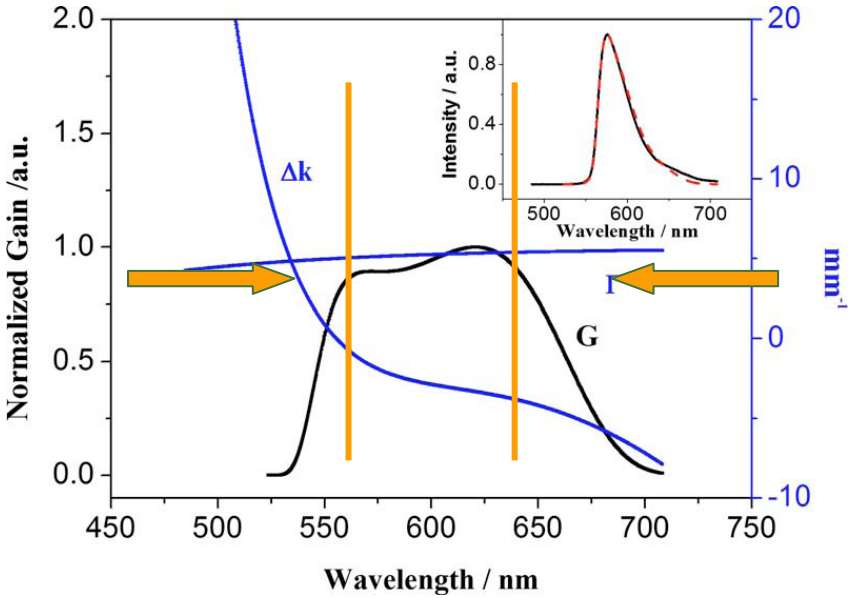
phase mismatch $\Delta k = k_p(\theta) - k_s \cos\alpha - k_i \cos\beta$



$\alpha = 3.76°,\ \theta = 31.3°$

a maximum gain bandwidth around central peak.

Distortion!



$\alpha = 3.9°,\ \theta = 31.7°$

Critically choosing α and θ spectral width > **2500 cm^{-1}**.

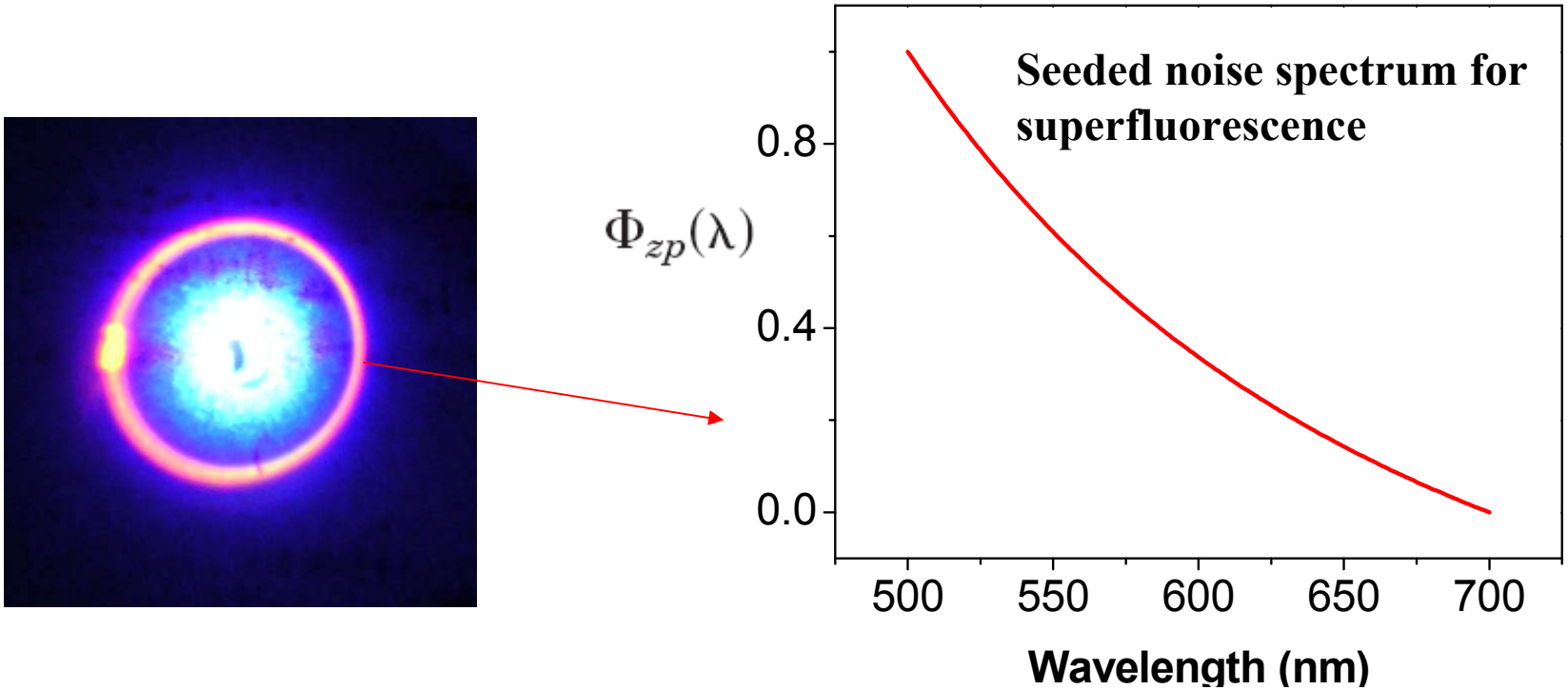
Very difficult!

应用真空量子噪声放大谱作为内禀荧光光谱校正源

$$\Phi_{sf}(\lambda;\alpha,\theta) = \Phi_{zp}(\lambda)[G(\lambda;\alpha,\theta) - 1]$$

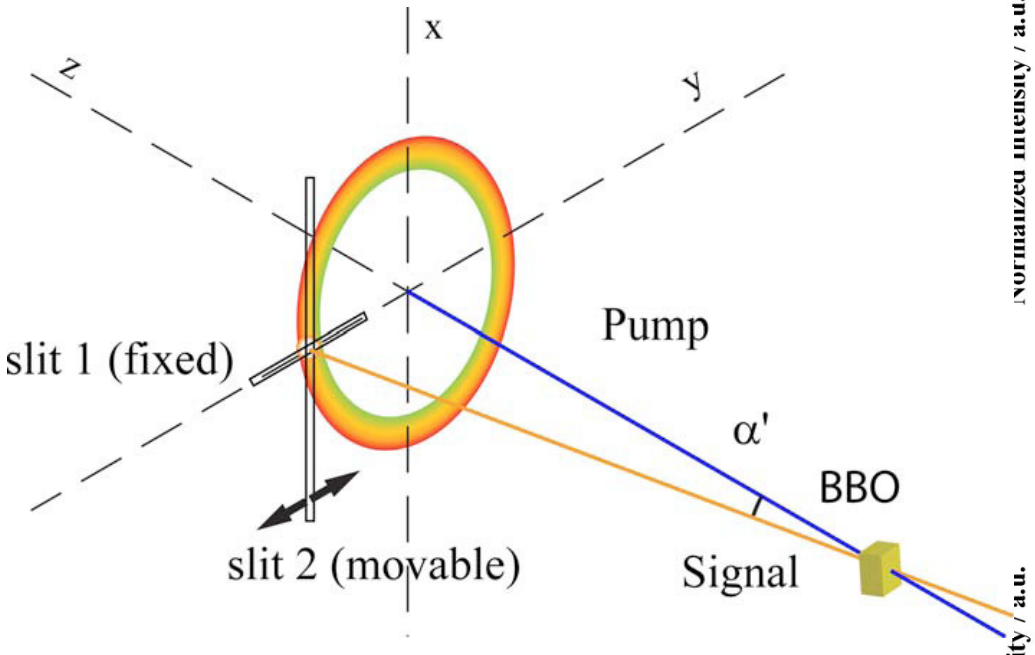
$\Phi_{sf}(\lambda;\alpha,\theta)$ **Experimentally measured**

the equivalent noise spectrum due to the zero-point fluctuations, : $hc^2/\lambda^3\, d\lambda$ in bandwidth $d\lambda$.

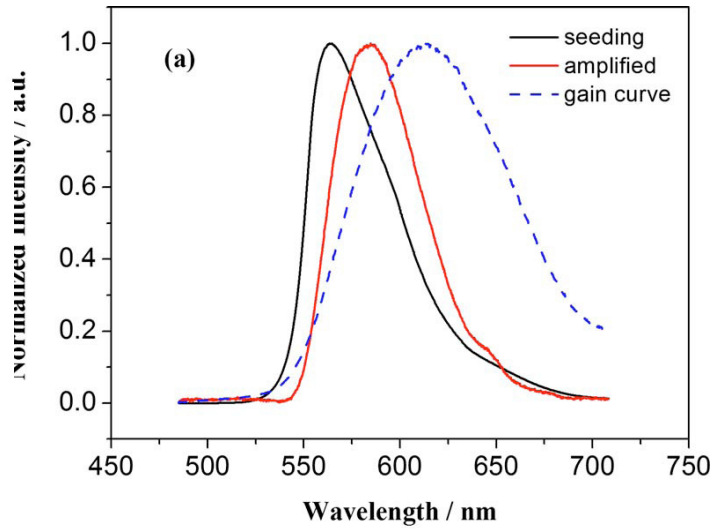


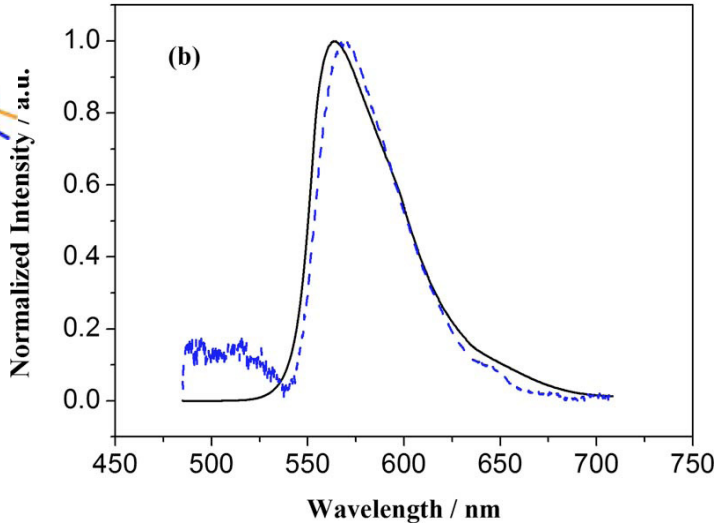
光　　实

Undistorted spectrum: 2500cm^{-1} at fixed angles



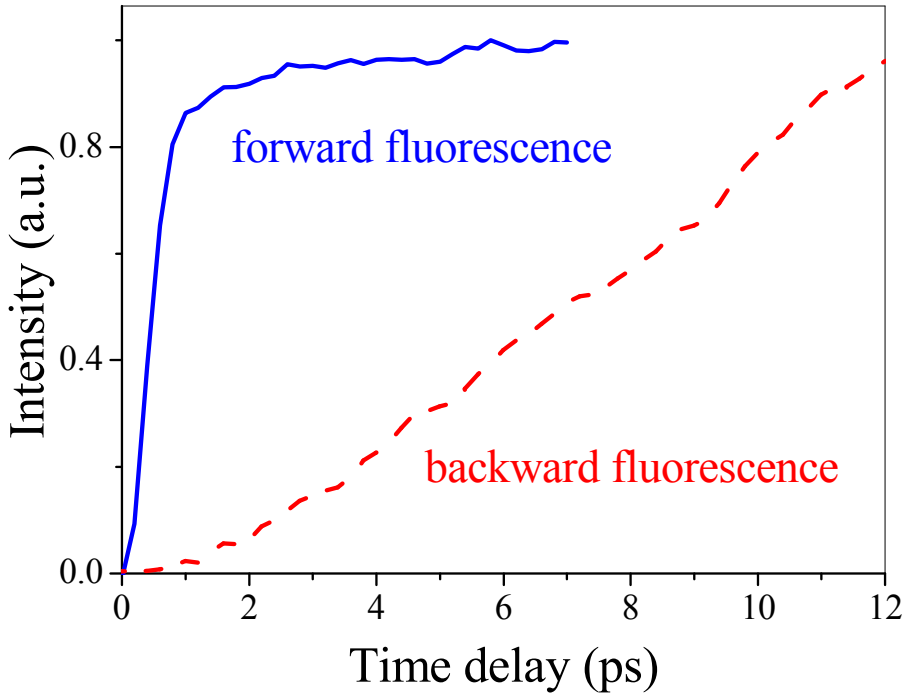
Determination of amplified noise spectrum

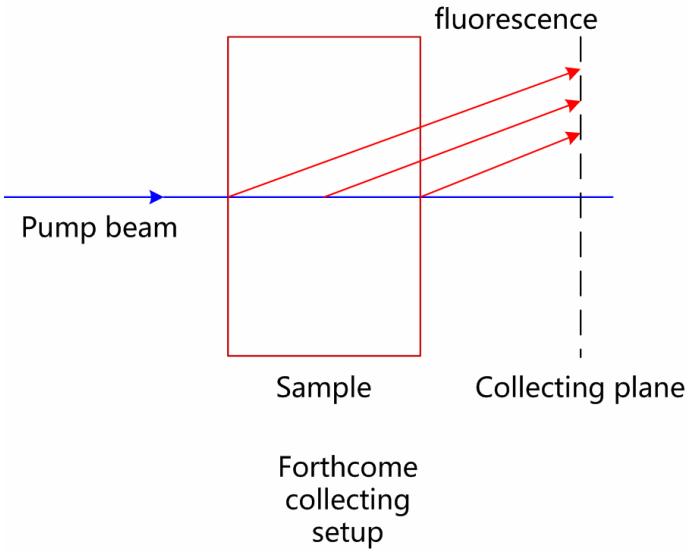




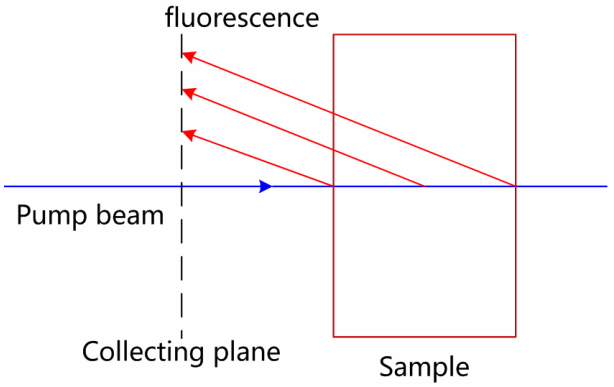
***Chen, HL, et al., Journal of Optical Society of America B*, 2009, 24(7), 1633-1638.**

光



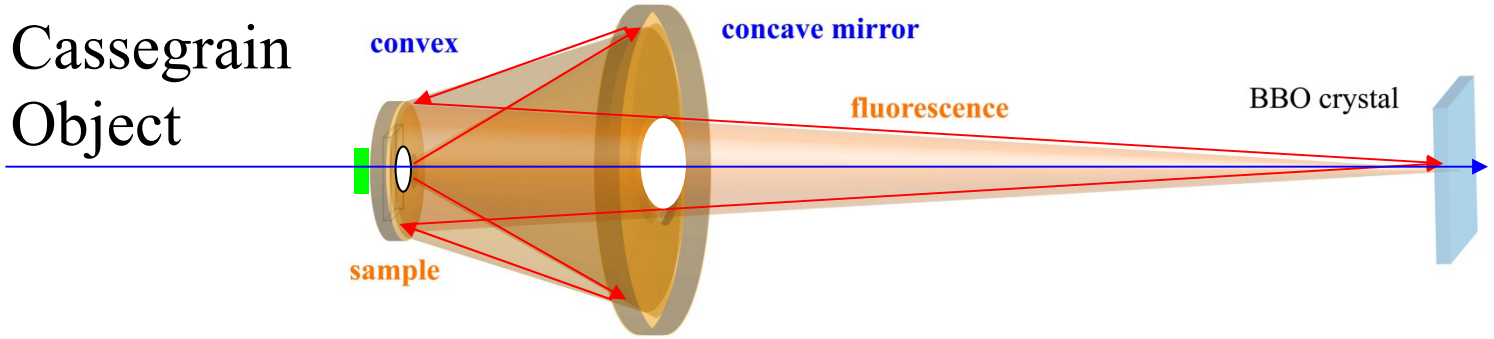


Forthcome collecting setup

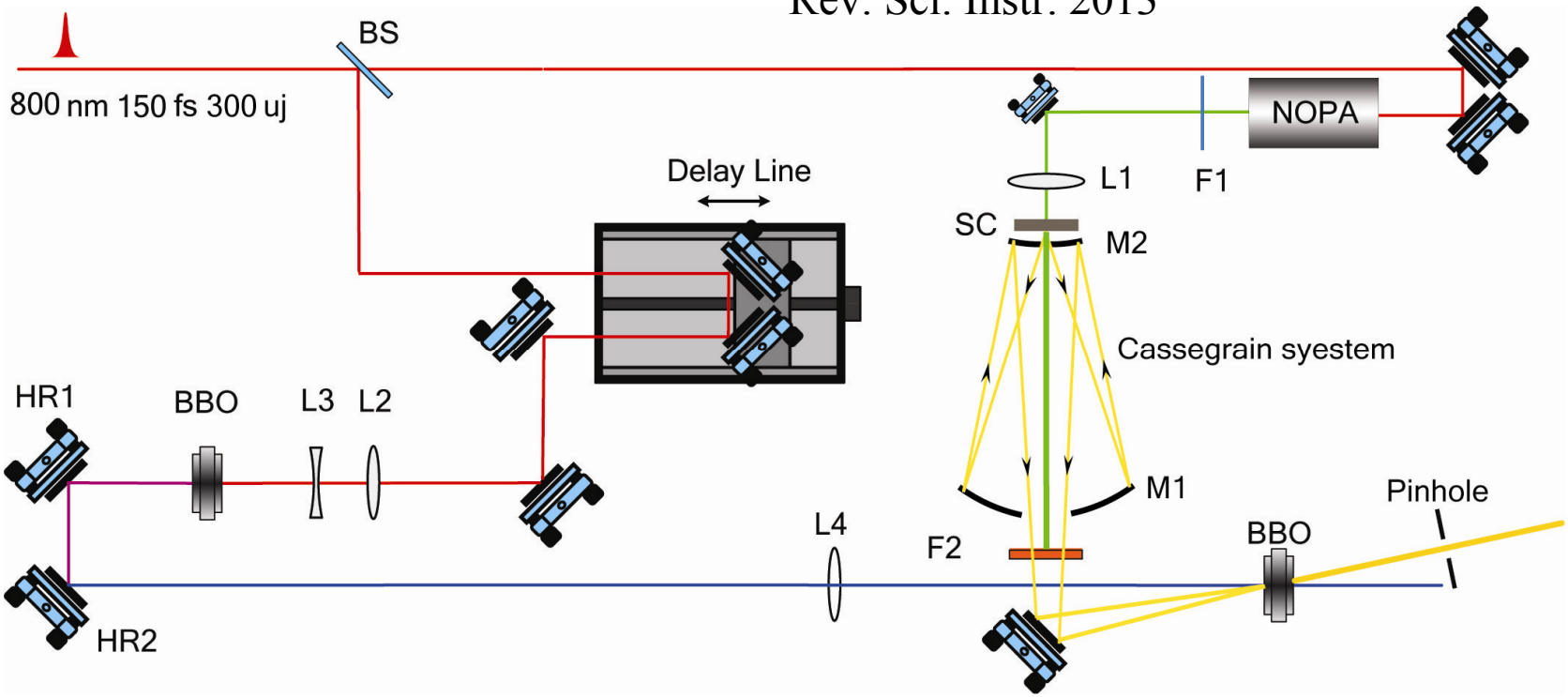


Backwards collecting setup

光　　光　　光

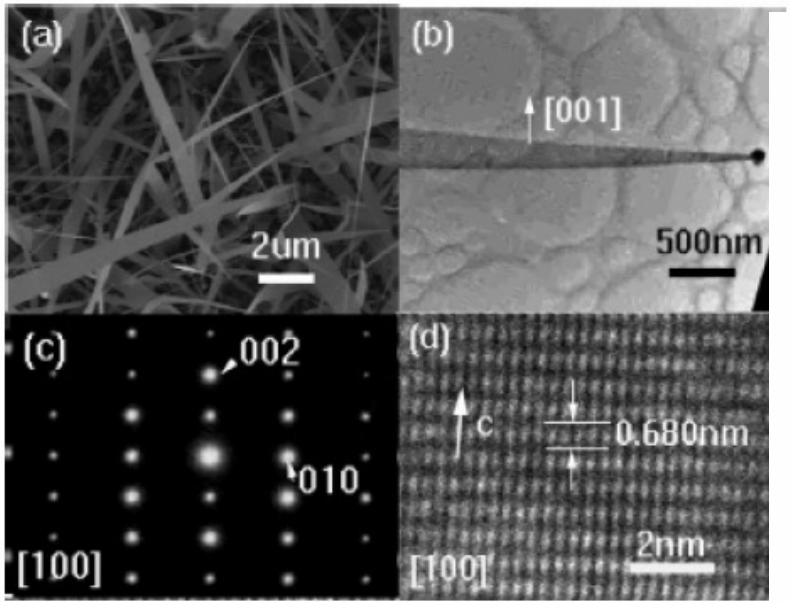


Rev. Sci. Instr. 2013

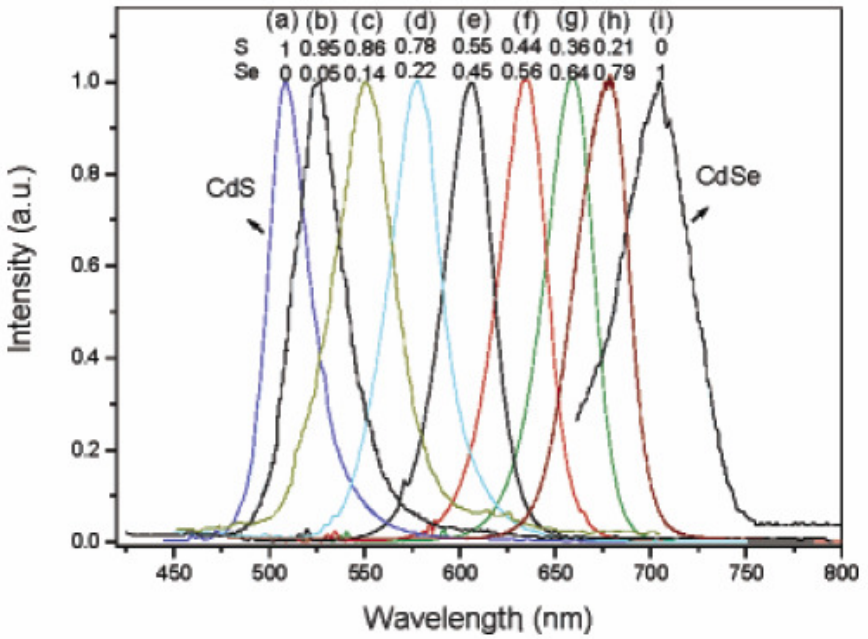


应用实例1：CdS_xSe_{1-x}时间分辨荧光光谱及超快驰豫动力学

新材料**CdS_xSe_{1-x}**纳米带　　J. Am. Chem. Soc. 2006, zhou etal



CdSxSe1-x纳米带

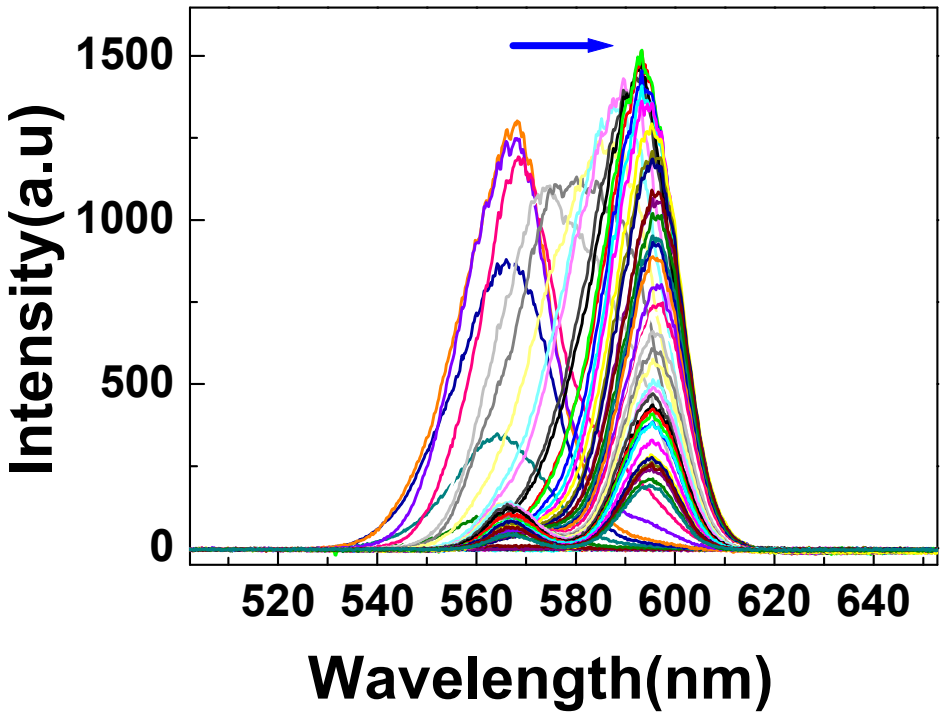


CdS_xSe_{1-x}发射光谱

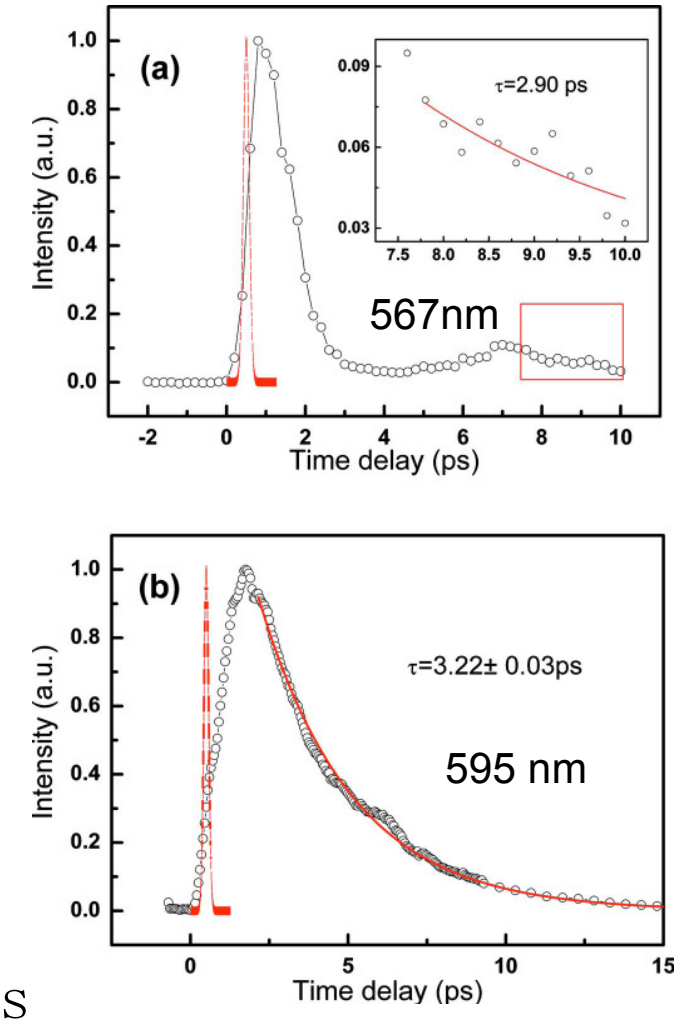
CdS_xSe_{1-x}　调节组分可改变发射光谱

应用实例：CdS_xSe_{1-x}时间分辨荧光光谱及超快驰豫动力学

Applied Physics Letter，92，032102，2008.

