2107年7月2日
台湾　国立交通大学理学院　SC102 at SBIII

増原塾　講義２

「光化学、分子光科学、光捕捉化学」

増原　宏

masuhara@masuhara.jp, http://www.masuhara.jp/

臺灣　国立交通大學　理学院応用化学系
講座教授

増原の略歴

1966年　東北大学理学部化学科卒業(小泉研)
1968年　東北大学大学院理学研究科化学専攻修士課程修了(小泉研)
1971年　大阪大学大学院基礎工学研究科化学系化学博士課程修了(又賀研)

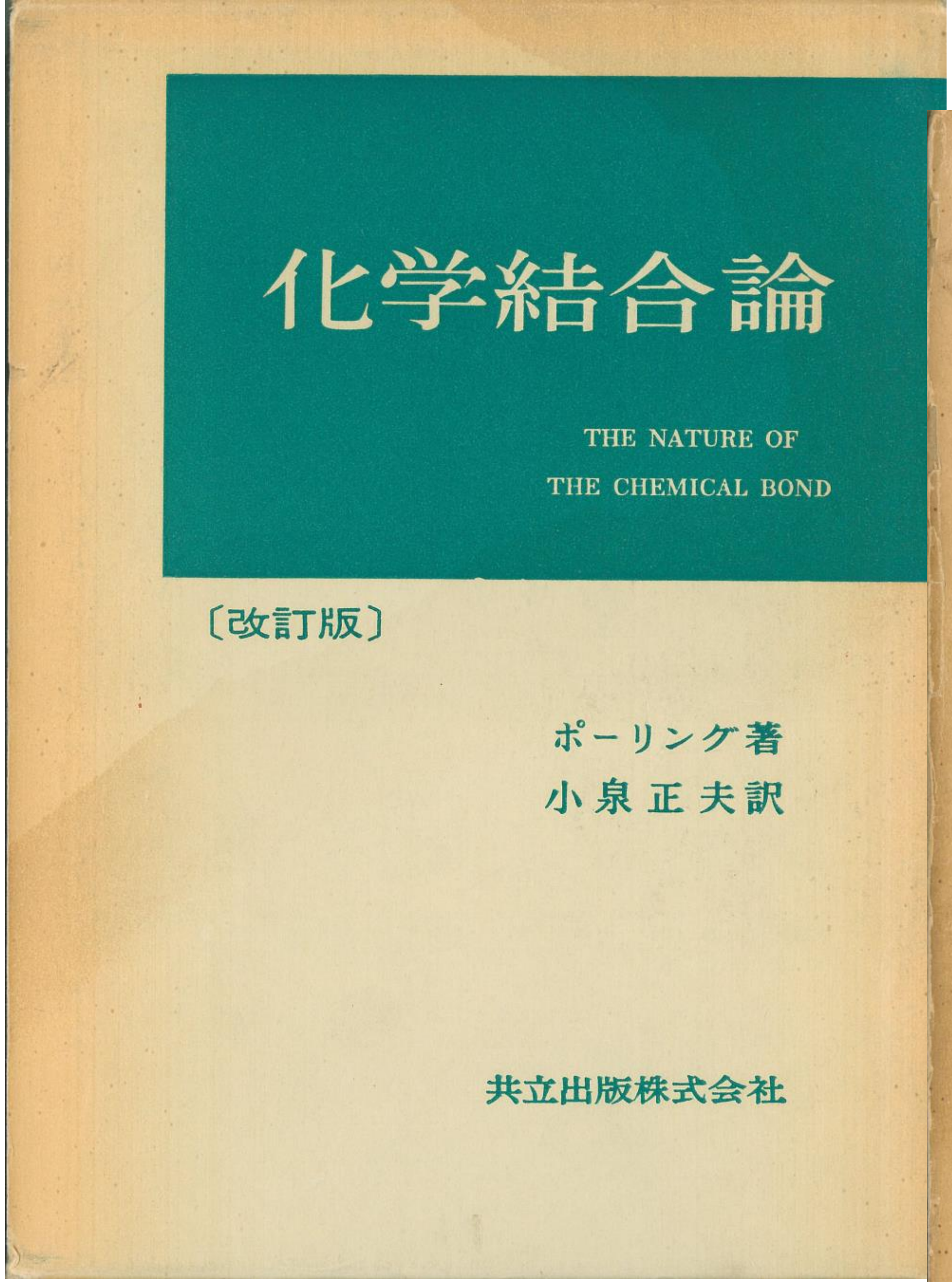
1972年　大阪大学基礎工学部合成化学科助手(又賀研)
1984年　京都工芸繊維大学繊維学部高分子学科教授
1991年　大阪大学工学部応用物理学科教授
2004年　大阪大学生命機能研究科兼任教授

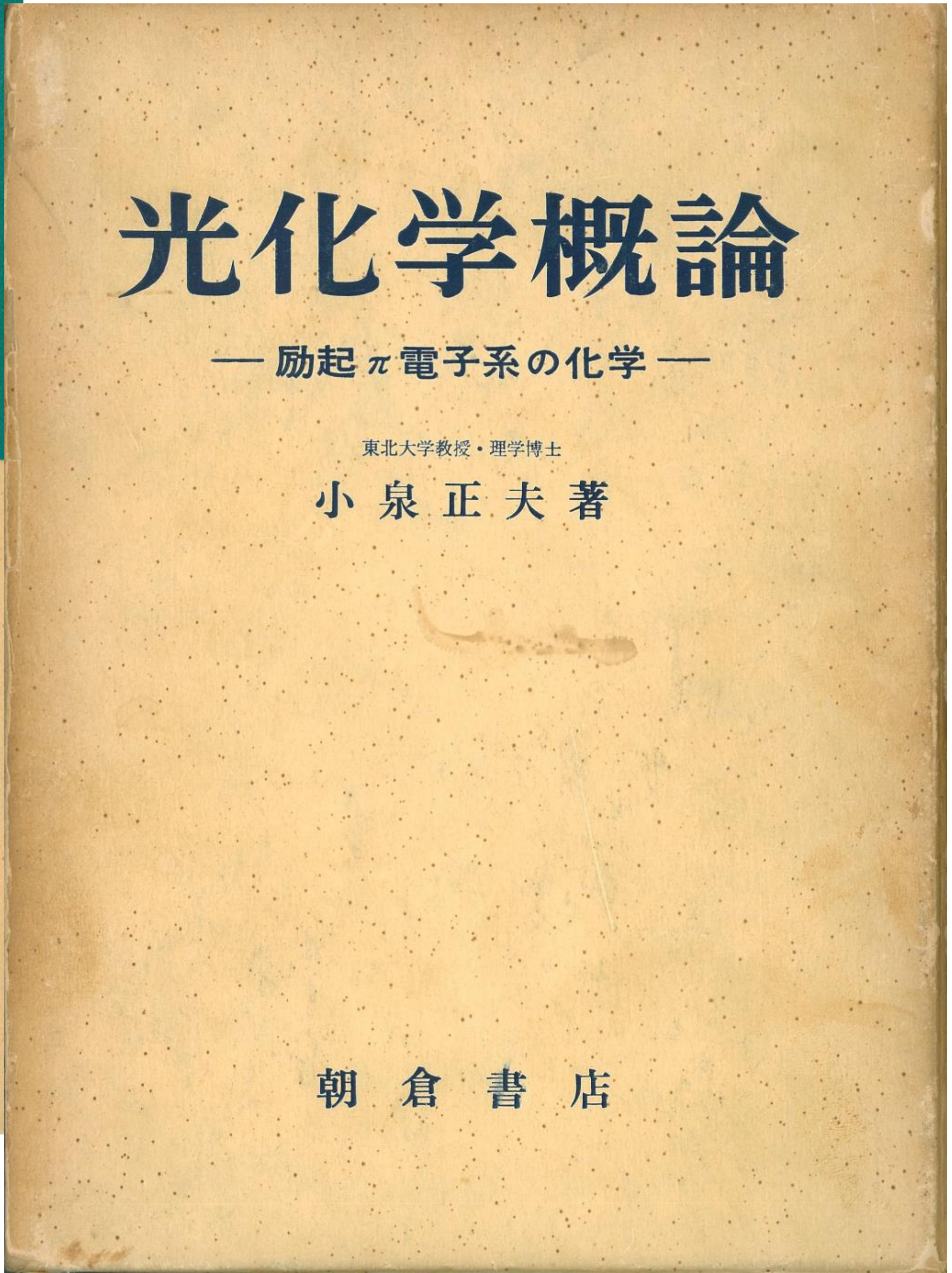
2007年　財団法人濱野生命科学研究財団主席研究員
2008年　奈良先端科学技術大学院大学物質創成科学研究科特任教授
2008年　国立交通大学理学院應用化學系及び分子科学研究所講座教授

小泉正夫先生

１９７３年東北大理化学ご退官

１９７４年ご逝去





Hybrid orbital　混成軌道と訳された

有機化学

無機分析化学

物理化学？？（1967年ごろ、修士時代）

構造、反応、物性、（機能）に関する研究

構造研究は絶対的な真理に繋がる研究

反応もそうであるけれど・・・？

反応の研究室は具体的な対象をもっている、豊な分野

阪大広田鋼蔵、同位体

東北大小泉正夫、光反応

東大田丸謙二、触媒

阪大叉賀昇、電子移動反応

・・・・・・

小泉研究室（1966-1968）

資源のない敗戦国の日本が生きていくために太陽光を使う＝＝＞光化学（昔）

化学反応の中間体を直接捕らえることにより化学反応を理解する＝＝＞光化学（1966年）

　　フラッシュホトリシス、剛性溶媒法

増原（1966－1968）

分子の電子状態から反応を理解したい

又賀研究室（1968－1984）

光化学反応の素過程を明らかにすることが出来る

レーザーを使って光化学の研究を可能にしてくれたら学位をあげる

将来すべての光源はレーザーに置き換わる、新しい現象が可能になる

物理化学とは？？（1970年代）

構造、反応、物性、（機能）に関する

①新しい研究方法論の開発

②新しい化学結合と反応に関する概念の提出

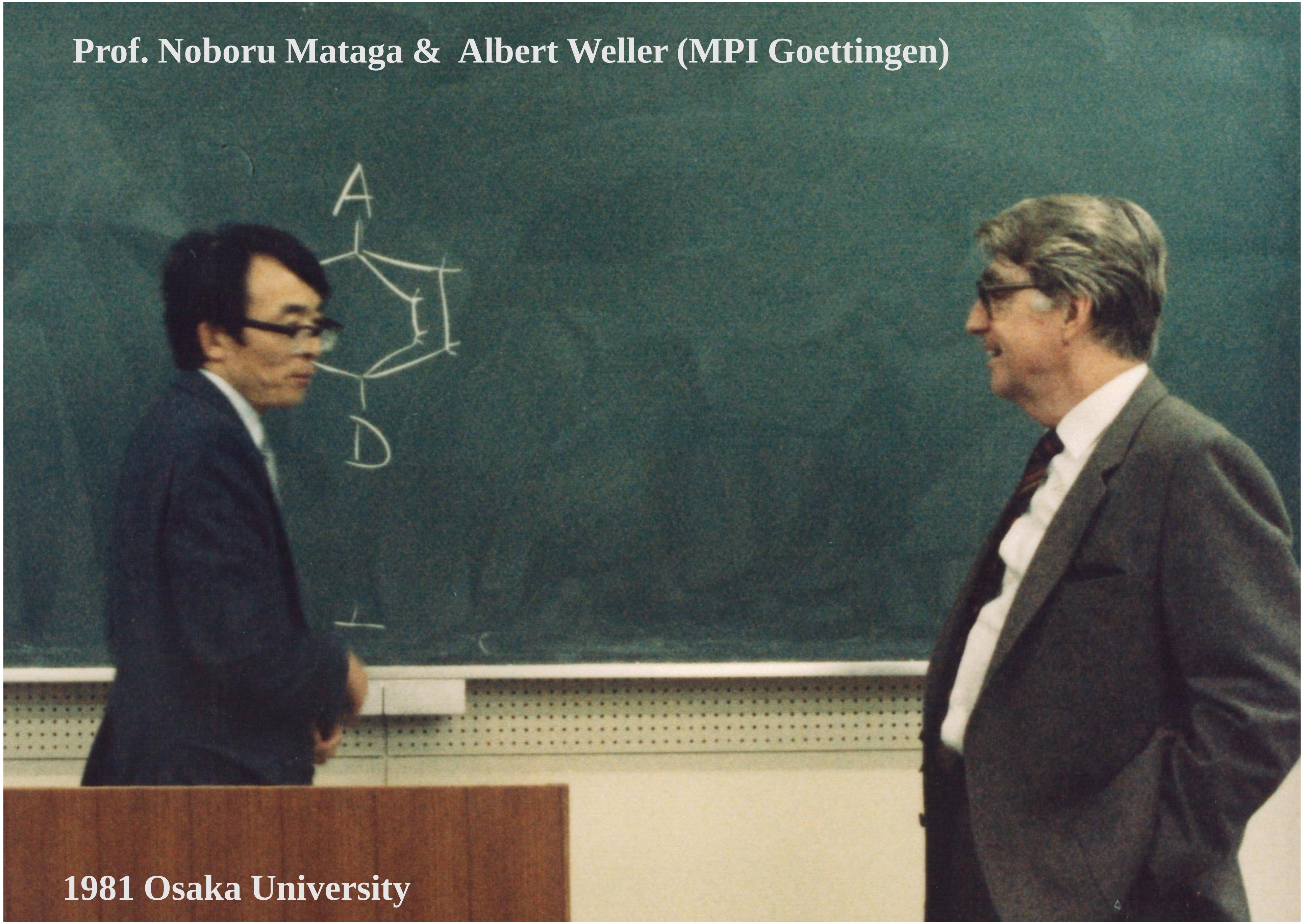
小泉、長倉、田中郁三、坪村、叉賀先生

化学反応の時々刻々の変化を直接見る、動的構造

1960年台～、光、レーザー、ビーム･･･

1970代後半、Pimentel Report,

レーザー、SOR、計算機



Prof. Noboru Mataga & Albert Weller (MPI Goettingen)

1981 Osaka University

Πορτερ Μεδαλ 1996,

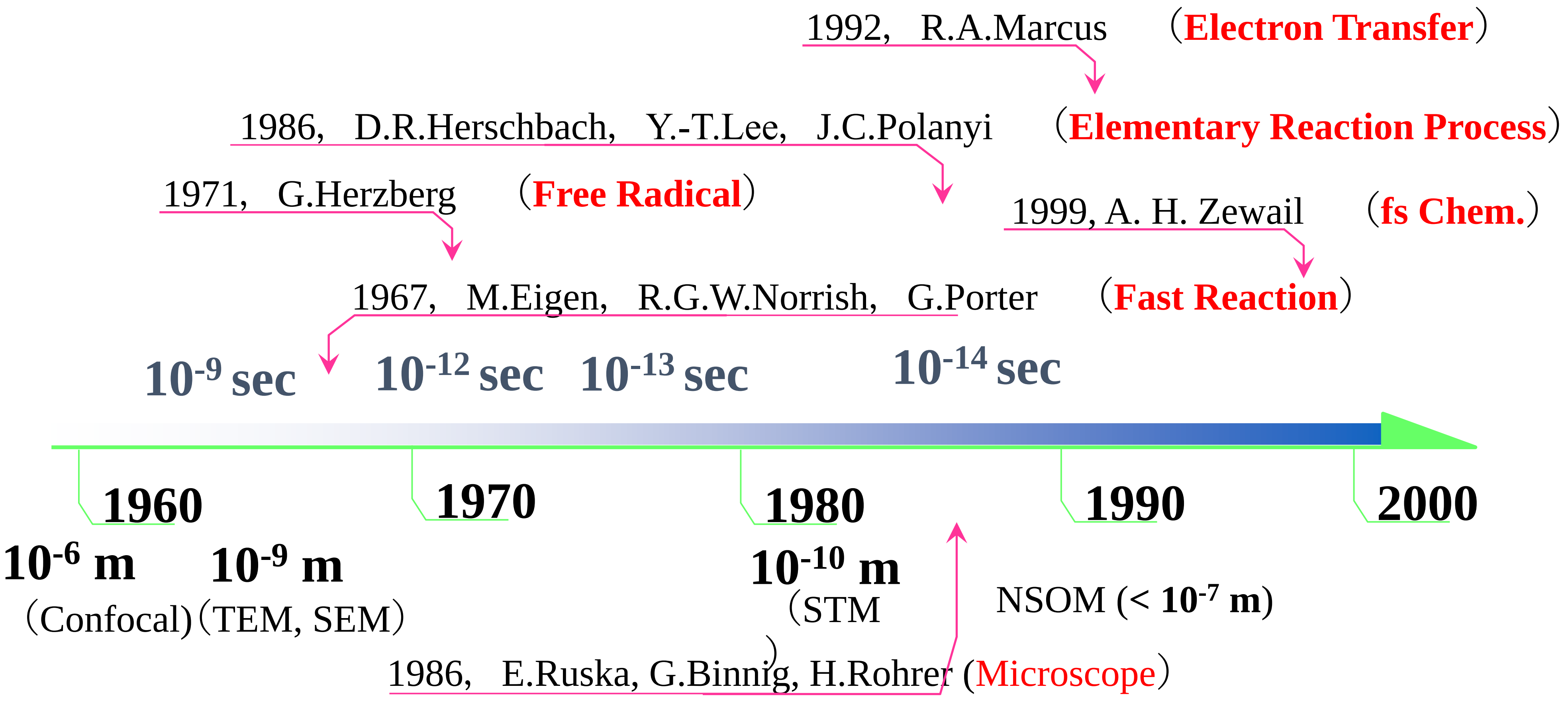
ΙΥΠΑΧ Σψμποσιυμ ον Πηοτοχηεμιστρψ, Ηελσινκι

桃李不言下自成蹊

「成蹊」という名は、司馬遷が「李将軍列伝」(史記)において李廣の人物を述べるため引用した諺「桃李不言下自成蹊」(桃李ものいはざれども、下おのづから蹊を成す)から採ったものです。意味は「桃や李(すもも)は、口に出してものを言うわけではないが、美しい花やおいしい実があるから自然と人がやって来て、そこに小道(蹊)ができる。つまり、桃や李は、人格のある人のたとえで、そういう徳のある人には、その徳を慕って人々が集まってくる。」ということです。

Laser Forming Frontiers in Chemistry

時間分解の化学



時間分解と空間分解の化学

Laser & Microscope have high potential in opening new molecular research !

Stage I; 時間分解分光と光化学過程

Time-resolved Spectroscopy and Photochemical Processes

(1965-1991)

増原の光化学入門：東北大小泉研

Quantum chemical and electronic spectroscopic studies on π-radicals,

Koizumi Laboratory at Tohoku University (1965-1968)

レーザーホトリシスによる電子移動過程の研究：阪大又賀研

Laser Photolysis Studies on Electron-Donor-Acceptor Systems,

Mataga Laboratory at Osaka University (1968-1984)

時間分解反射分光による不均一分子固体反応の測定：京都工芸繊維大学増原研

Time-resolved Reflection Spectroscopy on Films and Powders,

Kyoto Institute of Technology (1984-1991)

Stage II; 時間分解分光と光化学からマイクロ化学へ

From Spectroscopy and Photochemistry to Micro Chemistry

(1988-1994)

単一微粒子・液滴の操作、分光、化学

Spectroscopy, Photochemistry, and Electrochemistry of Single Trapped Nicro Particles and Droplests,

ERATO project (1988-1994)

単一マイクロ結晶の超高速分光

Ultrafast Spectroscopy of Single Micro Crystals,

ERATO project (1988-1994)

走査型電気化学顕微鏡による半導体表面の超微細加工

Surface Fabrication in Solution by Scanning Electro Chemical Microscope,

ERATO Project (1988-1994)

Stage III; マイクロ化学からレーザーナノ化学へ
From Micro Chemistry to Laser Nano Chemistry
(1991-2007)

ナノ分光とナノ光化学

Nano Spectroscopy and Nano Photochemistry,

Osaka University (1998-2007)

ナノトラッピングと光圧化学

Nano Manipulation and Chemistry of Photon Pressure,

ERATO project and Osaka University (1991-2007)

ナノアブレーションのダイナミクスとメカニズム

Nano Ablation Dynamics and Mechanism,

Kyoto Institute of Technology and Osaka University (1991-2005)

Stage IV; 高輝度レーザー光によるバイオおよび分子系の操作
Manipulation of Bio/Molecular Systems by Intense Laser Beams
(2003-present)

レーザー捕捉結晶化

Laser Trapping Crystallization,

Hamano Foundation (2007), NAIST (2008-2011), and NCTU (2008-)

レーザー制御結晶成長

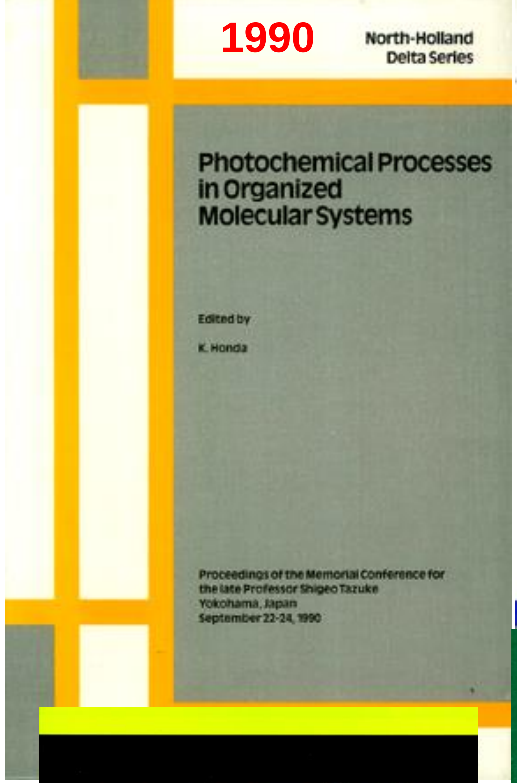
Laser-Controlled Crystal Growth,

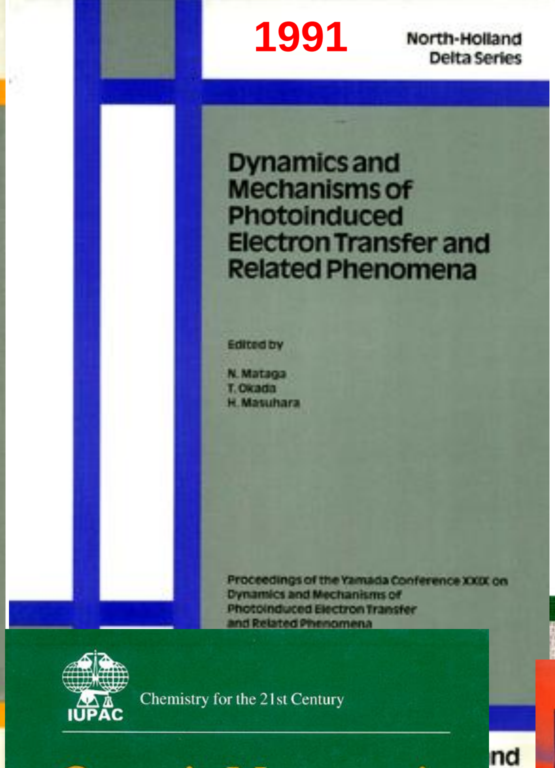
Osaka University (2006-2007), NAIST (2008-2011), and NCTU (2008-)