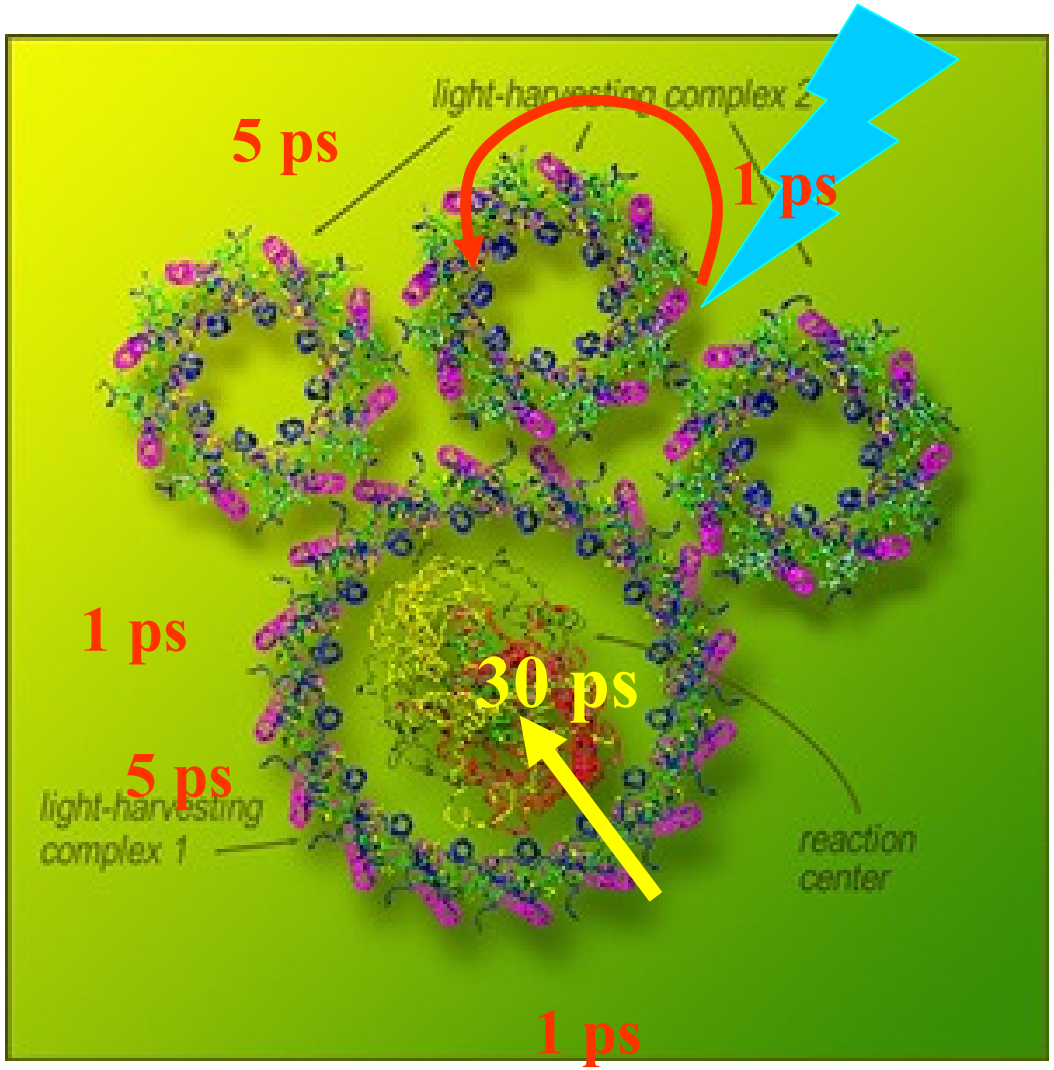


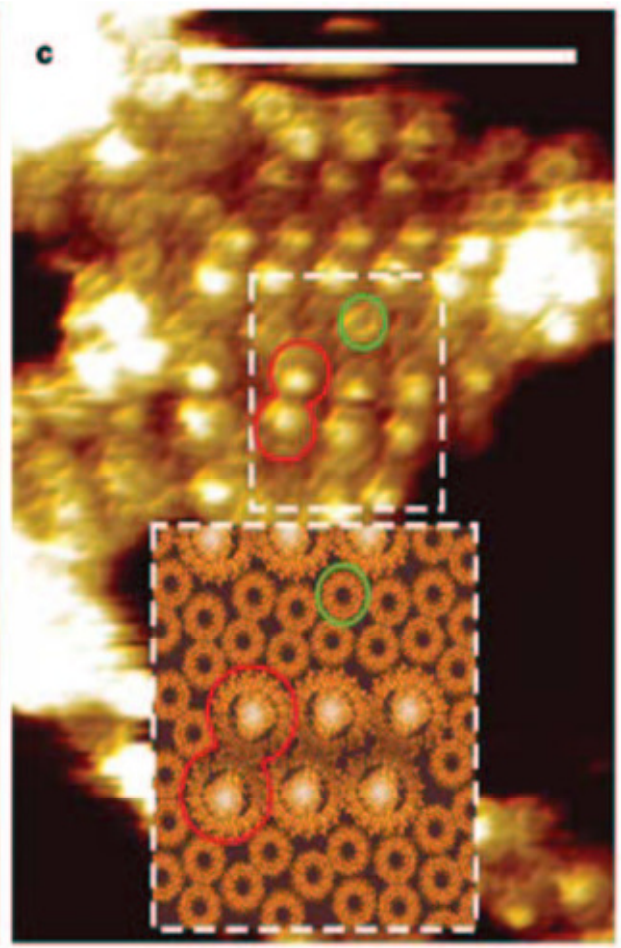
时间分辨荧光光谱 时间间隔0.2 ps



驰豫动力学: 迟滞荧光

光合作用　光


5 ps
1 ps
1 ps
30 ps
5 ps
light-harvesting
complex 1
reaction
center
1 ps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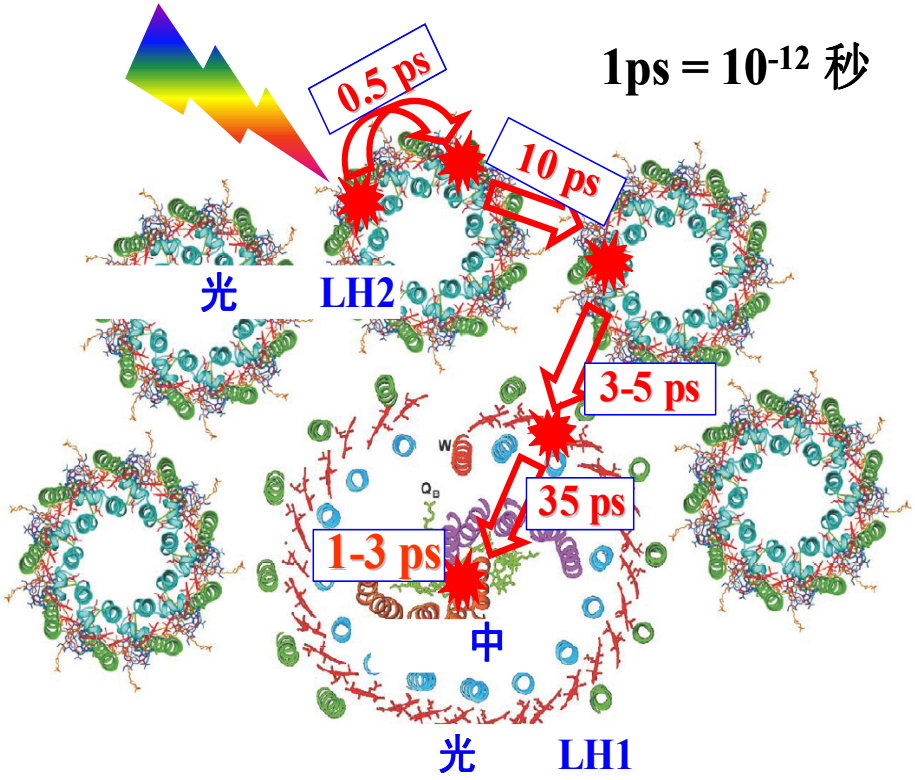
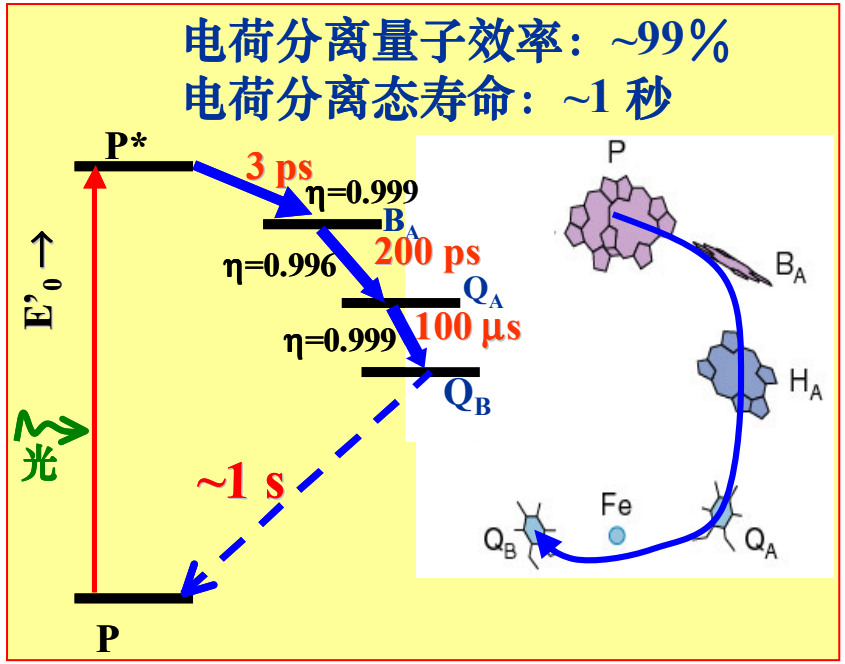
天然光合作用与超快光谱研究





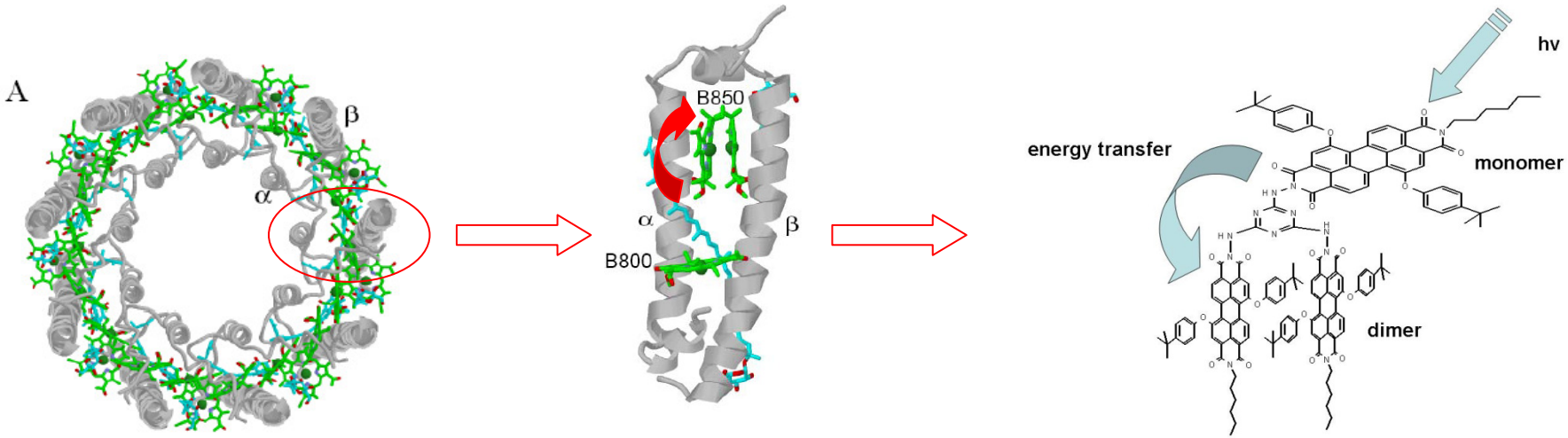
光合作用　　中
光　→　　学

多个功能单元（多元）协同作用

多步、高效率、电荷分离长寿命

应用实例2:光合模拟系统超快传能研究

Mimicry of energy transfer from the monomer to dimer in LH2

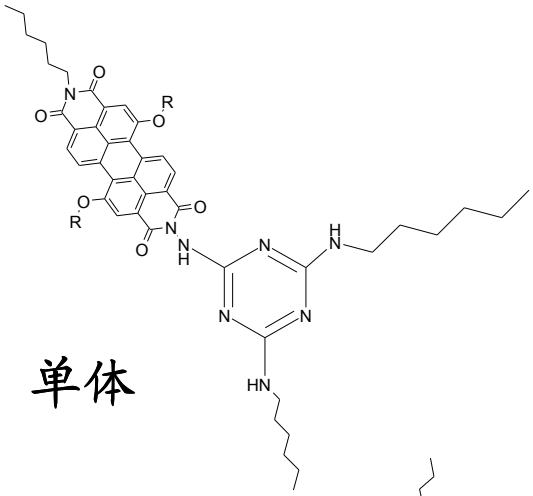


Photosynthetic Antenna complex LH2

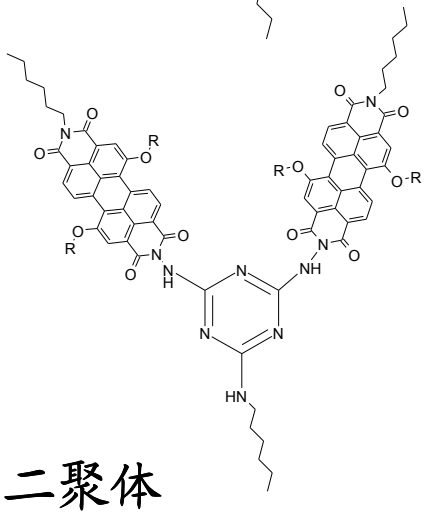
Subunit

Artificial system

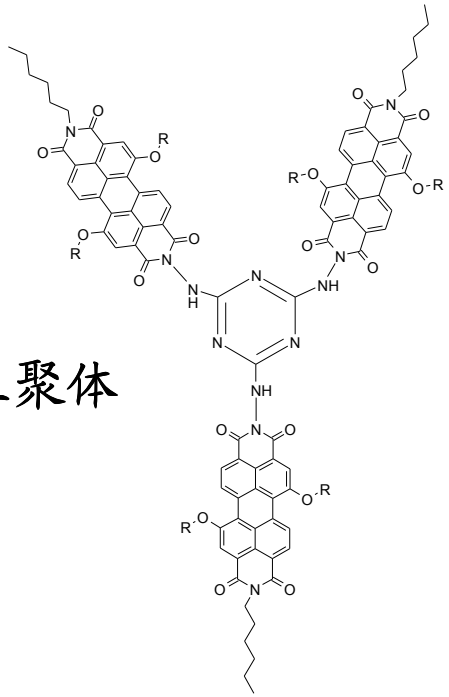
苝四甲酰二亚胺



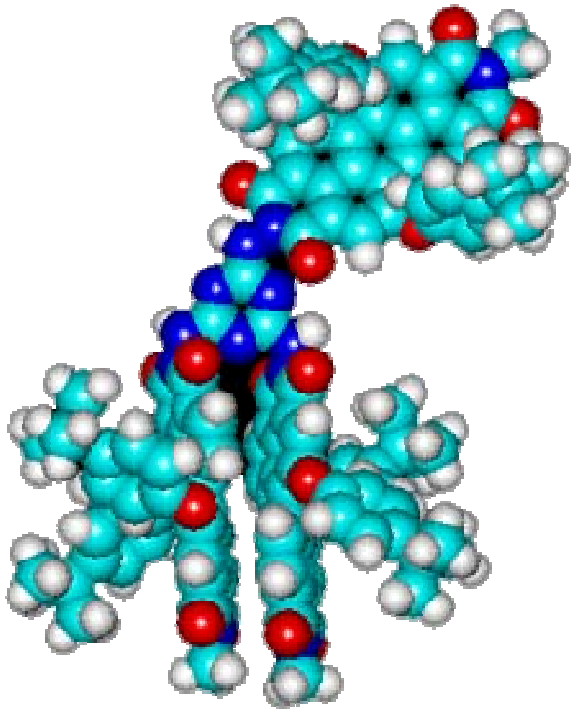
单体



二聚体



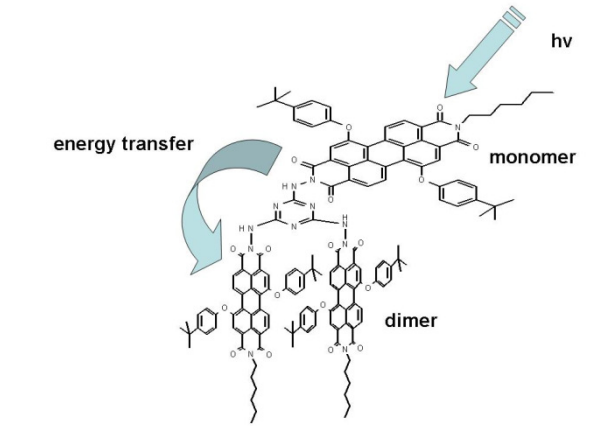
三聚体

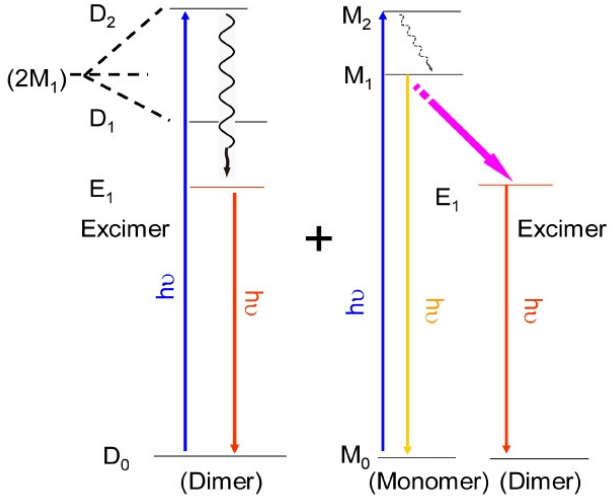


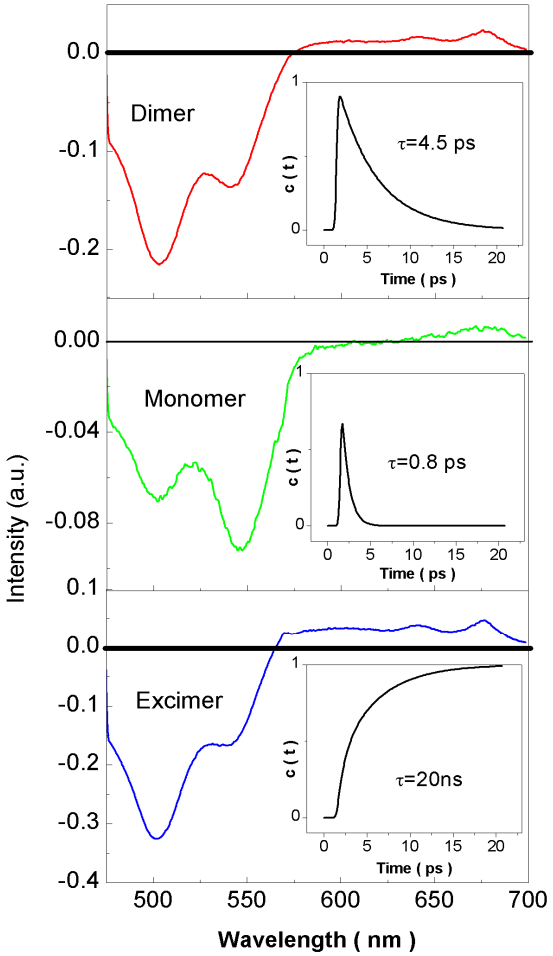
Perylenetetracarboxylic diimide (PDI)

三聚体分子内单体向二聚体能量转移的超快光谱研究

J. Am. Chem. Soc., **2009**, *131* (1), pp 30–31

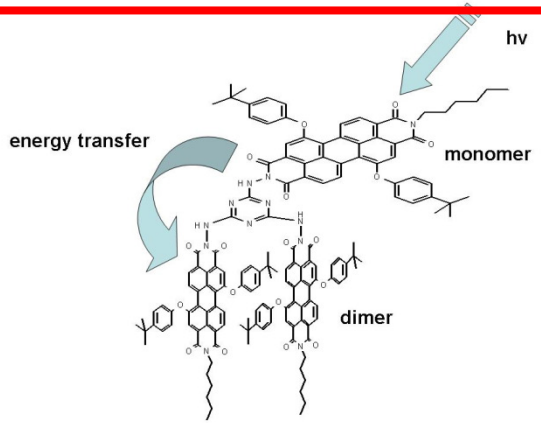




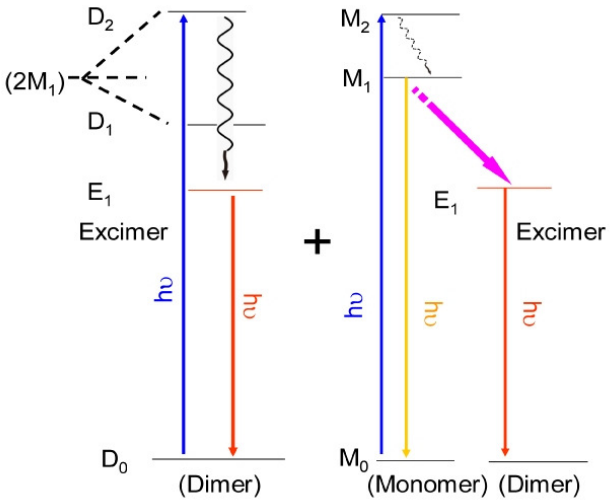


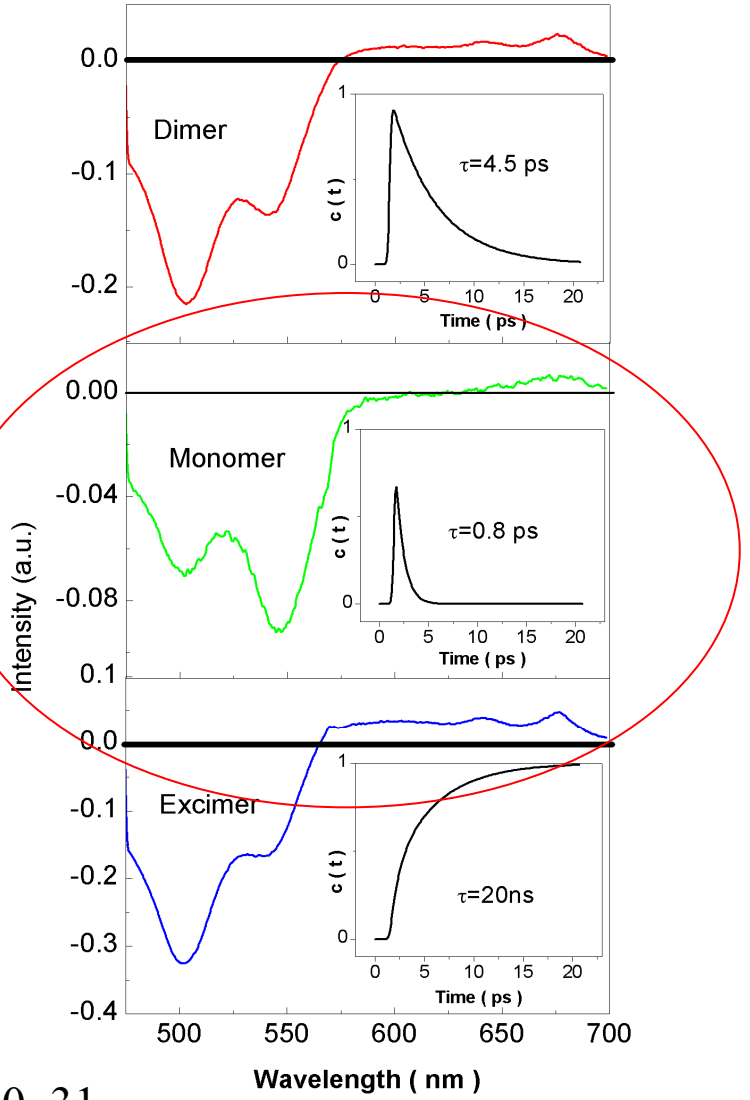
与山大李希友合作

由飞秒瞬态吸收光谱推断的单体到二体的超快传能过程



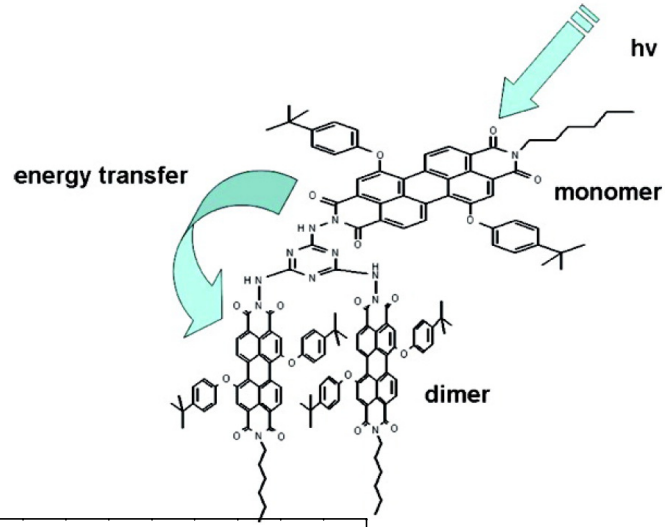
Perylenetetracarboxylic Diimide (PDI)



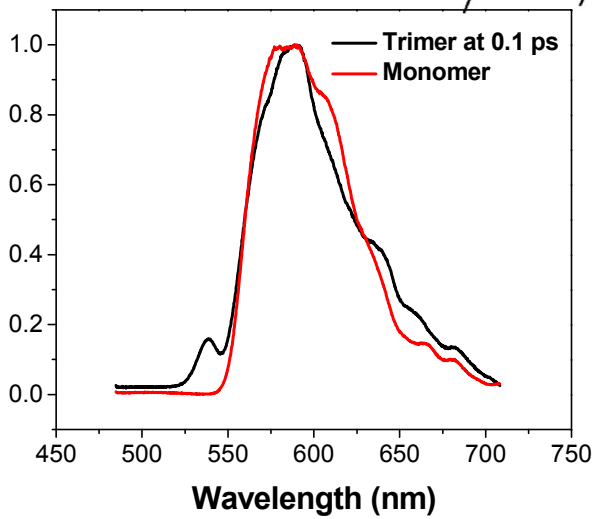


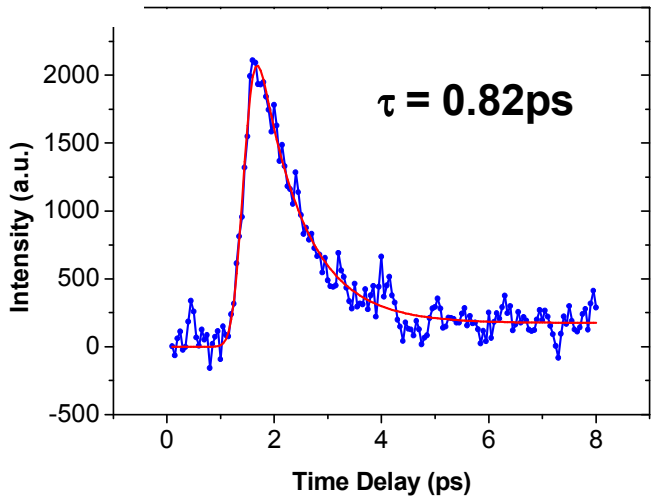
Wang, Y. F. et al., J. Am. Chem. Soc., **2009**, *131* (1), 30–31

飞秒时间分辨瞬态荧光光谱证实的超快传能过程



Energy transfer between dimer and monomer



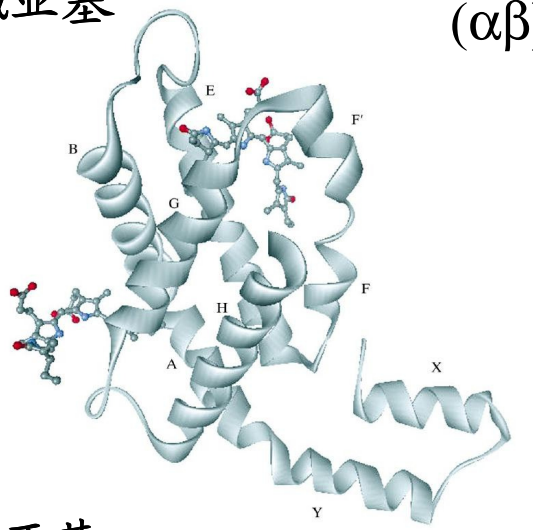


CHINESE JOURNAL OF CHEMICAL PHYSICS, 2011

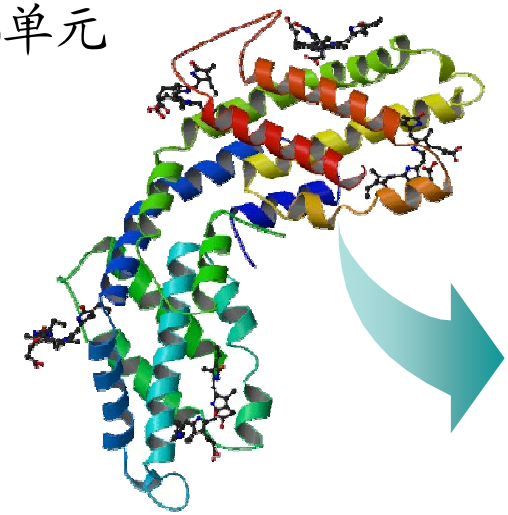
应用实例3. 海藻光合天线的超快传能过程研究

R-藻红蛋白基本结构

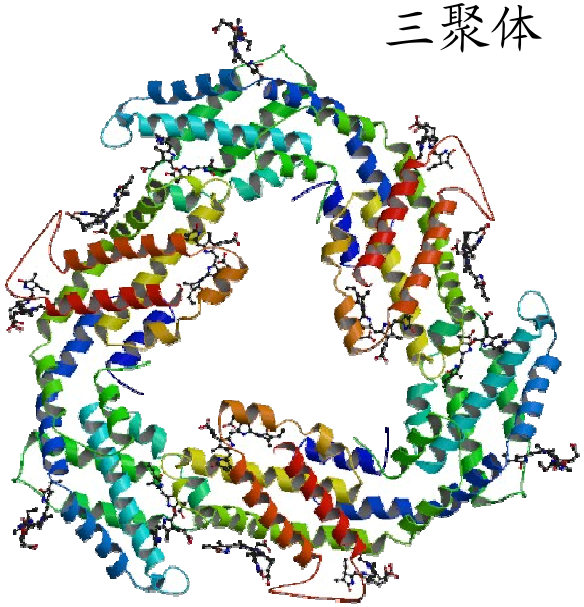
α亚基



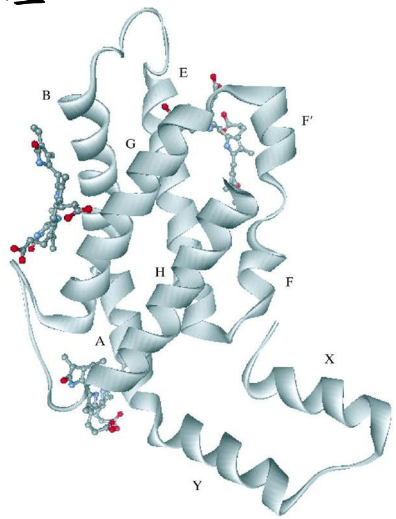
(αβ)单元

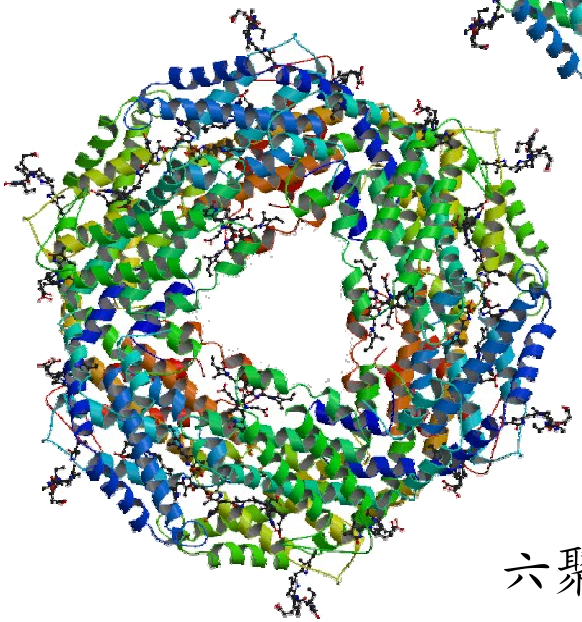


三聚体



β亚基

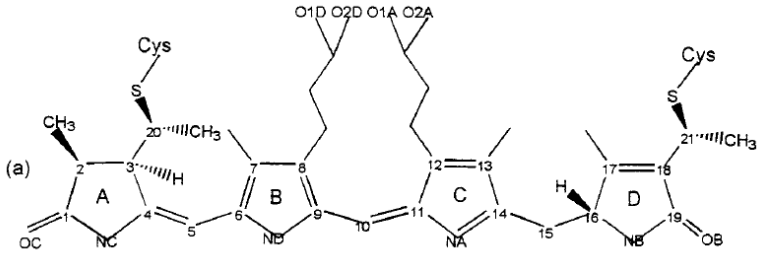




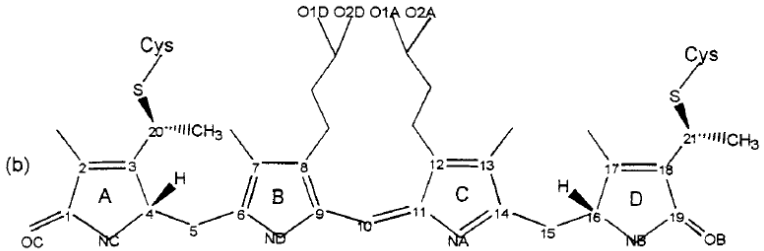
六聚体

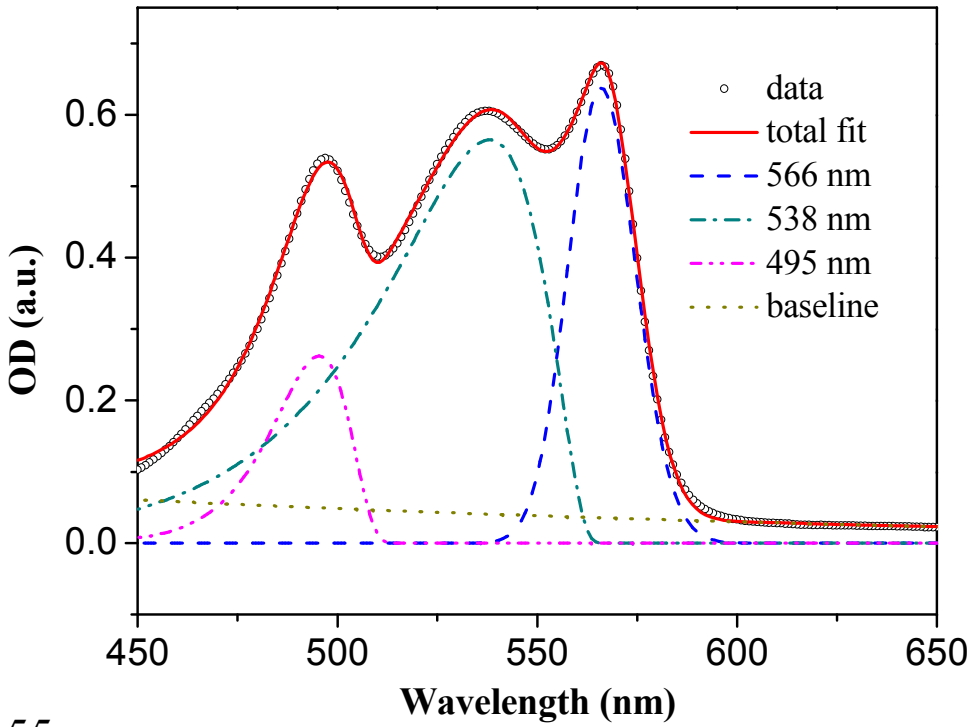
发色团性质

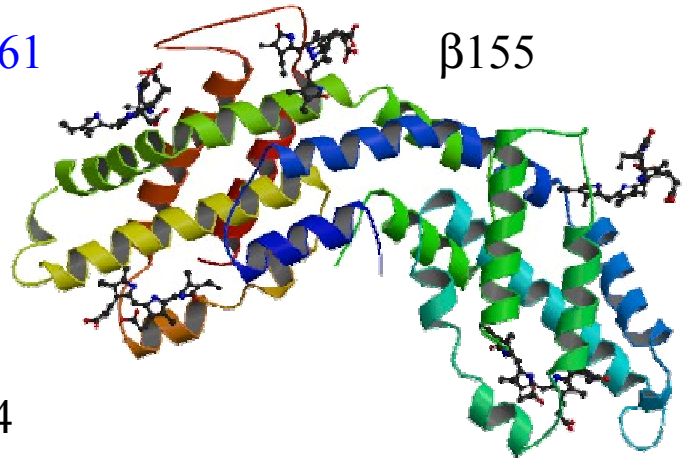
Phycoerythrobilin (PEB)