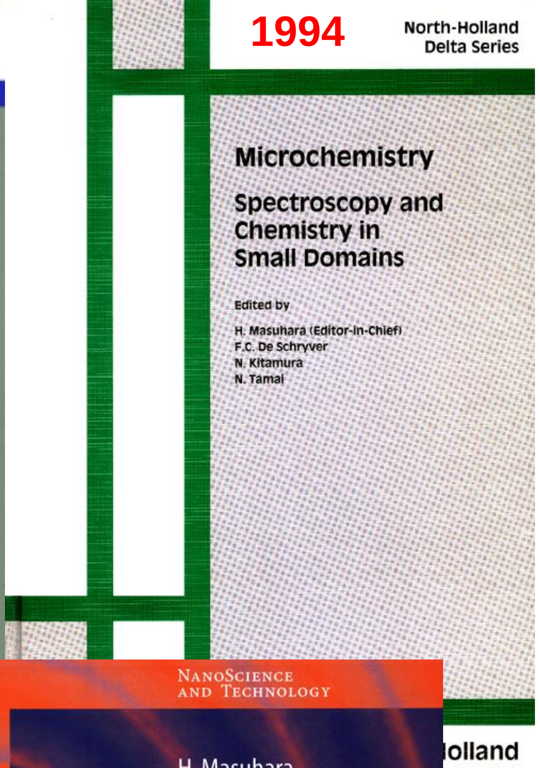
フェムト秒レーザーブレークダウンによる単一細胞の操作と機能制御

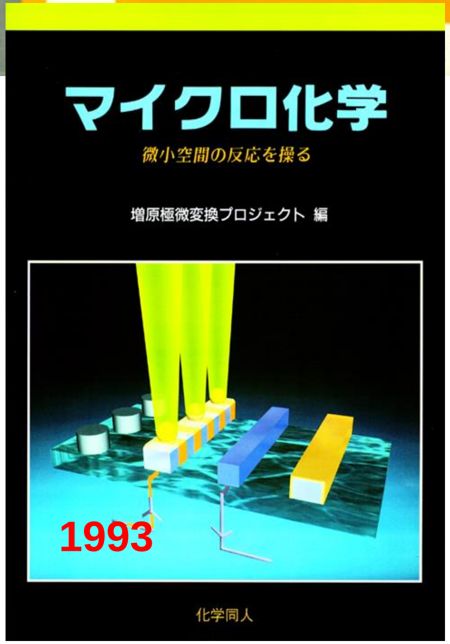
Femtosecond Laser Manipulation and Functionallization of Single Living Cells

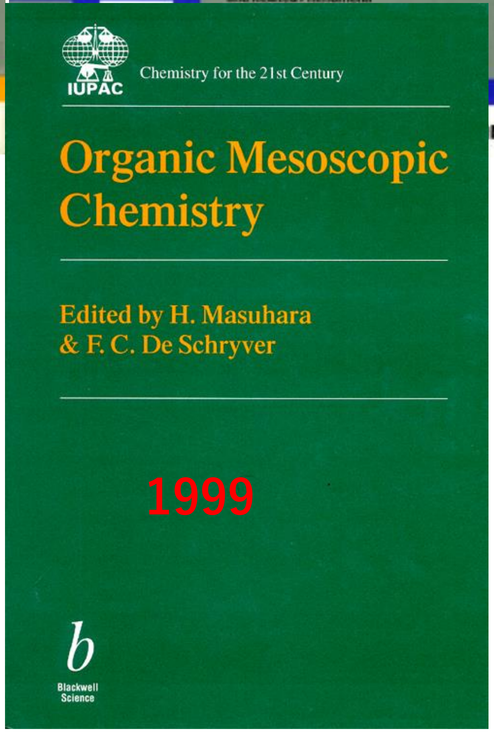
Osaka University (2003-2007), NAIST (2008-2011), and NCTU (2008-2015)

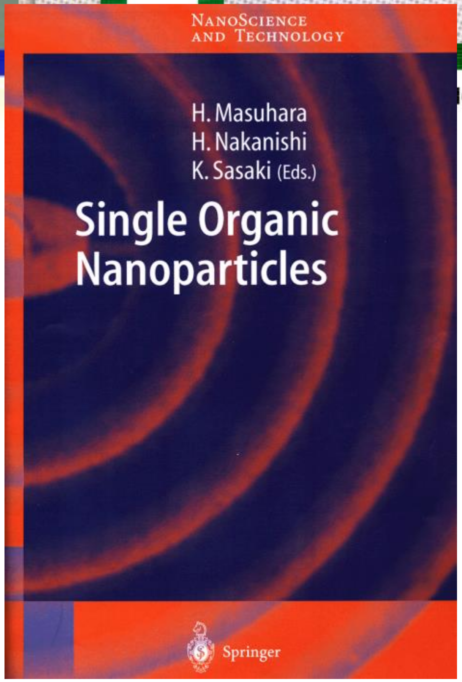








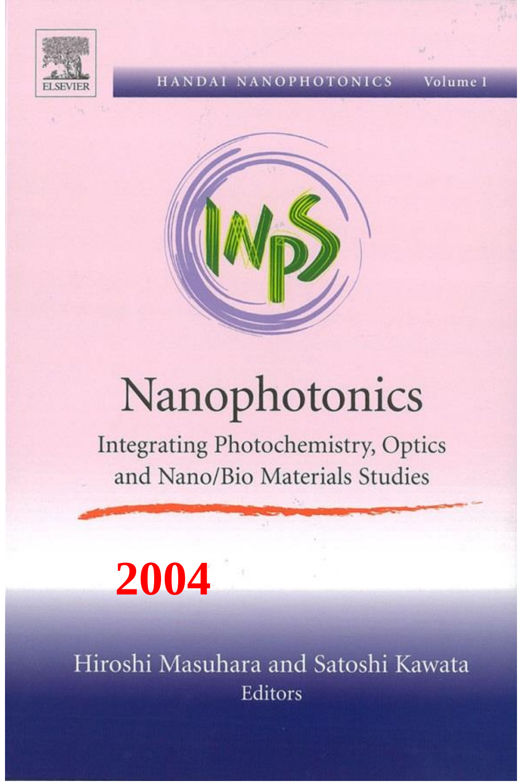


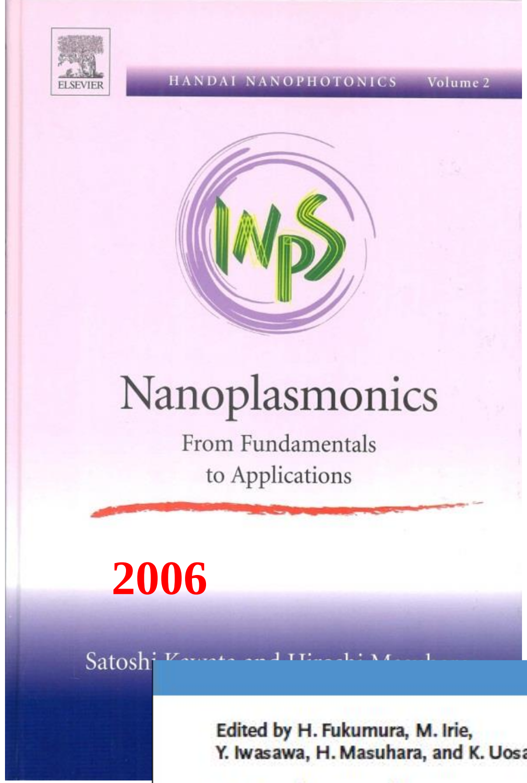


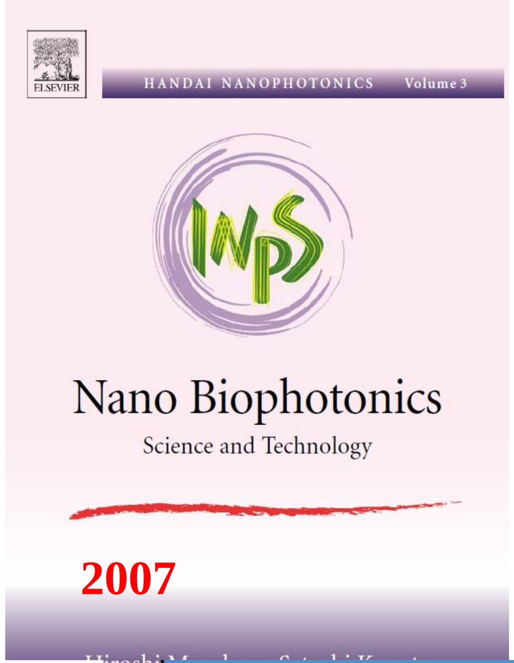
2005

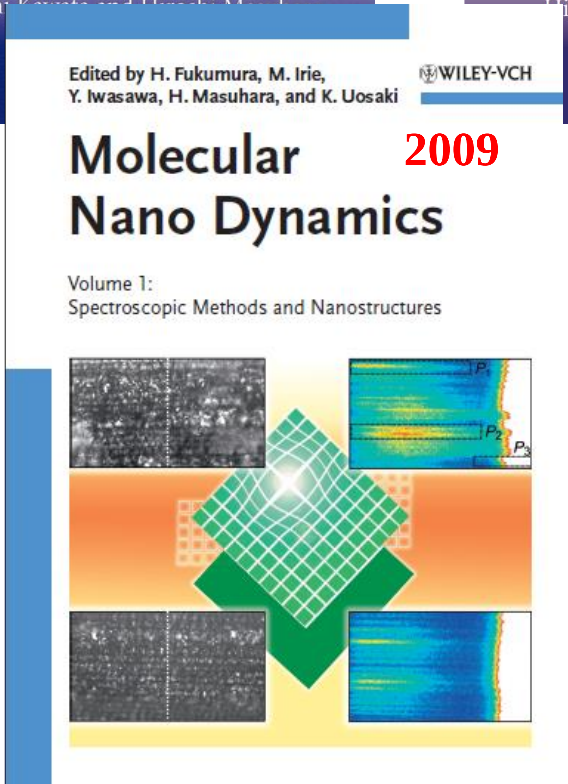
2003

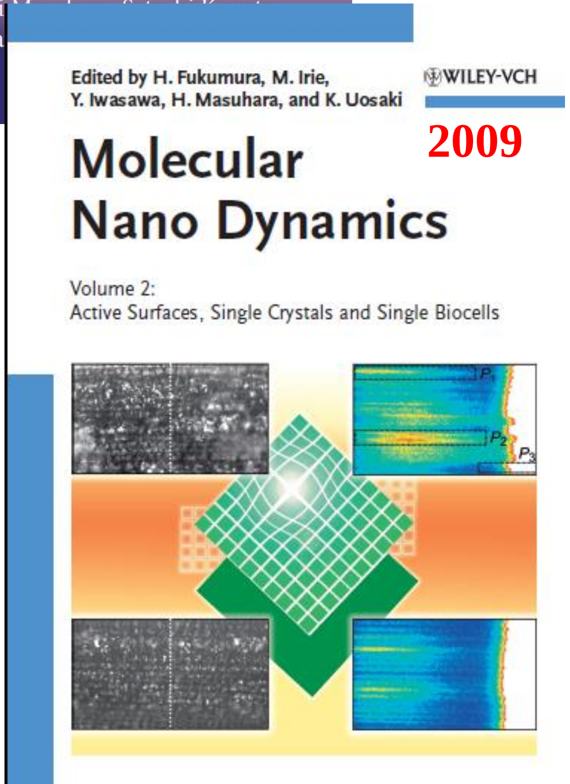
Books Edited and Written by Masuhara et al.











Books Edited and Written

by Masuhara et al.

Porter Medal 2006,

IUPAC Symposium on Photochemistry, Kyoto

Thanks to funding and support

MOE (Ministry of Education) ATU (Aiming-Top-University) Project (National Chiao Tung University), Taiwan

MOST (Ministry of Science and Technology), Taiwan

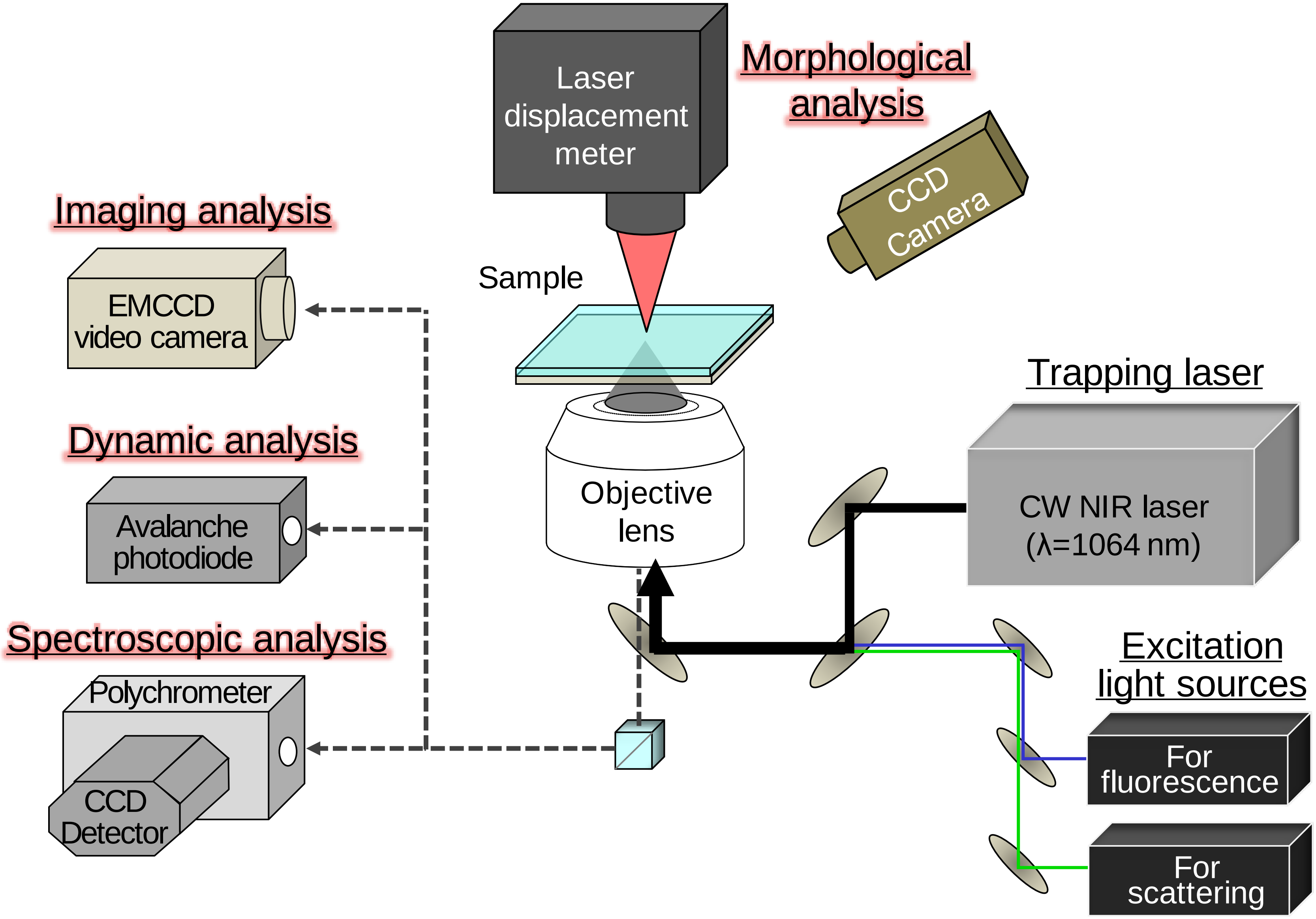
JSPS (Japan Society for Promotion of Science), Japan

And

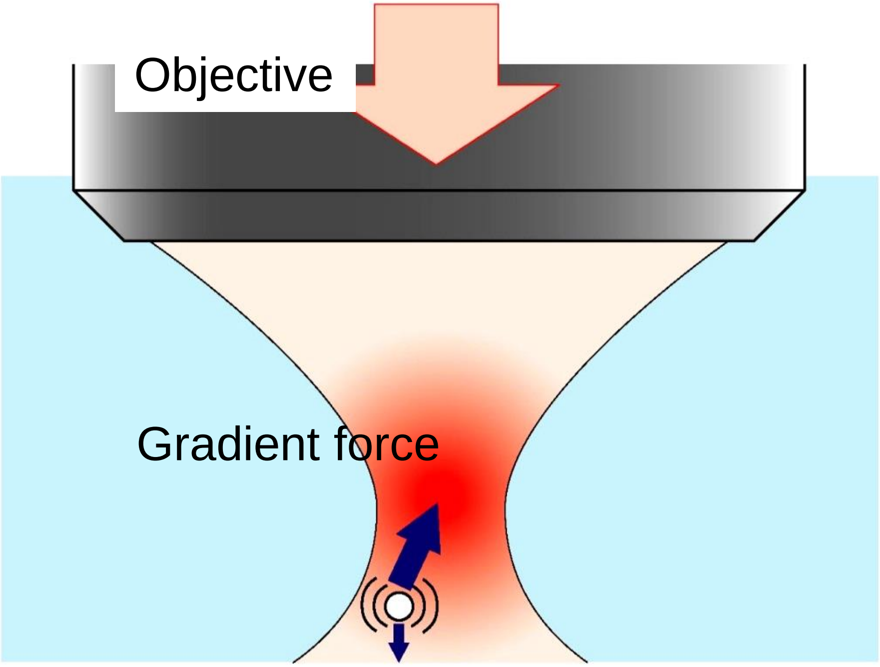
Prof. Yuan-Pern Lee of National Chiao Tung University, Taiwan

Introduction

Sugiyama, Yuyama, Masuhara,
"Laser trapping chemistry: From polymer assembly to amino acid crystallization"
Acc. Chem. Res., 2012, 45, 1946-1954


Laser displacement meter
Morphological analysis
CCD Camera
Imaging analysis
Sample
EMCCD video camera
Trapping laser
Dynamic analysis
Objective lens
CW NIR laser (λ=1064 nm)
Avalanche photodiode
Spectroscopic analysis
Excitation light sources
Polychrometer
For fluorescence
CCD Detector
For scattering

Principle of laser trapping of nanometer-sized particles



$$\mathbf{F}_{phot} = \mathbf{F}_{grad} + \mathbf{F}_{scat} + \mathbf{F}_{abs}$$

$$\mathbf{F}_{phot} \cong \mathbf{F}_{grad}$$

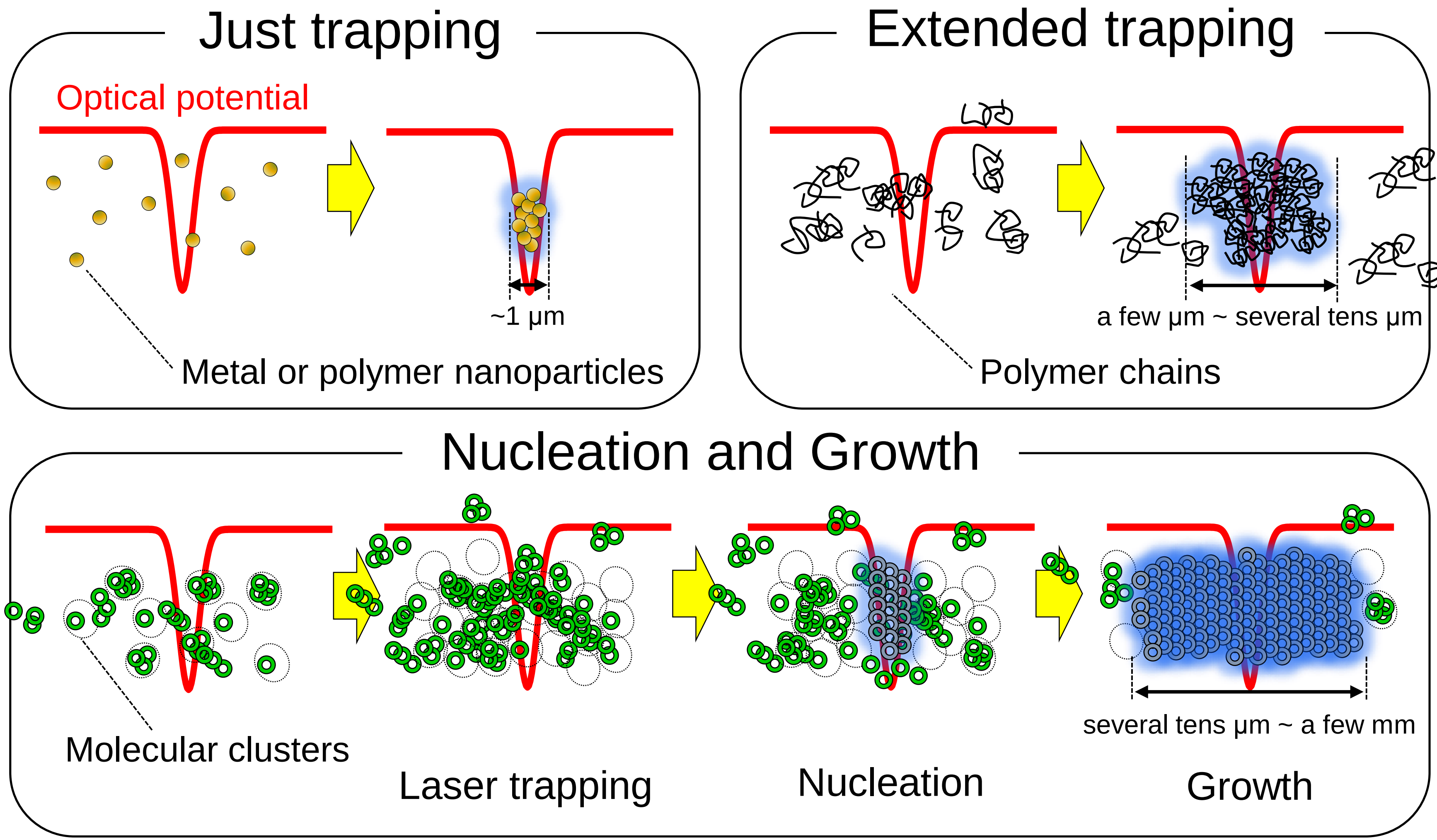
$$= \frac{1}{2}\varepsilon_m |\hat{\alpha}| \nabla |\mathbf{E}|^2$$

$$\hat{\alpha} = 3V' \frac{\hat{\varepsilon}_p - \varepsilon_m}{\hat{\varepsilon}_p + 2\varepsilon_m}$$

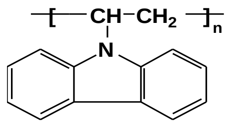
$$V' = 4\pi \int_0^a r^2 \, exp\left(\frac{r - a}{\delta}\right) dr$$

$$\left(\delta = \lambda_0 / 2\pi\kappa_p\right)$$

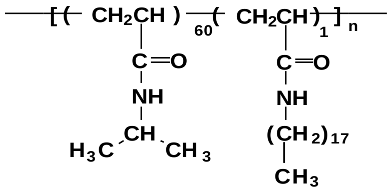
“Trapping, Assembling, and Nucleation Phenomena”



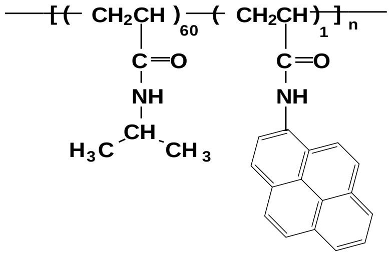
Laser trapping of polymers inside solution reported by us in 1990's



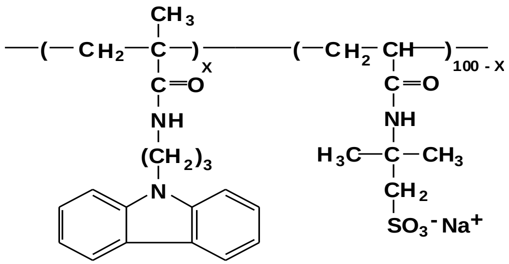
Poly(n-vinylcarbazole)



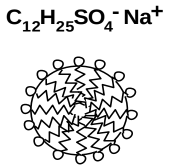
PNIPAM / alkanoic acid copolymer



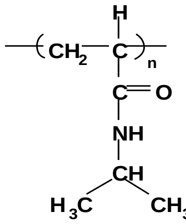
Pyrene-labeled PNIPAM



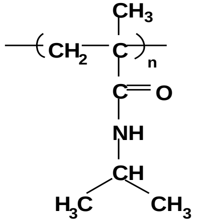
Amphiphilic copolymer with carbazolylalkyl groups