Phycourobilin (PUB)

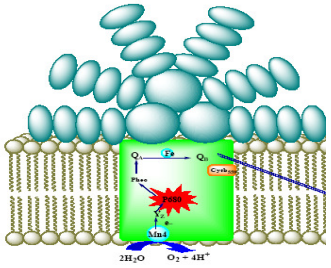


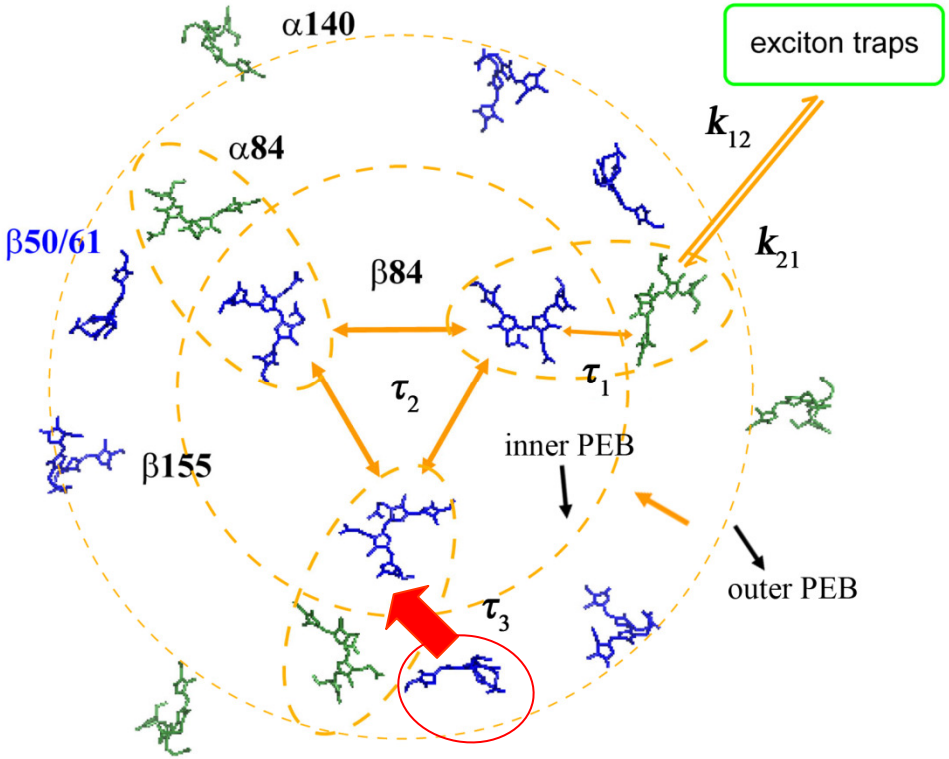




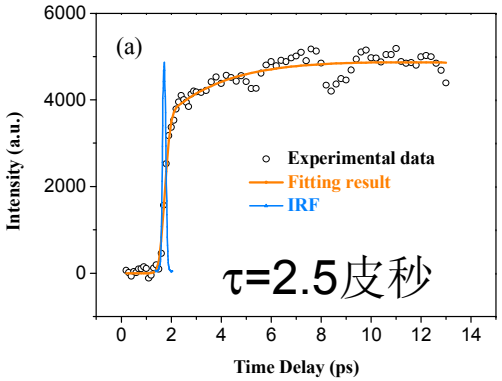
R-PE吸收光谱

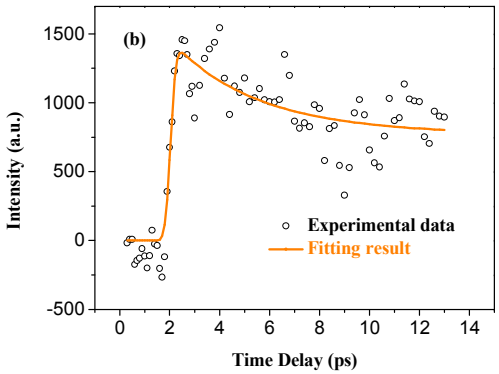
海藻光合天线的超快传能过程

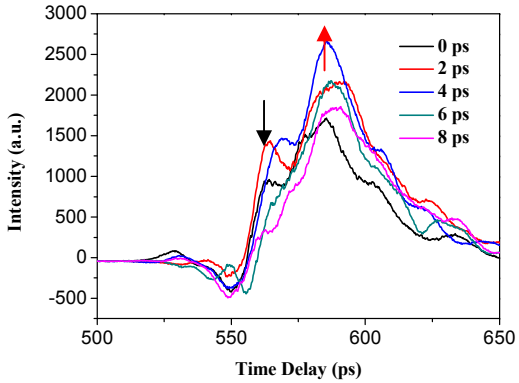




Chen, et al., Photosynthesis Research , 2011

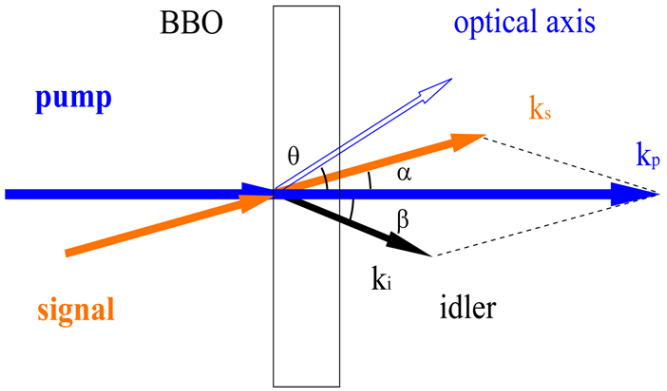


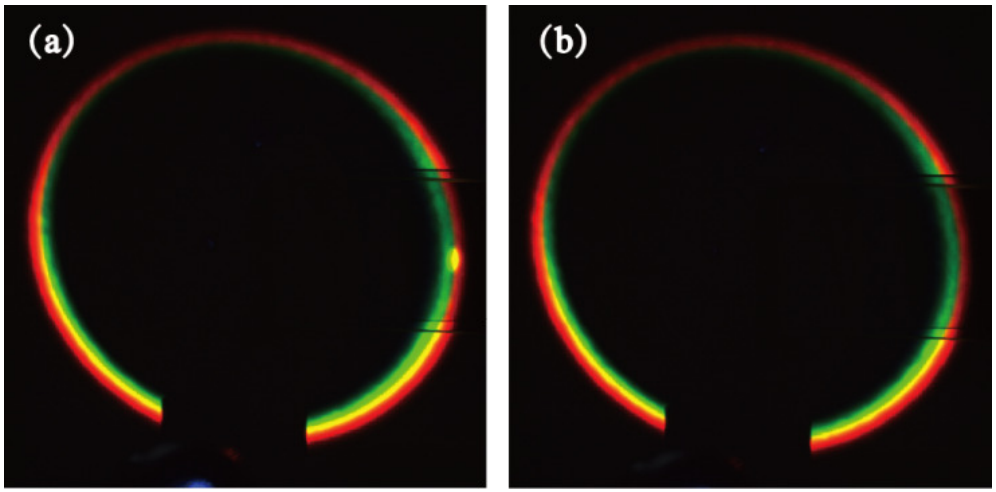




荧光放大系统的改进

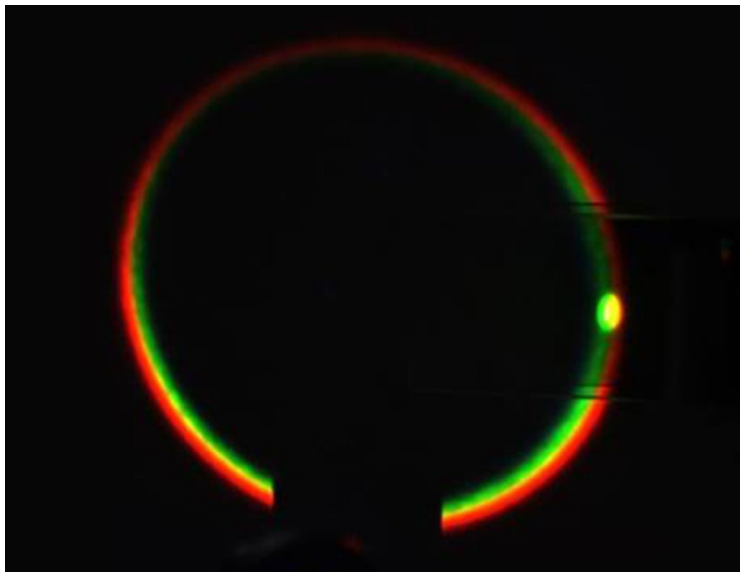
- 真空量子噪声被泵浦光放大产生荧光环
- 荧光环与信号时间和空间均不可分开
- 量子噪声完全随机无法减掉

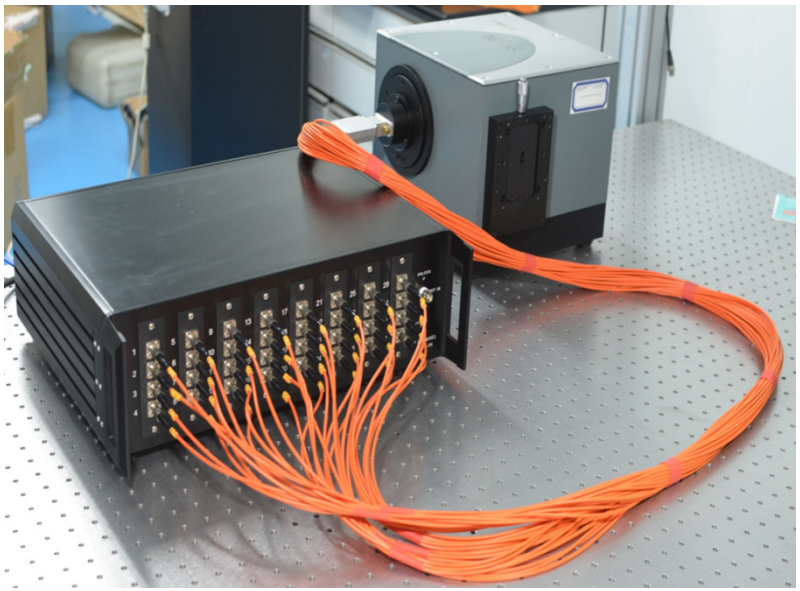




10^{-3} M与10^{-5} M罗丹明6G溶液被放大效果投影图

实验系统的改进

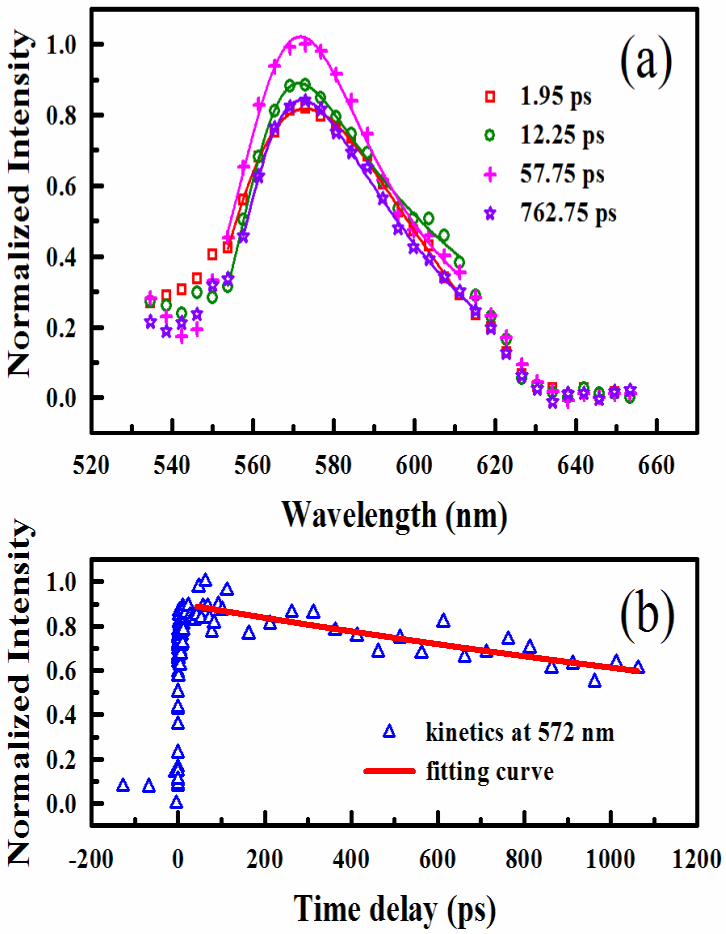


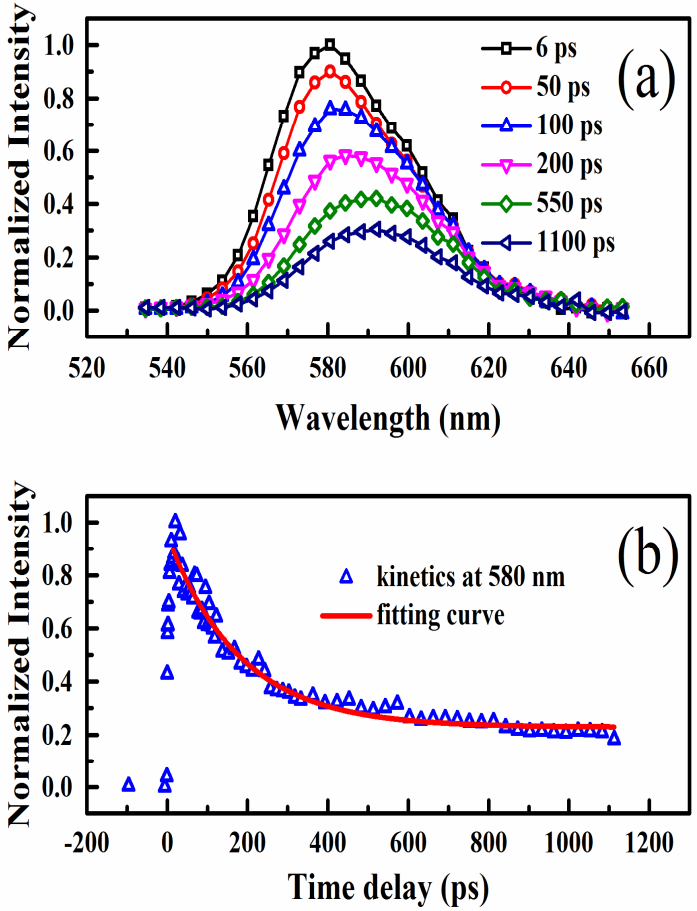


合作研发的光纤接口32通路并行数字锁相放大器

- 荧光环抑制能力: 1/300—1/100
- 动态范围100 dB,响应极限10^{-13} A
- 同时摄谱122 nm或256 nm

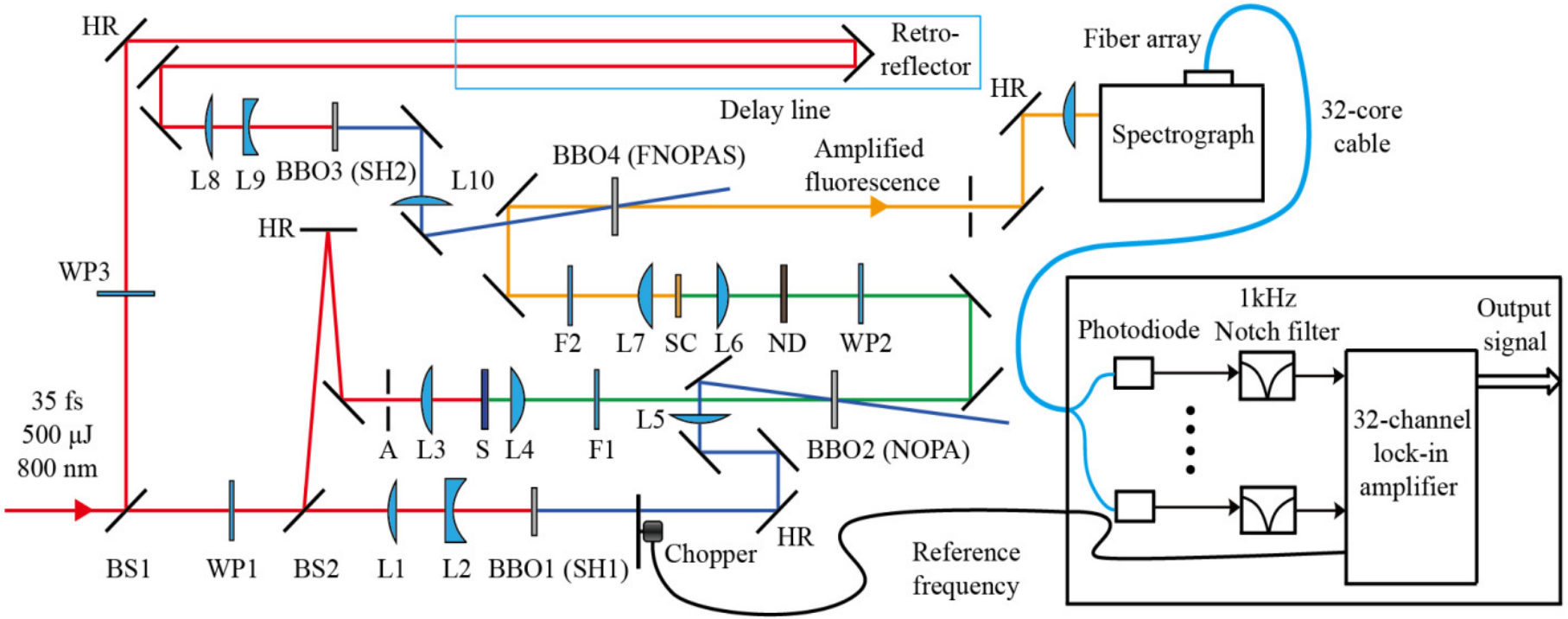
Rev. Sci. Instr. 2016





10^{-5} M与10^{-3} M的R6G乙醇溶液的时间分辨光谱与峰值处的动力学曲线

荧光放大系统简介

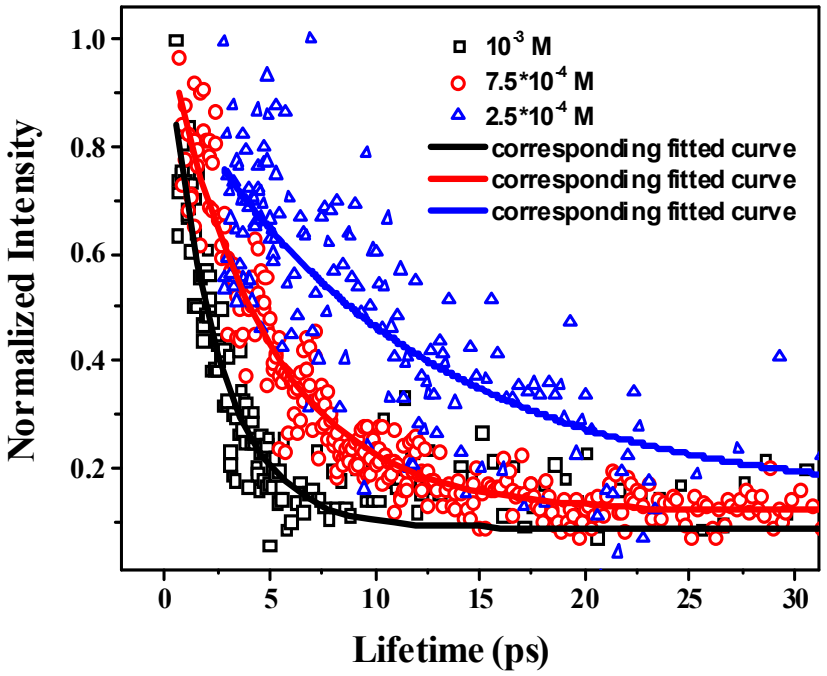


优点：时间分辨率**100 fs**

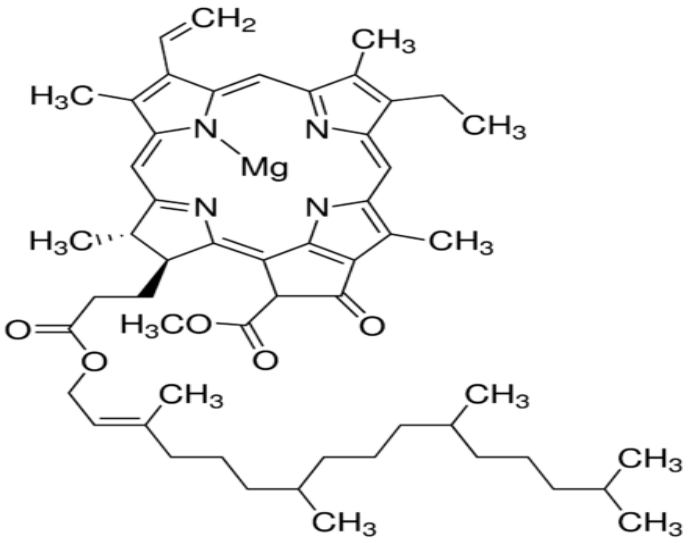
有增益测量，探测极限**13个非相干光子**

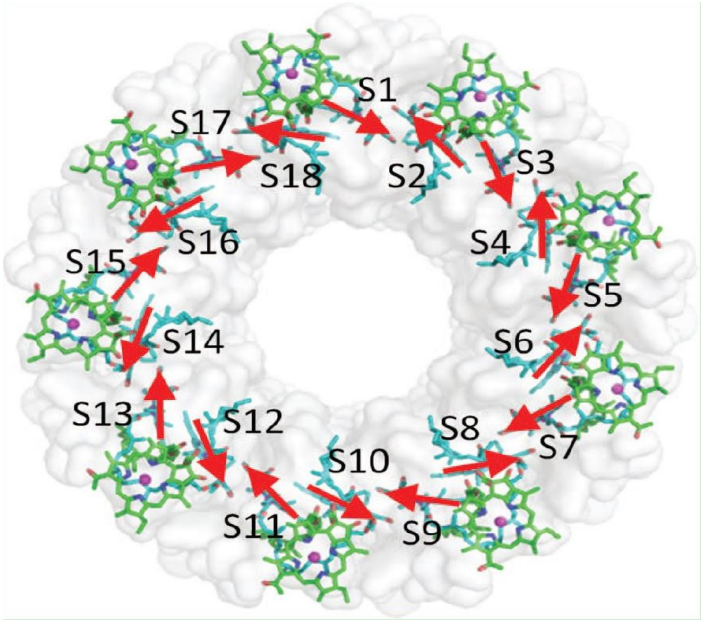
可见光区域单次放大光谱范围 **110 nm (2500 cm^{-1})**

改进后系统的应用（叶绿素a）



叶绿素a的荧光寿命随浓度的变化关系



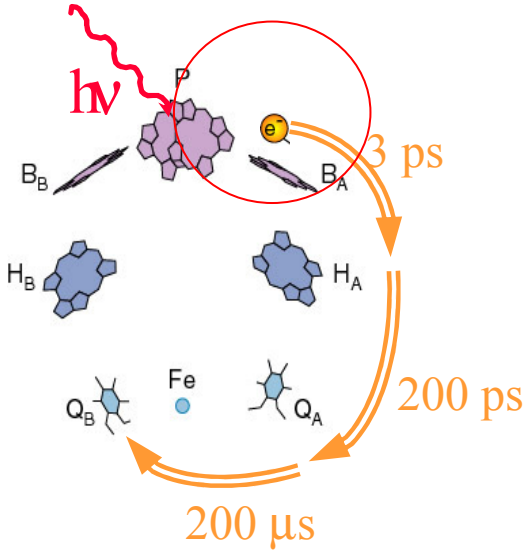


科研

中国科学院物理研究所
北京凝聚态物理国家实验室 SM6组供稿 第71期 2015年12月31日

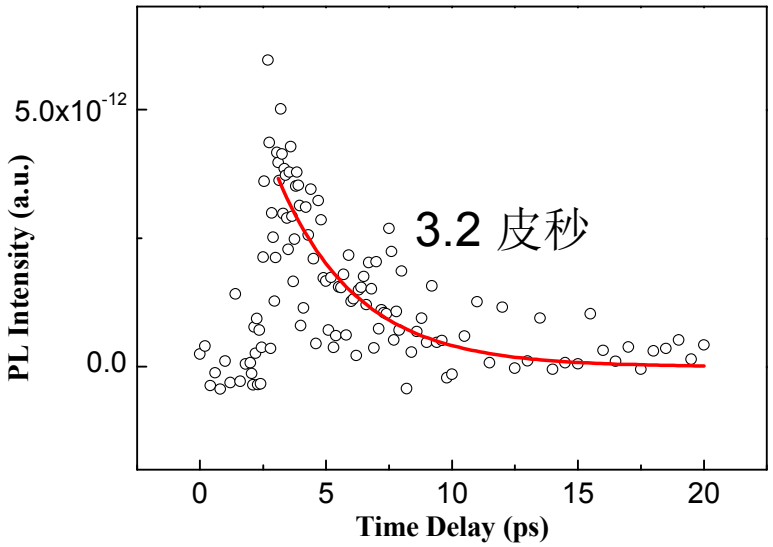
相干焉否单光子？成败荣辱一噪声—飞秒时间分辨荧光光谱新方法取得新进展

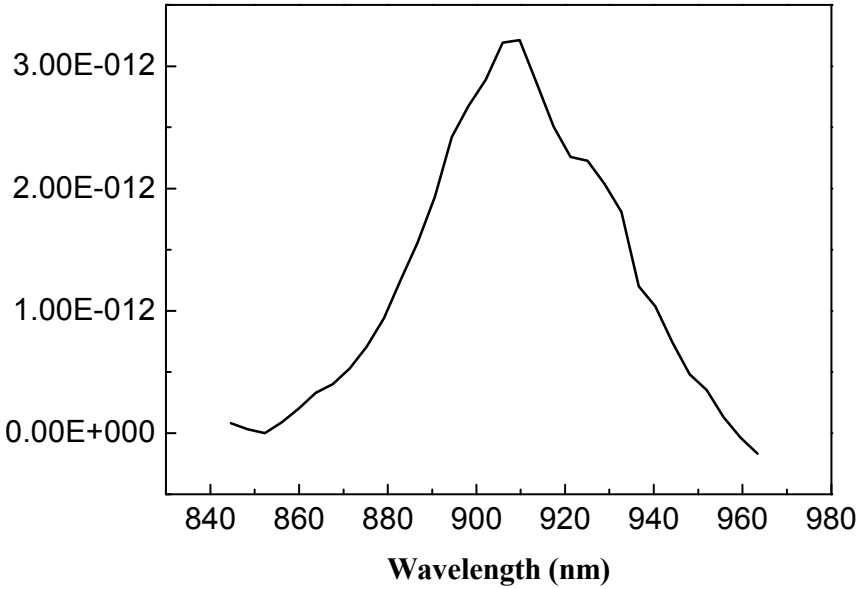
"与其临渊羡鱼，不如退而结网"这一谚语是告诫那些手中没有工具的人，不要在别人收获的季节去凑热闹，幻想着去分一杯羹，而是静下心来，好好去打造自己的工具，等待属于自己的机会。这句古训不仅仅是古人生存经验的总结，对今日现代科学研究的指点也寓意犹新。