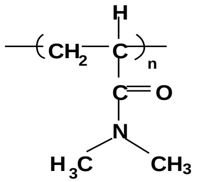
Swelled micelles



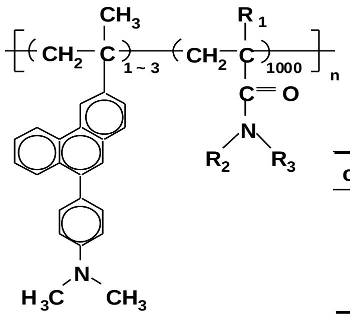
Poly(*N*-isopropylacrylamide)



Poly(N-isopropylmethacrylamide)

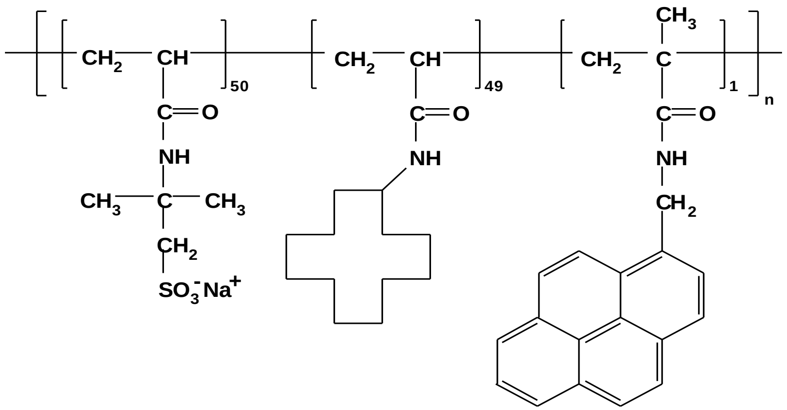


Poly(*N, N*-dimethylacrylamide)

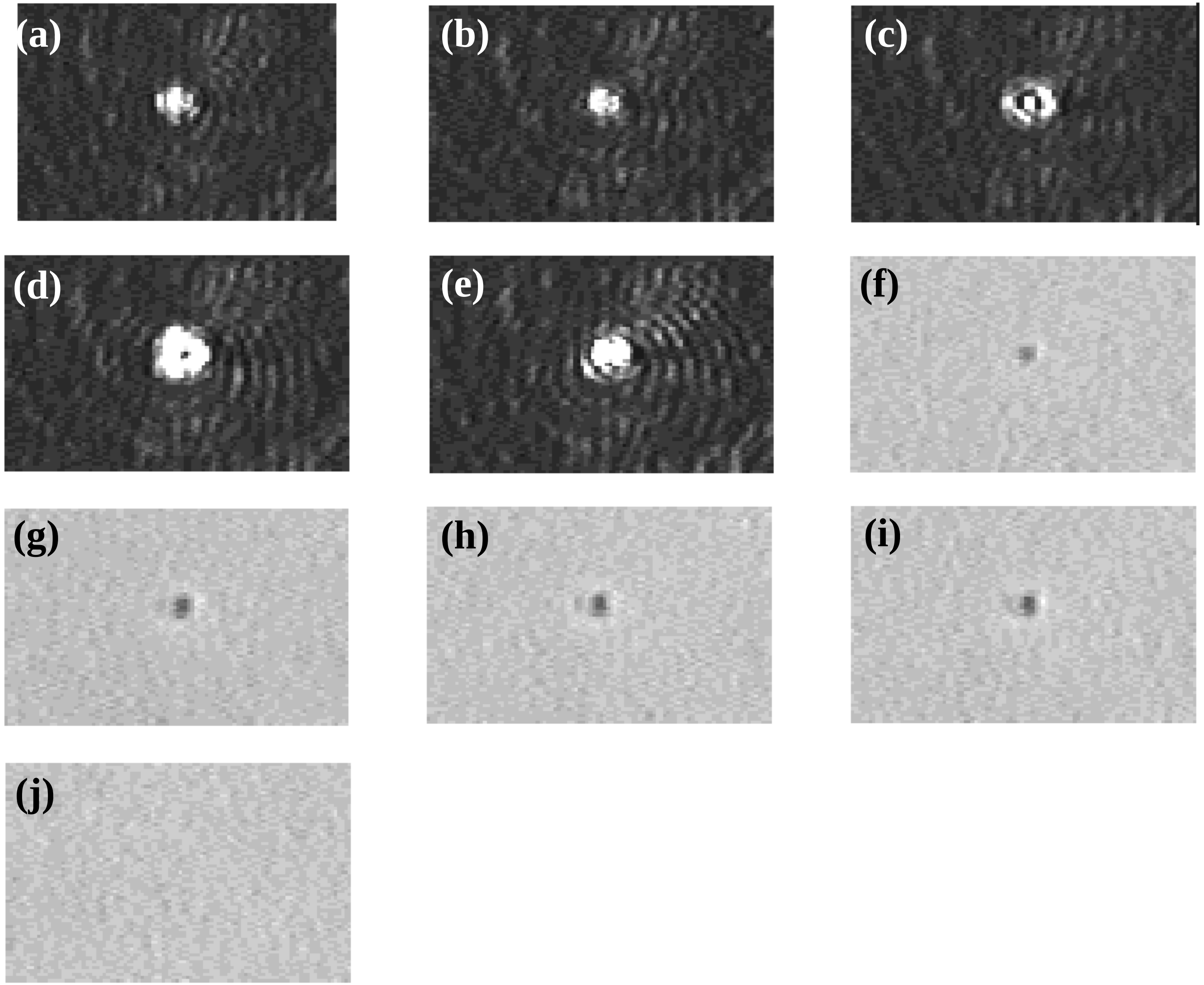


comonomer	R_1	R_2	R_3
NIPAM	-H	$-CH(CH_3)_2$	-H
NIPMAM	$-CH_3$	$-CH(CH_3)_2$	-H
DMAM	-H	$-CH_3$	$-CH_3$

P(VDP-co-comonomer)

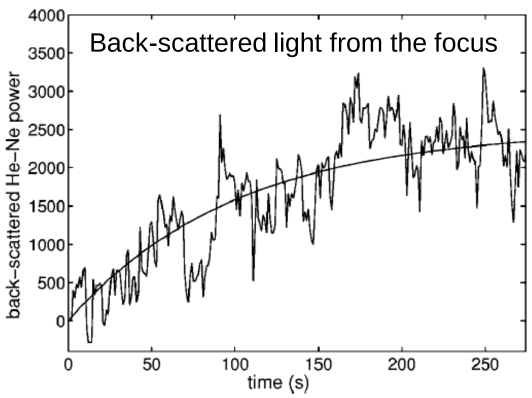


Pyrene-labeled poly (2-(acrylamido)-methylpropanesulfonate-co-*N*- cyclododecylmethacrylamide)


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)

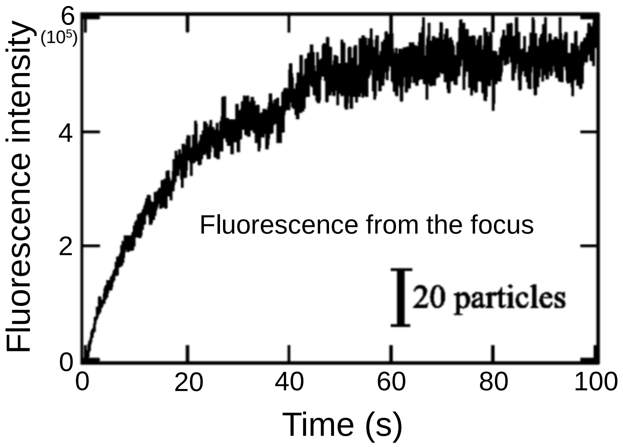
Laser Trapping Assembling inside Solution
Forming a Single Sphere

PEO polymer
(Molecular weight:100-900 kDa)



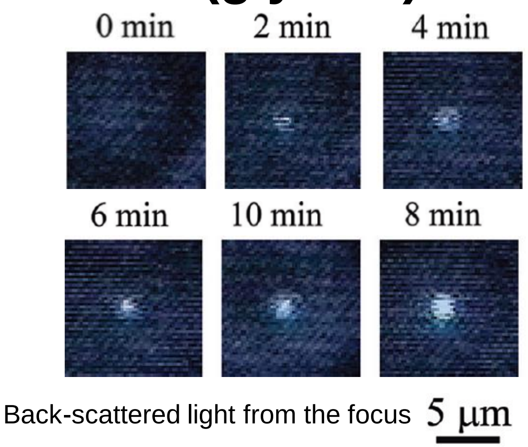
Singer W. *et al., Phys. Rev. E*
2007, *75*, 011916

Dye-doped Polystyrene NPs
(Particle size:100 nm)



Hosokawa C. *et al., Phys. Rev. E*
2007, *70*, 0614140

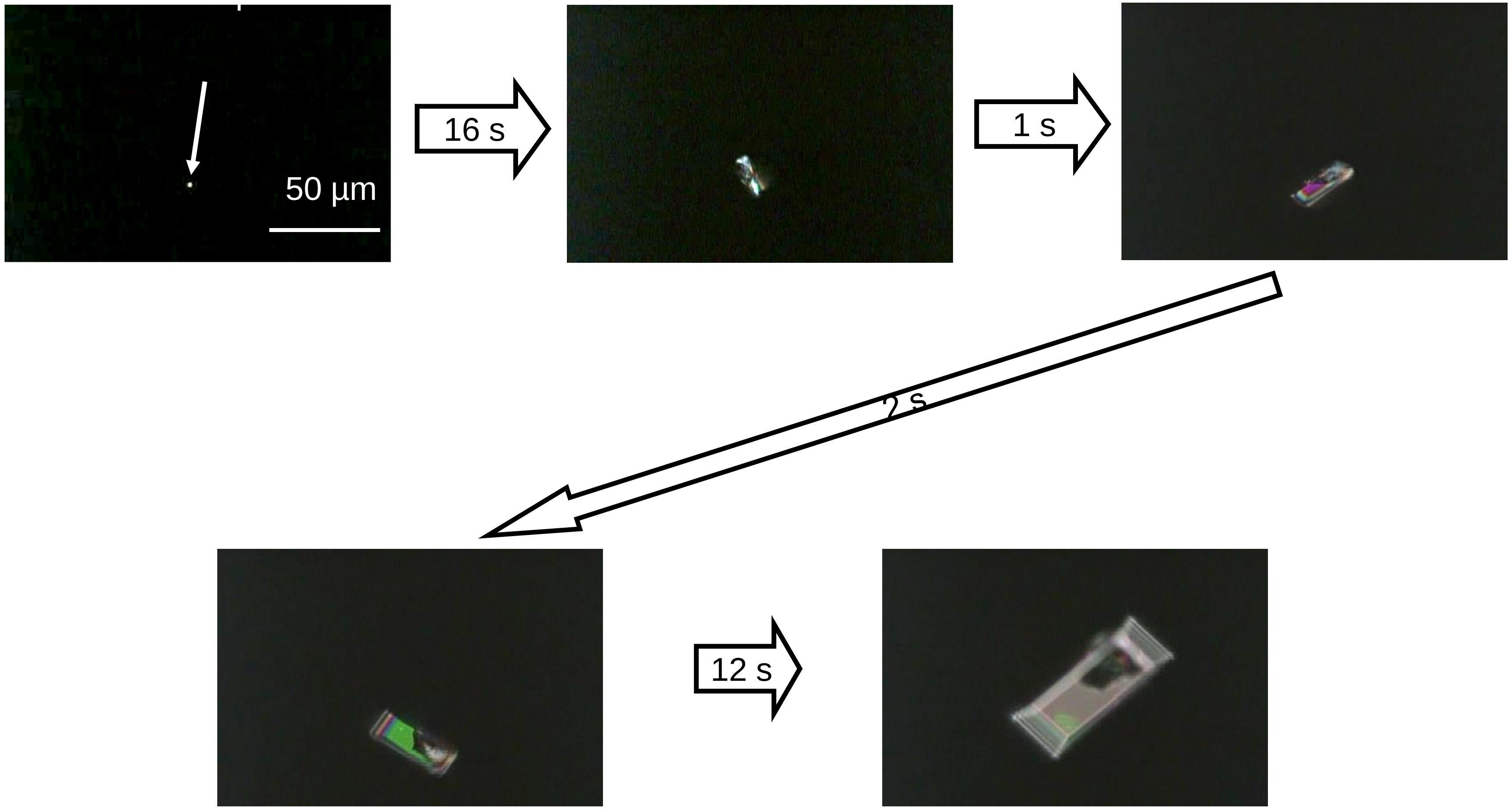
Amino acid (glycine)



Tsuboi Y. *et al., J. Phys. Chem. C*
2013, *114*, 5589

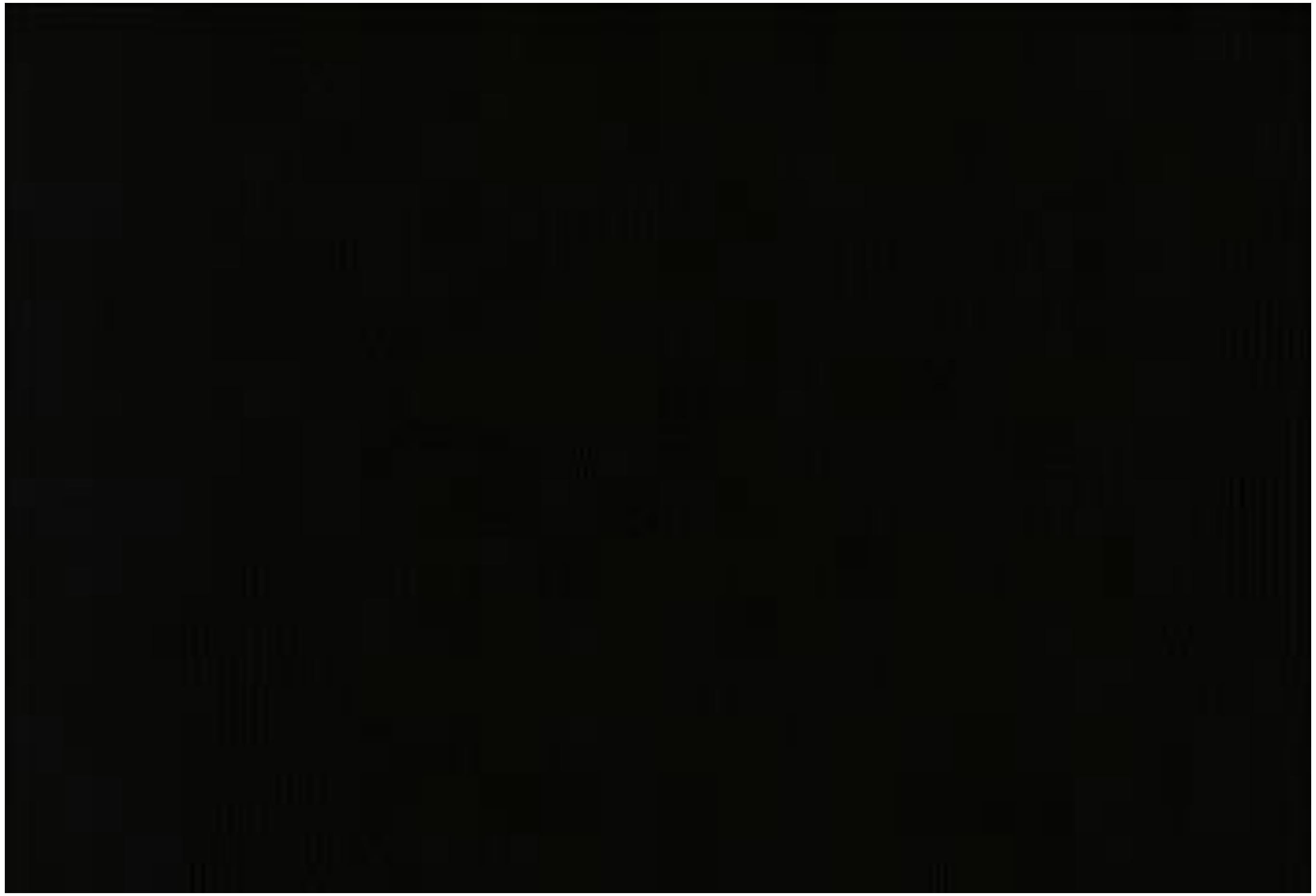
- ➢ **Nanometer-sized objects like polymers, nanoparticles, amino acids are sequentially trapped in the focal volume, and the local concentration is increased with irradiation time.**

Laser Trapping of Amino Acids at Solution Surface Inducing Crystallization



Glycine in heavy water

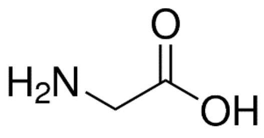
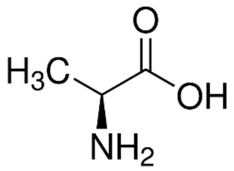
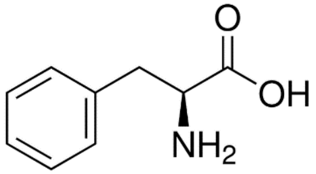
Sugiyama, Adachi, Masuhara, Chem. Lett., 2007, 36, 1480

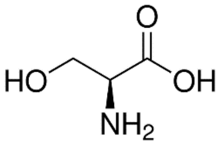
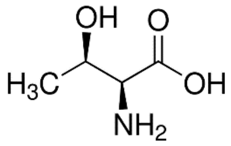
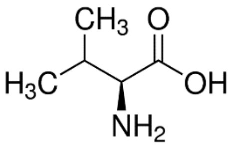
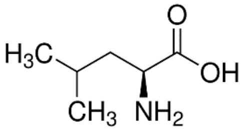
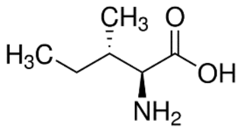


A near infrared CW laser focused at an air/solution interface induced crystallization of glycine, giving a length of 50 micrometer.

Sugiyama, Adachi, Masuhara, Chem. Lett., 36, 1480, 2007

Laser trapping crystallization of amino acids

Name	**Glycine**	**Alanine**	**Phenylalanine**
Structure			
	Rungsimanon, Yuyama, Sugiyama, Masuhara, Tohani, Miyata, *J. Phys. Chem. Lett.*, **2010**, 1, 599 Rungsimanon, Yuyama, Sugiyama, Masuhara, *Cryst. Growth Des.*, **2010**, 10, 4686 Yuyama, Rungsimanon, Sugiyama, Masuhara, *Cryst. Growth Des.*, **2012**, 11, 2427 Sugiyama, Yuyama, Masuhara, *Acc. Chem. Res.*, **2012**, 45, 1946	Yuyama, Ishiguro, Sugiyama, Masuhara, *Proc. of SPIE*, **2012**, 8458, 84582D-1	Yuyama, Sugiyama, Masuhara, *J. Phys. Chem. Lett.*, **2013**, 4, 2436 Yuyama, Wu, Sugiyama, Masuhara, *Photochem. Photobio. Sci.*, **2014**, 13, 254

Name	**Serine**	**Threonine**	**Valine**	**Leucine**	**Isoleucine**
Structure					

<Unpublished>

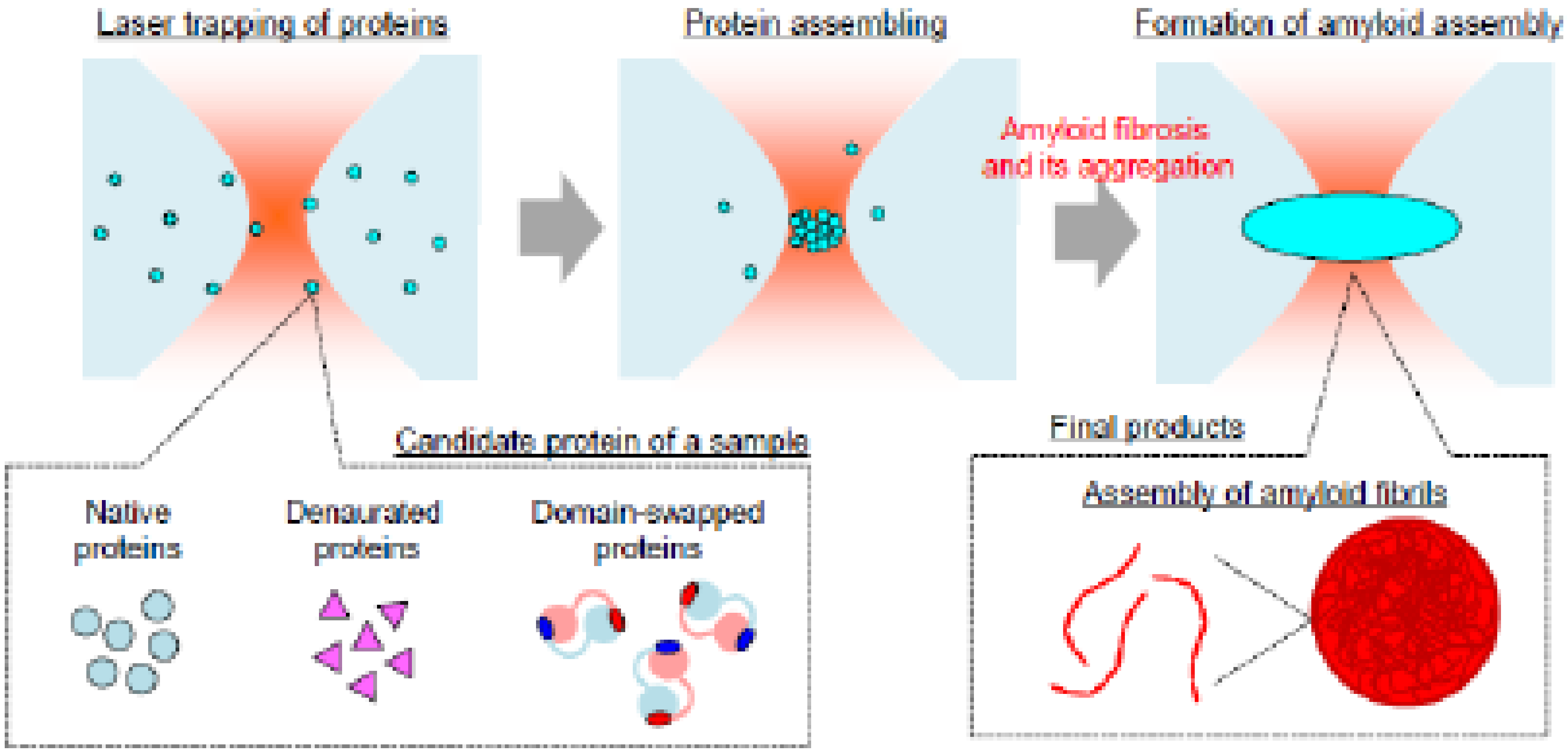
https://www.sigmaaldrich.com/japan.html/

Laser trapping amyloid formation
in solution

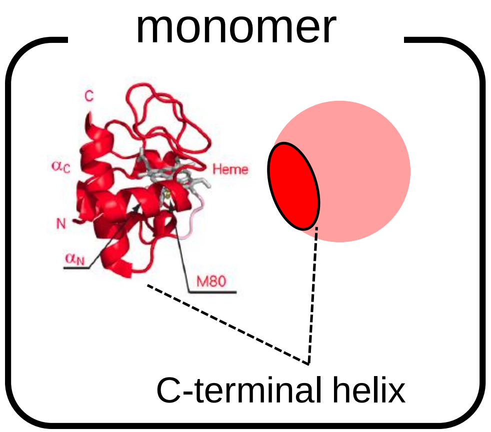
Cytochrome c

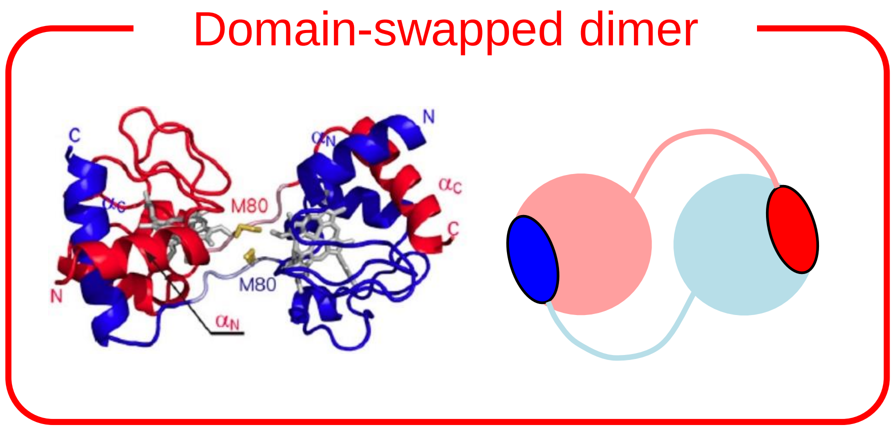
Yuyama, Ueda, Nagao, Sugiyama, Hirota, Masuhara
In preparation (2016)

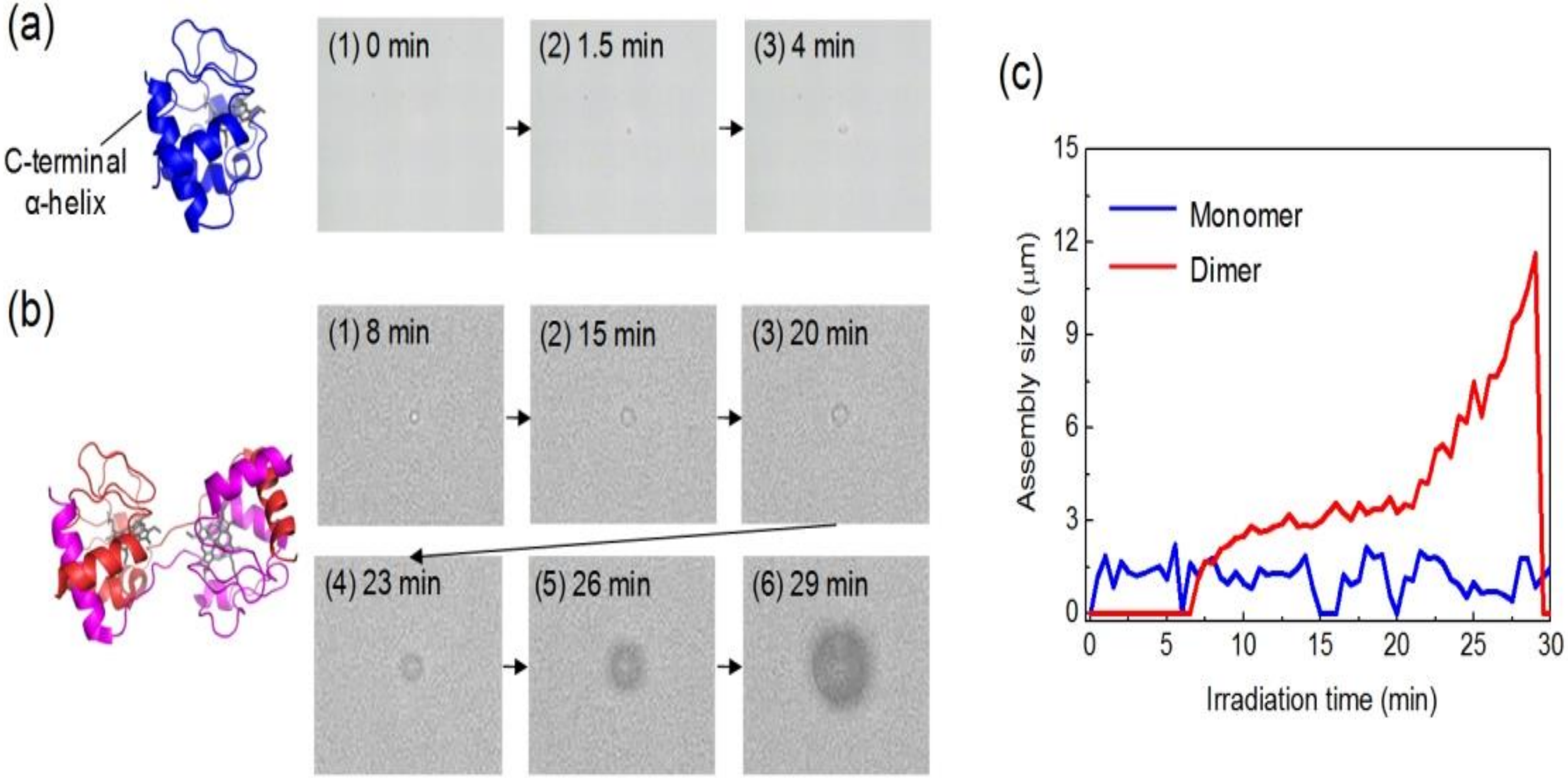
Formation of amyloid fibril by laser trapping



Horse hear cytchrome c

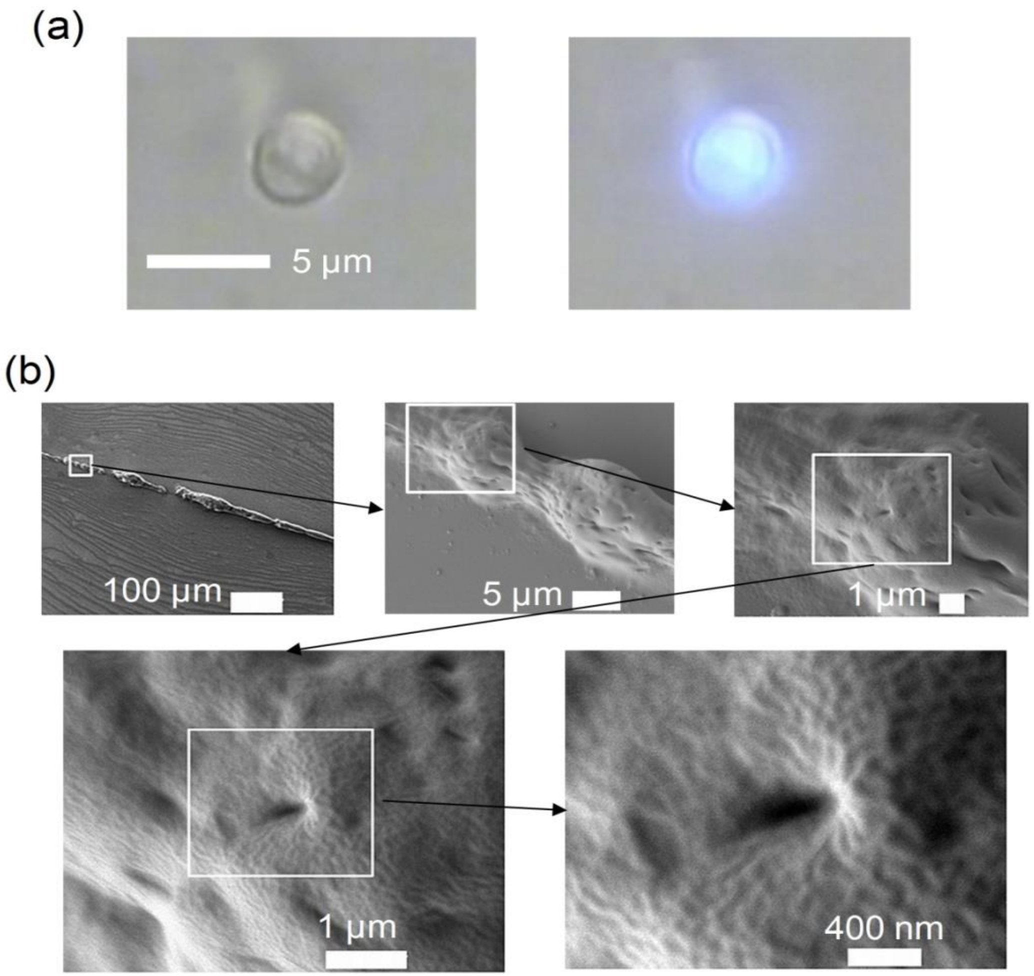






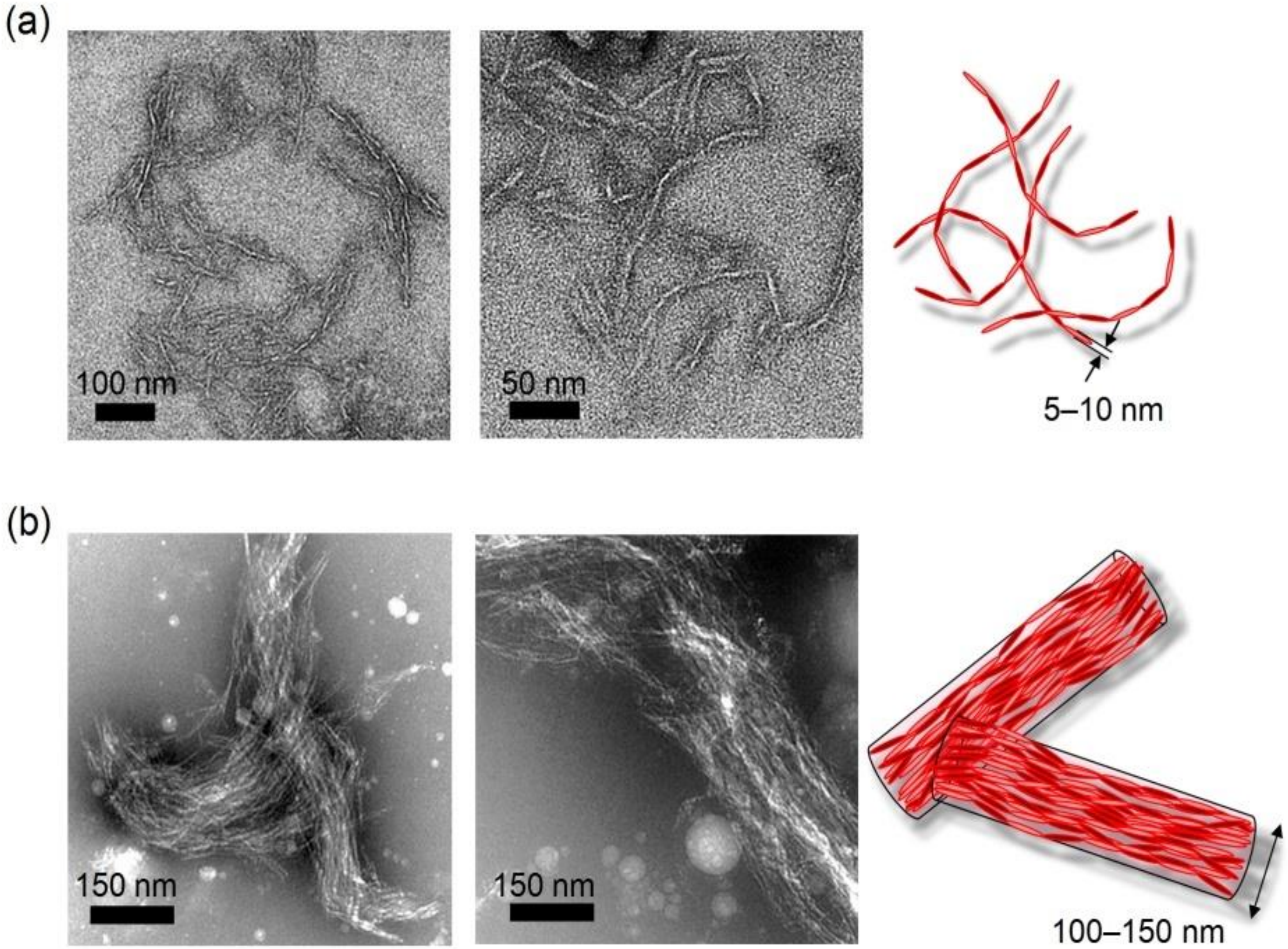
(a)
C-terminal
α-helix
(1) 0 min
(2) 1.5 min
(3) 4 min
(b)
(1) 8 min
(2) 15 min
(3) 20 min
(4) 23 min
(5) 26 min
(6) 29 min
(c)
Monomer
Dimer
Assembly size (μm)
Irradiation time (min)
0
3
6
9
12
15
0
5
10
15
20
25
30

Fluorescence characterization of amyloid formation by thioflavin T

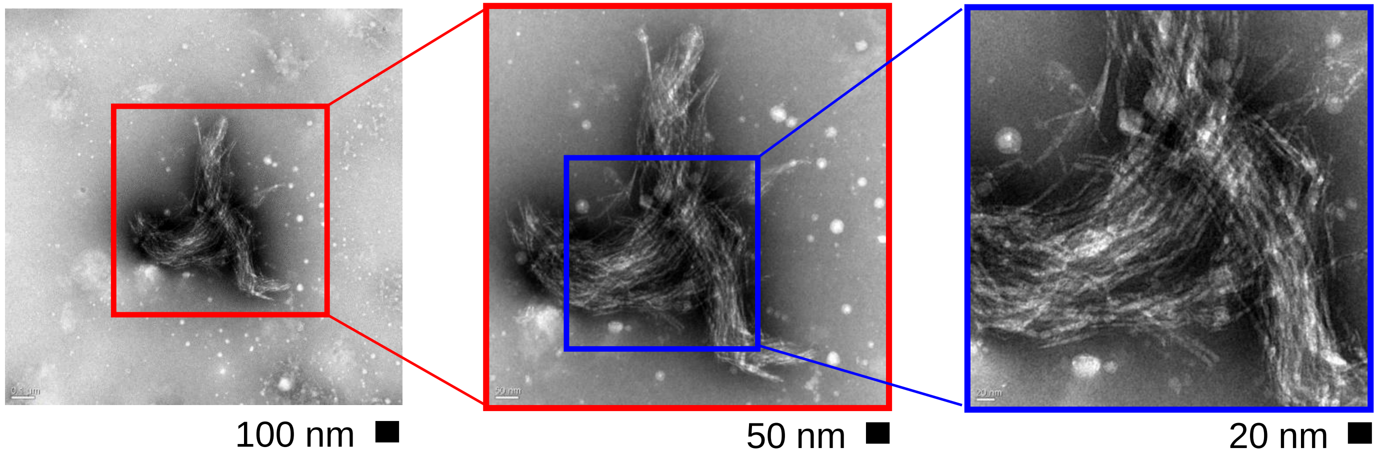


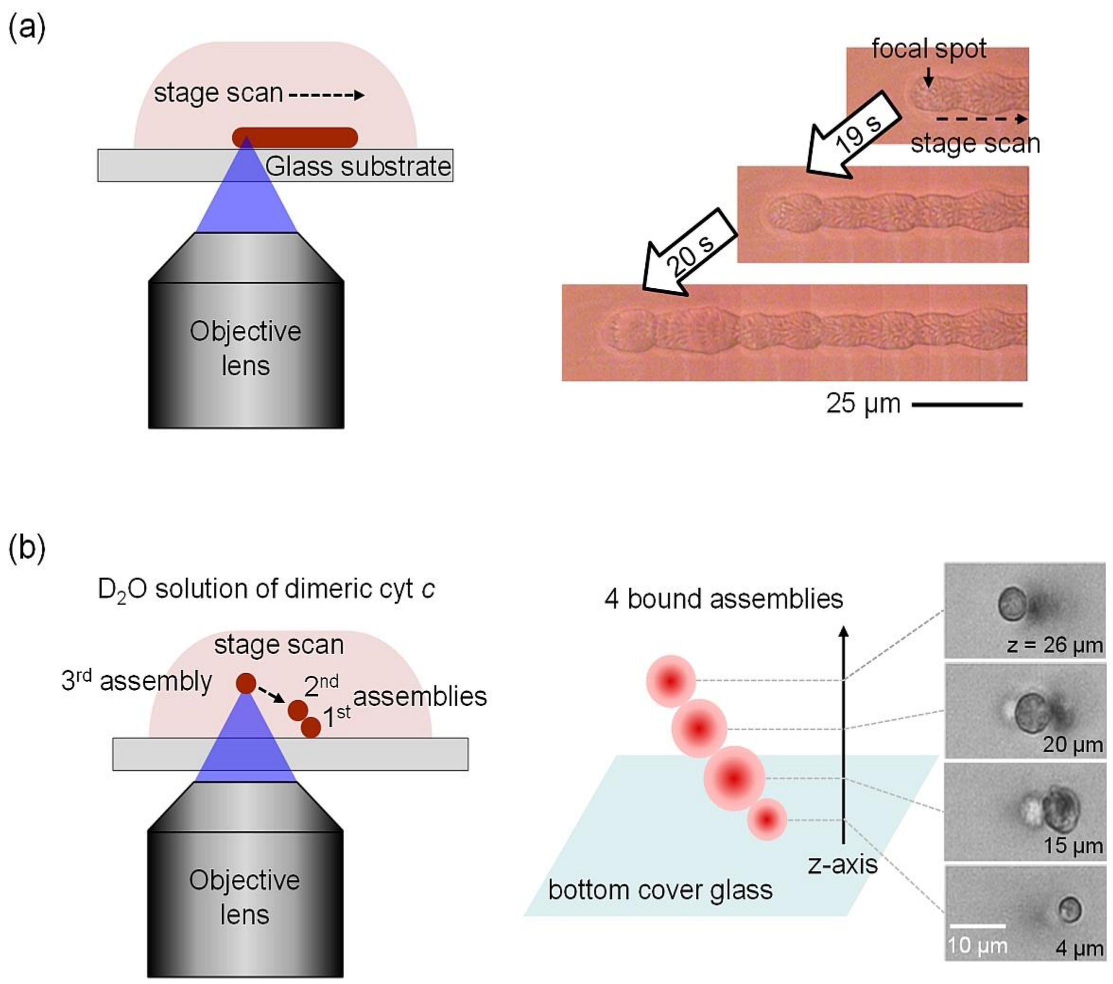
SEM observation

TEM observation



TEM observation



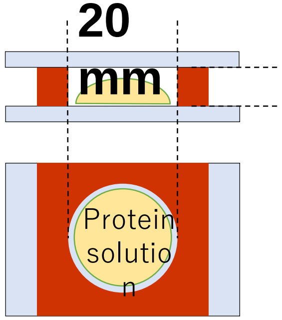

(a)
stage scan
Glass substrate
Objective lens
focal spot
19 s
stage scan
20 s
25 μm
(b)
D2O solution of dimeric cyt c
stage scan
3rd assembly
2nd
1st
assemblies
Objective lens
4 bound assemblies
z-axis
bottom cover glass
z = 26 μm
20 μm
15 μm
4 μm
10 μm

Protein crystallization upon switching trapping laser off at glass/solution interface

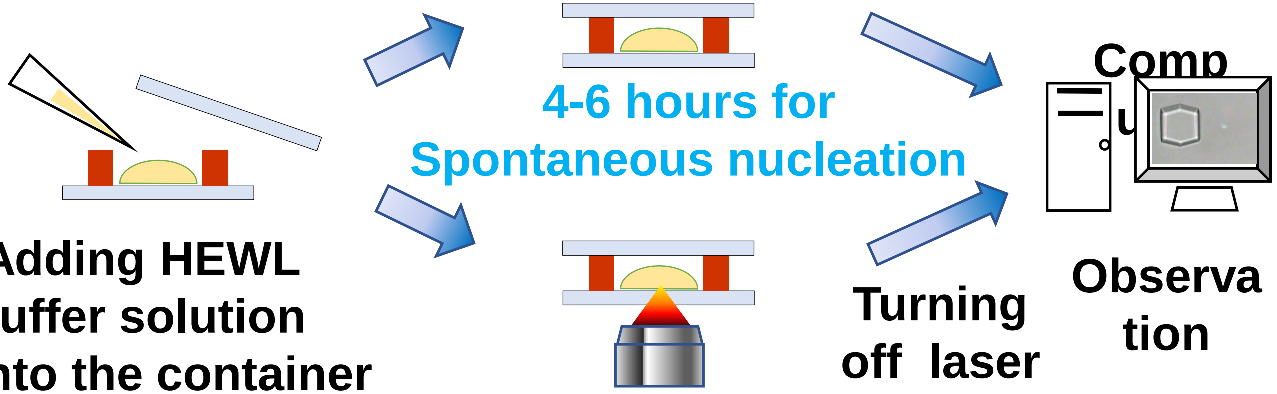
Lysozyme

Yuyama, Chang, Tu, Sugiyama, Masuhara
In preparation, 2016

Preparation procedure of HEWL buffer solution

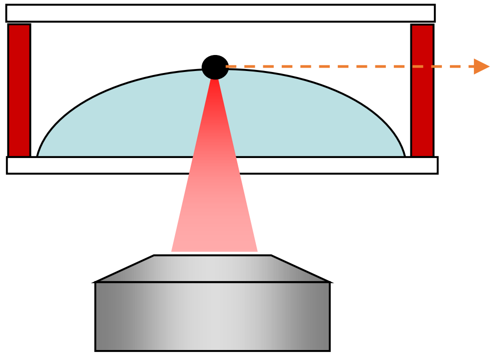


Concentration (Total Volume)	40 mg HEWL in 1.0 ml D_2O buffer (80 μL)
NaCl	2.7 %
Laser power	0.5, 0.8 and 1.1 W
Laser Polarization	Linear, Right- and Left-handed Circular, Depolarized
Irradiation time	30, 60, and 90 min

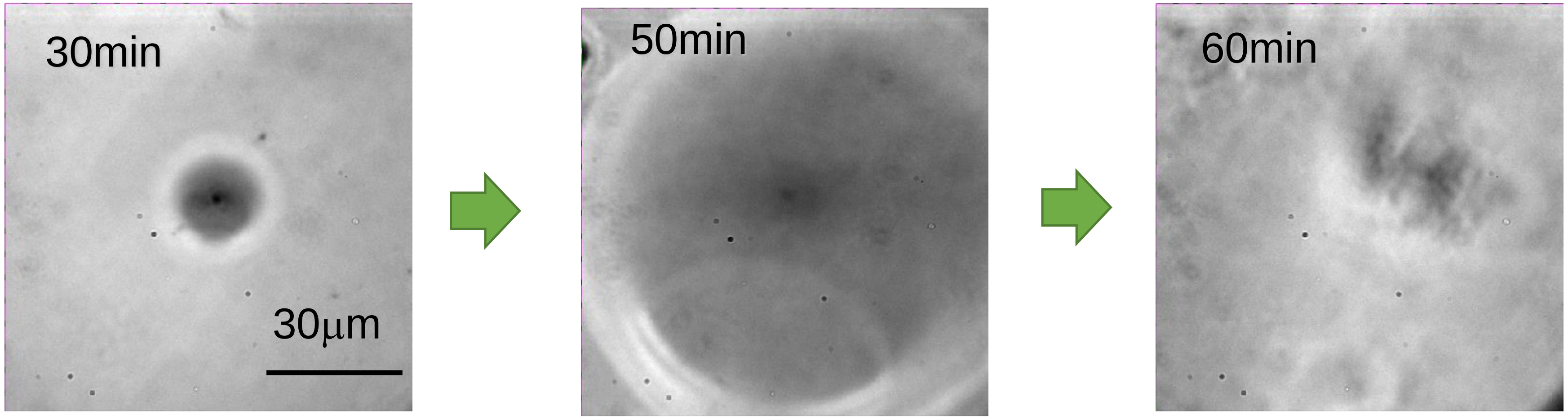


Laser trapping of protein at solution surface gives a single disc-like assembly instead of a crystal