荧光量子效率1%

3.0 ps – 4.0 ps averaged





(2)飞秒时间分辨可见及中红外瞬态吸收光谱

有机小分子半导体薄膜中存在光生自由载流子的实验证明

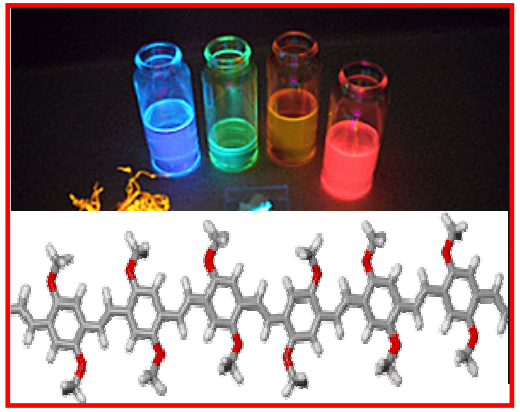
长春应化所闫东航研究组合作

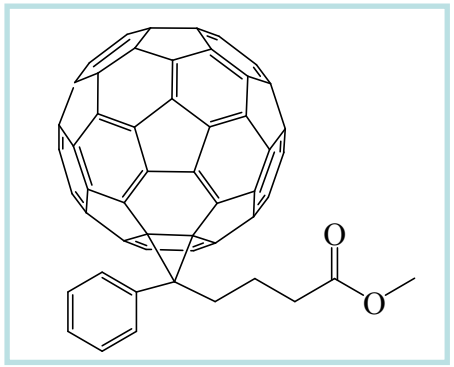
Scientific Reports 2015

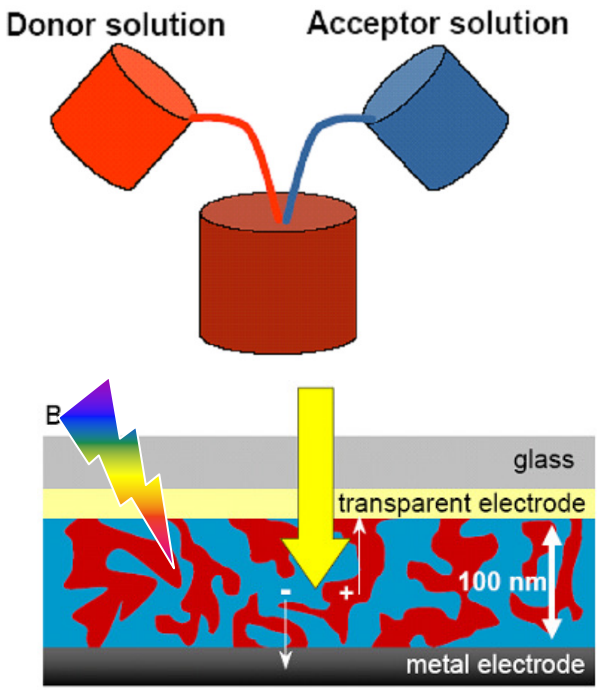
35飞秒激光器

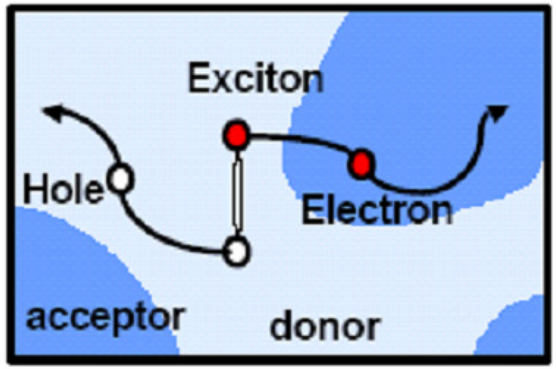
软

两种有机半导体材料：1.共轭长链高分子



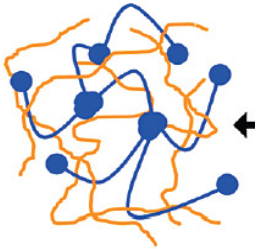




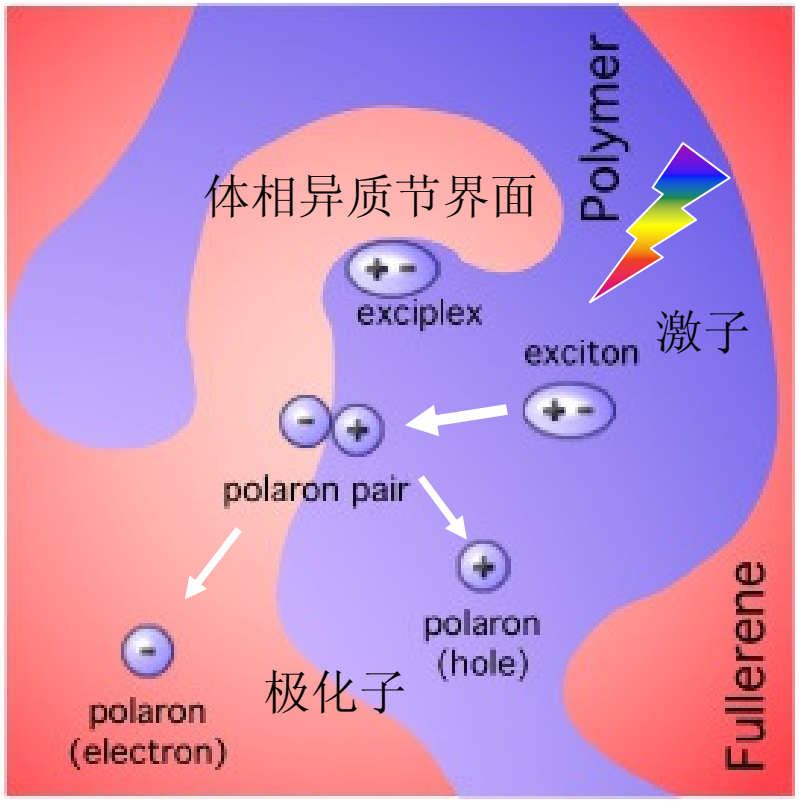


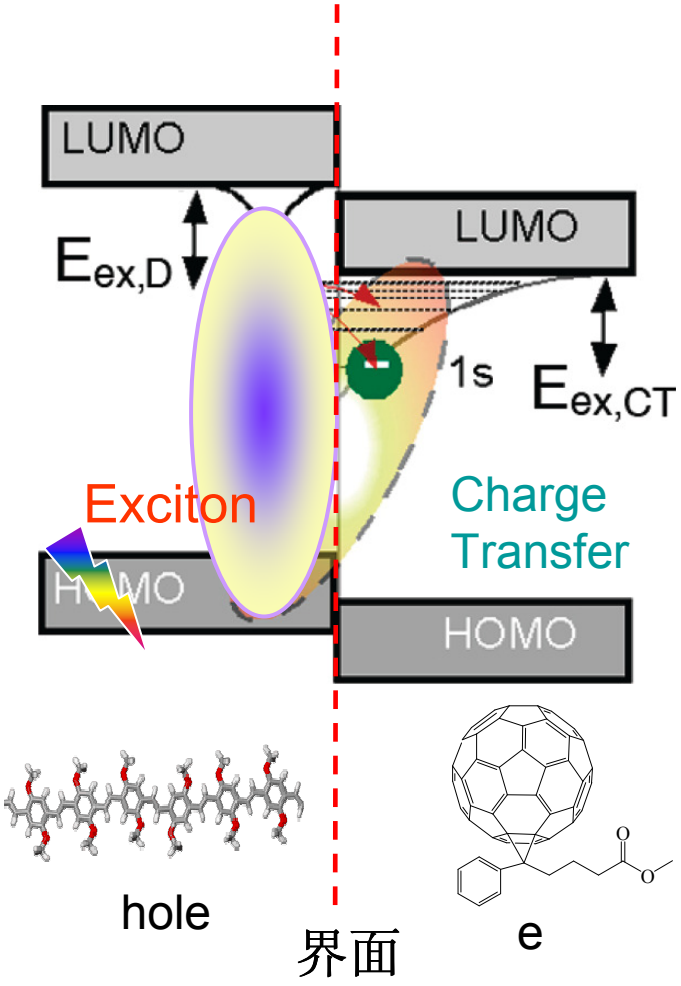
Bulk Heterojuction

激子扩散长度决定光电转换效率

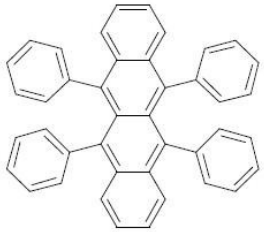


高分子聚合物一般难以形成完整的晶格，无法形成能带结构

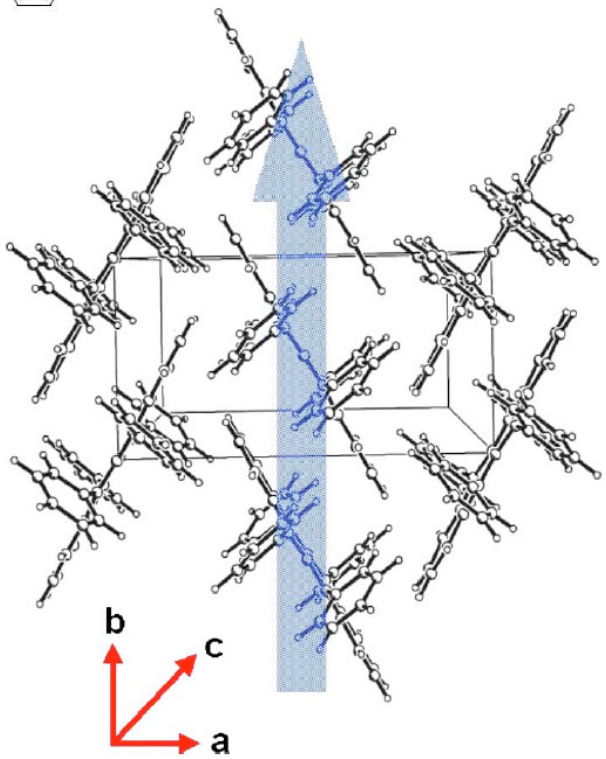


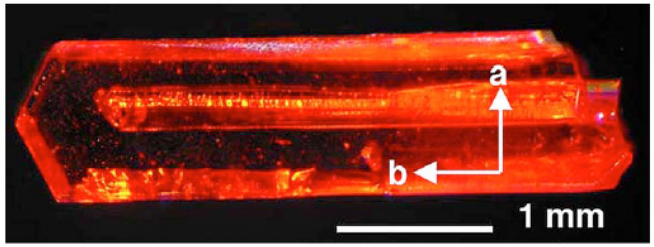


两种有机半导体材料：2.平面共轭有机小分子



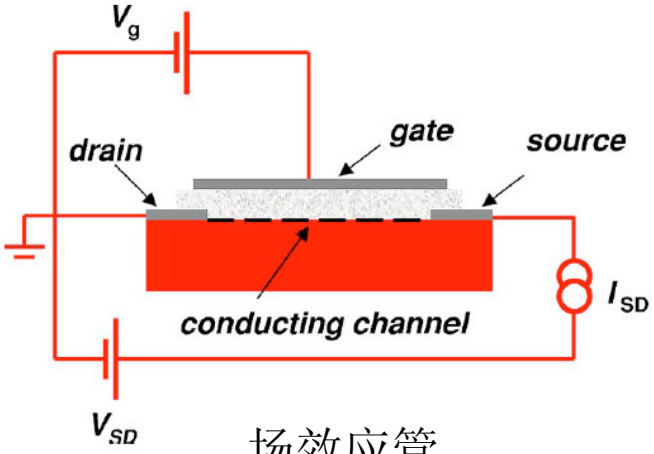
Rubrene 红荧烯





2008THz 瞬态光电导实验提出可能存在光生自由载流子

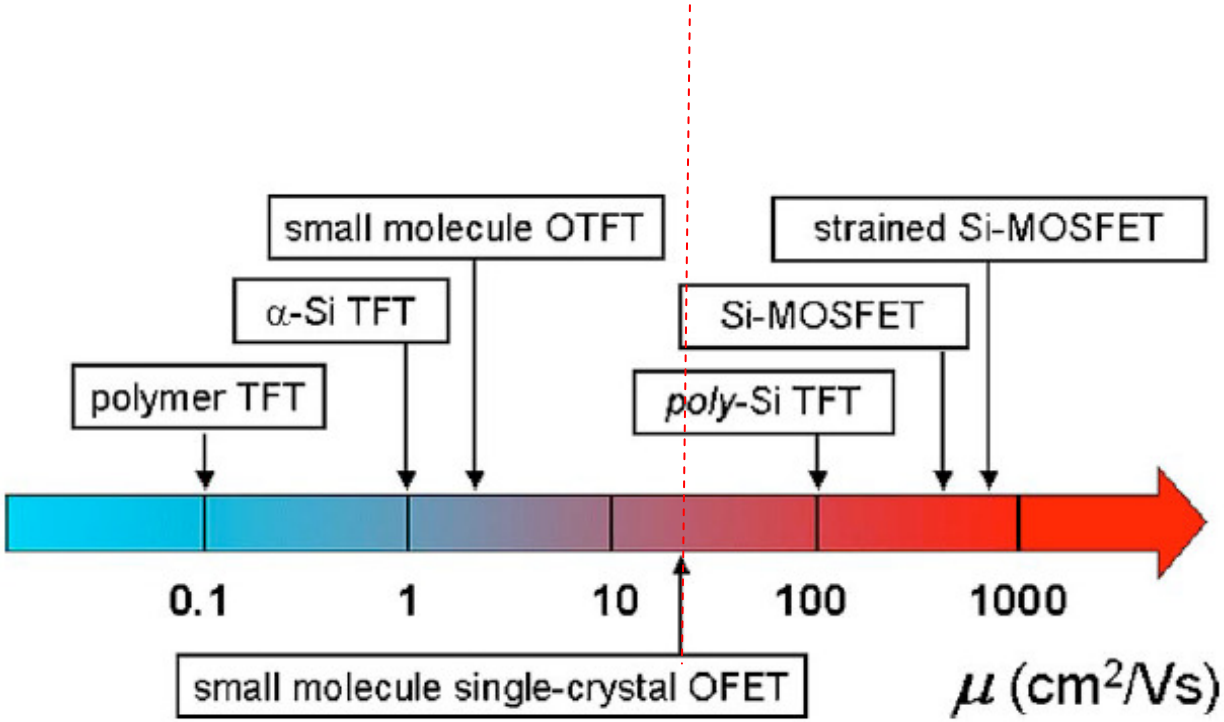
Ostroverkhova, APL, 2006, 88, 162101



场效应管

Gershenson, M.; Podzorov, V.; Morpurgo, A. *Rev. Modern Phy.* **2006,** *78* (3), 973.

有机场半导体和无机半导体迁移率的差异

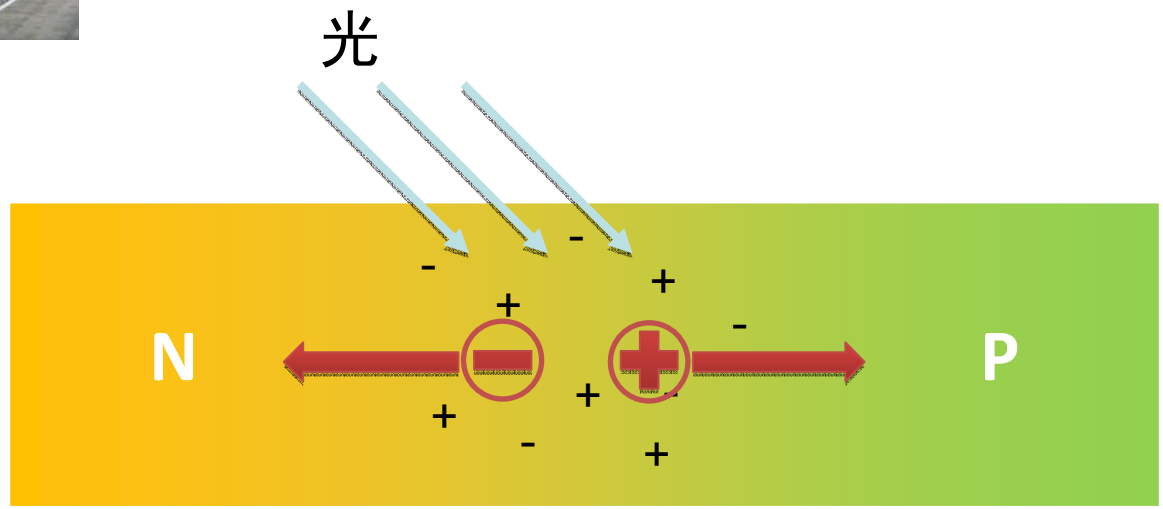


Gershenson, M.; Podzorov, V.; Morpurgo, A. *Reviews of Modern Physics* **2006,** *78* (3), 973

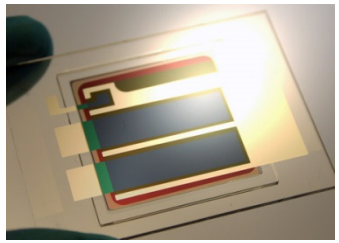
光　　光

1.共价键作用，相邻原子间作用强

2.介电常数大，对电荷屏蔽作用大



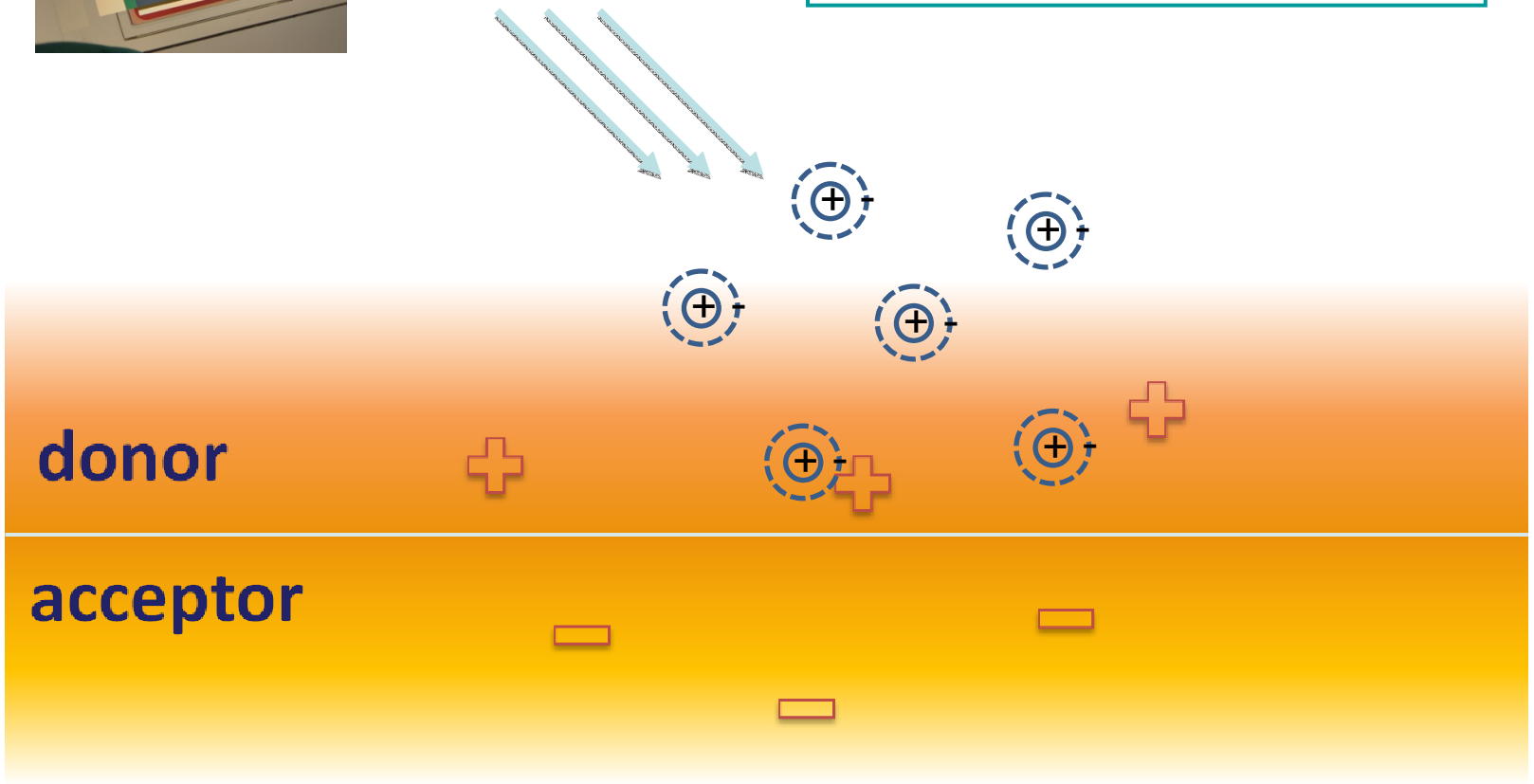
光



光

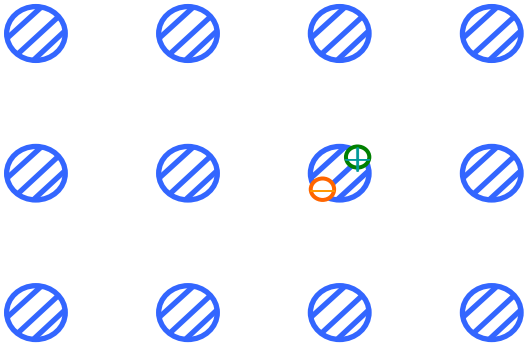
1. 有机材料中分子间耦合作用弱

2. 有机材料内介电常数低

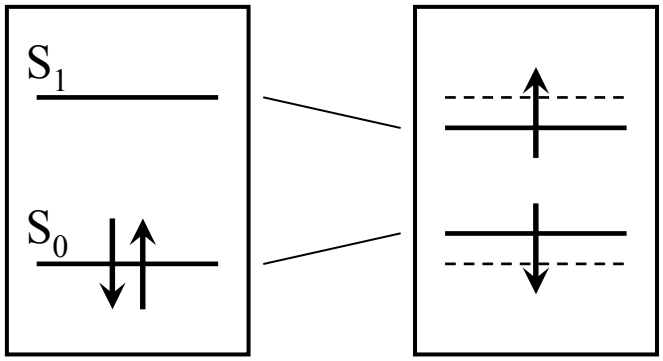


有机小分子半导体是否存在本征光生自由载流子

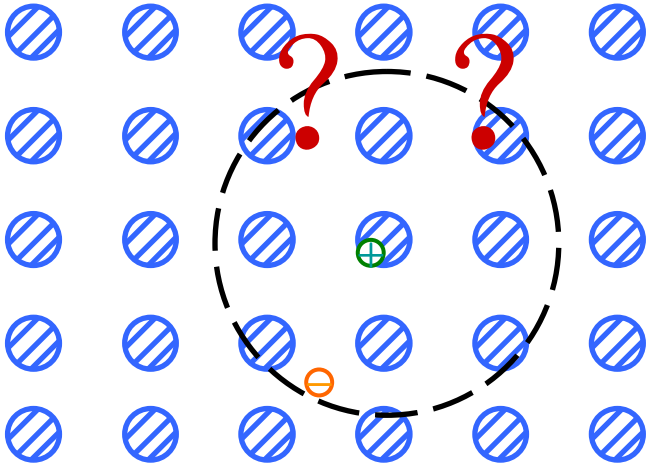
(a) Frenkel Excition



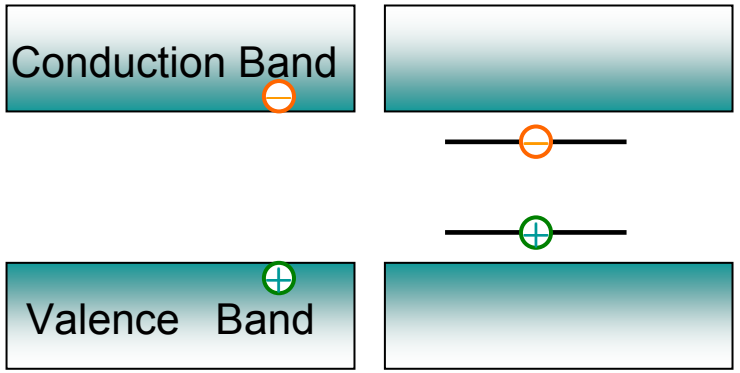
Molecular picture



(b) Wannier Excition



Semiconductor picture



何谓本征光生载流子

光

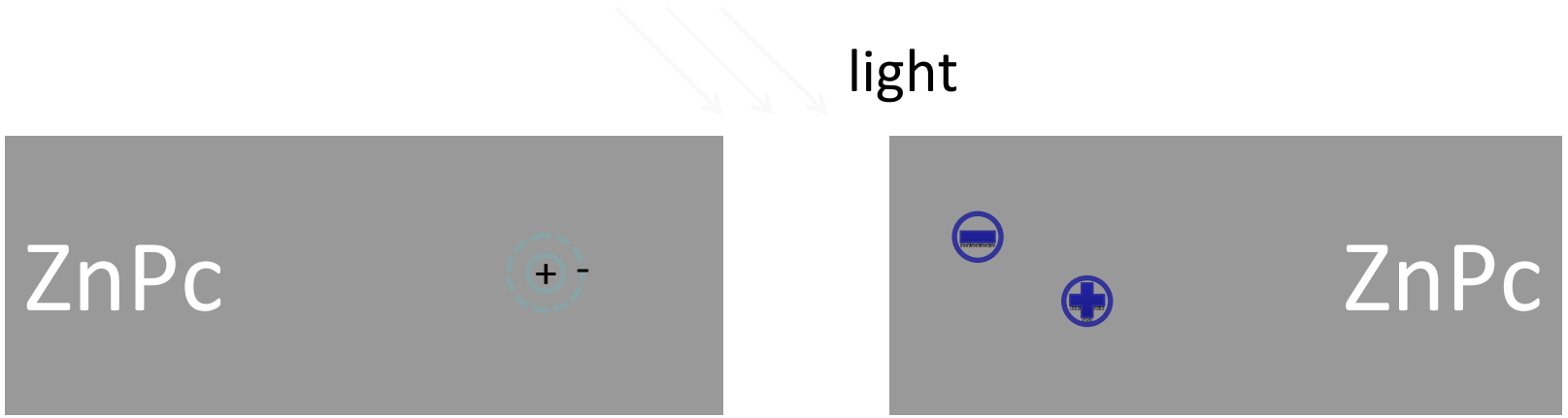
学

要求非接触测量

光学测量

科学

有机小分子晶体中是否存在本征载流子?



Drude 光

$$\alpha(\omega) \propto Re(\sigma(\omega)) = Re(\frac{ne^2}{m}\frac{\tau}{1-i\omega\tau}) = \frac{ne^2}{m}\frac{\tau}{1+(\omega\tau)^2}$$

$$\alpha(\lambda) \propto \frac{ne^2}{m}\frac{\tau}{1+(\omega\tau)^2} \propto \frac{\tau\lambda^2}{\lambda^2+(c\tau)^2}$$

光

理

$$\alpha(\lambda) \propto \frac{ne^2}{m}\frac{\tau}{1+(\omega\tau)^2} \propto \frac{\tau\lambda^2}{\lambda^2+(c\tau)^2}$$

$$c\tau >> \lambda$$

$$\alpha(\lambda) \propto \lambda^p = \lambda^2; \quad p = 2$$

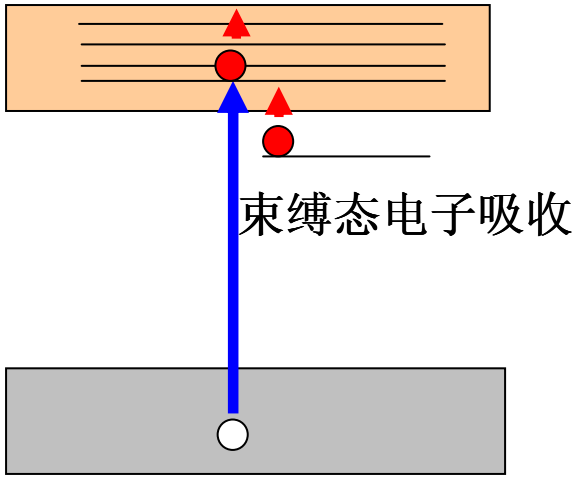
Beard, et al., *Phys. Rev. B* **2000**, *62*, 15764–15777

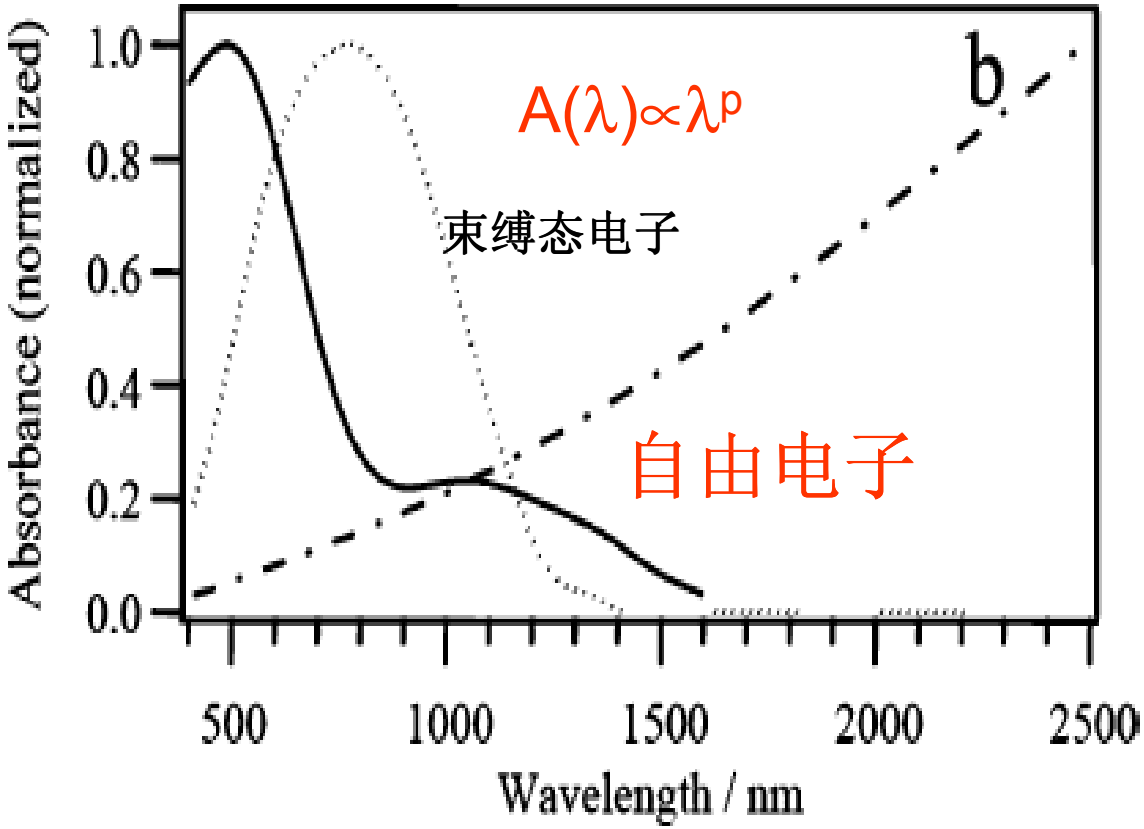
光生导带及束缚态电子的红外光谱表征

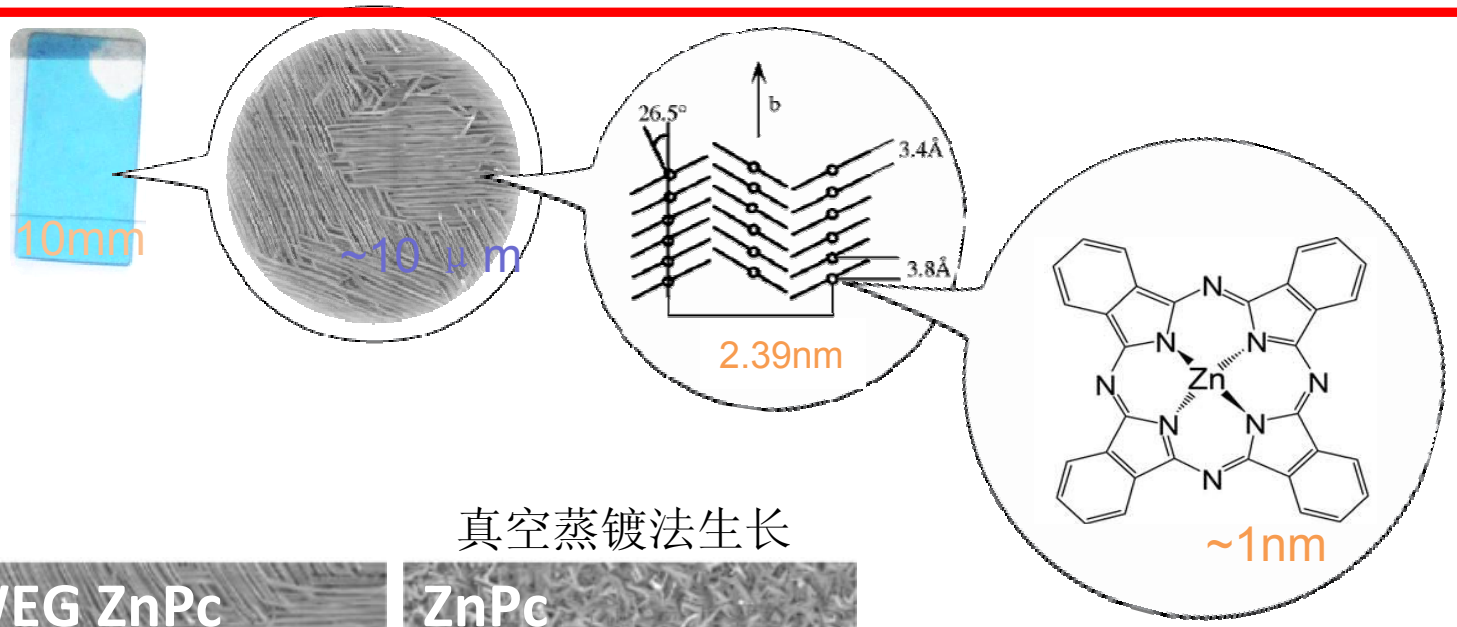
导带自由吸收光谱线型：
$A(\lambda) \propto \lambda^p$