Lysozyme 40mg/ml with 2% NaCl, Transmittance images

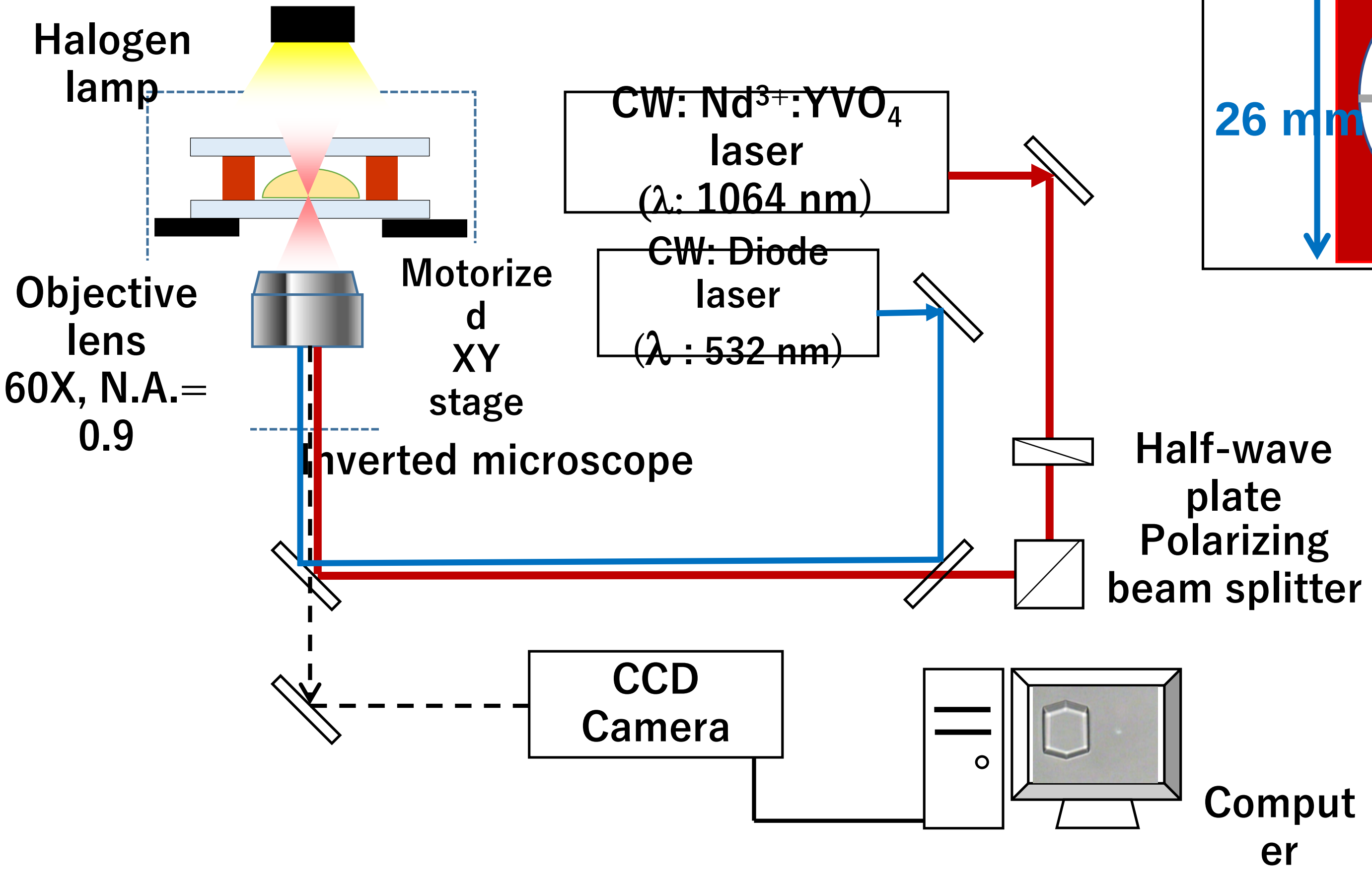


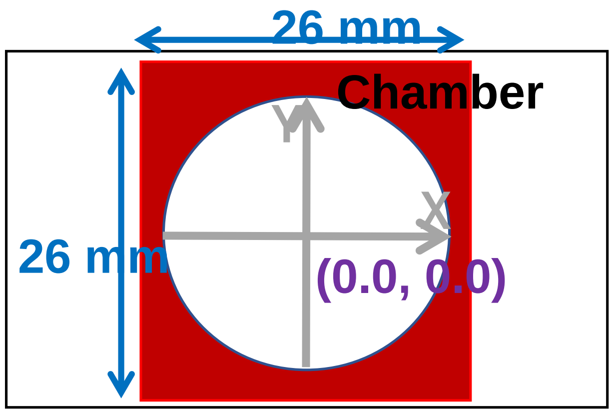
Transmittance images



Laser trapping inside the solution gave no crystal and assembly, but we found many crystals were formed upon stopping laser trapping.

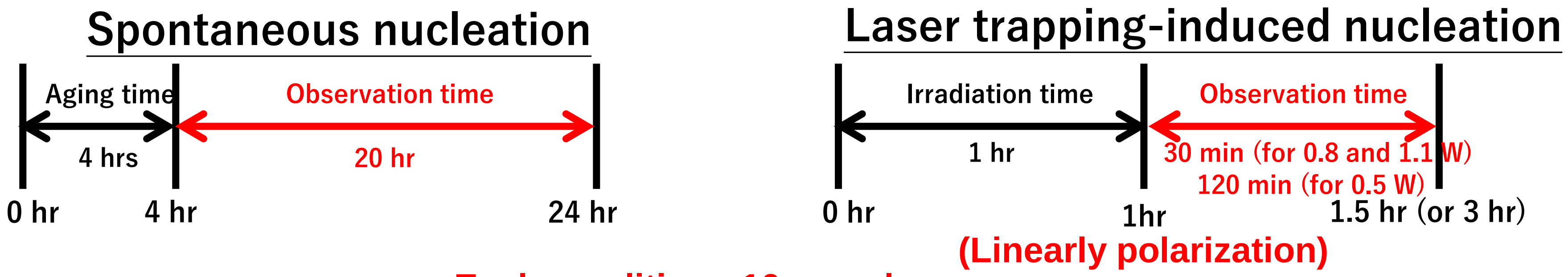
Optical Setup



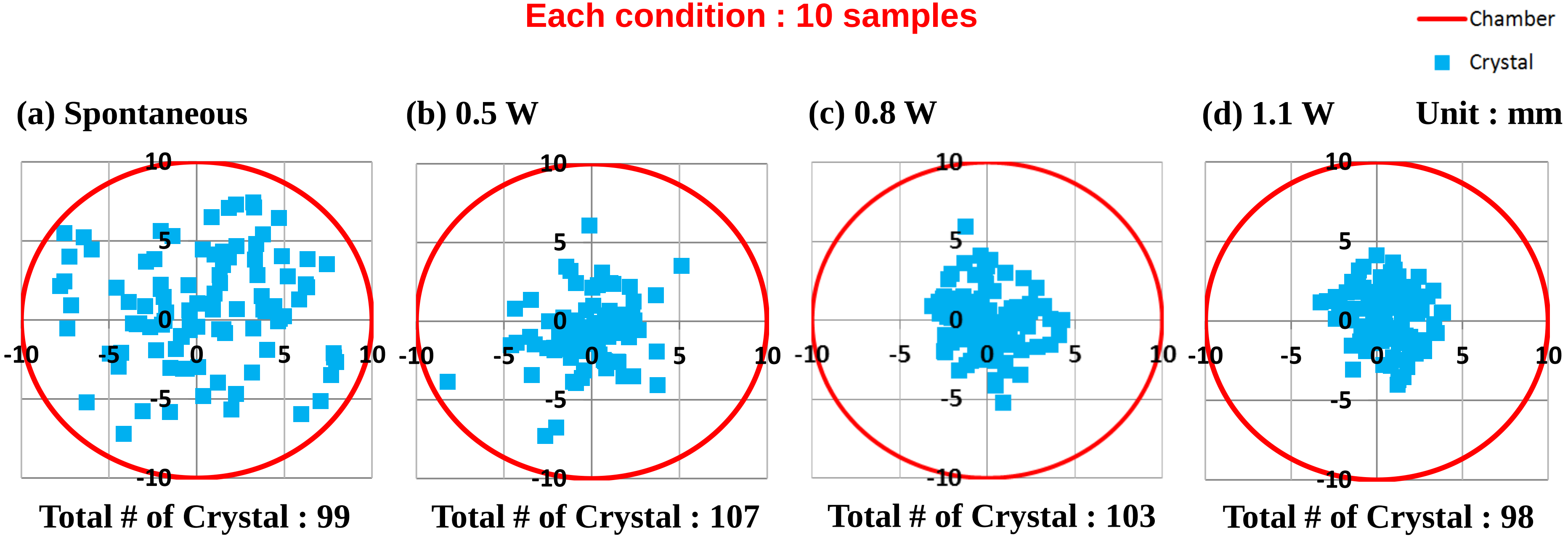


Glass substrate

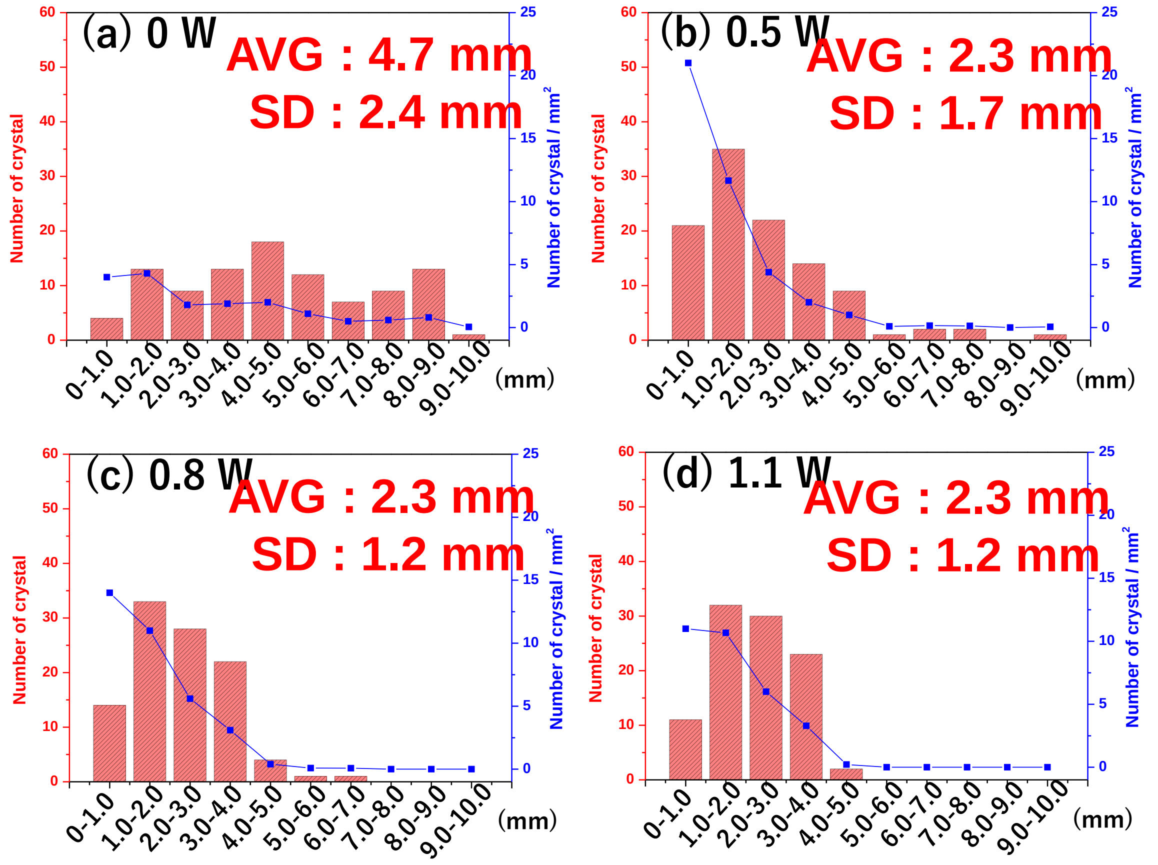
Distribution of crystallization position depending on laser power



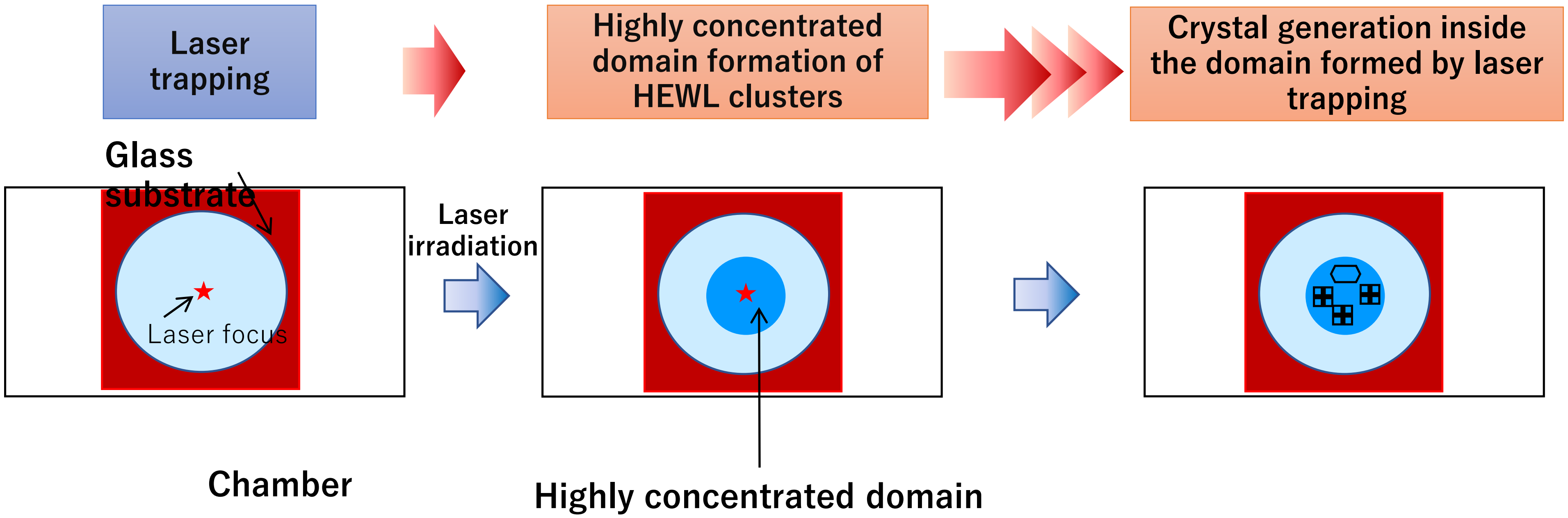
Each condition : 10 samples



The position distribution of HEWL crystal depending on laser power

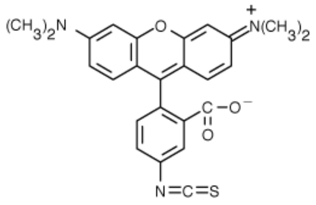


We proposed that a large highly concentrated domain formed around the focus by laser trapping. Here we extend systematic study toward control of HEWL nucleation through the domain.

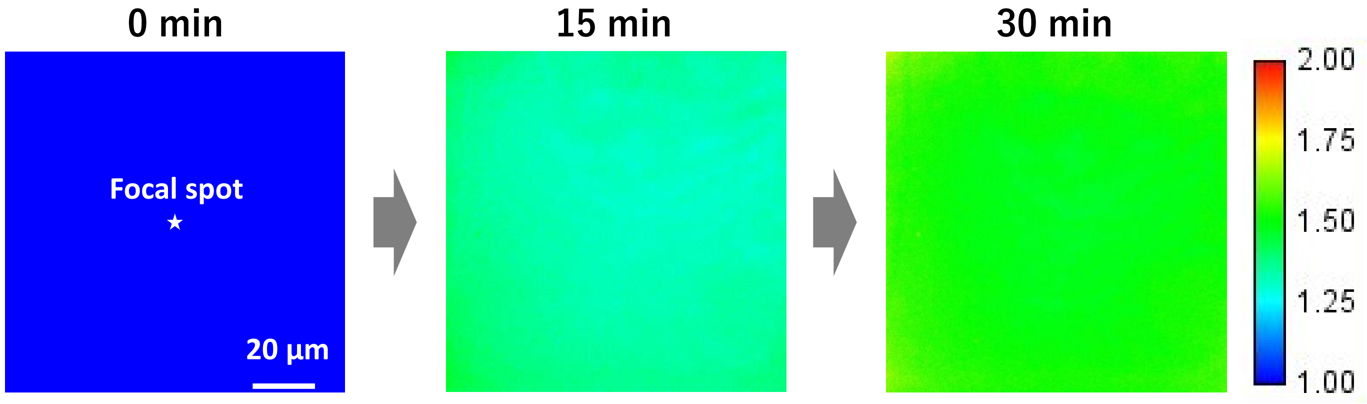


Fluorescence study on highly concentrated domain formation in D_2O

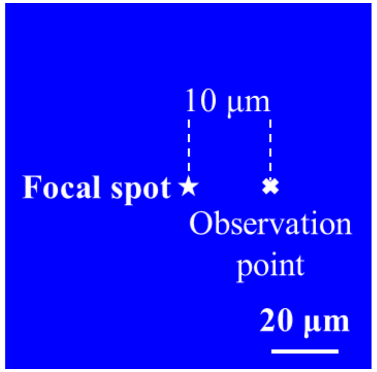
5-TRITC
(Tetramethylrhodamine
-5-isothiocyanate)

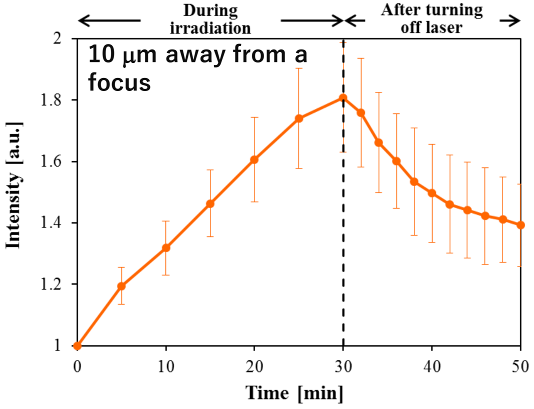


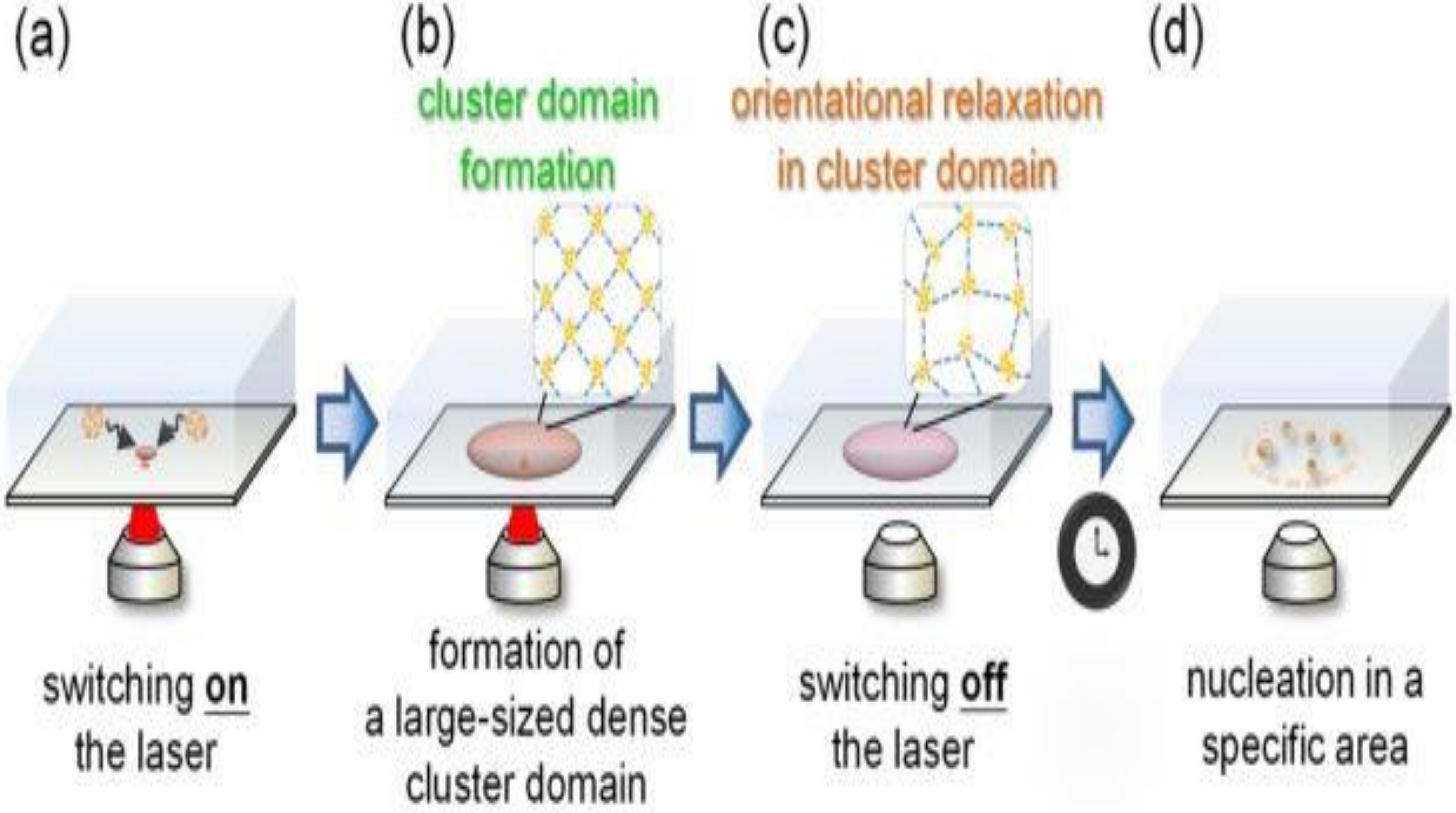
HEWL : F-HEWL = 16000 : 1
(F-HEWL is 5-TRITC labeled HEWL)



Temporal change in distribution of fluorescence intensity by laser trapping







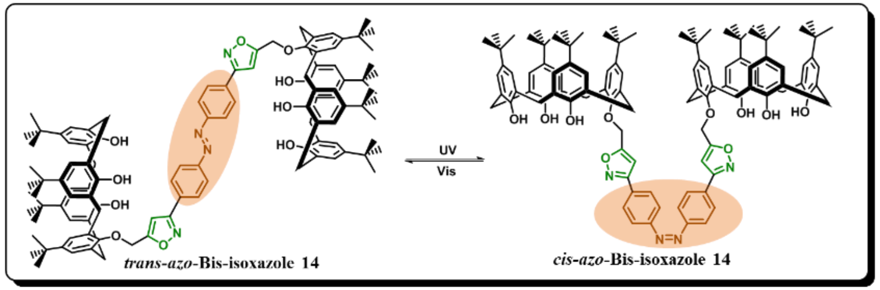
(a)
(b)
(c)
(d)
cluster domain formation
orientational relaxation in cluster domain
switching **on** the laser
formation of a large-sized dense cluster domain
switching **off** the laser
nucleation in a specific area

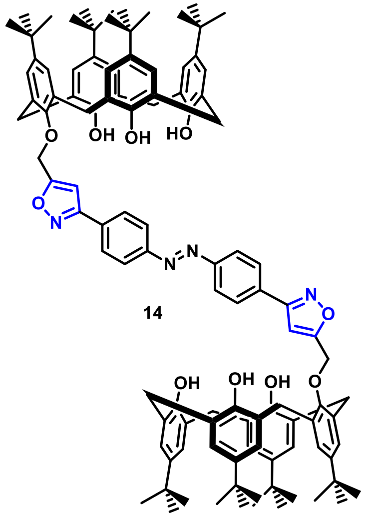
Supramolecular assembling upon switching trapping laser on and off at solution surface

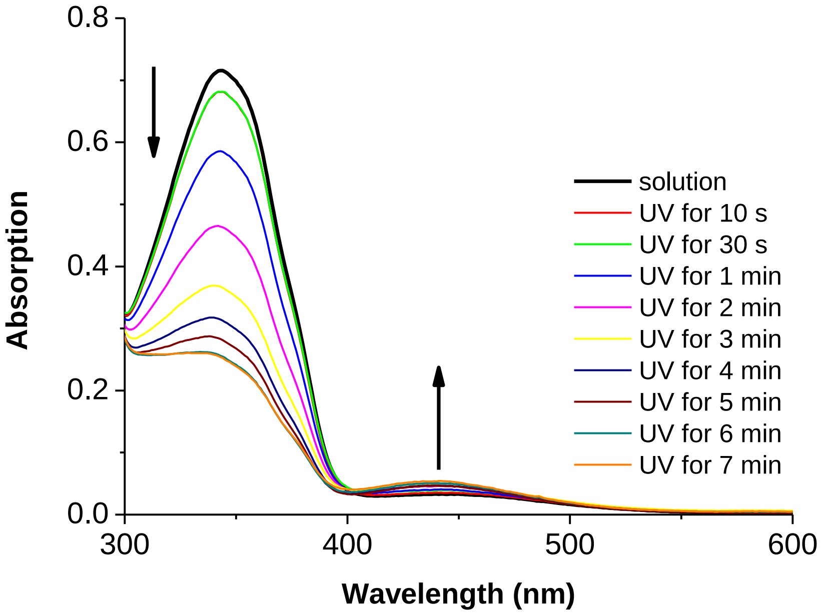
azobenzene-based bis-calix[4]arene

Yuyama, Marcelis, Su, Chung, Masuhara
In preparation, 2016

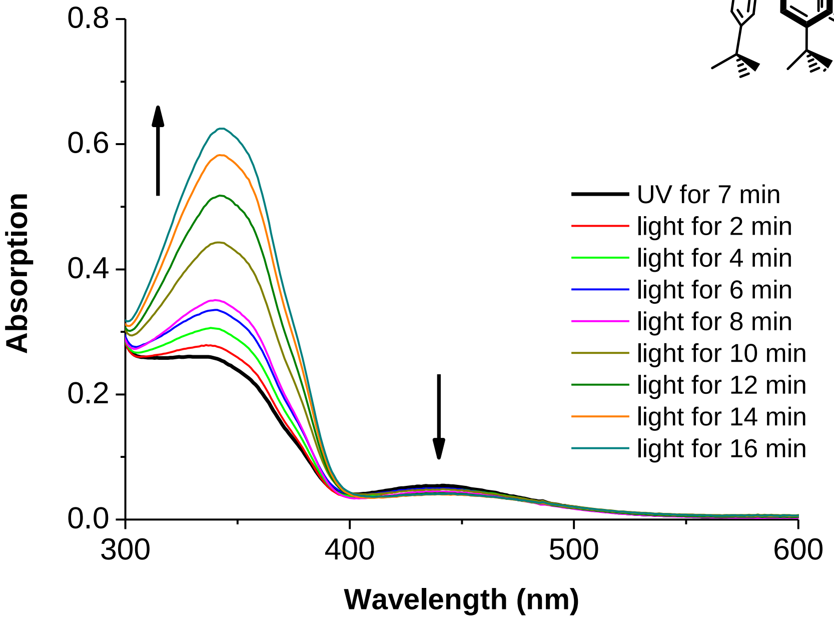
Absorption spectra of *trans-cis* isomerization of compound 14 (bis-isoxazole)





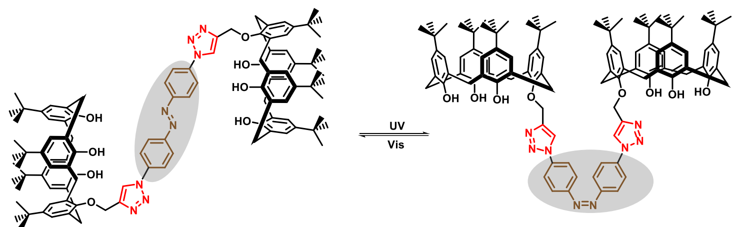


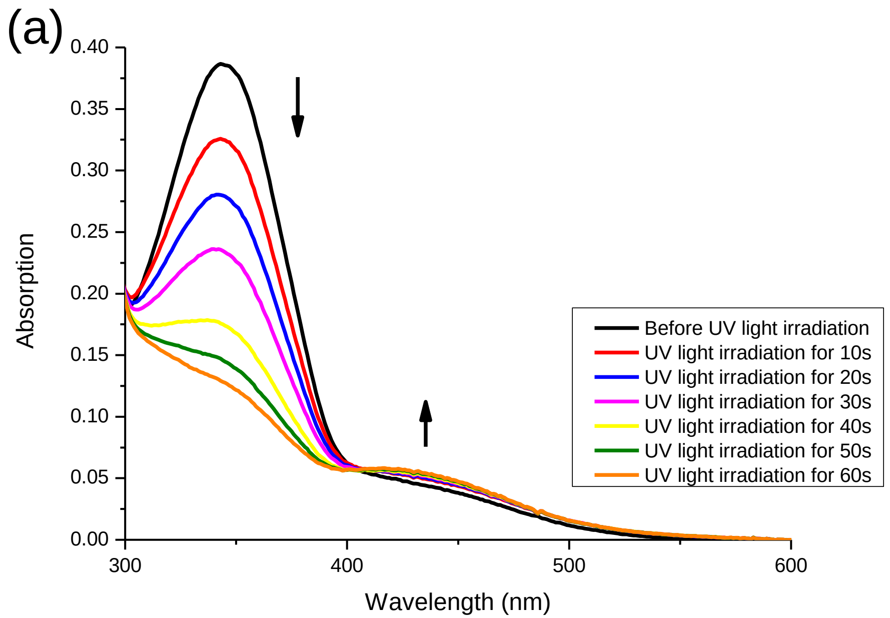
(a) 10^{-5} M in CH_2Cl_2/MeOH = 1/5 under UV light (365 nm) irradiation for different times



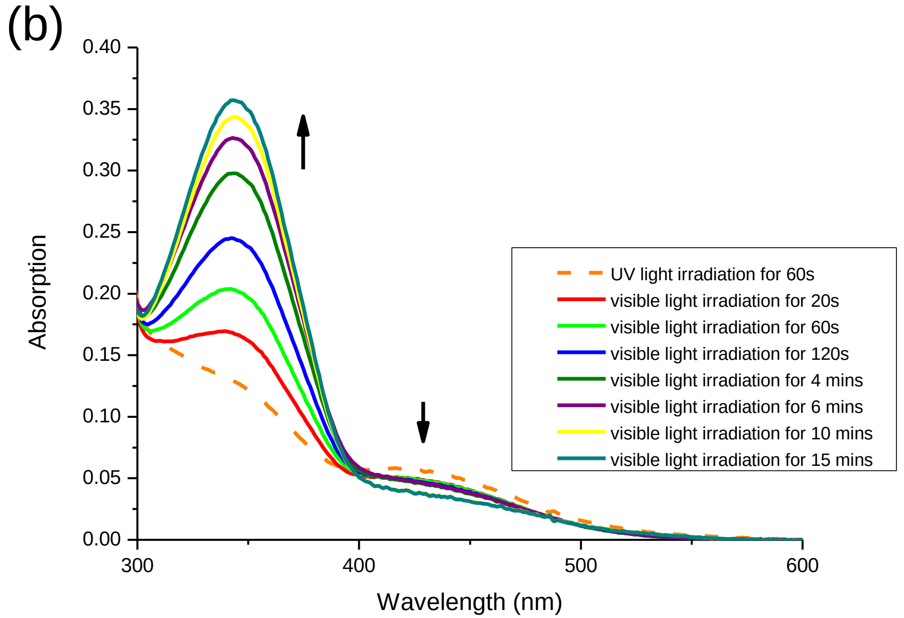
(b) 10^{-5} M in CH_2Cl_2/MeOH = 1/5 under UV light irradiation for 7 mins and further visible light irradiation for different times

Absorption spectra of *trans-cis* isomerization of compound 7 (tri-oxazole)





(a) Absorption spectrum of compound **7** in Acetonitrile (1 x 10 $^{-5}$ M), using 365 nm irradiation for different times



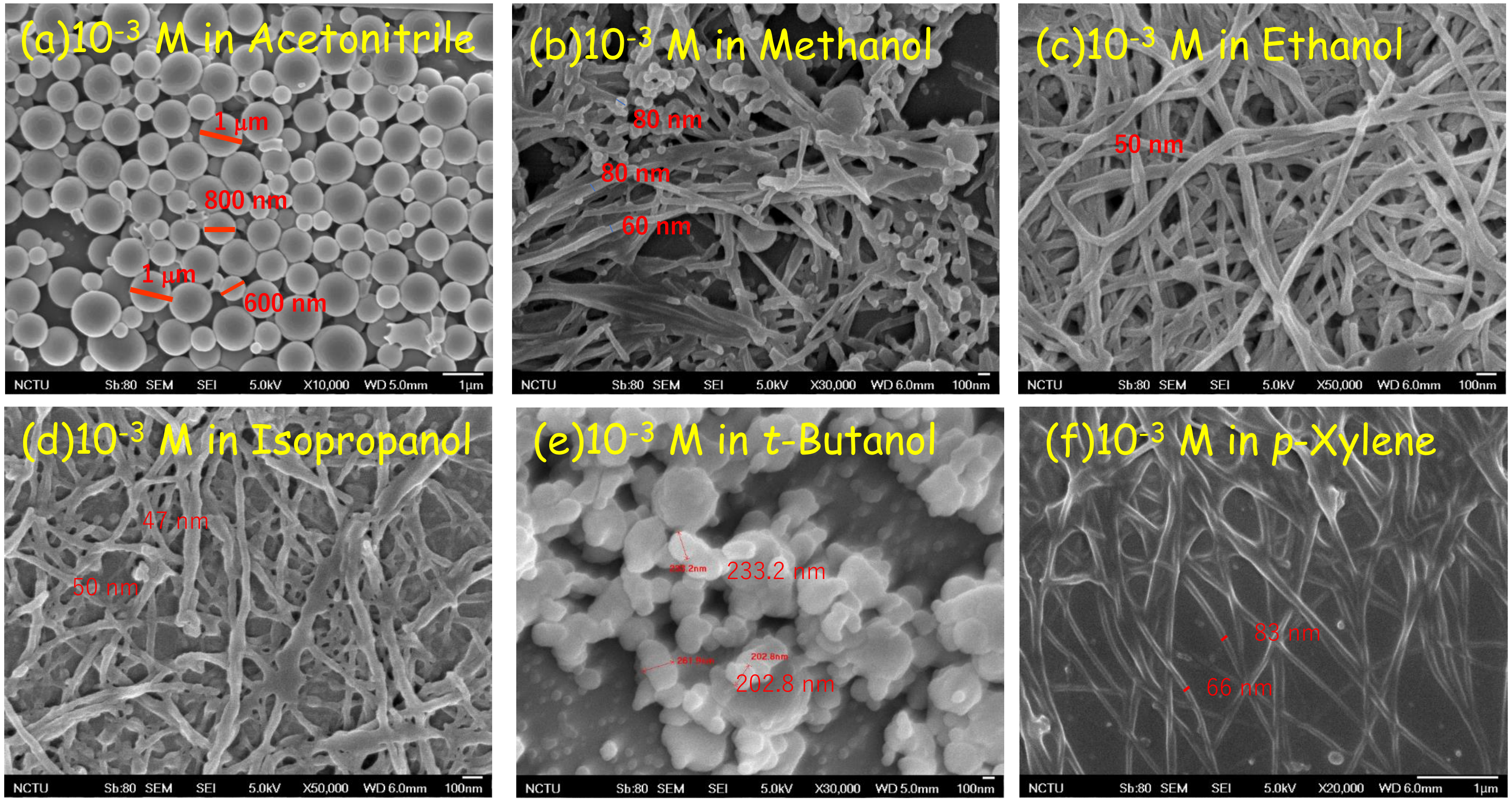
(b) Absorption spectrum of compound **7** in Acetonitrile (1 x 10 $^{-5}$ M), after UV light irradiation for 60 s, and further using tungsten irradiation for different times

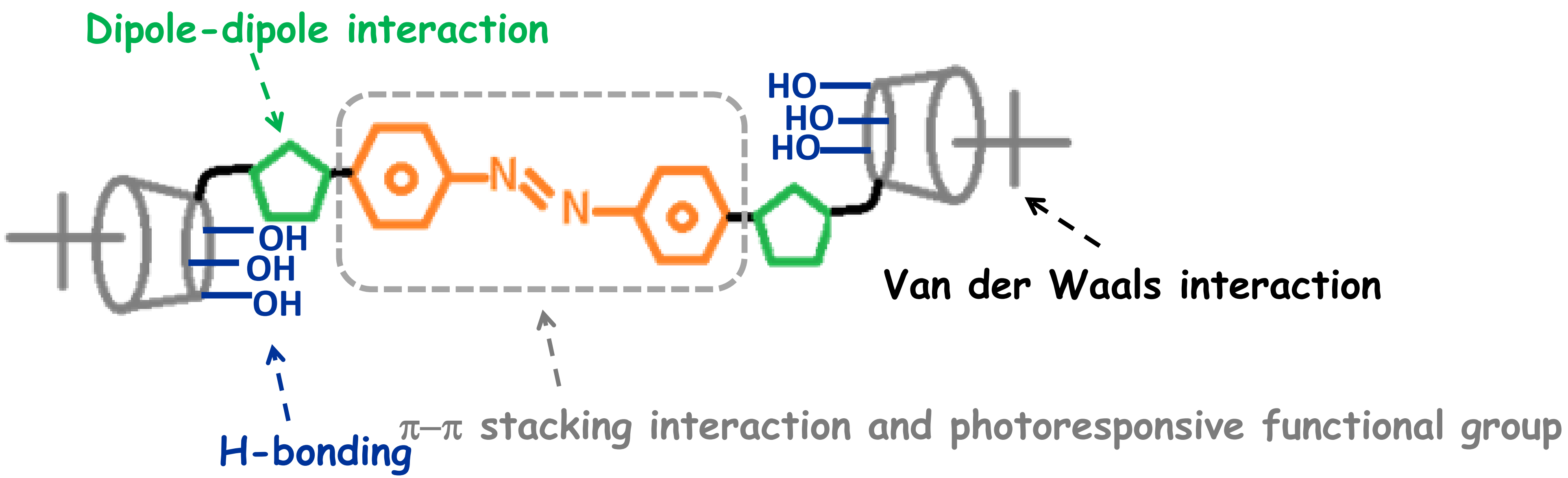
Gelation properties for compound 7 and 14 in different organic solvents

Solvent	7 (Bis-triazole)	14 (Bis-isoxazole)
CH_2Cl_2	S[a]	S
$CHCl_3$	S	S
1,2-dichloroethane	S	P
DMSO	S	S
DMF	S	S
THF	S	S
Benzene	P[b]	P
Toluene	S	P
p-Xylene	G[c] (3.73, 33 mg/mL)[d]	P
p-Dioxane	S	S
Pyridine	S	S
Ethyl acetate	S	S
Acetone	S	S
Acetonitrile	G (1.79, 14 mg/mL)	P
n-Hexane	I[e]	I
MeOH	G (0.19, 1.5 mg/mL)	I
EtOH	G (0.20, 1.6 mg/mL)	I
n-Propanol	G (0.56, 4.5 mg/mL)	P
Isopropanol	G (0.24, 1.9 mg/mL)	I
n-Butanol	G (0.87, 7.1 mg/mL)	P
t-Butanol	G(0.67, 5.3 mg/mL)	I
Cyclohexane	S	S
Cyclopentanone	S	S
Cyclohexanone	S	S

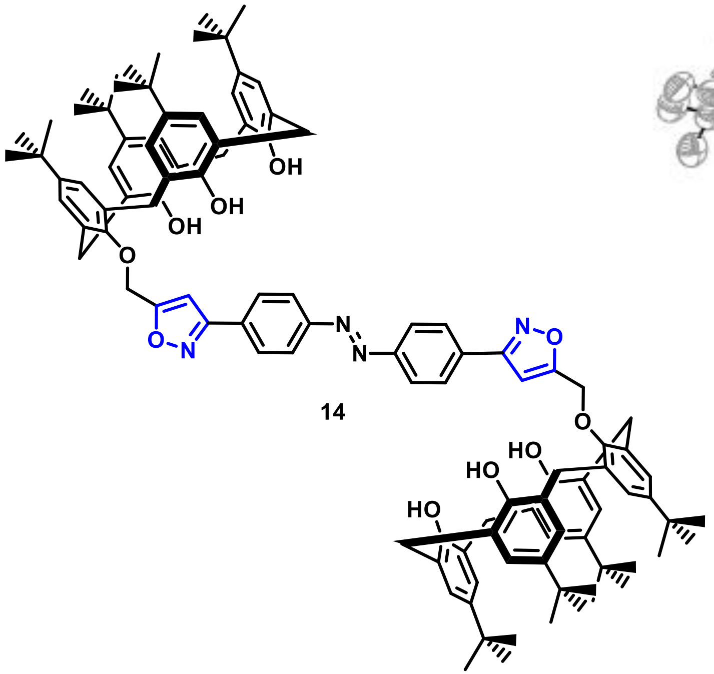
[a]S = solution (溶液); [b]P = Precipitate (沉澱); [c]G = gel (凝膠) ; [d]( ) : wt %; [e]I = Insoluble.(不溶解); [f]PG= Partial gel (部分凝膠)

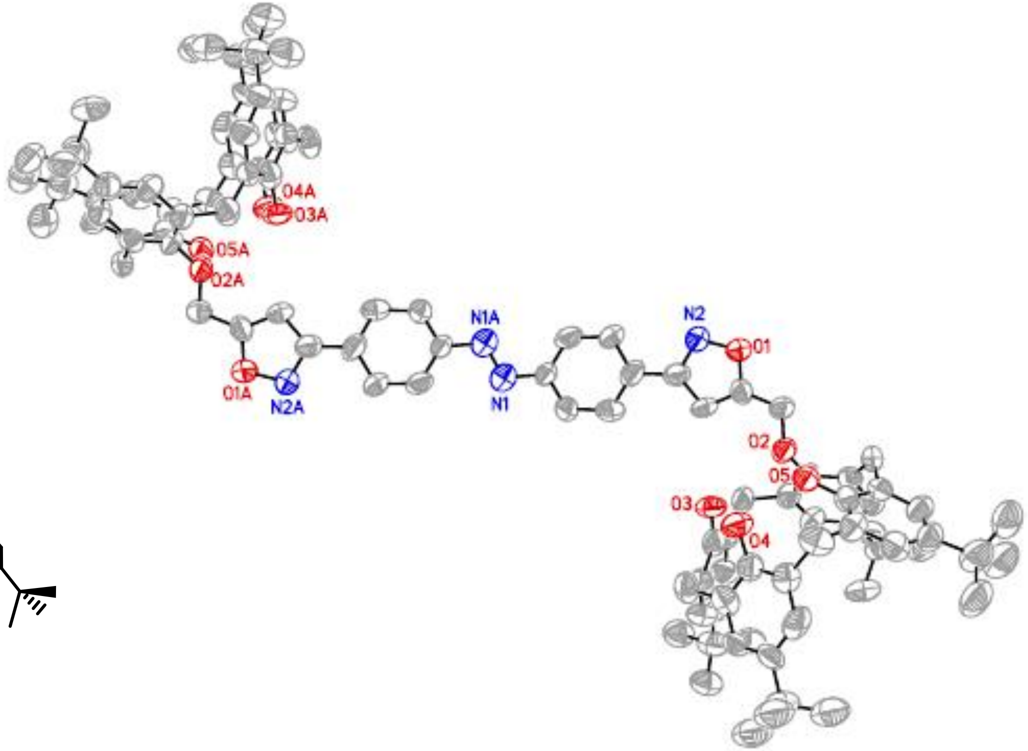
SEM images of compound 7




Dipole-dipole interaction
HO
HO
HO
N
N
OH
OH
OH
Van der Waals interaction
H-bonding
π–π stacking interaction and photoresponsive functional group

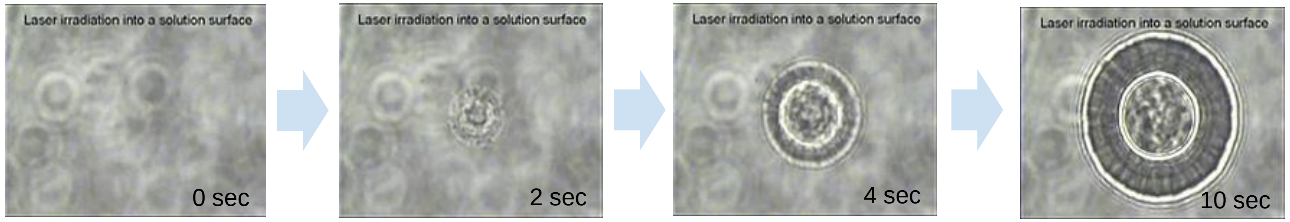
The X-ray structure of compound 14





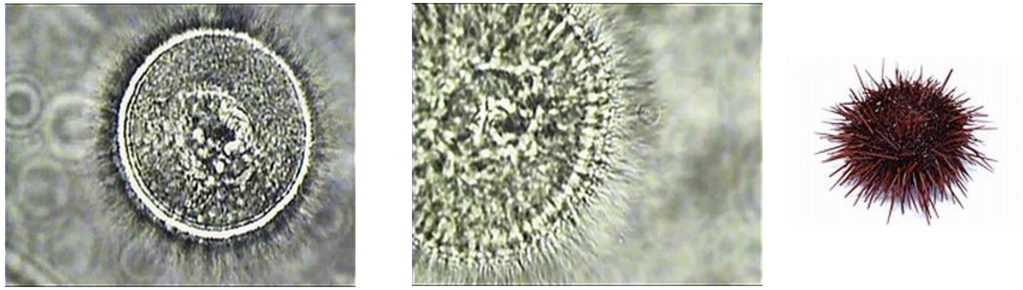
Assembly formation by laser trapping at a solution surface

Switch on trapping laser



sea urchin like structure

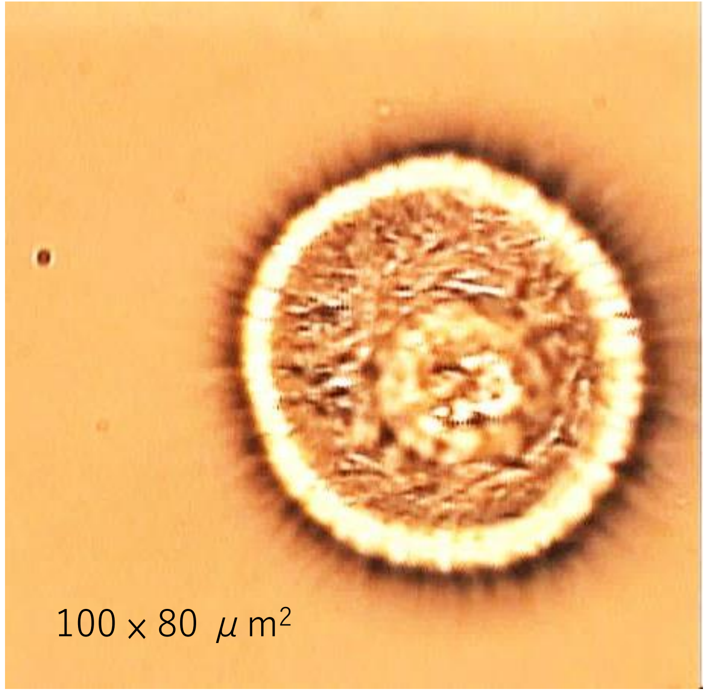
Switch off trapping laser



Size of images; 80×60 μm^2

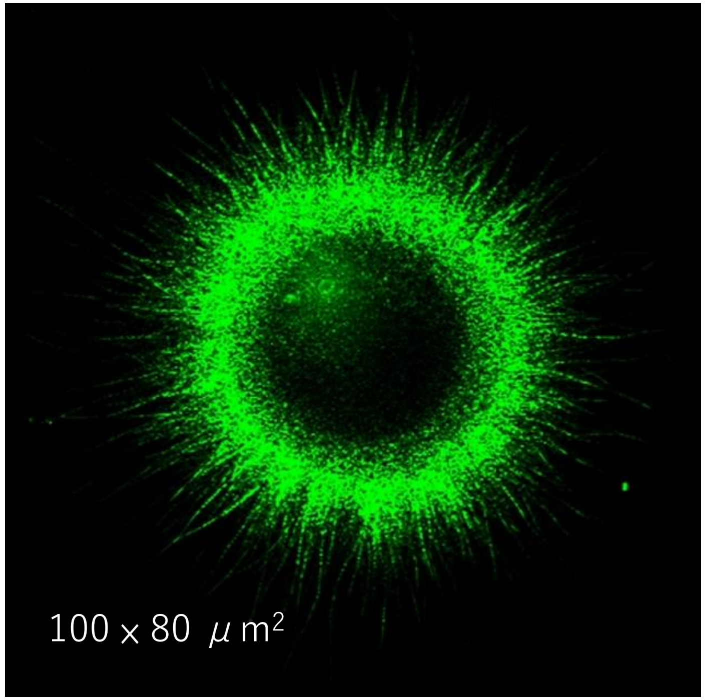
Assembly morphology after switching off trapping laser