P=1.5 conduction band electron

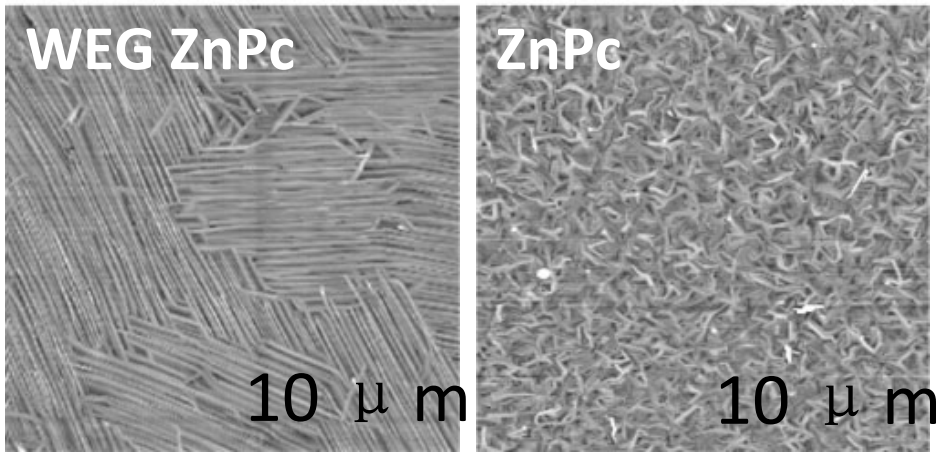
P=2.5 trapped electron





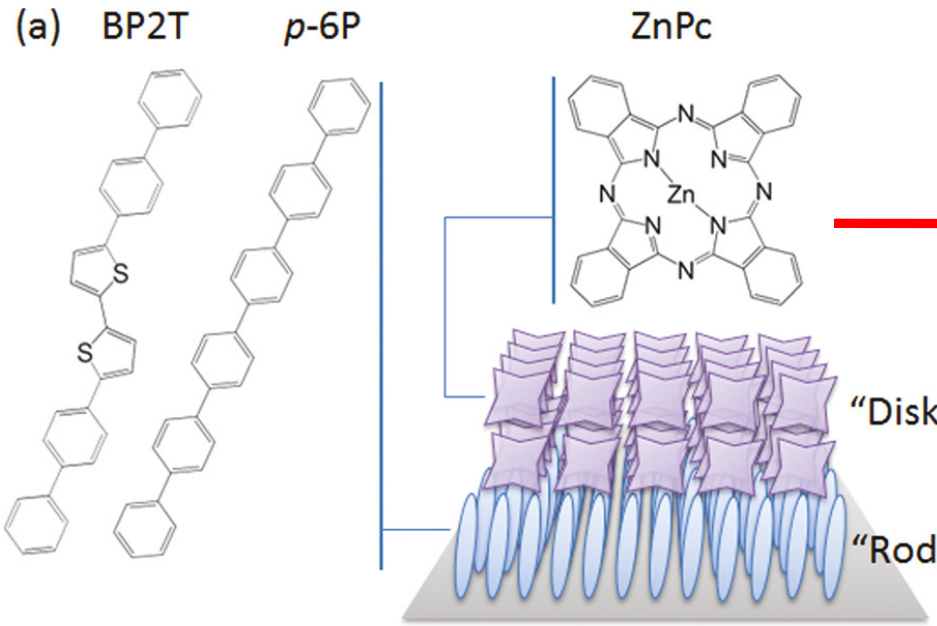


真空蒸镀法生长

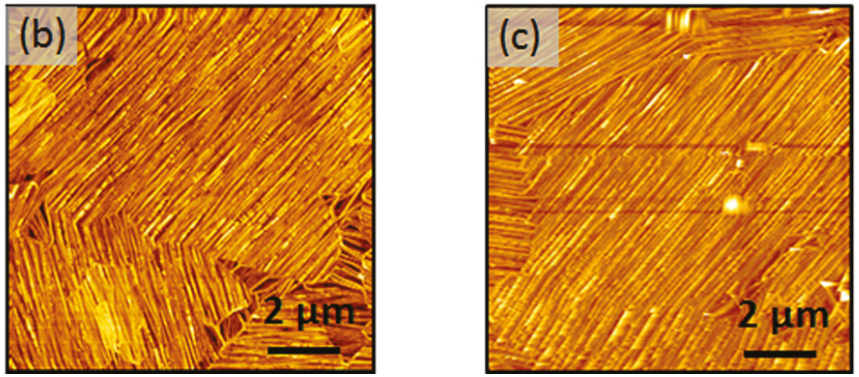


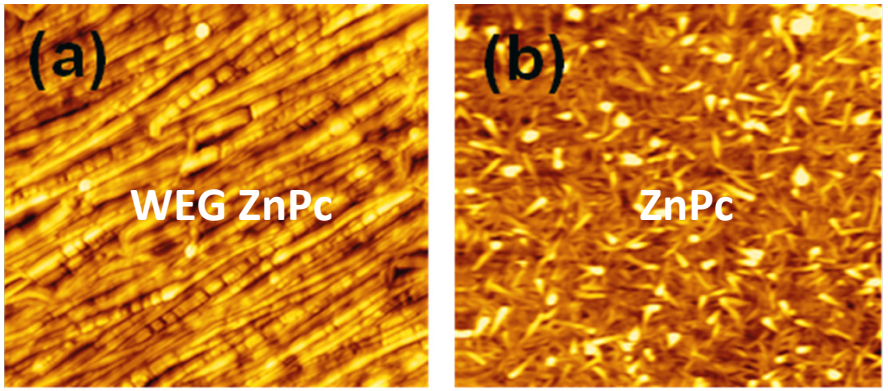
AFM形貌图

Wang, H., Zhu, F., Yang, J., Geng, Y., & Yan, D. (2007). Weak Epitaxy Growth Affording High-Mobility Thin Films of Disk-Like Organic Semiconductors. *Advanced Materials*, *19*(16), 2168–2171.



我们样品中的Rods是BP2T





4*4 μm

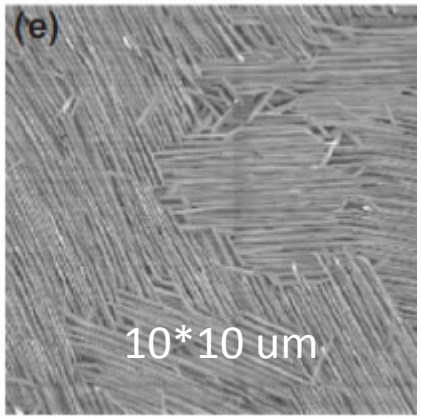
Figure 1. (a) Molecular structure of ZnPc, BP2T, and p-6P. Schematic
diagram of weak epitaxy growth of disklike molecules on rodlike molecules. (b, c) AFM image of ZnPc/BP2T and ZnPc/p-6P, respectively.

Zhu, F., Grobosch, M., & Treske, U. (2011). Hole Transparent and Hole Blocking Transport in Single-Crystal-Like Organic Heterojunction: When Rods Hold up Disks. *ACS Applied Materials & Interfaces*, *3*, 2195–2199. Retrieved from http://pubs.acs.org/doi/abs/10.1021/am200512d

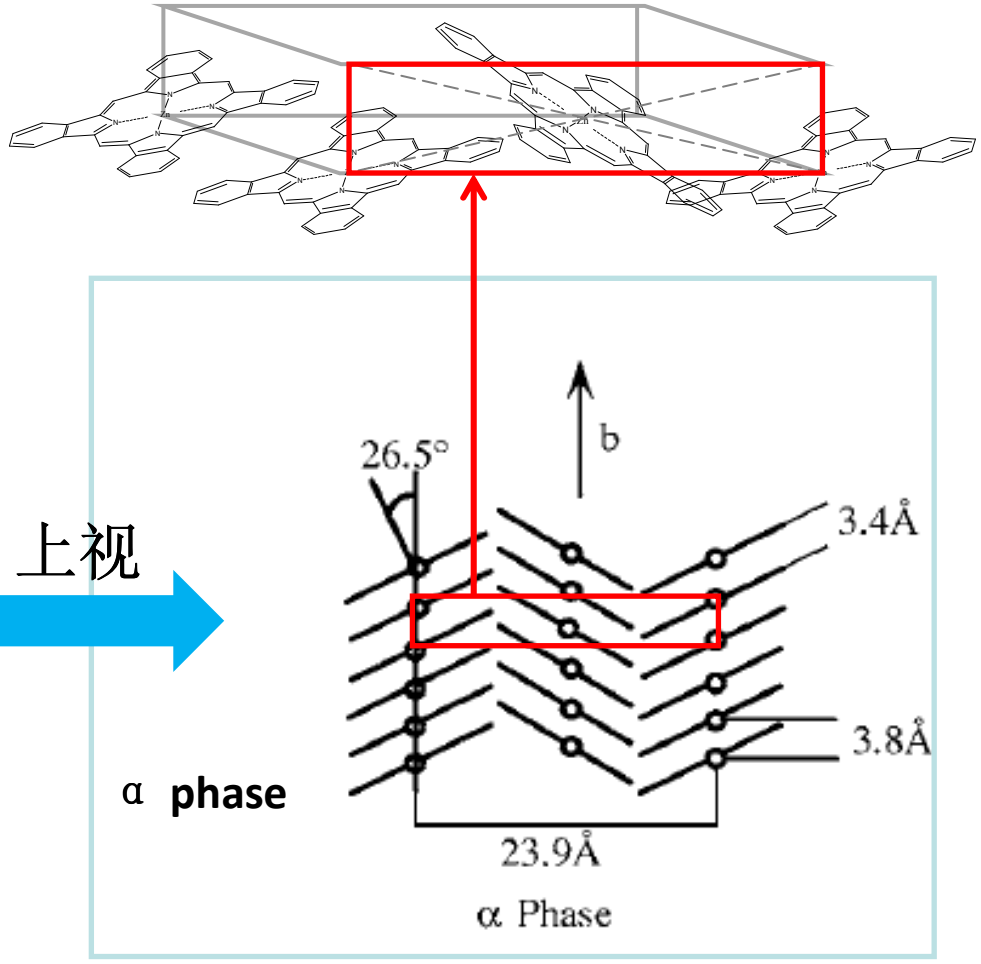
Yang, J., Zhu, F., Yu, B., Wang, H., & Yan, D. (2012). Simultaneous enhancement of charge transport and exciton diffusion in single-crystal-like organic semiconductors. *Applied Physics Letters*, *100*(10), 103305. doi:10.1063/1.3692106

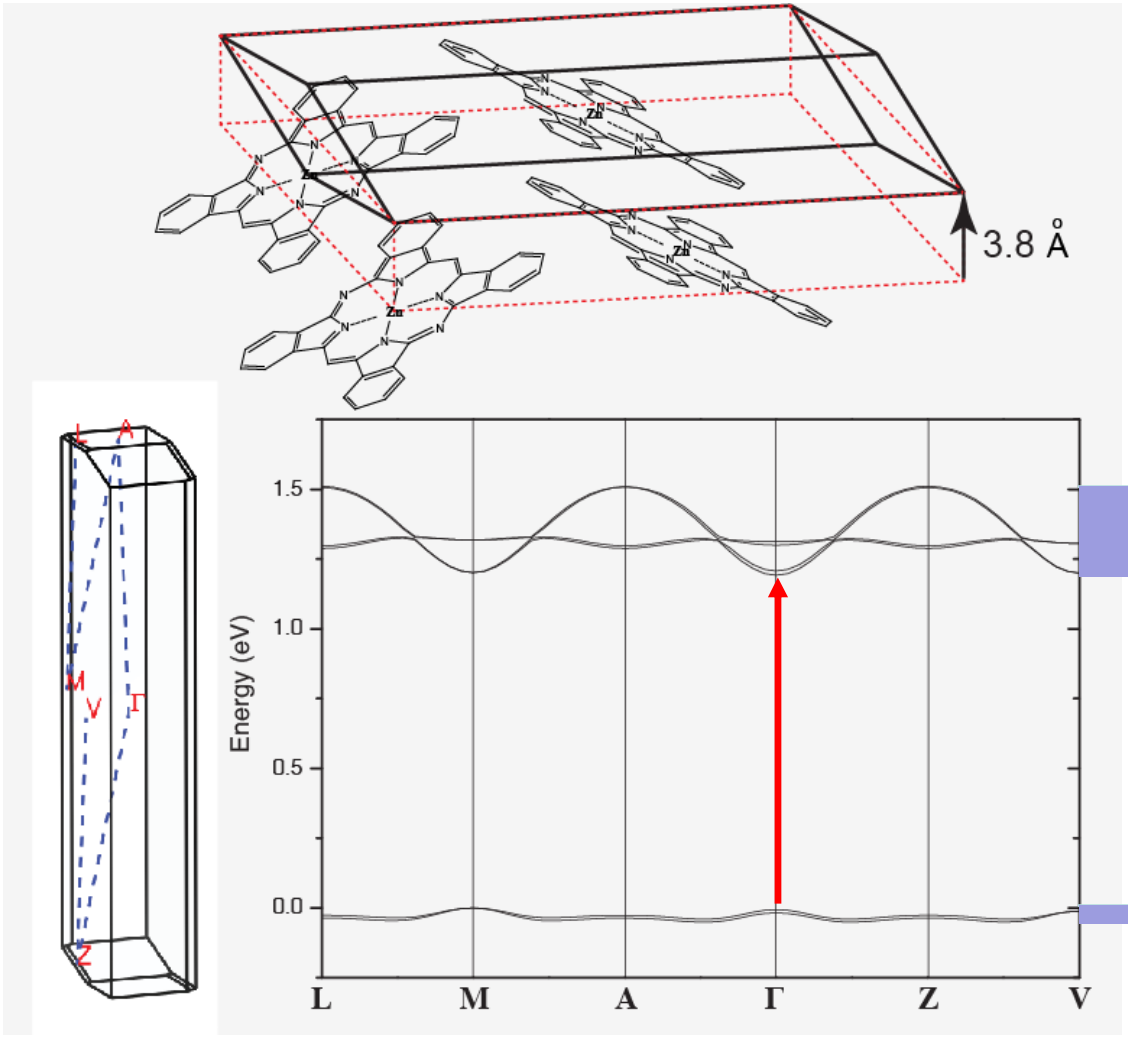
晶胞中大致的构型

一个单胞中有两个不同的平移对称分子，导致光谱中的每个能级分裂成两子能级



上视





DFT in Dmol3
GGA
BLYP

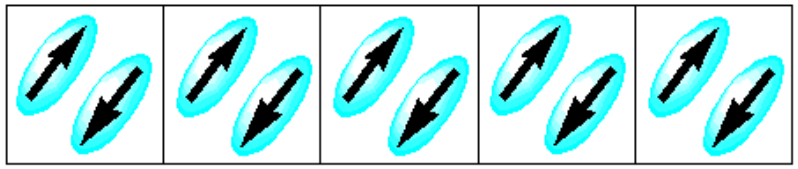
直接带隙

0.318 eV

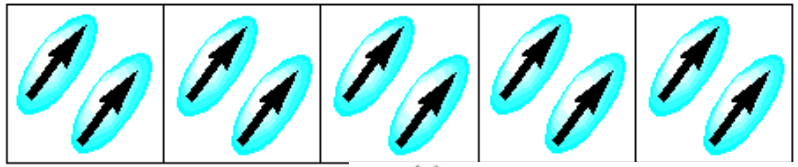
0.057 eV

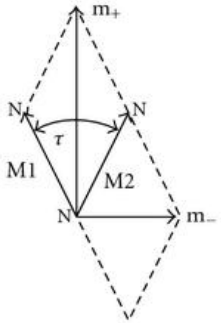
Davydov Splitting in Molecular Aggregates

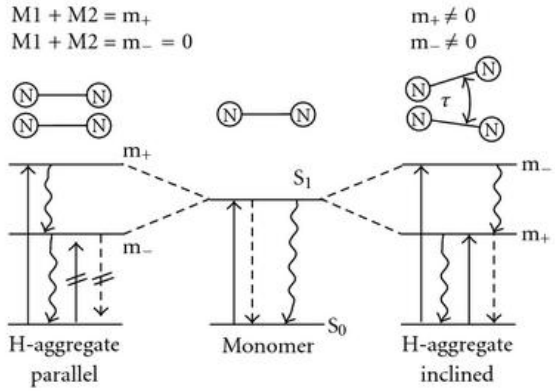
Davidov Splitting: low energy transition



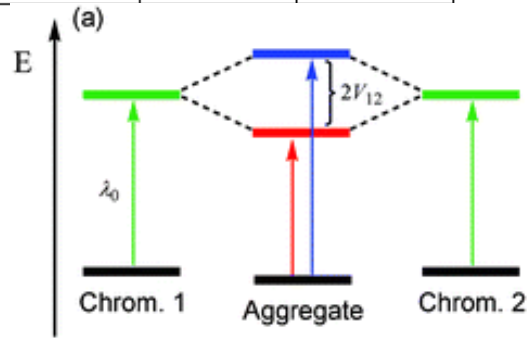
Davidov Splitting: high energy transition

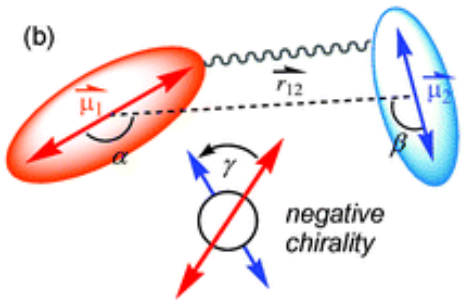


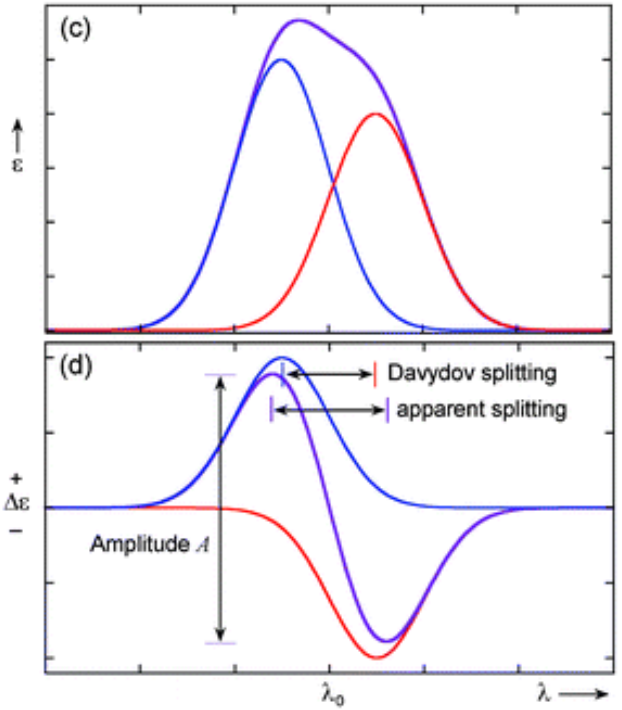




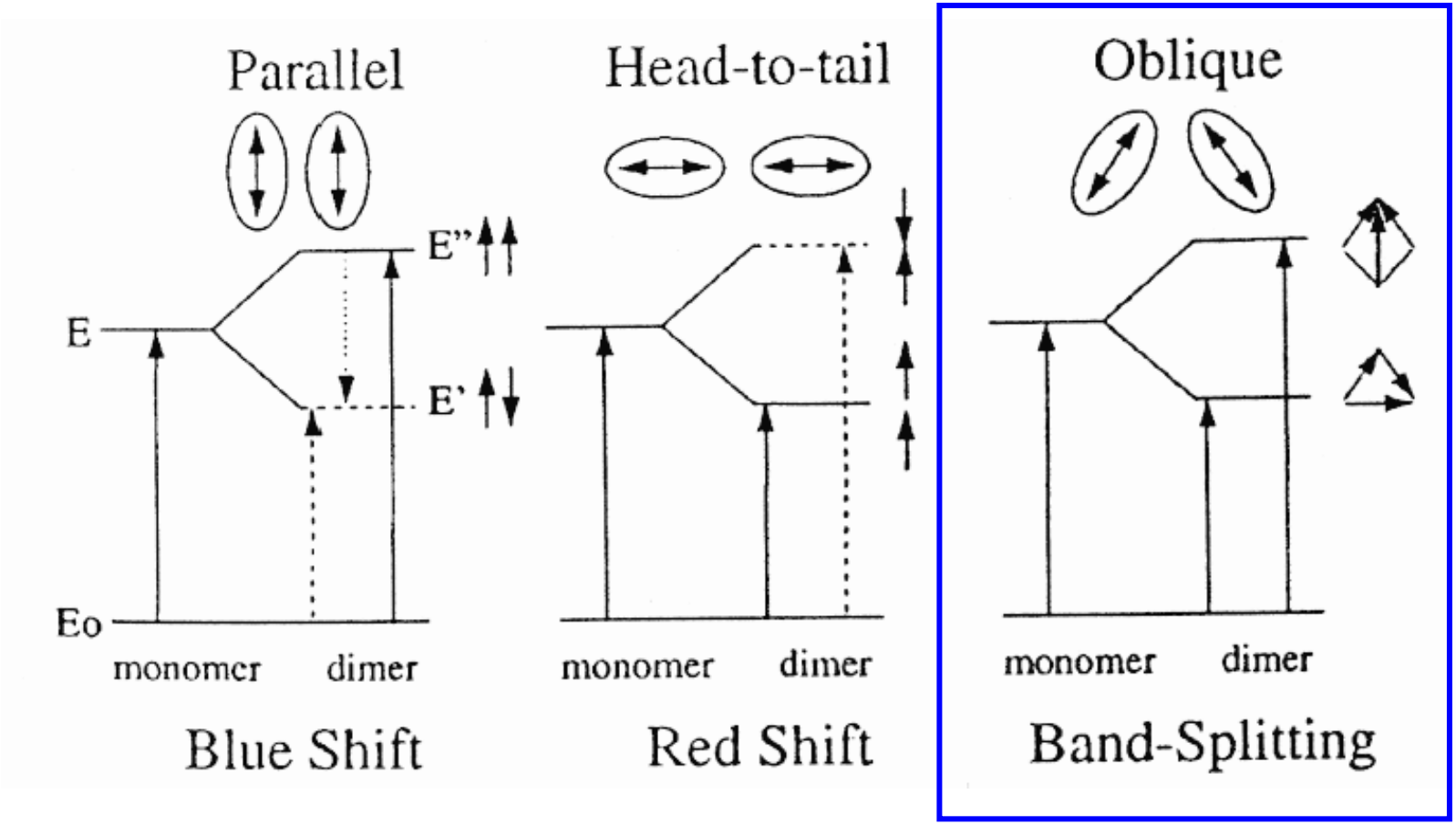
τ: angle between M1 and M2
M1, M2: molecular transition dipoles
m+ , m−: resulting Davydov components