Transmission image



Rayleigh scattering image

(with confocal scanning microscope)



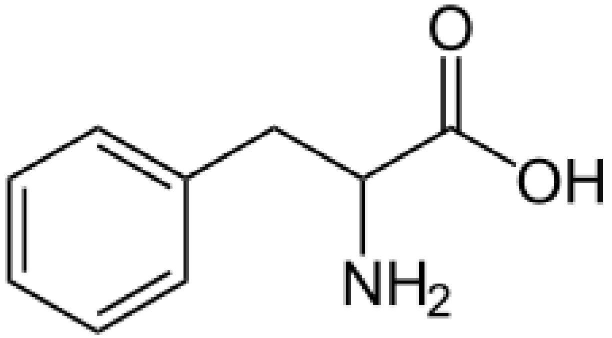
A large mm-sized domain of liquid-like clusters where crystallization takes place
at solution surface

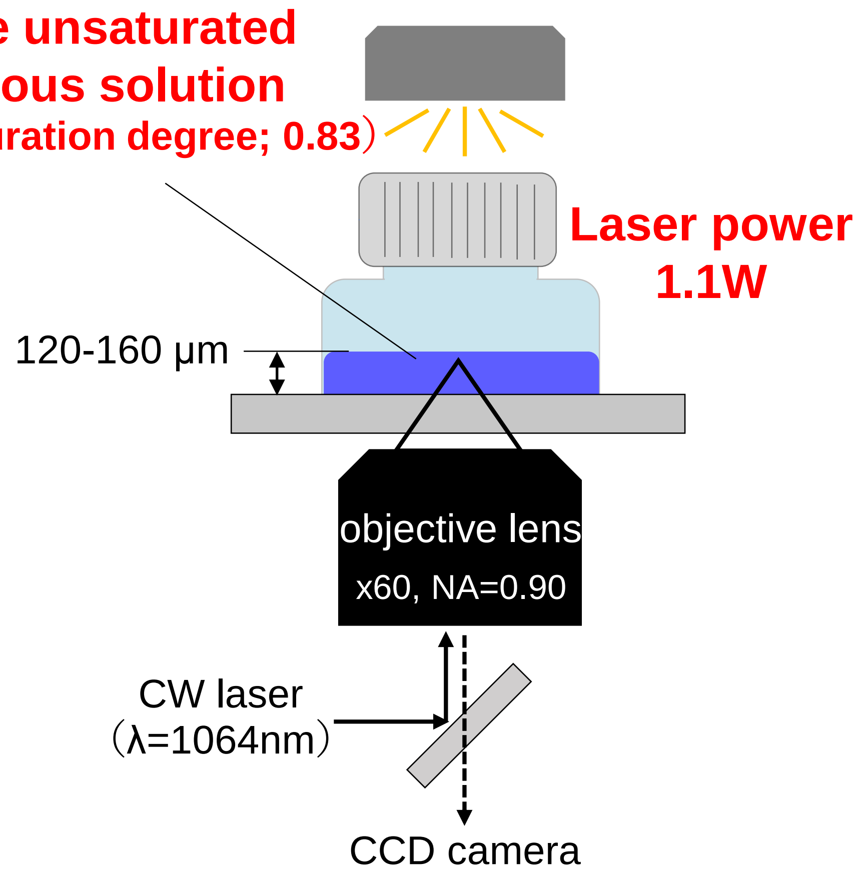
L-Phenylalanine

Yuyama, Sugiyama, Masuhara
J. Phys. Chem. Lett., 2013, 4, 2436-2444
Yuyama, George, Thomas, Sugiyama, Masuhara
Cryst. Growth Des., 2016, 16(2), 953-960

Laser trapping crystallization of L-phenylalanine

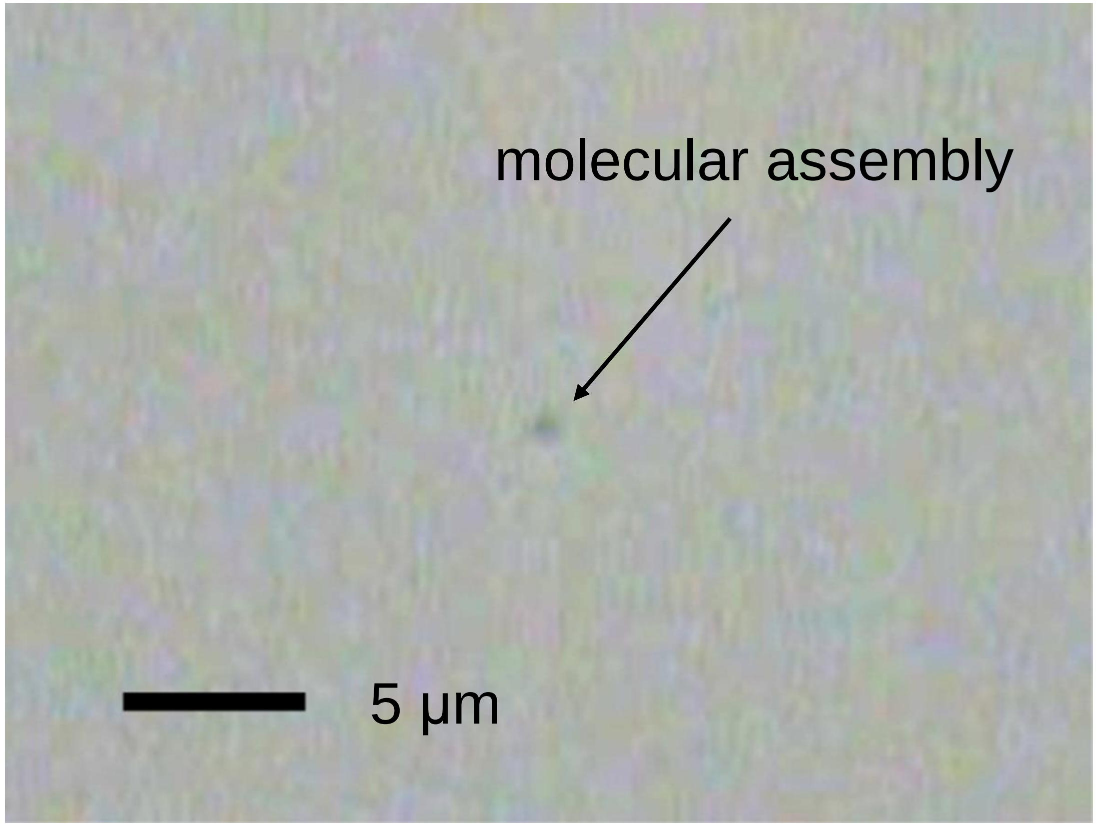
L-phenylalanine (L-Phe)





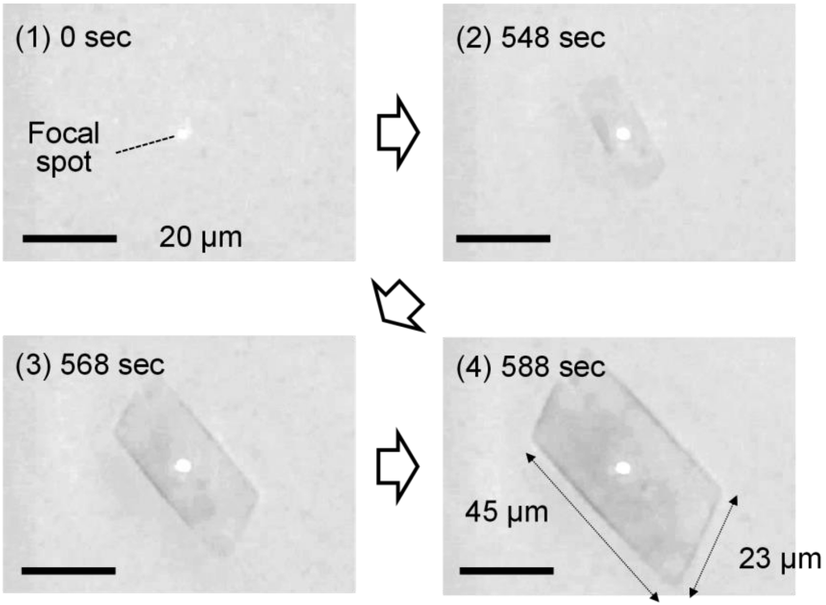
Laser trapping of L-Phe inside solution

Under unsaturated condition

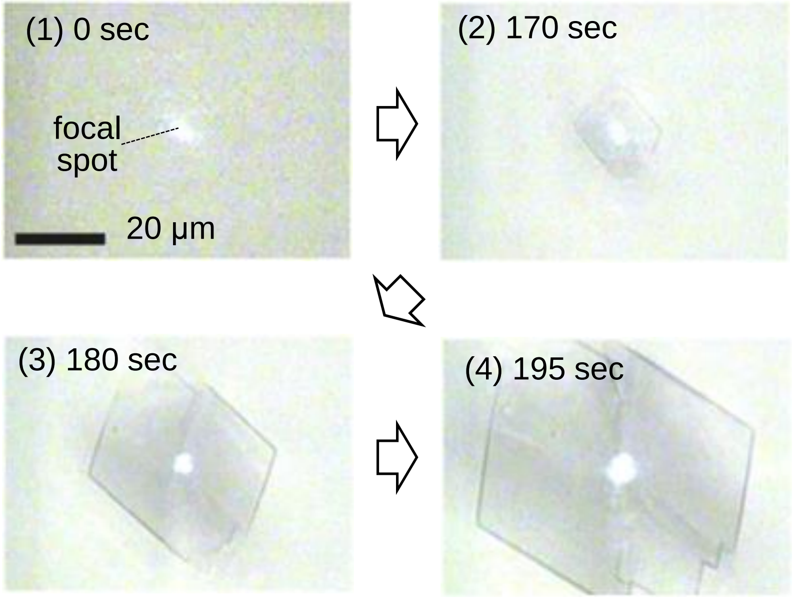


Crystallization of L-phenylalanine

Crystallization behavior (SS=0.67)



Crystallization behavior (SS=0.83)

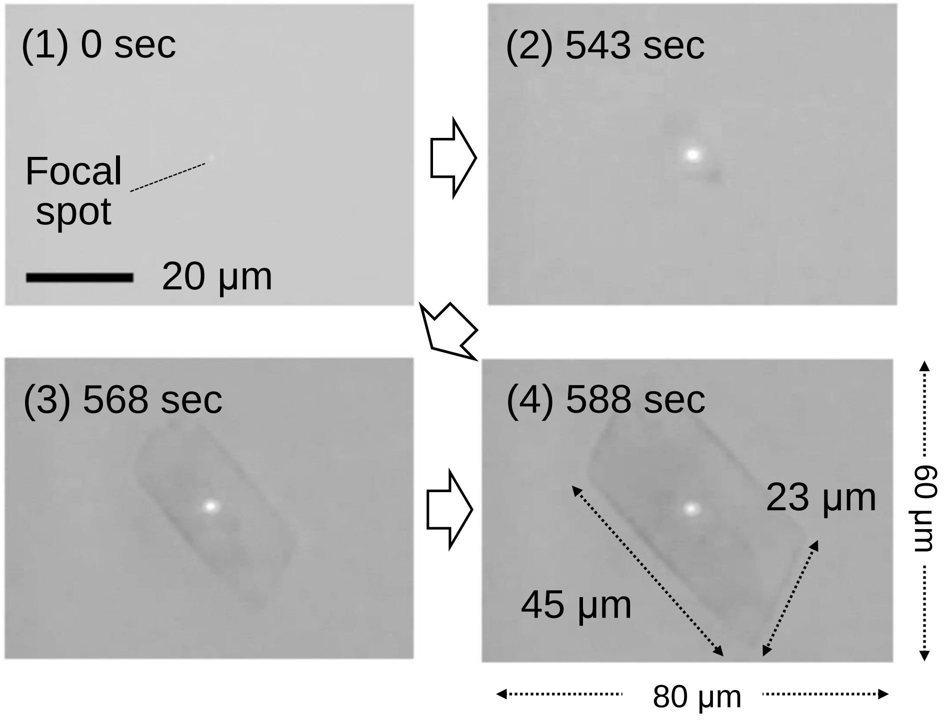


- The formation of the plate-shaped anhydrous crystal from the focal spot
- The 100% crystallization probability (unsaturated and saturated solutions)

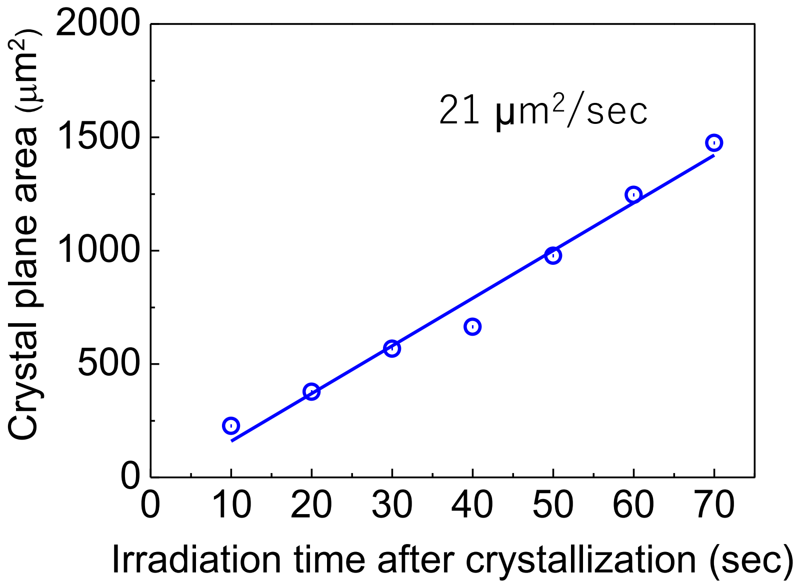
Laser trapping crystallization of L-Phe at solution surface

Under unsaturated condition

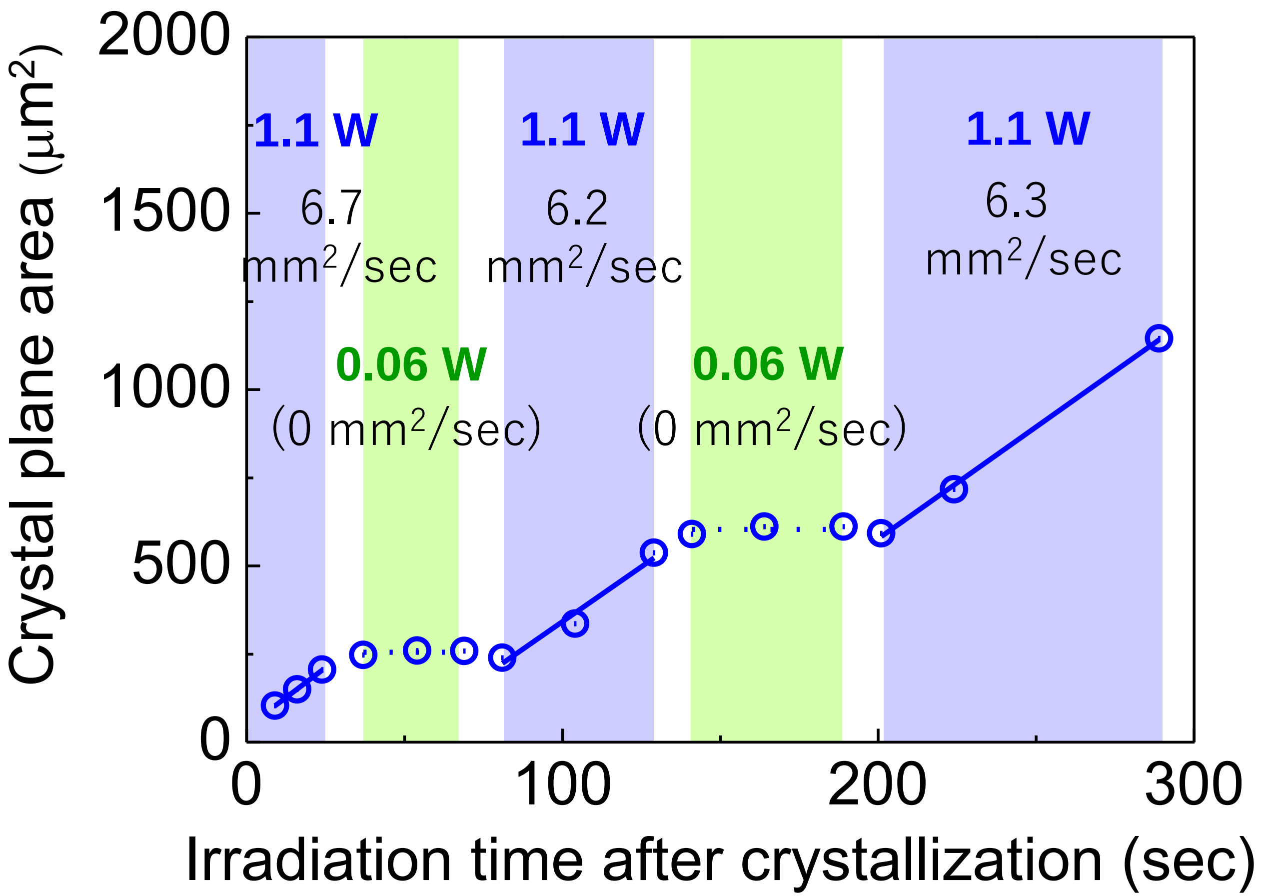
<CCD image>



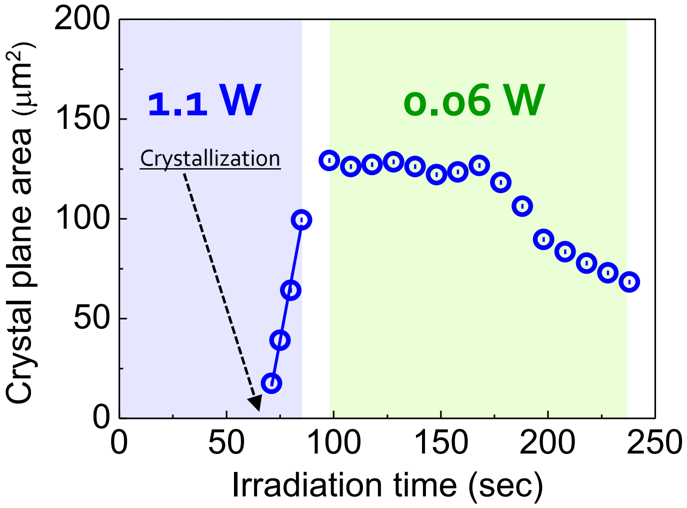
<Time evolution of crystal plane area>



Crystal growth control



Crystal dissolution



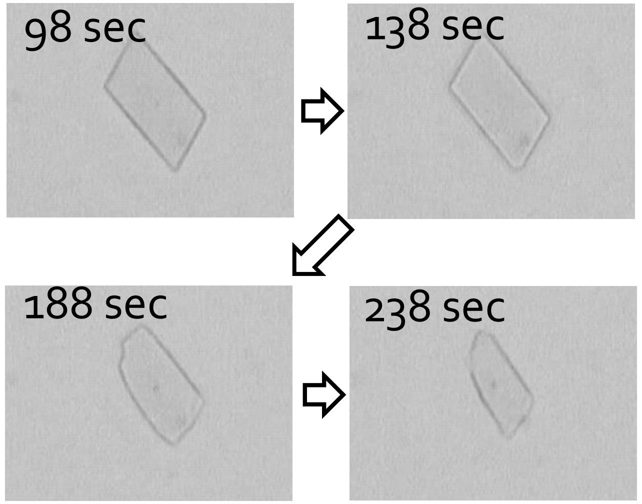
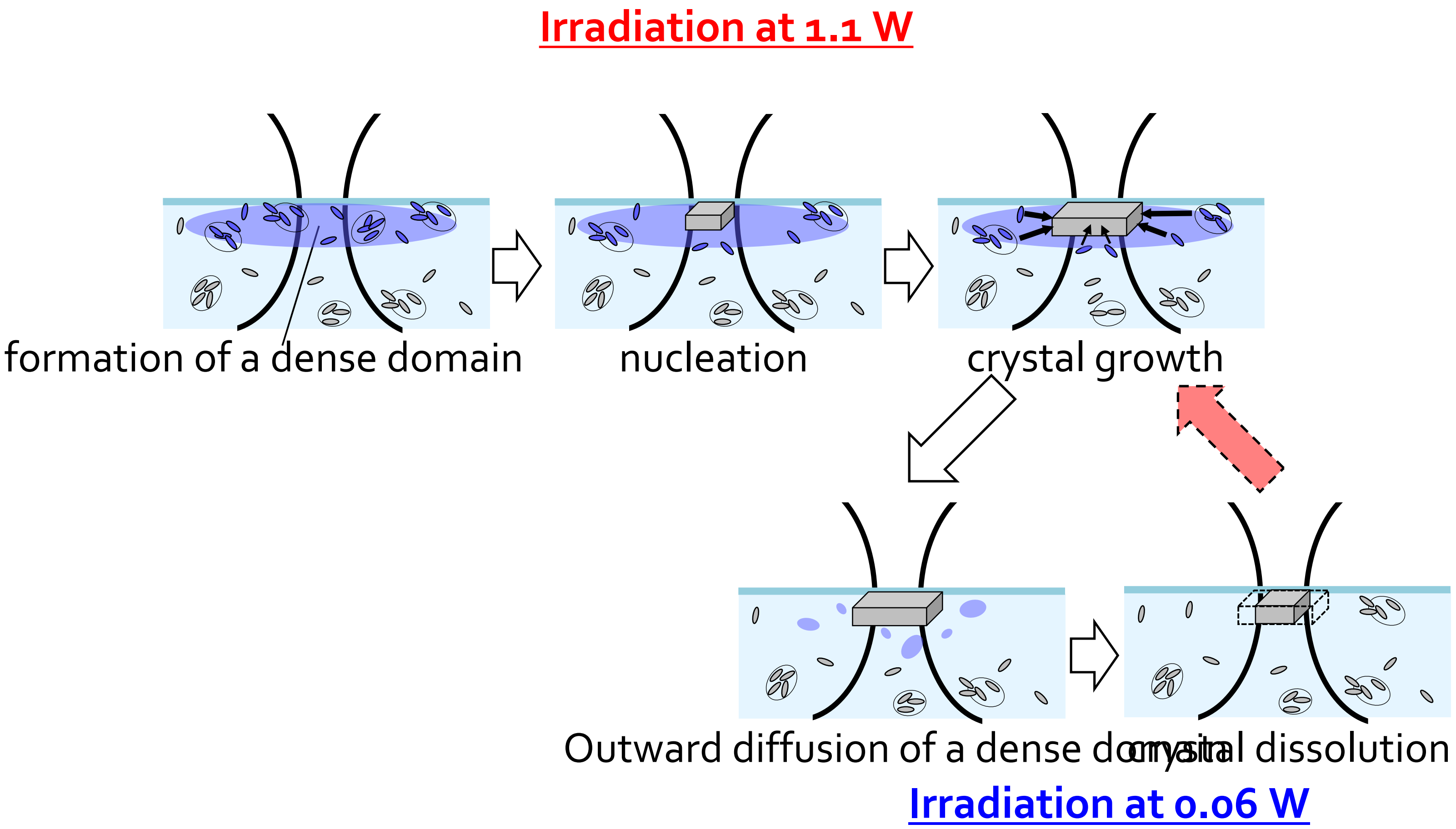


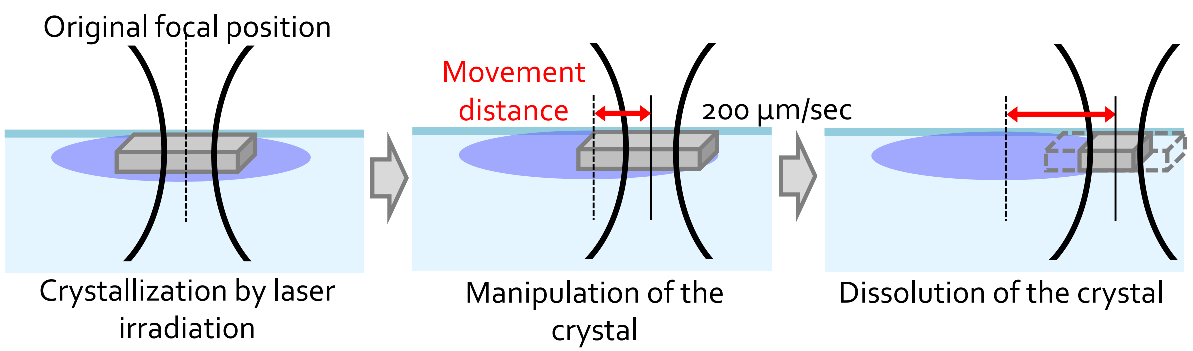
Image size; 40 × 30 μm²

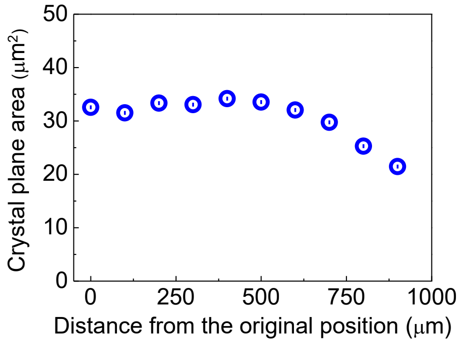
Crystal size is decreased through crystal dissolution.