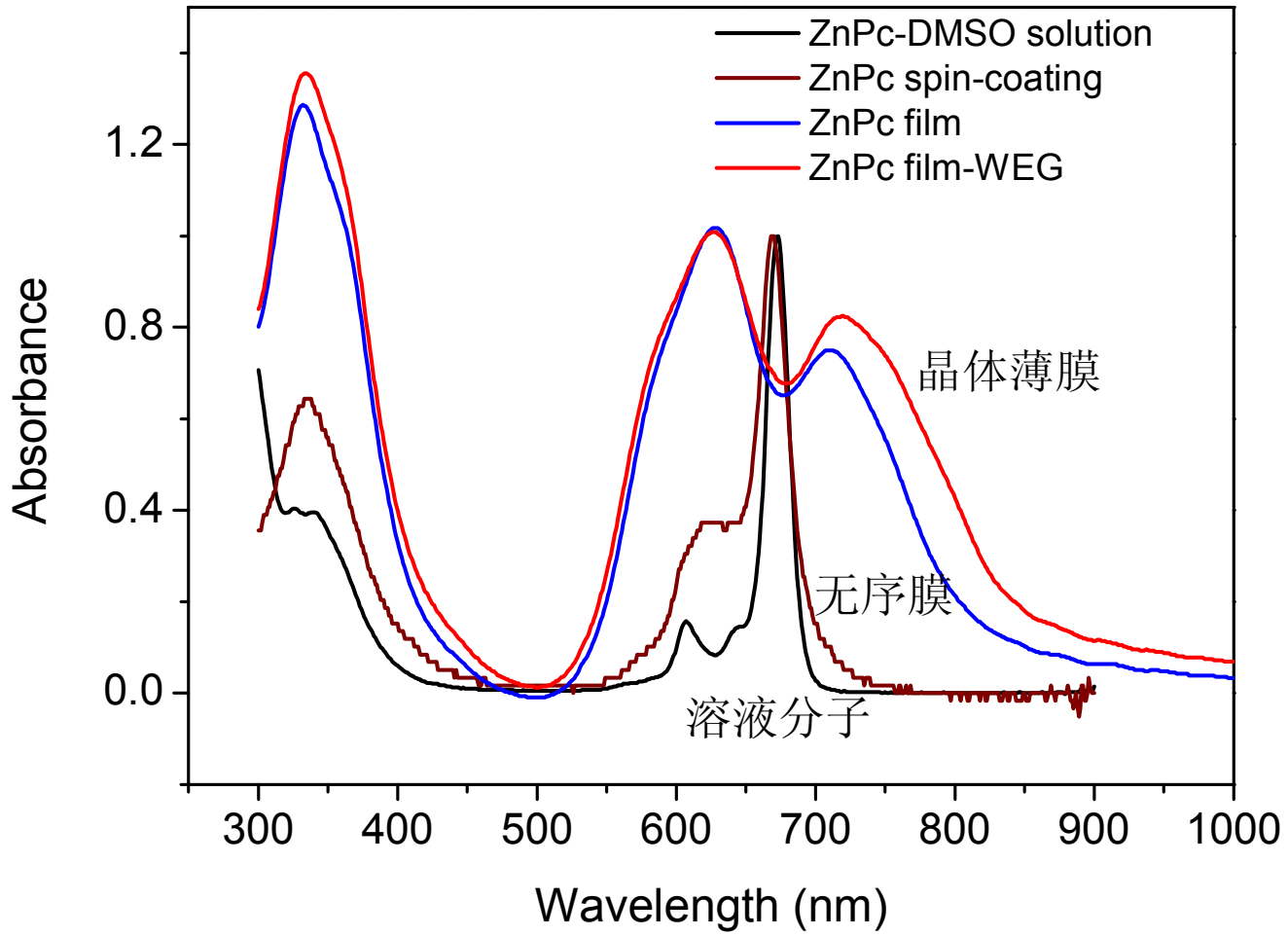




二聚体分子能级的Davydov Spliting

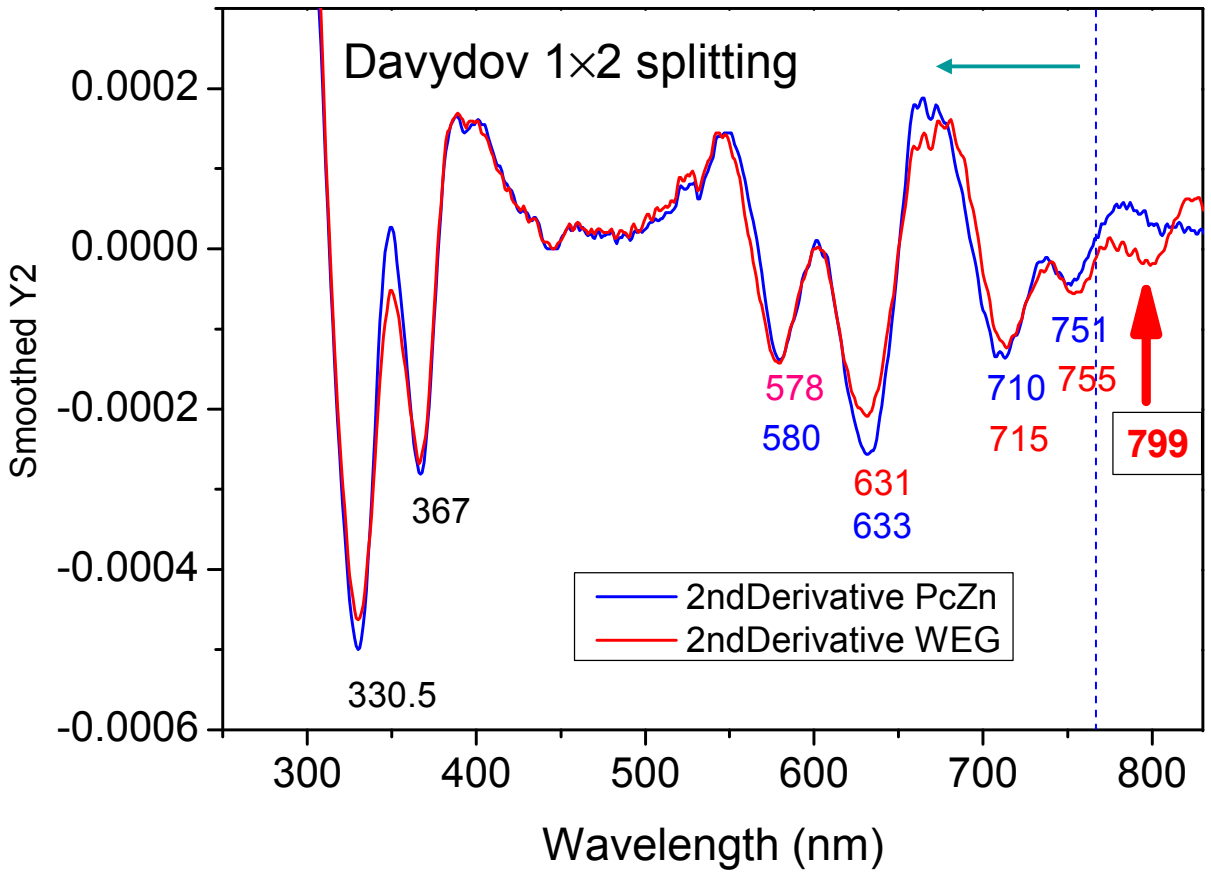


吸收光谱出现的Davydov 劈裂

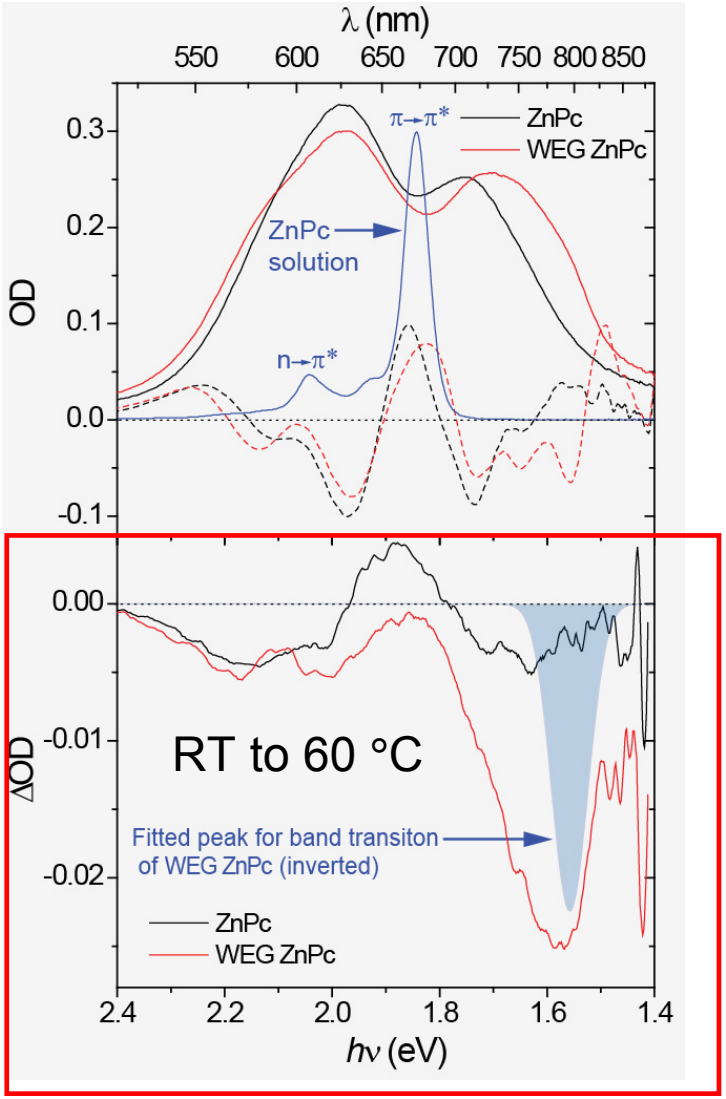


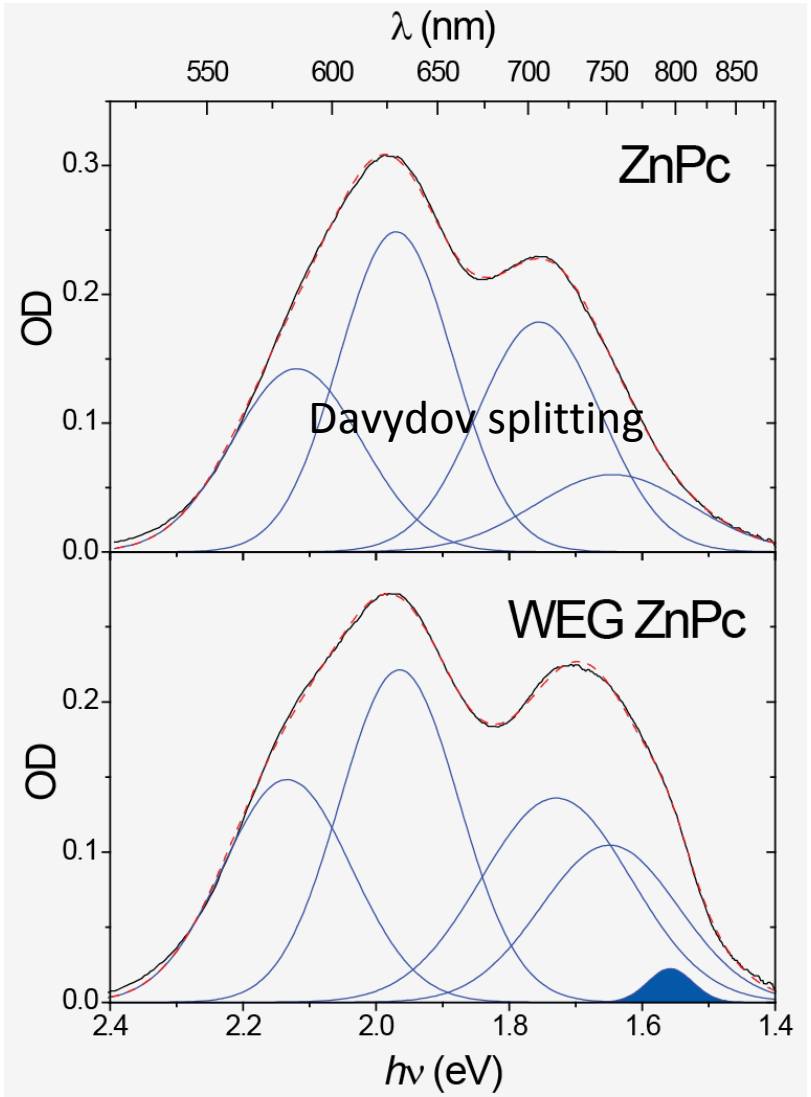
ZnPc和ZnPc WEG二阶导数峰位比较：带隙跃迁峰的发现

ZnPc WEG 在799 nm处多出一峰！

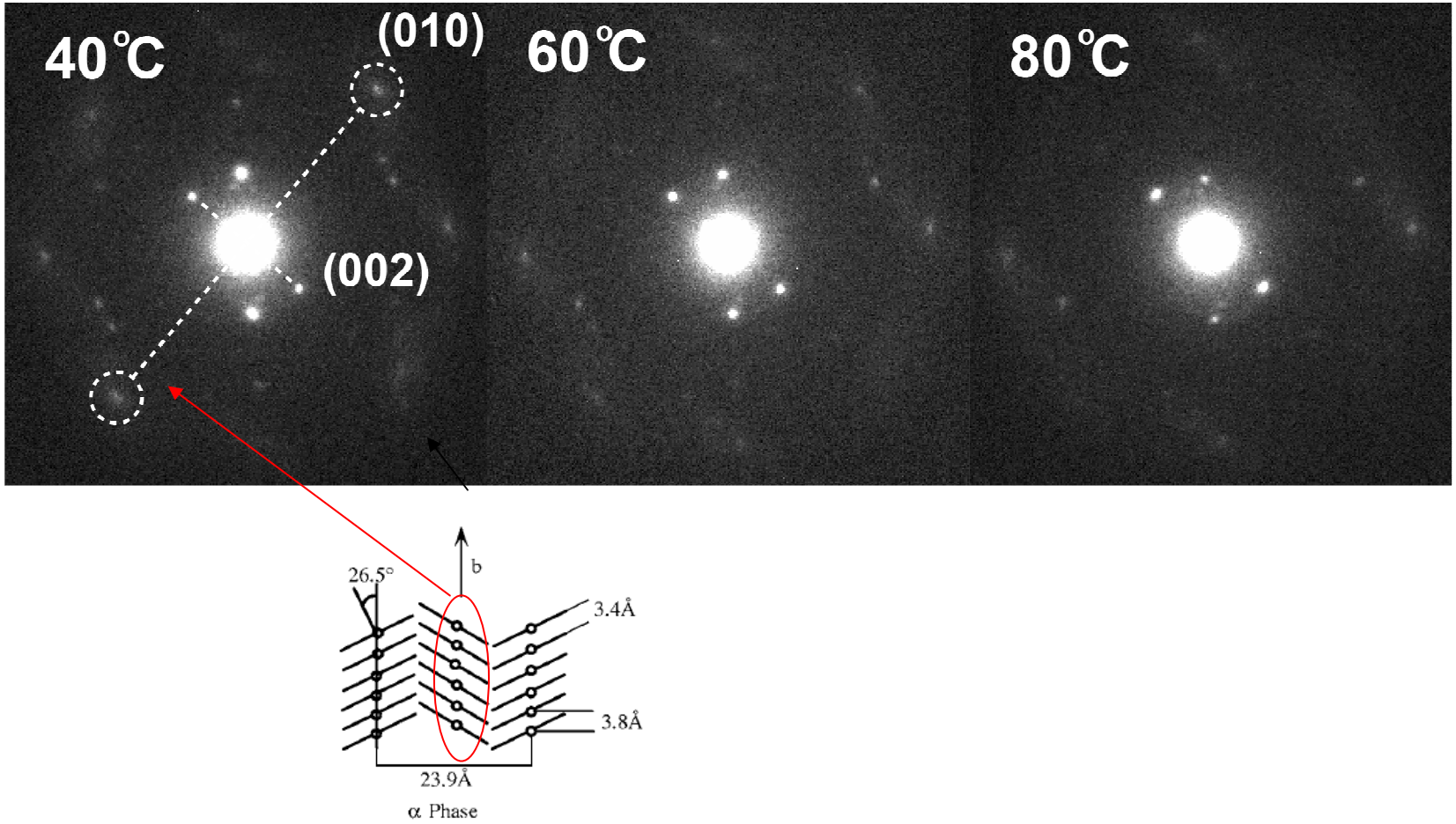


光　中

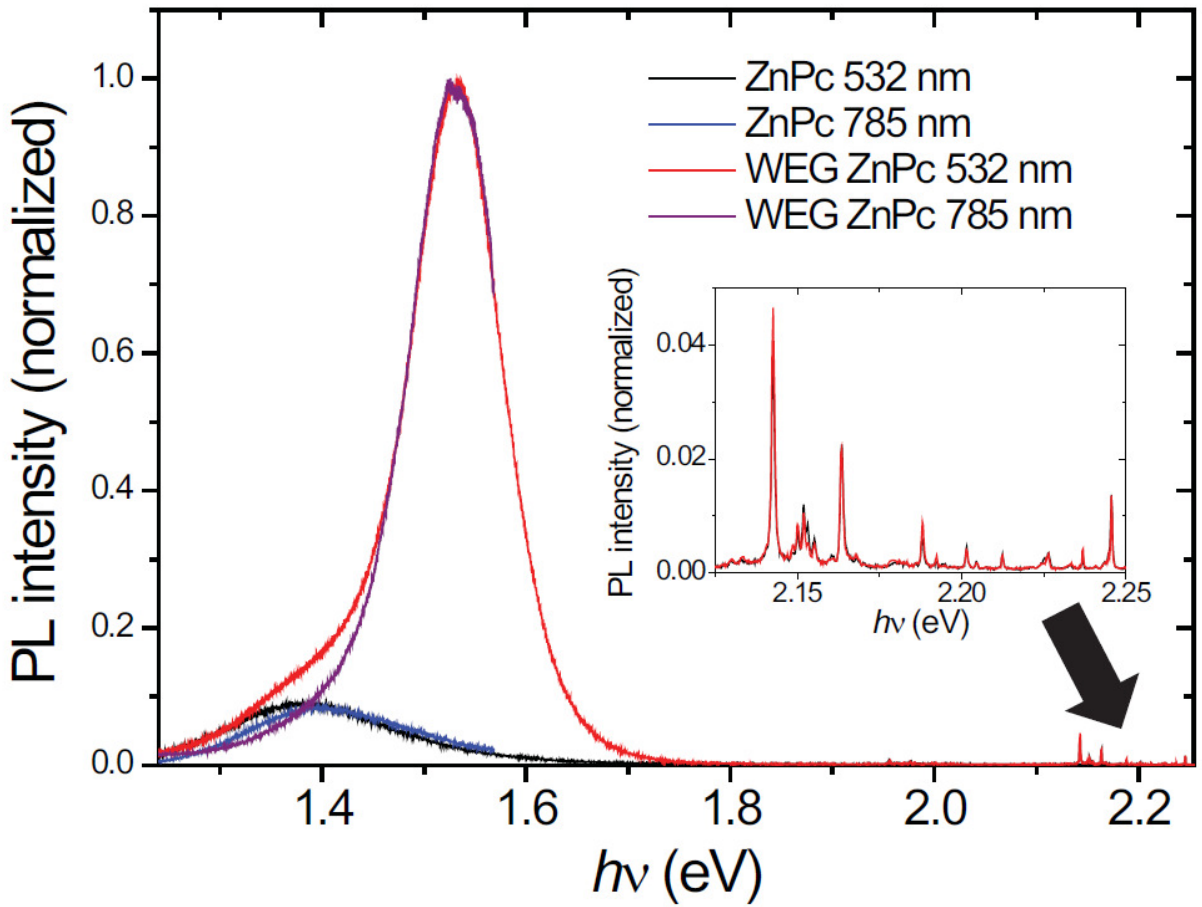

λ (nm)
550 600 650 700 750 800 850
OD
0.3
0.2
0.1
0.0
-0.1
π→π*
n→π*
ZnPc
WEG ZnPc
ZnPc
solution
ΔOD
0.00
-0.01
-0.02
RT to 60 °C
Fitted peak for band transiton
of WEG ZnPc (inverted)
ZnPc
WEG ZnPc
2.4 2.2 2.0 1.8 1.6 1.4
hν (eV)


λ (nm)
550 600 650 700 750 800 850
OD
0.3
0.2
0.1
0.0
ZnPc
Davydov splitting
WEG ZnPc
2.4 2.2 2.0 1.8 1.6 1.4
hν (eV)

变温选区电子衍射证明升温导致晶格长程有序度变差，导致能带结构被破坏

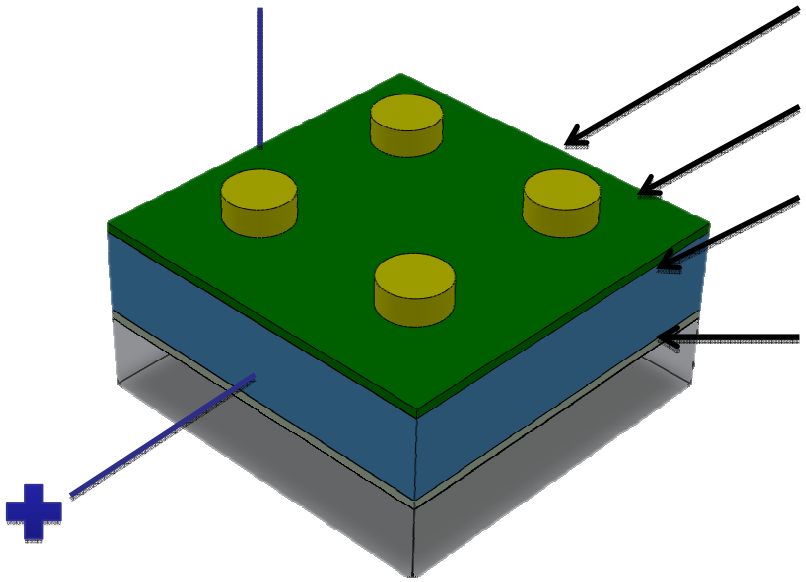


光　　光　　光


ZnPc 532 nm
ZnPc 785 nm
WEG ZnPc 532 nm
WEG ZnPc 785 nm
PL intensity (normalized)
hν (eV)
1.0
0.8
0.6
0.4
0.2
0.0
1.4
1.6
1.8
2.0
2.2
0.04
0.02
0.00
2.15
2.20
2.25

光

Perpendicular



Au电极

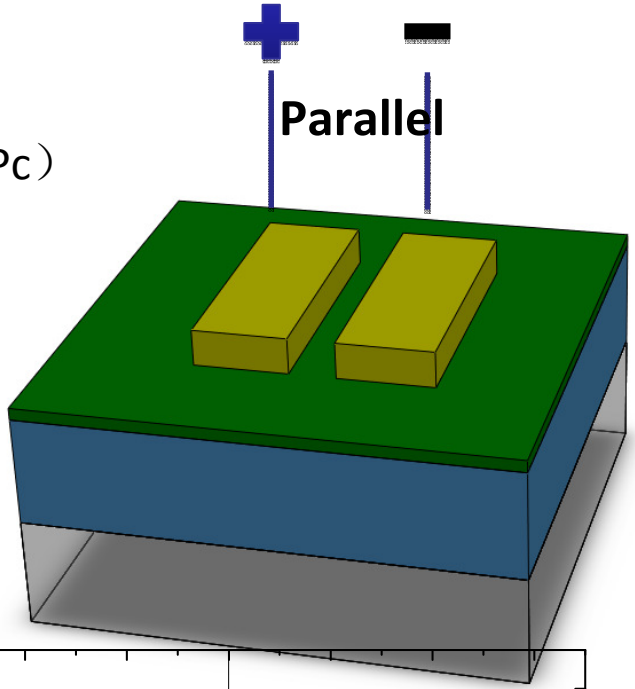
过渡层（F16CuPc）

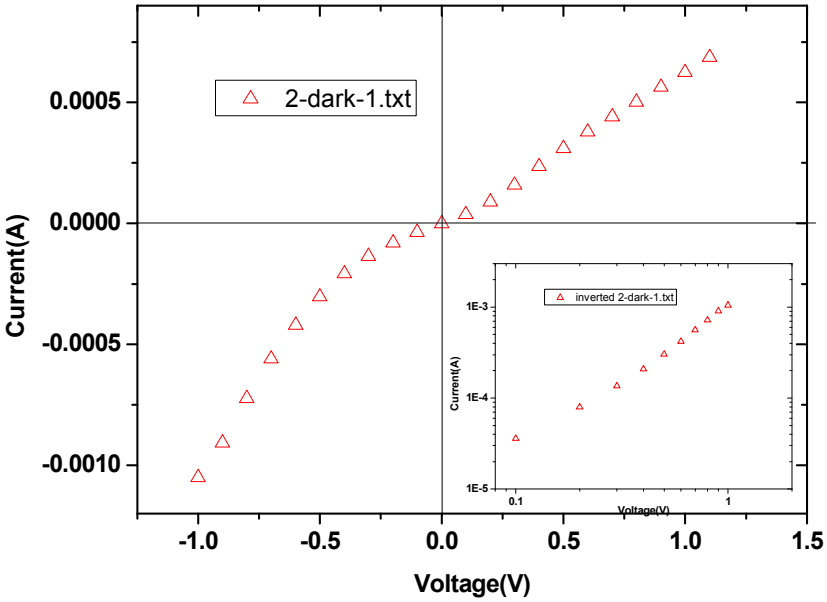
WEG ZnPc

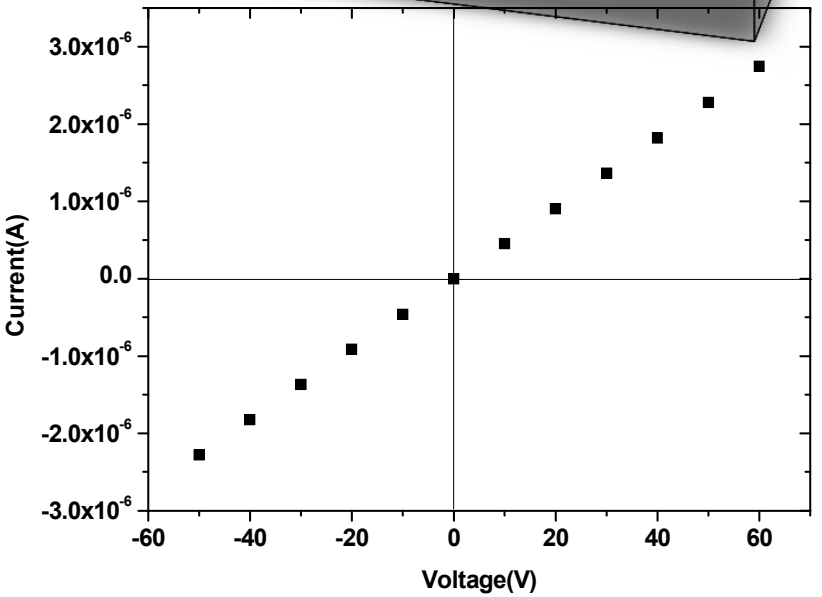
PEDOT:PSS

ITO glass

Parallel







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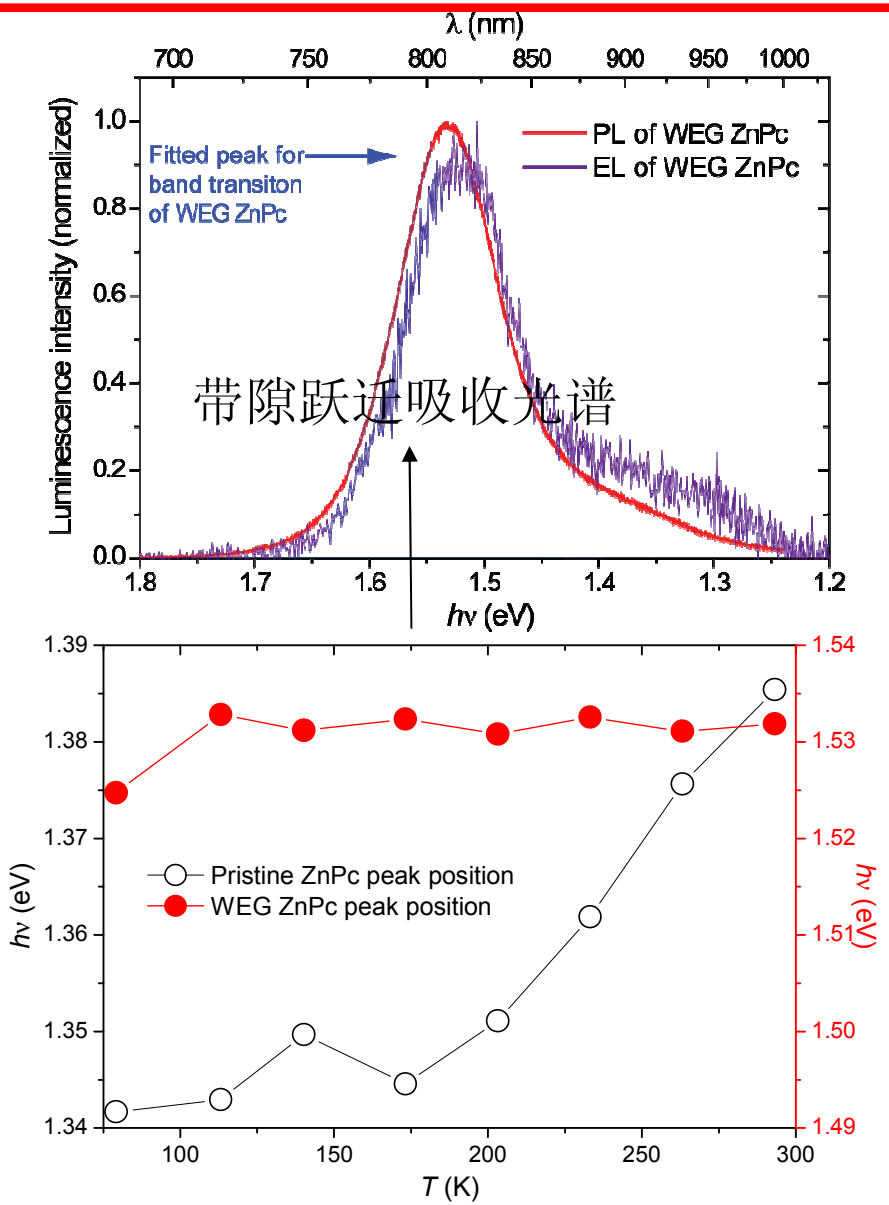
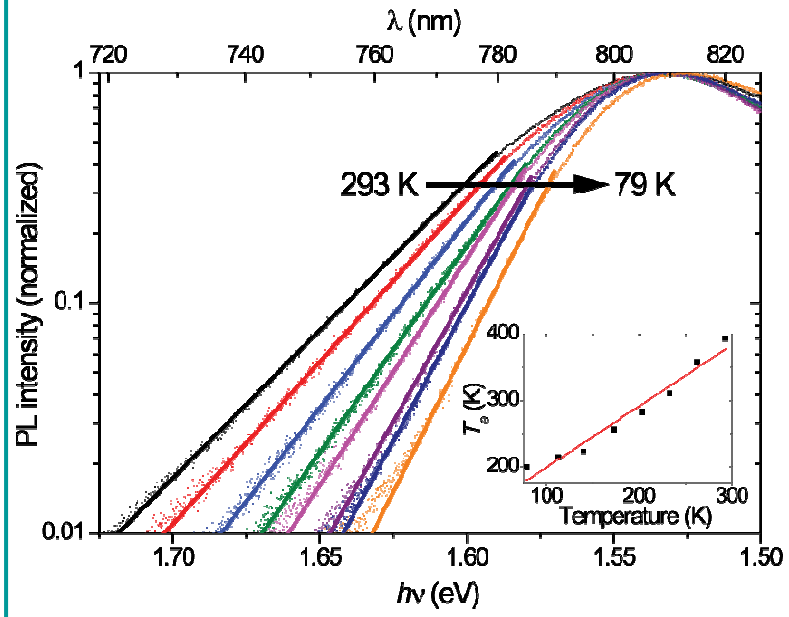




$$\propto e^{-E/k_B T_e}$$

变温光谱线型符合载流子Bolzman发表

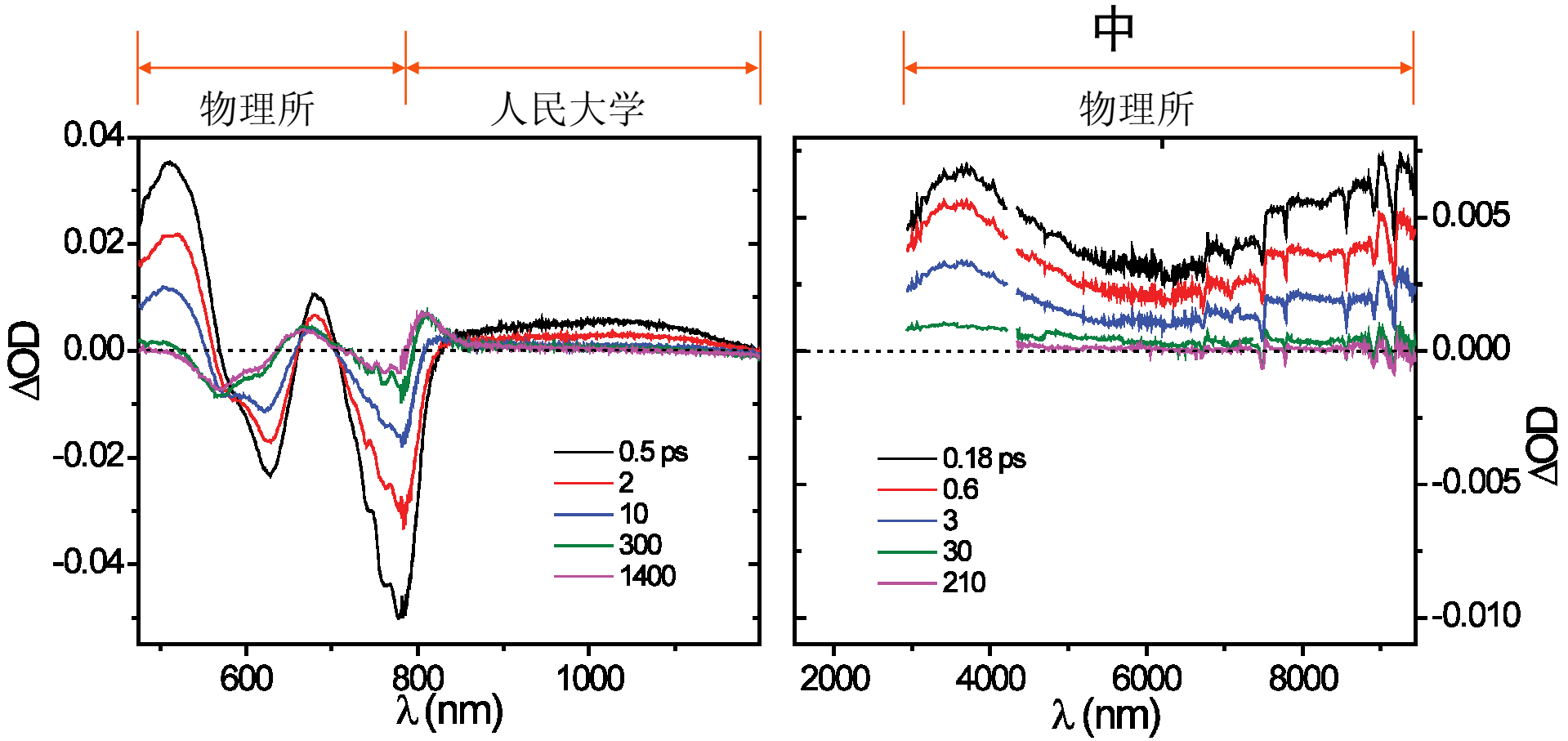
Arnaudov, B., et al.. *Physical Review B*, *64*(4), 045213.

时间　　光

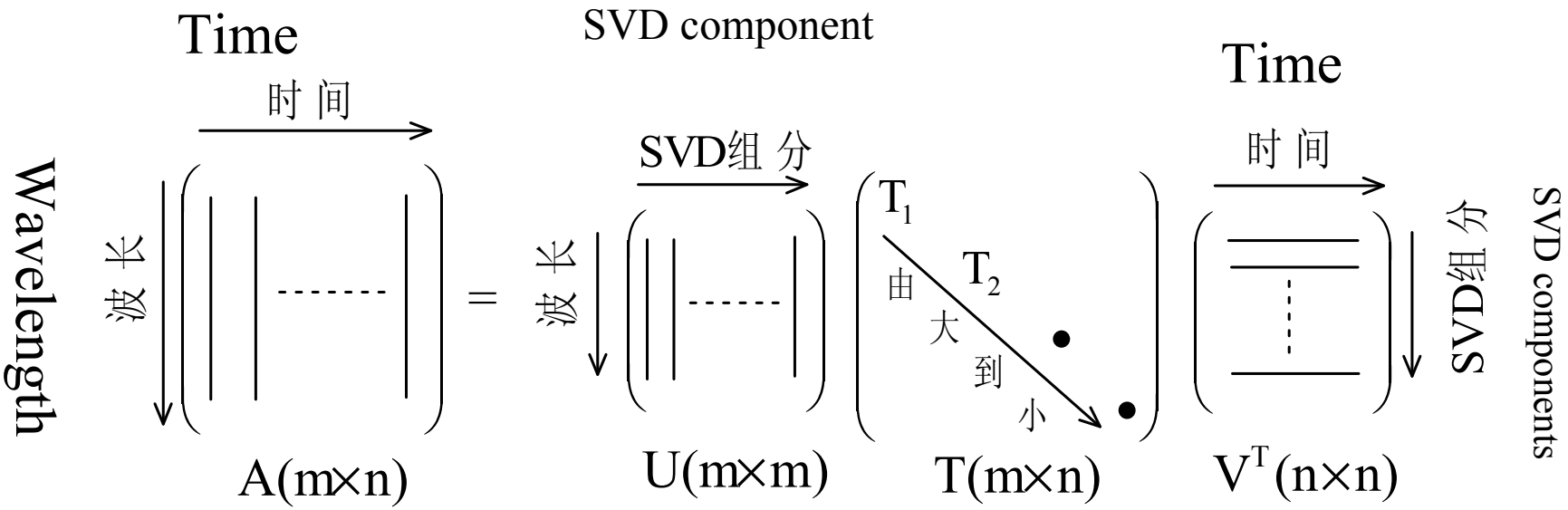
ZnPc

ZnPc

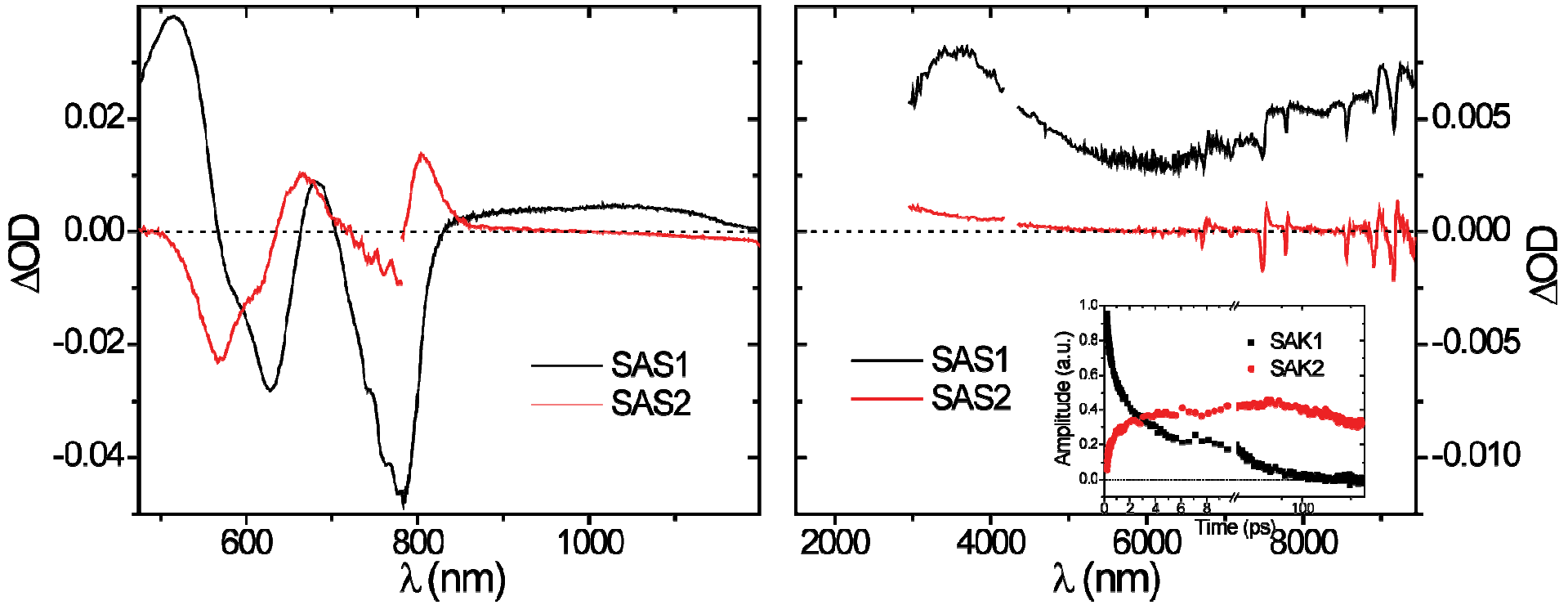
飞秒时间　　中


物理所
人民大学
中
物理所
0.04
0.02
0.00
-0.02
-0.04
ΔOD
0.5 ps
2
10
300
1400
600
800
1000
λ (nm)
0.005
0.000
-0.005
-0.010
ΔOD
0.18 ps
0.6
3
30
210
2000
4000
6000
8000
λ (nm)

Singular Value Decomposition (SVD)-global fitting analysis



光



可见+近红外

中红外

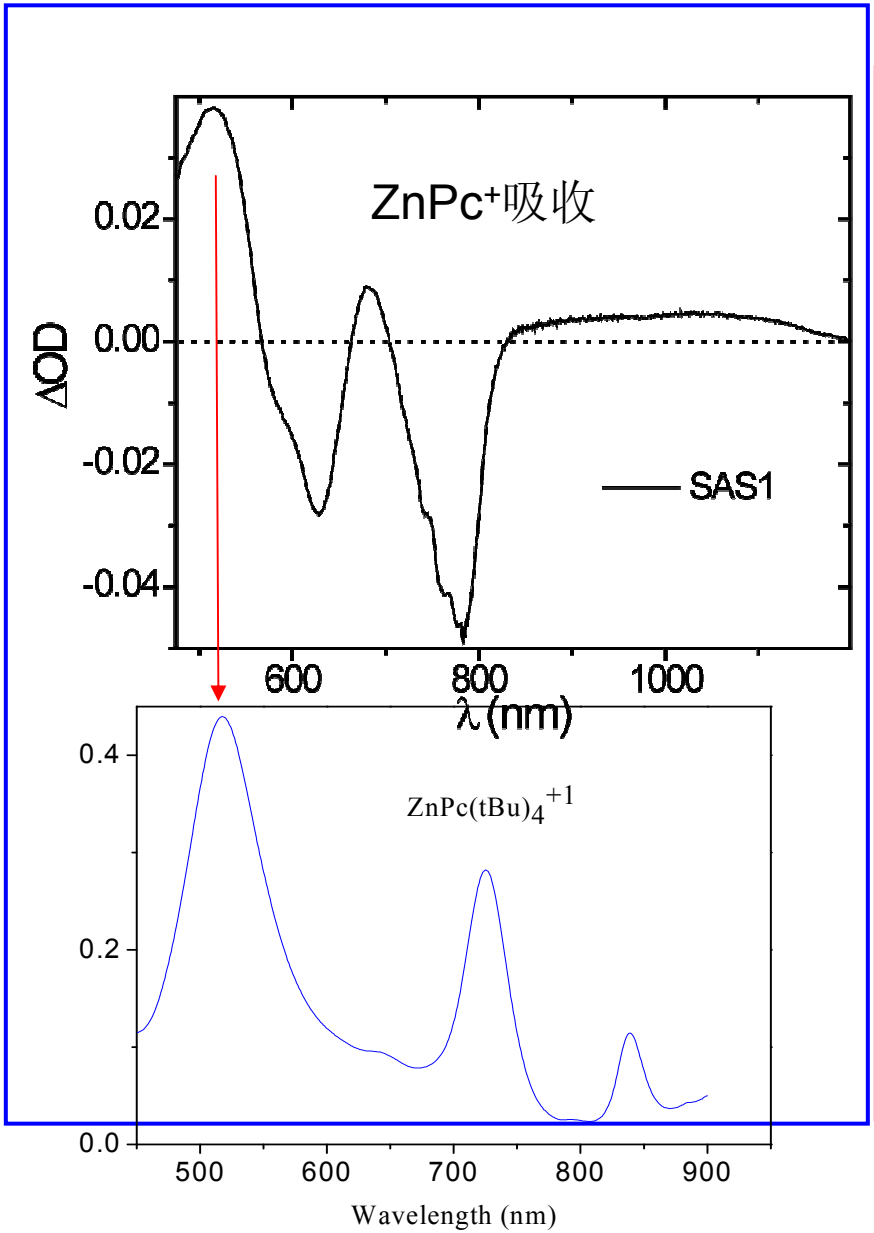
A+B

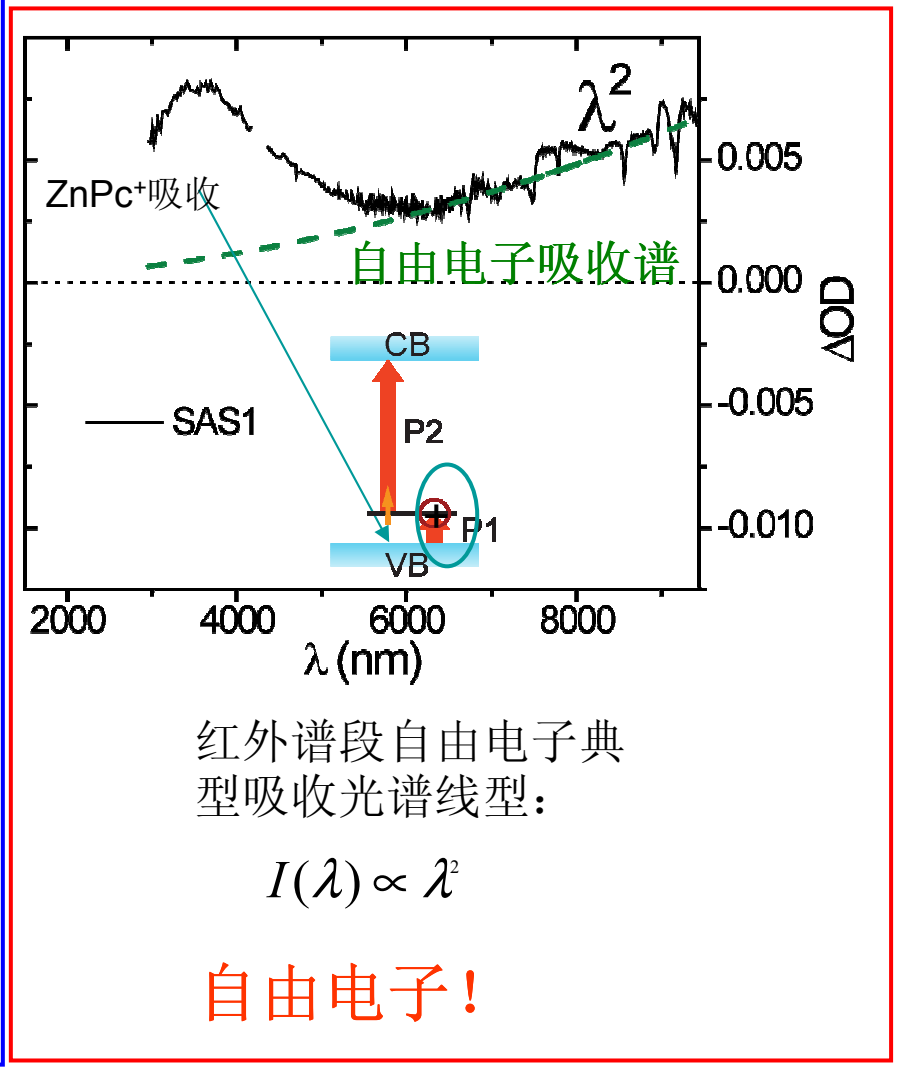
SVD

A

B

光生空穴和自由电子光谱指认（快分量）



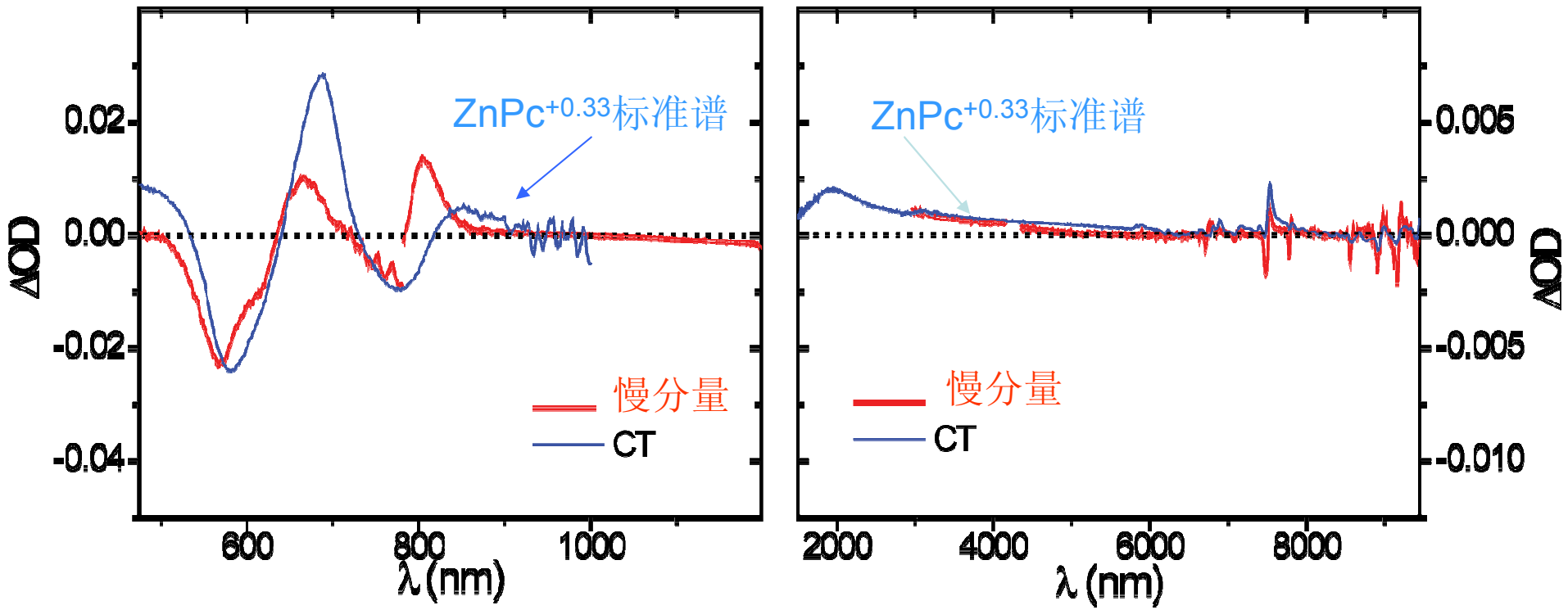


红外谱段自由电子典型吸收光谱线型：

$$I(\lambda) \propto \lambda^2$$

自由电子！

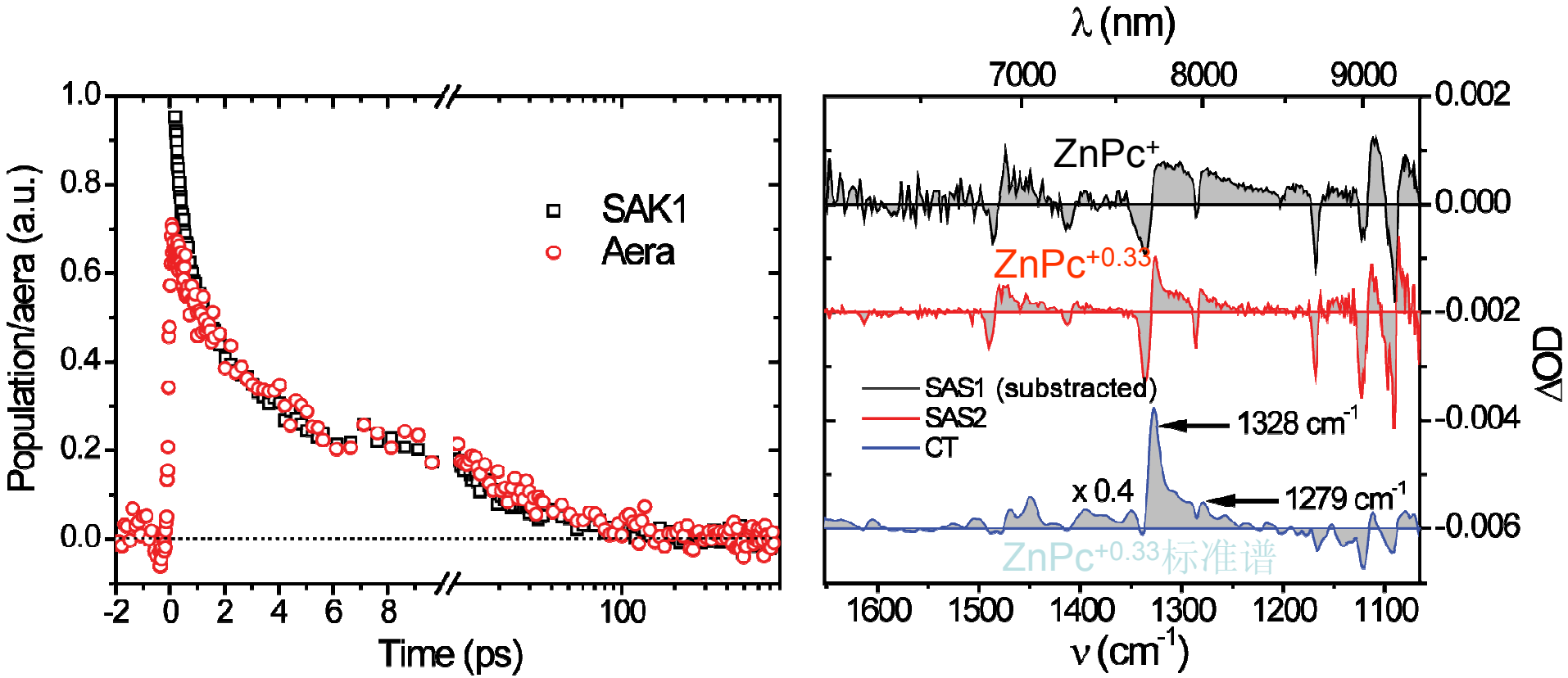
$ZnPc^{+0.33}$光



Vinogradskii, A. (1990). Degree of solid-phase oxidation of nickel and cobalt phthalocyanines by halogens. *Theoretical and Experimental Chemistry*, *25*(5), 488–493.

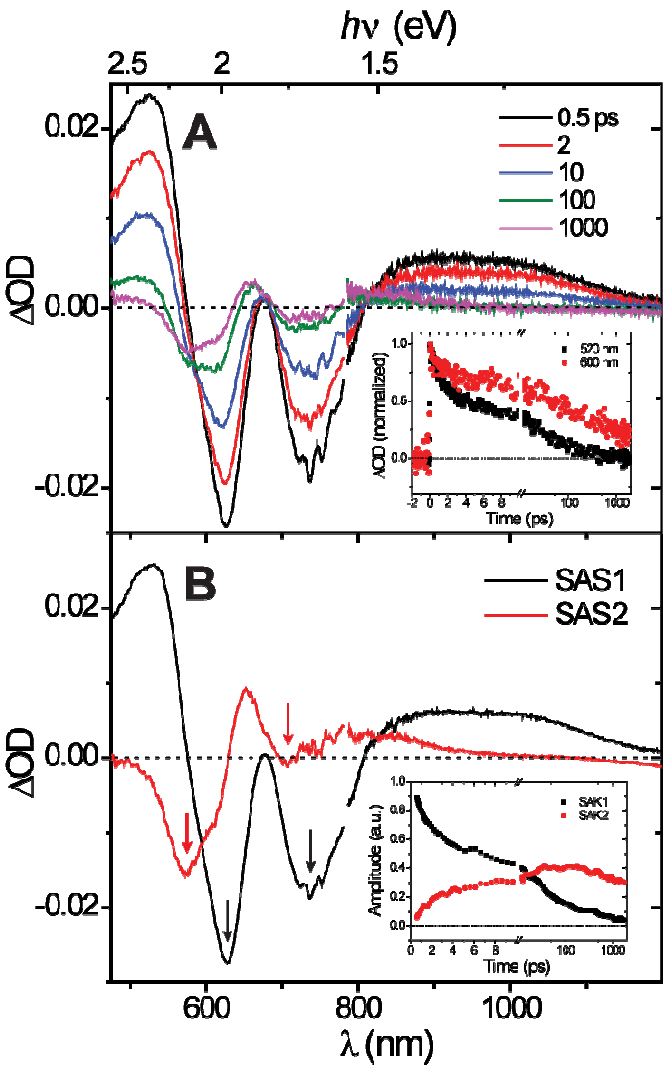
$ZnPc^{+0.33}$ CT exciton

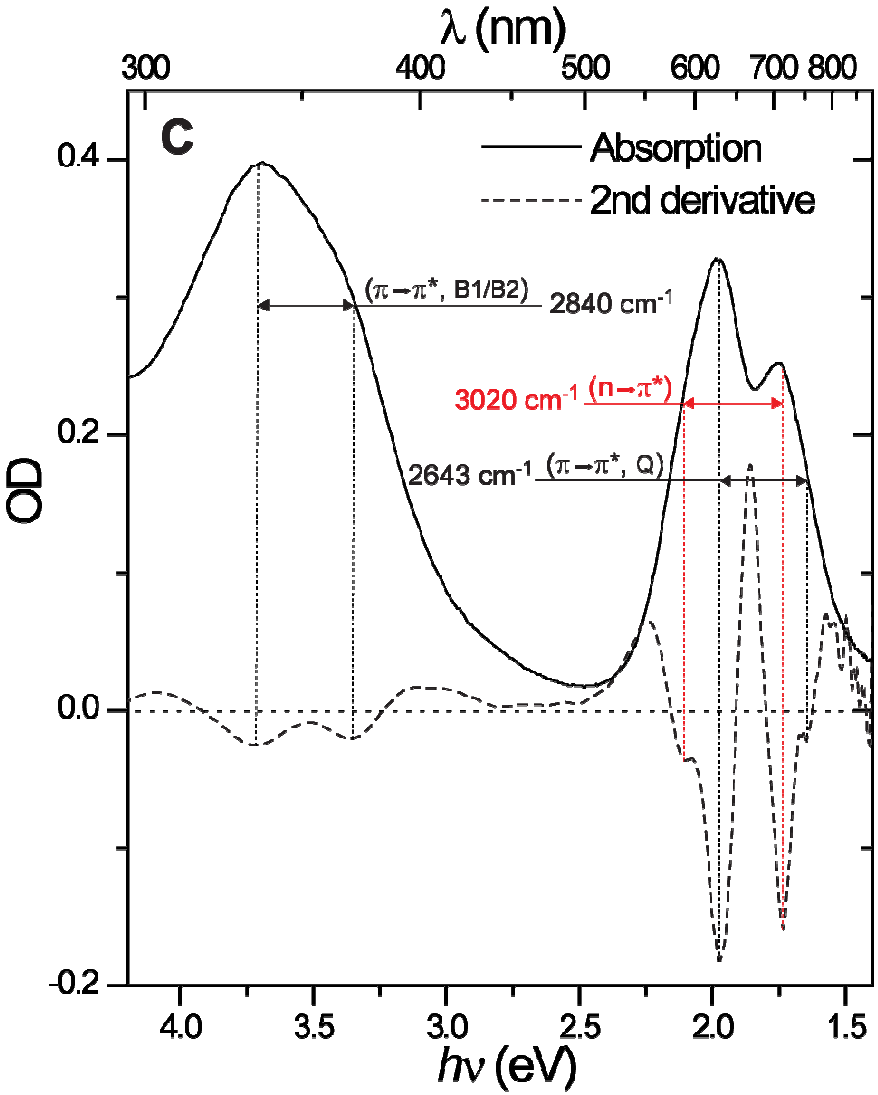
离域的$ZnPc^+$ 时间 光

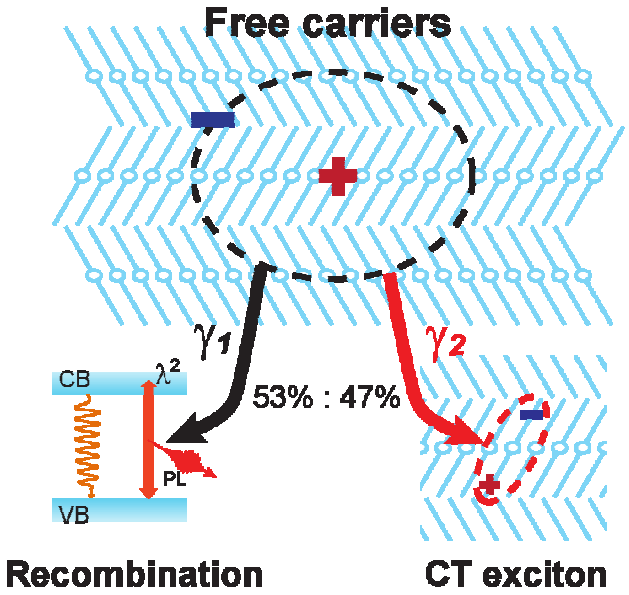


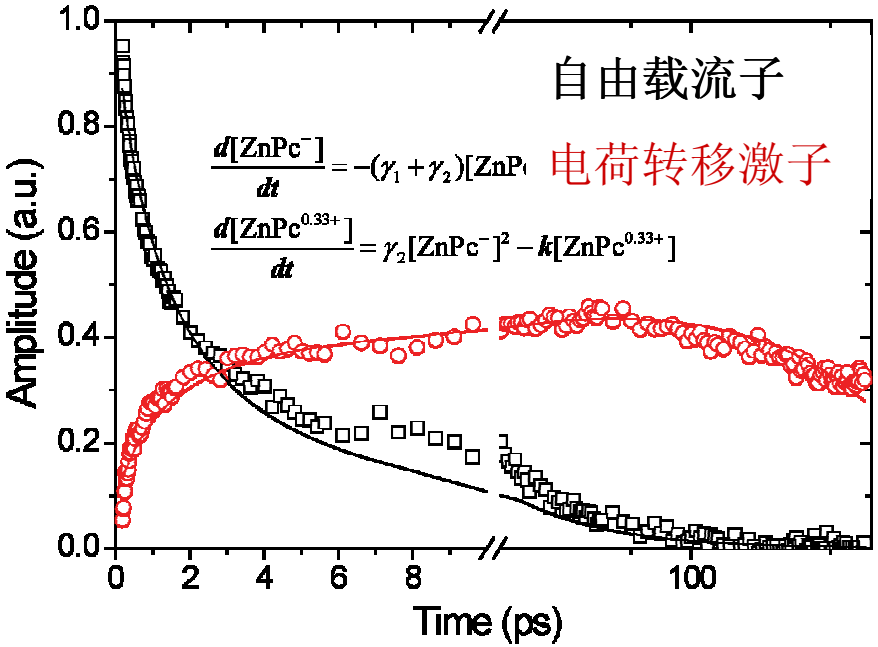
振动峰面积弛豫动力学和自由电子复合动力一致，说明来自于离域的$ZnPc^+$

合飞秒时间　　光　　Davydov splitting






Free carriers
γ1
γ2
CB
λ2
PL
VB
53% : 47%
Recombination
CT exciton


自由载流子
电荷转移激子
Amplitude (a.u.)
Time (ps)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
100

实 中

光

总结

1. 在10皮秒时间尺度观测到了自由电子和离域的空穴
2. 空穴的离域尺度大于11个分子
3. 自由载流子寿命约6.8皮秒
4. 自由载流子复合后形成部分电荷转移的电荷转移态激子 $ZnPc^{+0.33}$，寿命大于1纳秒
5. $ZnPc^{+0.33}$的激子束缚能为0.28eV

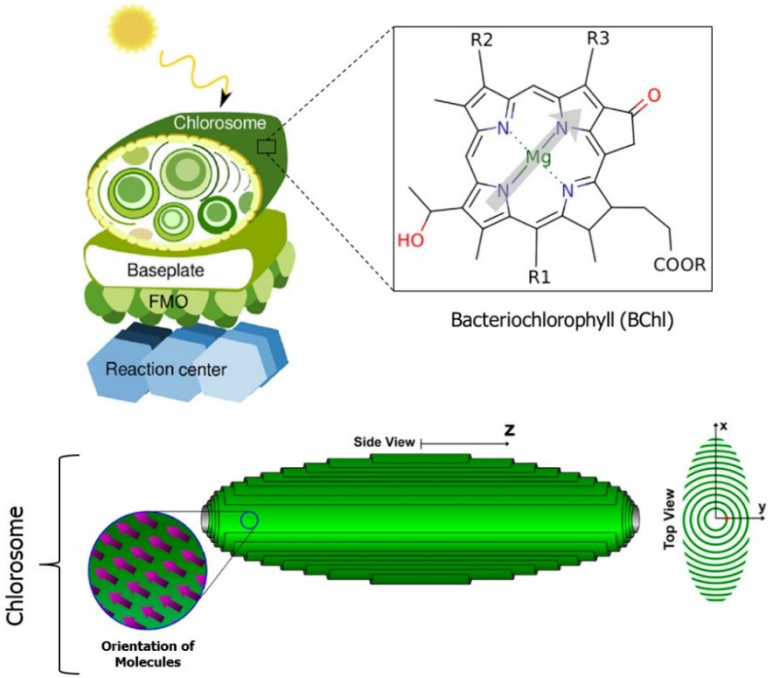
展望

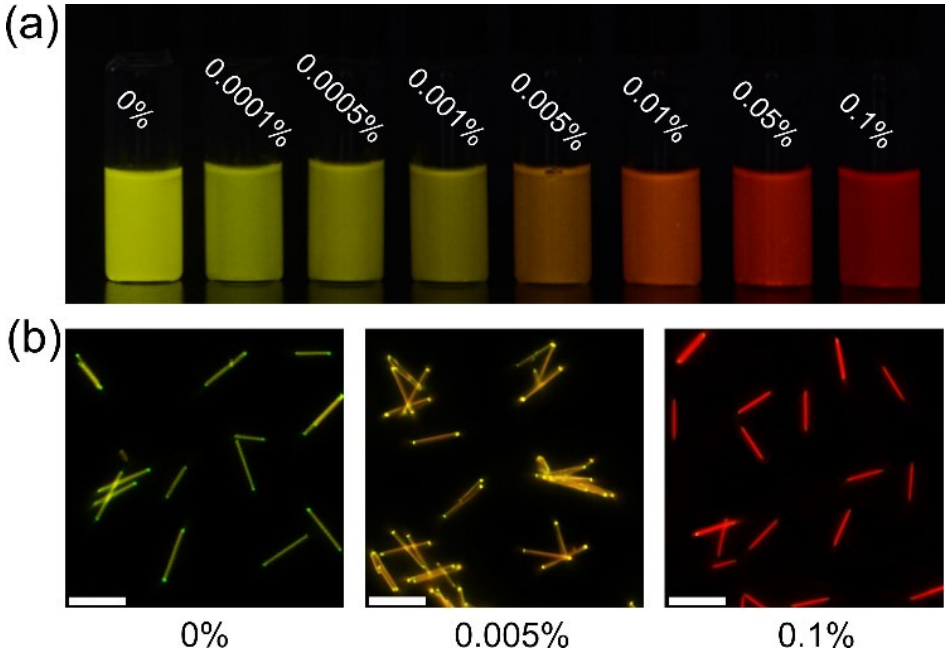
飞秒时间分辨二维可见电子态光谱仪研究离域相干态传能

光合　　光

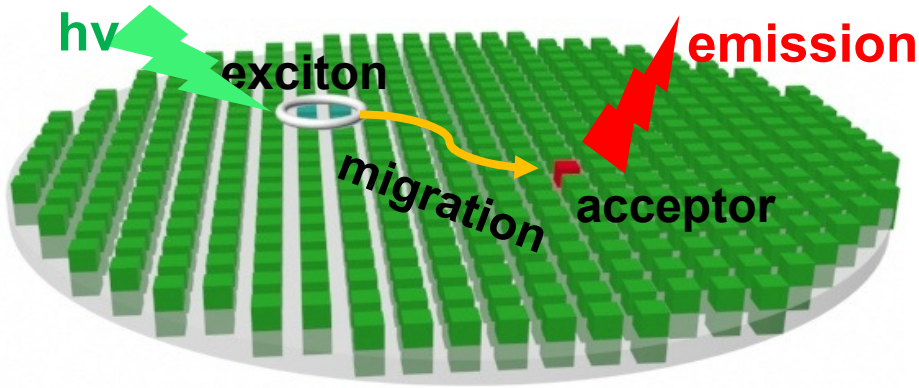
Angew. Chem. Int. Ed. 2016, 55, 2759 –2763

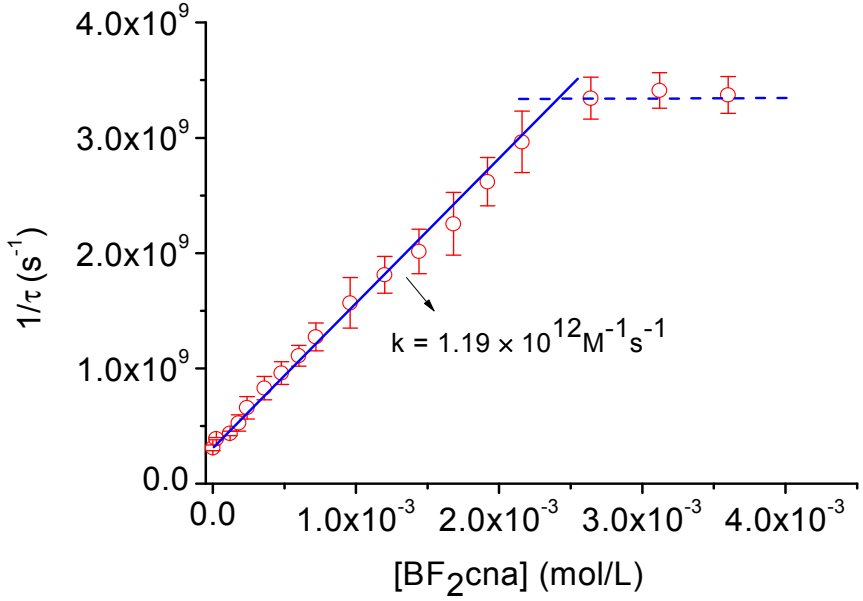
北京师范大学杨清正教授组合作

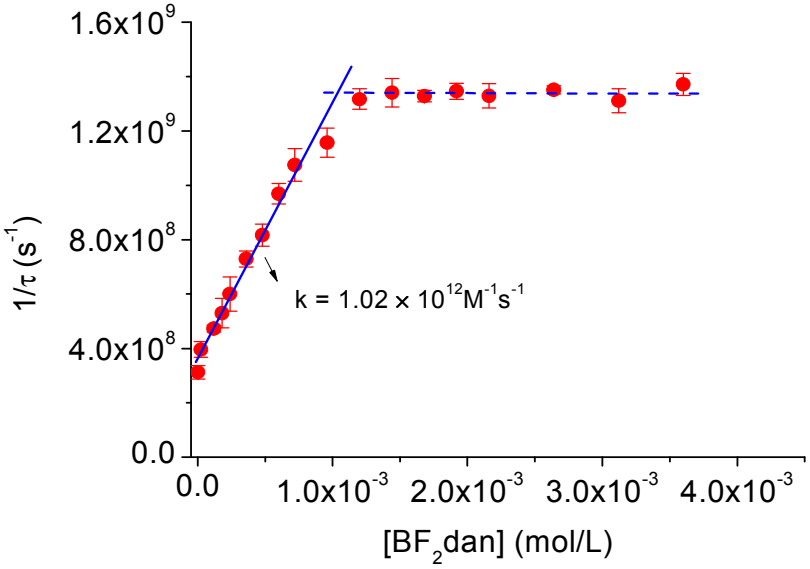




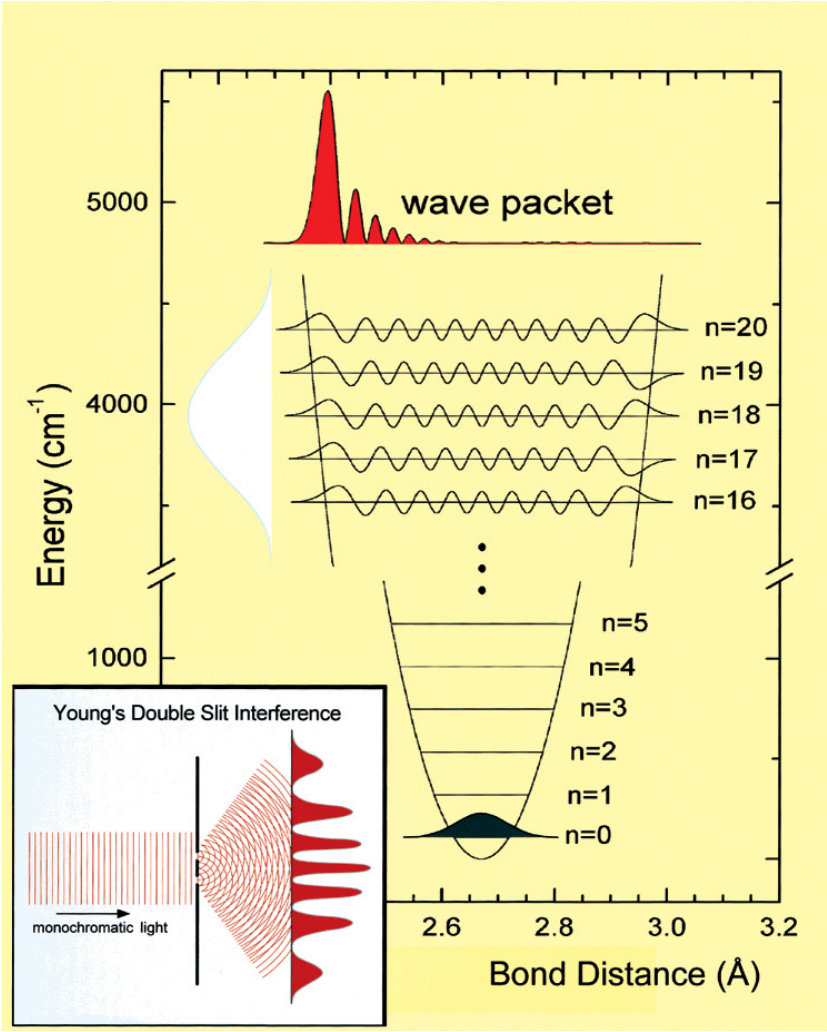
给受体有机纳米共晶中能量传递的相干激子态迁移机制及两种不同受体分子对给体荧光的浓度淬灭关系



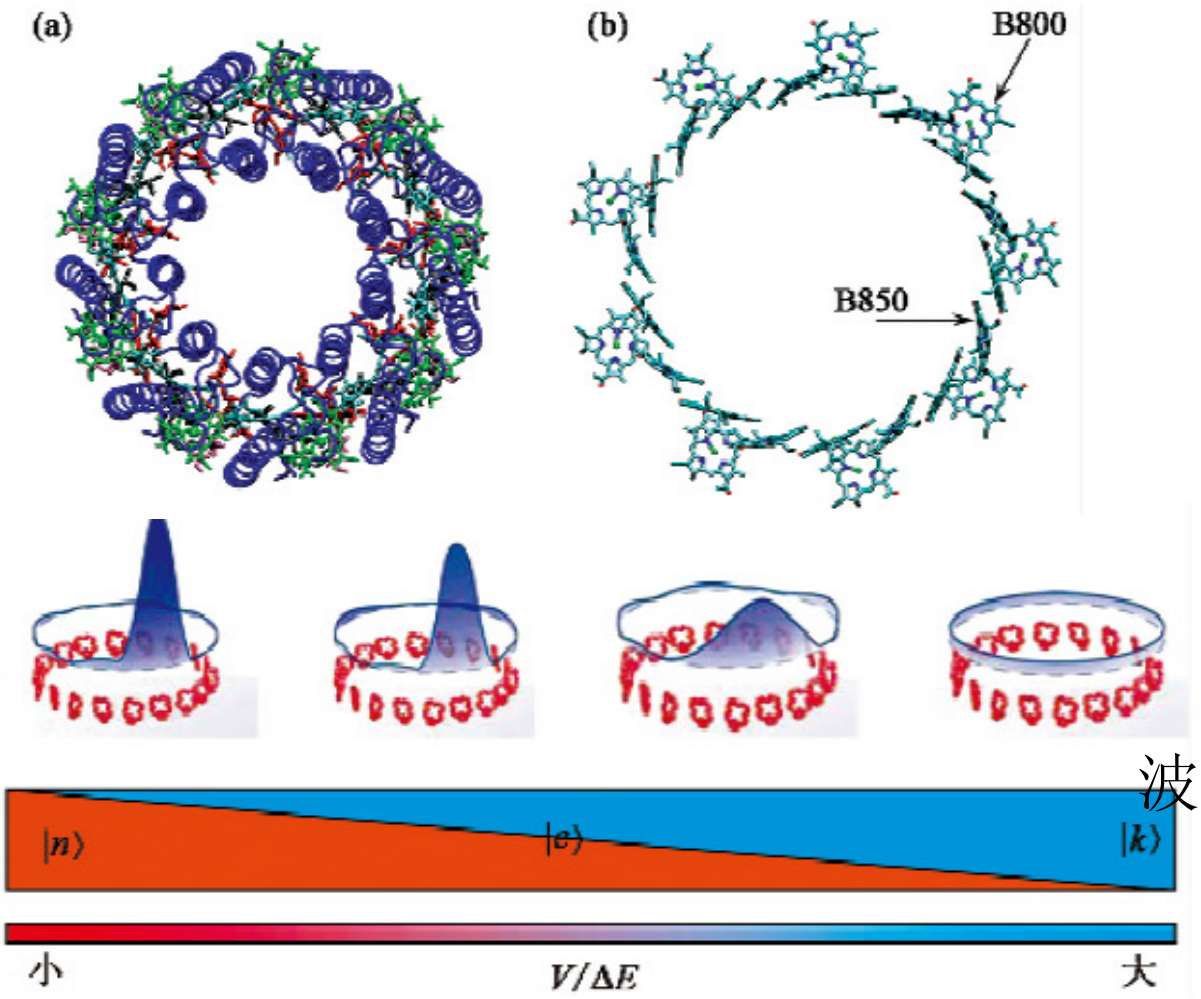




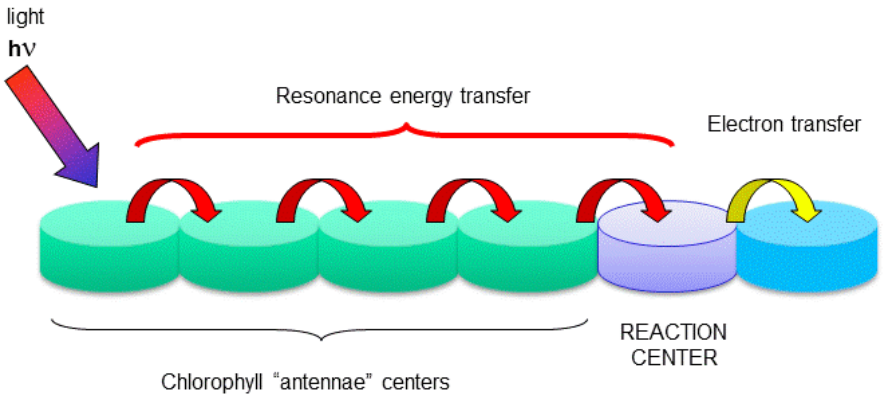
何谓相干态？

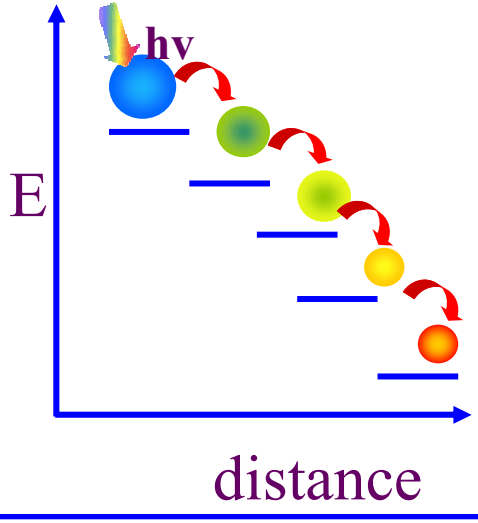

wave packet
5000
4000
1000
Energy (cm-1)
n=20
n=19
n=18
n=17
n=16
n=5
n=4
n=3
n=2
n=1
n=0
2.6
2.8
3.0
3.2
Bond Distance (Å)
Young's Double Slit Interference
monochromatic light

光合细菌外周天线LH2的相干态

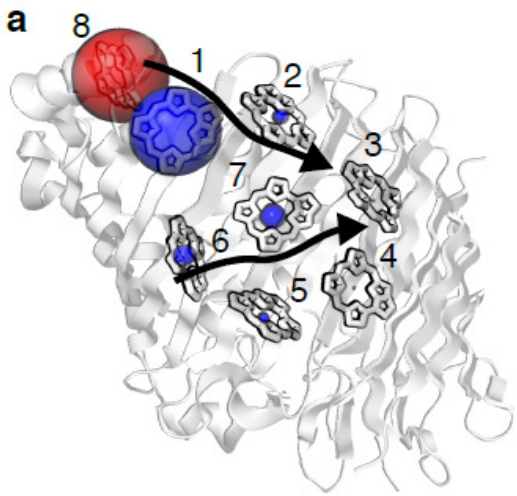


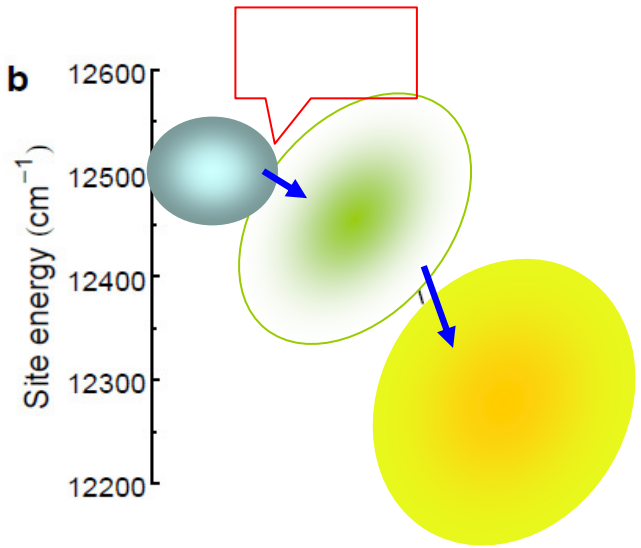
波的性质


light
hν
Resonance energy transfer
Electron transfer
REACTION
CENTER
Chlorophyll "antennae" centers


hν
E
distance

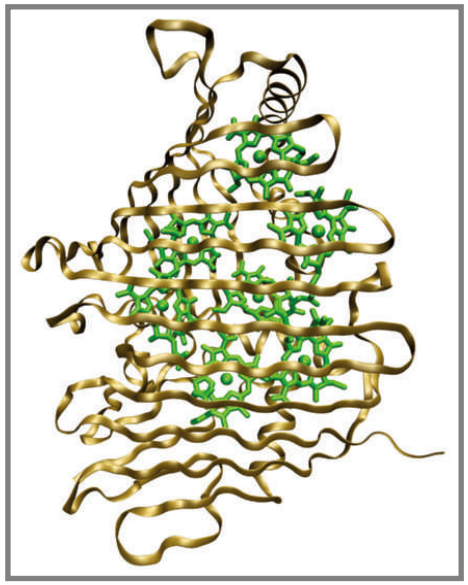
光合
FMO


a
8
1
2
3
7
6
4
5

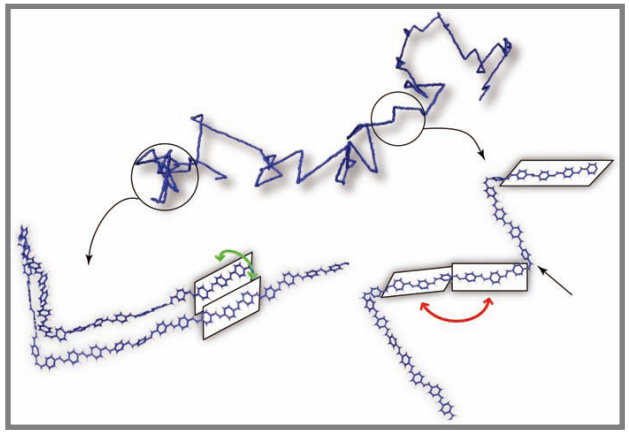

b
12600
12500
12400
12300
12200
Site energy (cm^{-1})

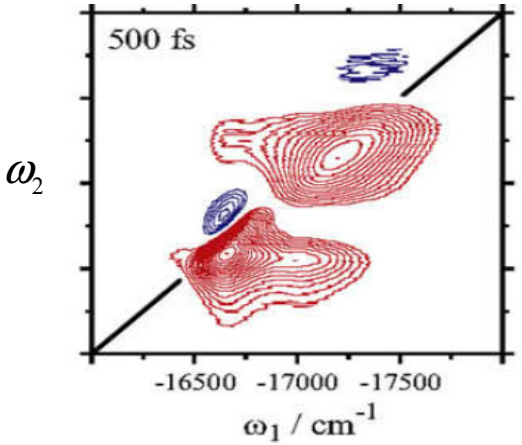
光合　　室　　实验验

Graham R. Fleming, Nature 2007
(FMO)　　77K　　660飞秒

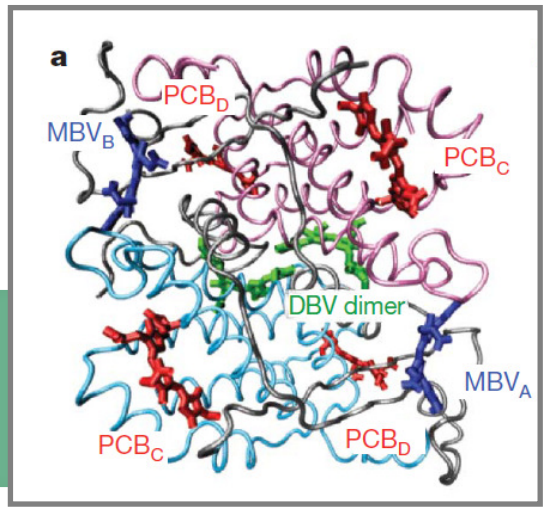


Gregory D. Scholes , Science　2009
(MEH-PPV)　　250飞秒



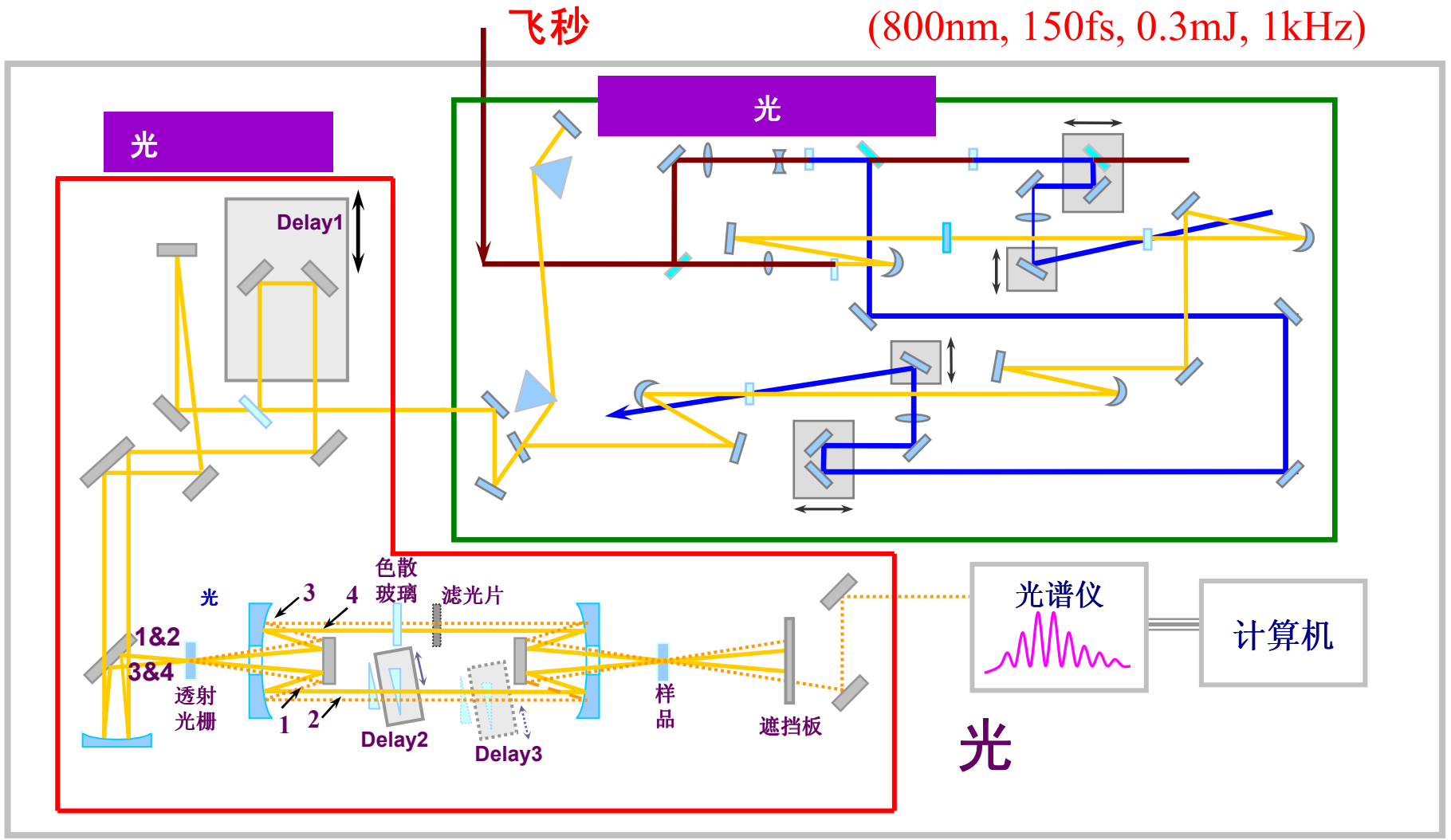


Gregory D. Scholes, Nature　2010
(PC645)　　660飞秒



实验　　光

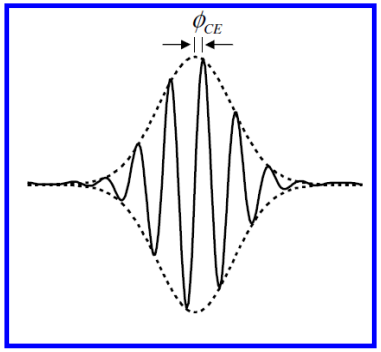
光

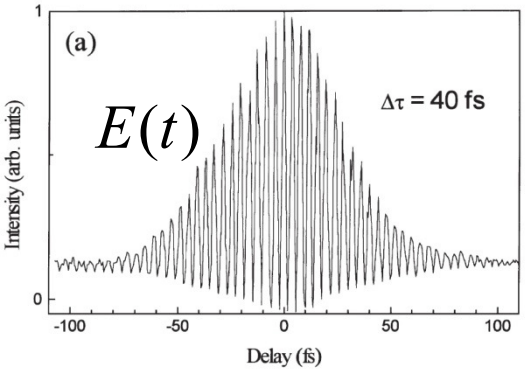

飞秒
(800nm, 150fs, 0.3mJ, 1kHz)
光
光
Delay1
光
色散
玻璃
滤光片
3
4
1&2
3&4
透射
光栅
1
2
Delay2
Delay3
样
品
遮挡板
光谱仪
计算机
光

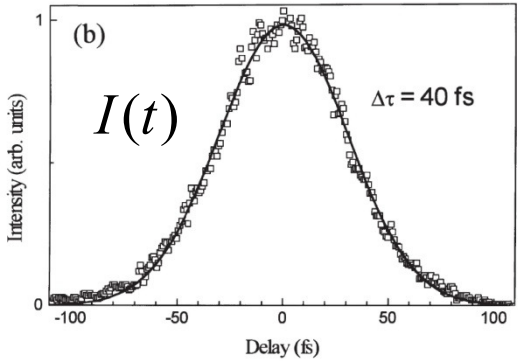
时　　光　　$I(\omega)$　　$E(\omega)$

$$I=E^2$$

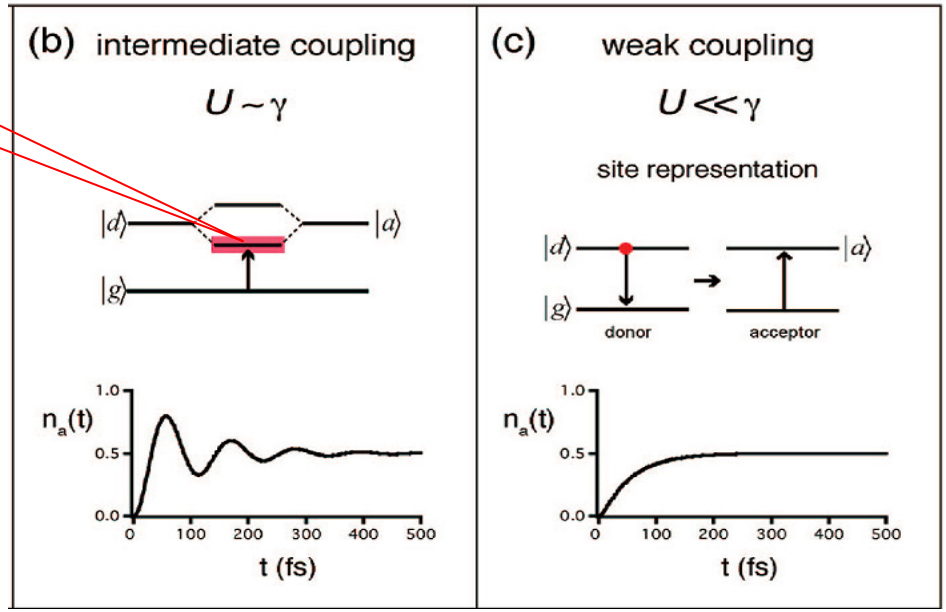
$$I(\omega)=FFT(I(t)),\quad E(\omega)=FFT(E(t))$$



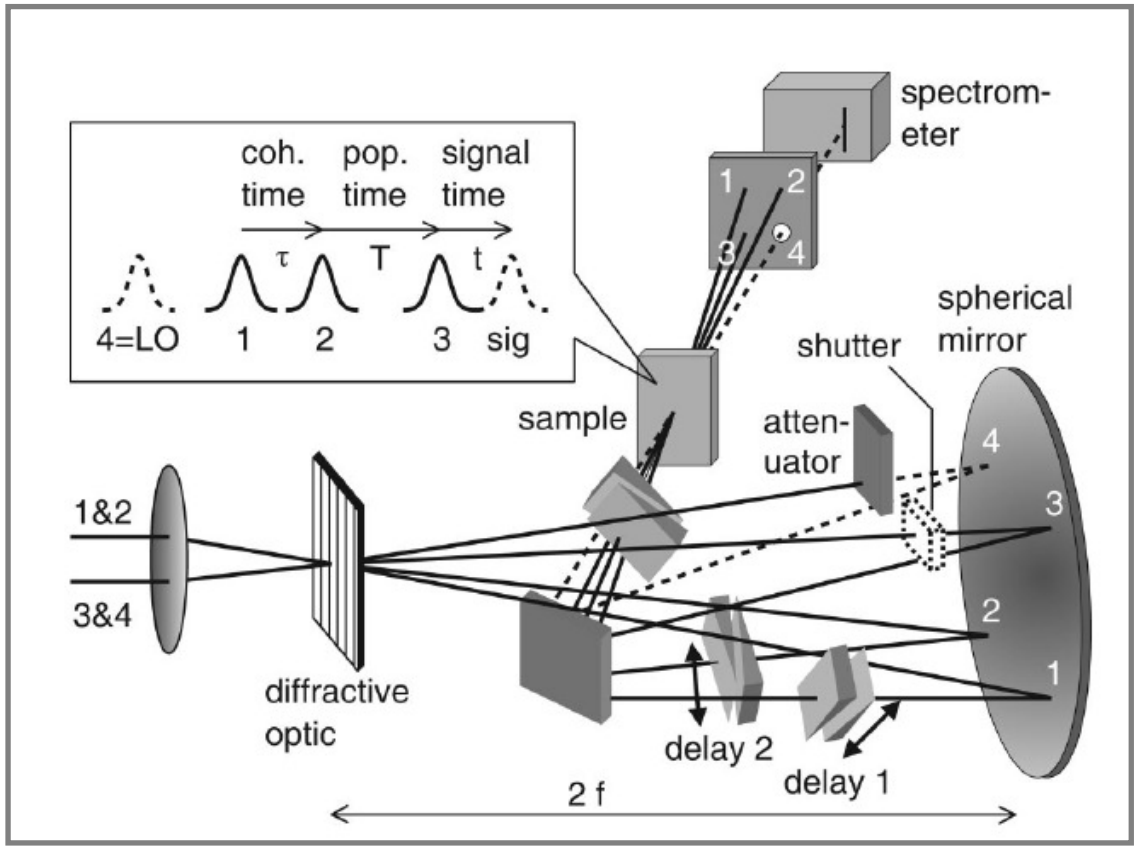




ΔE



发展飞秒时间分辨二维可见光谱研究相干态传能



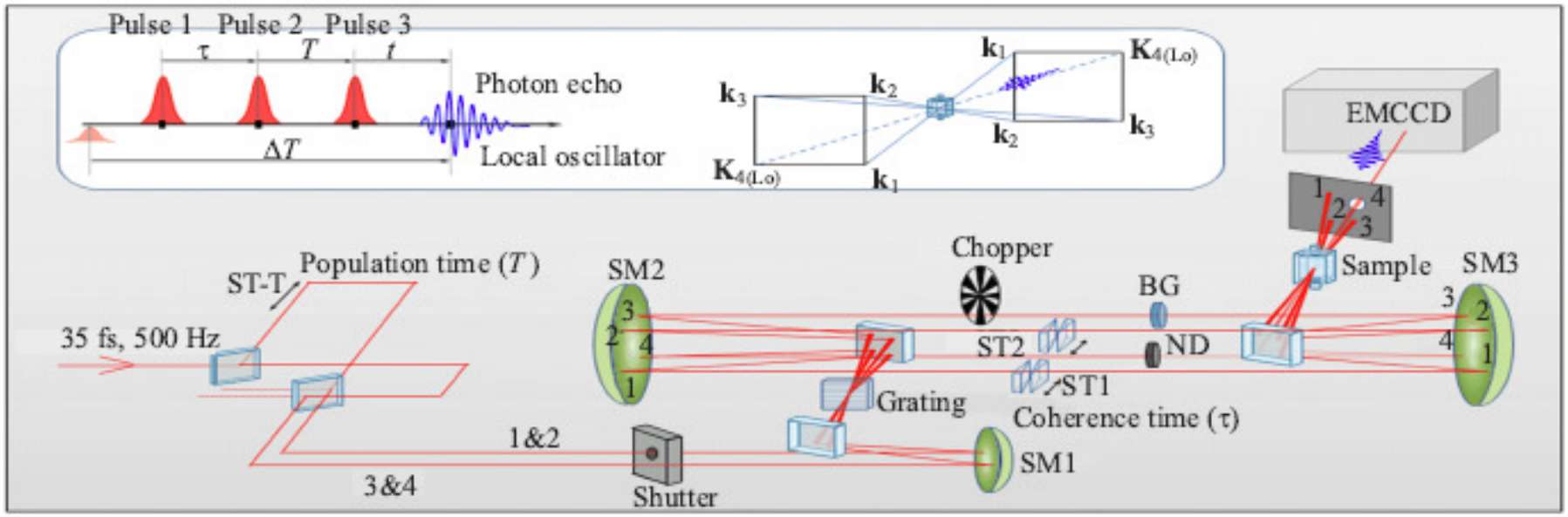
50l/mm 透射式光栅

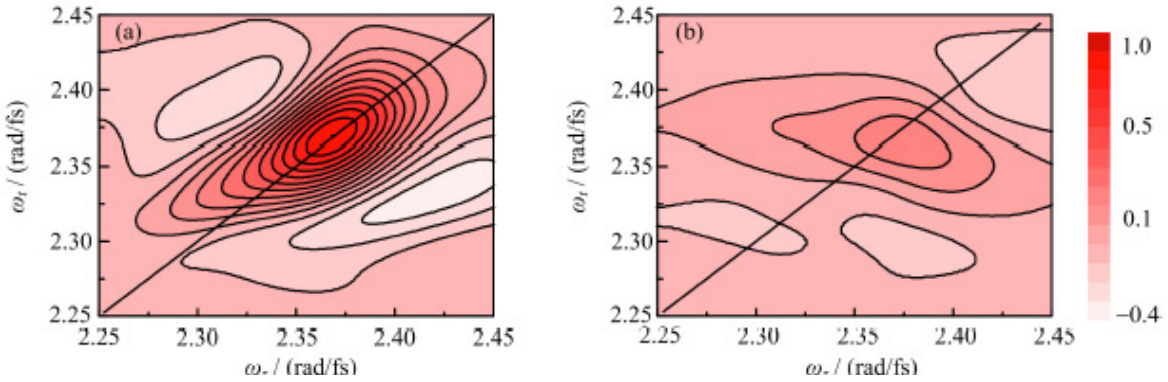
石英光楔

2 inch直径凹面银镜

精密电控平移台

光





Phase stability: 1/90λ

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