Possible mechanism



A highly concentrated domain surrounding the crystal





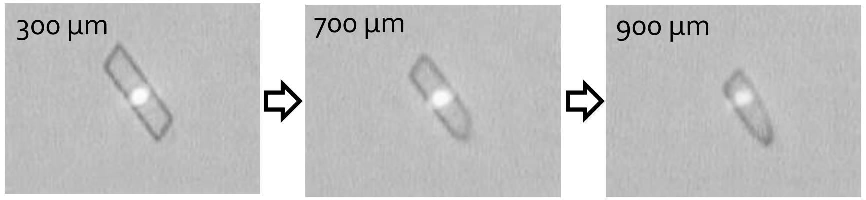


Image size; 30 × 22.5 μm²

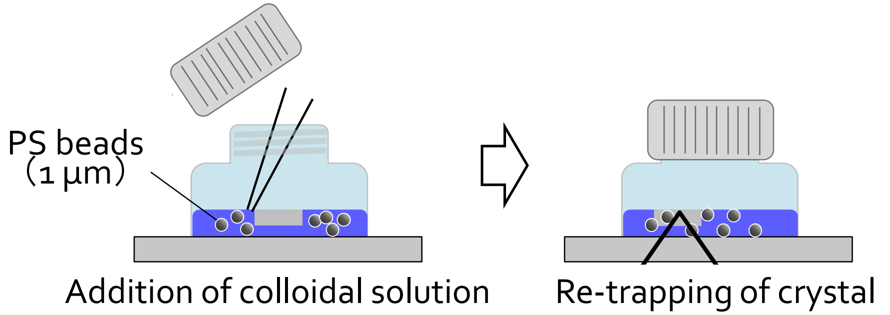
Lateral manipulation of the crystal at the surface suggests that the crystal is surrounded with a dense domain.

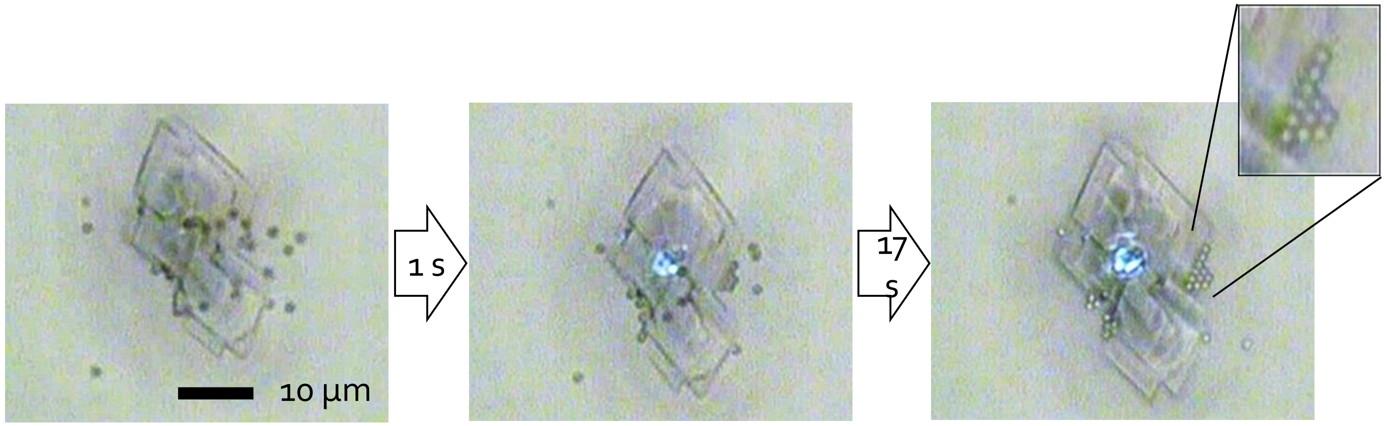
Laser trapping coupled with optical scattering/propagation gives a single crystal at solution surface

L-Phenyalanine

Yuyama, Sugiyama, Masuhara
J. Phys. Chem. Lett., 2013, 4, 2436-44
Yuyama, George, Thomas, Sugiyama, Masuhara
Cryst. Growth Des., 2016, 16(2), 953-960

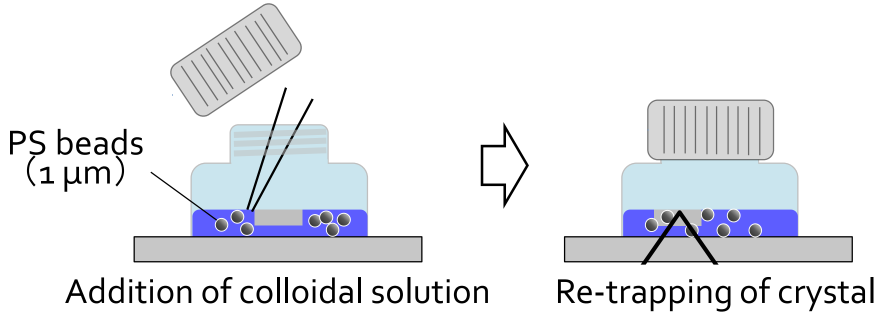
Trapping at the crystal edge (1.1 W)



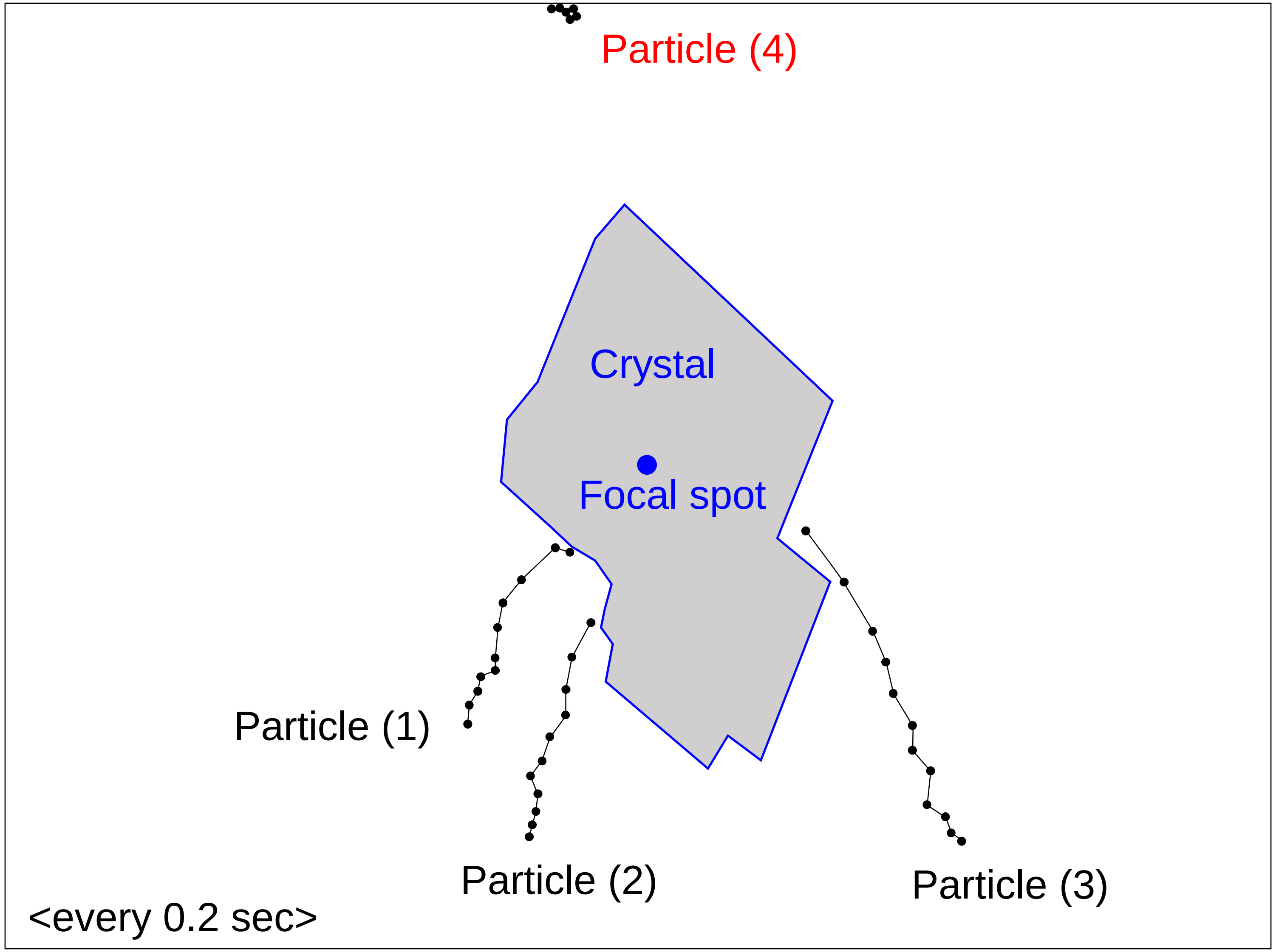


Trapping at the crystal edge is possible.

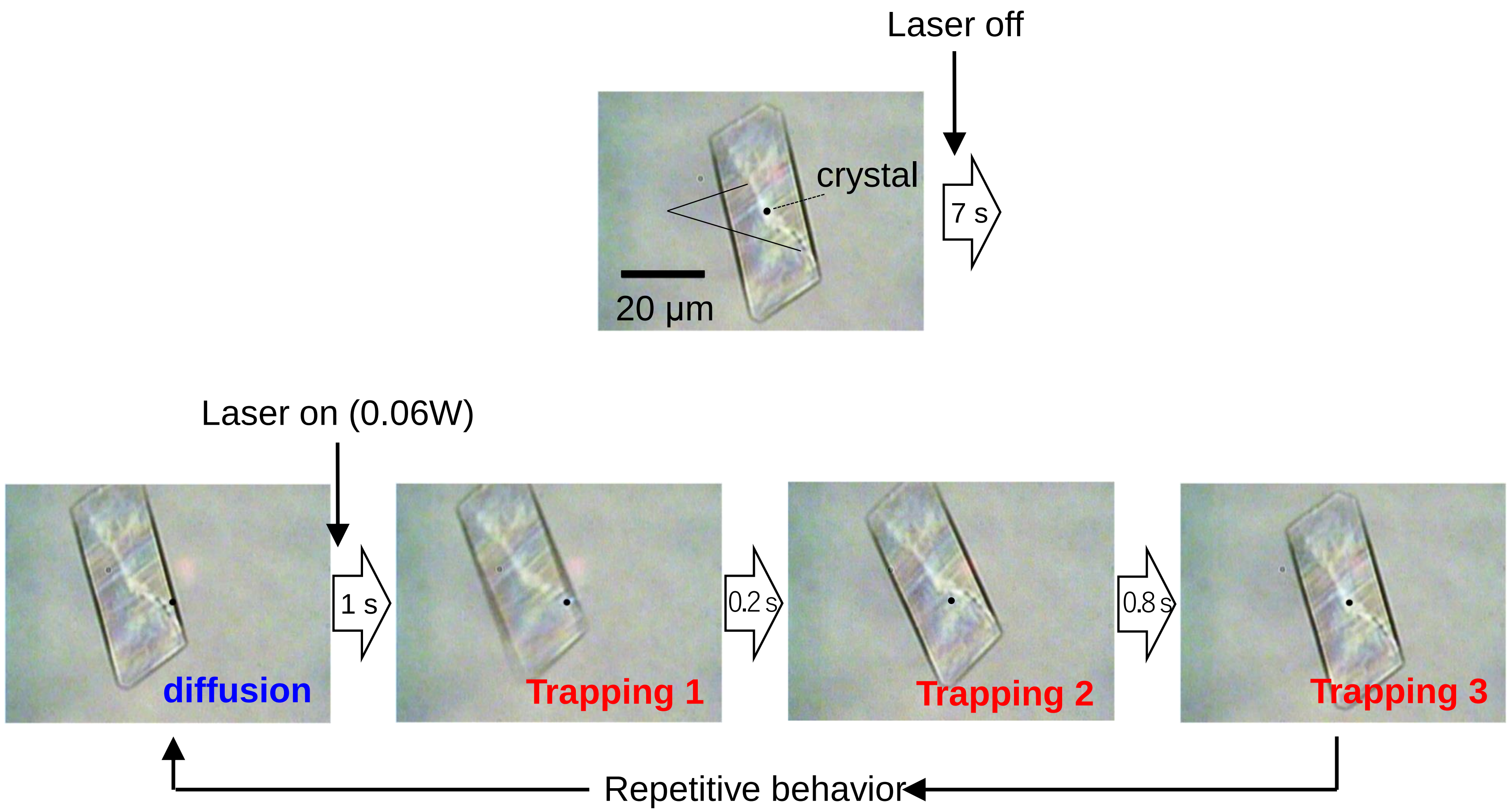
Trapping at the crystal edge



Trajectories of PS beads



Laser trapping of L-Phe crystal



Trapping site shift from the focal point to the edge surface of the growing crystal

(1) Crystallization

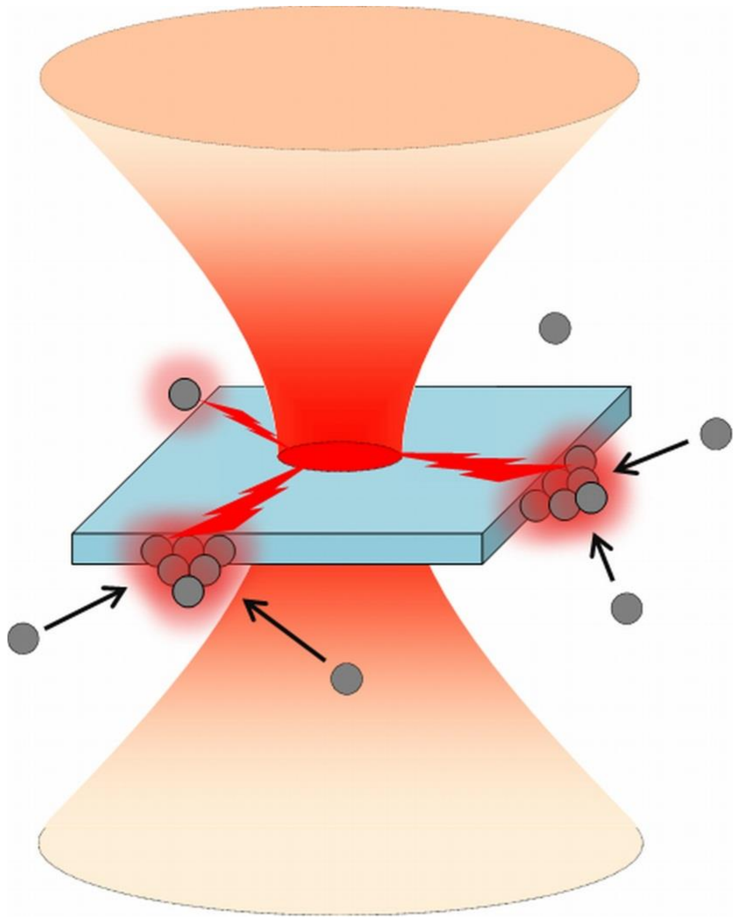
(2) Crystal growth

- Crystal nature of L-Phe
- Trapping laser

peculiar structure

(3) Efficient light scattering
or light propagation

(3) Further crystal growth

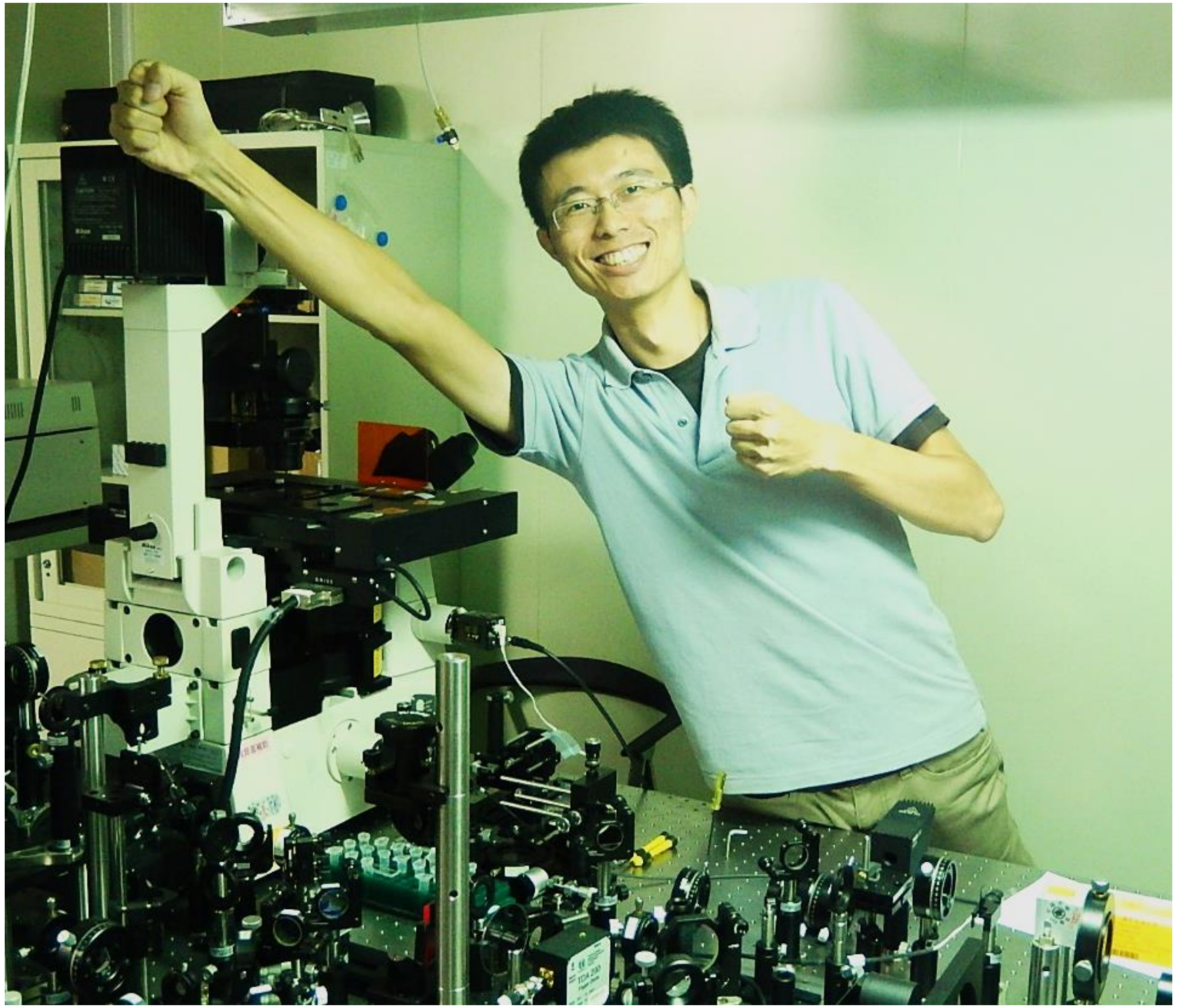


Laser trapping coupled with optical scattering and propagation gives a single assembly at solution surface

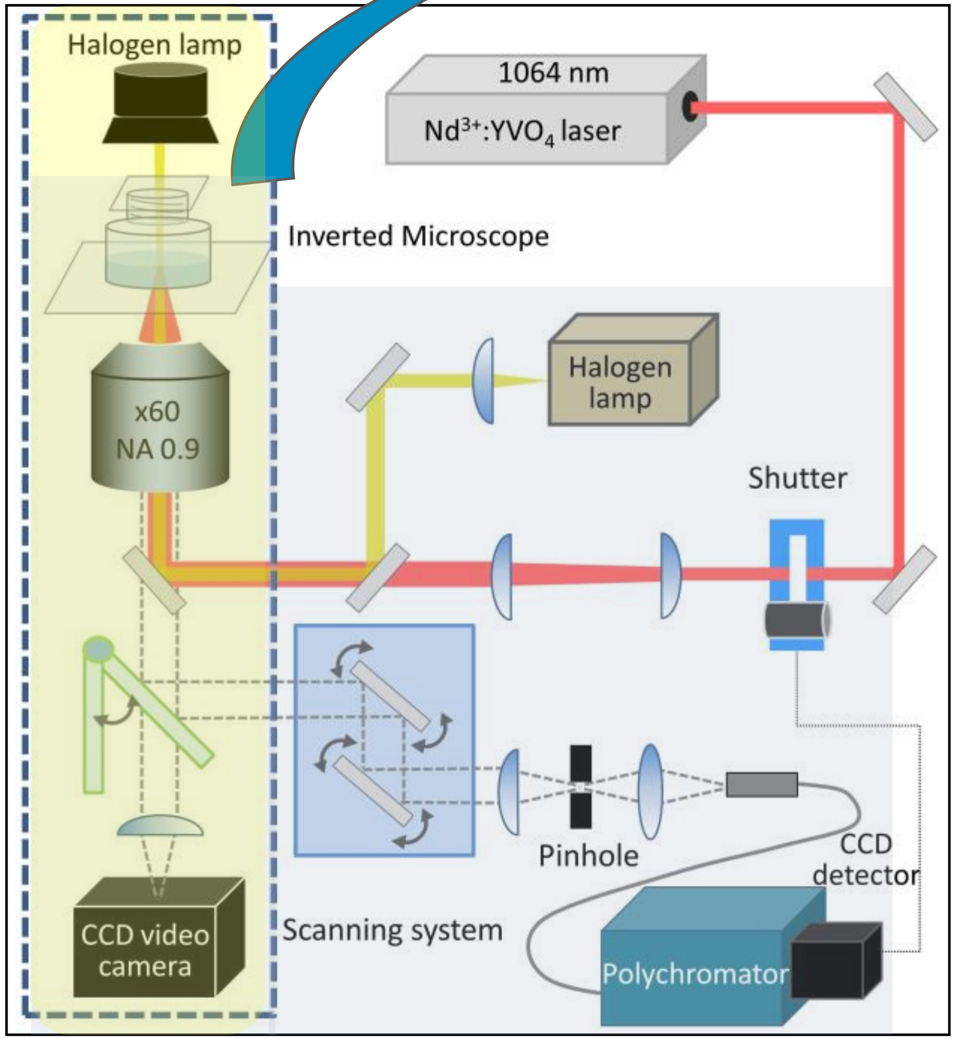
Polystyrene nanoparticles

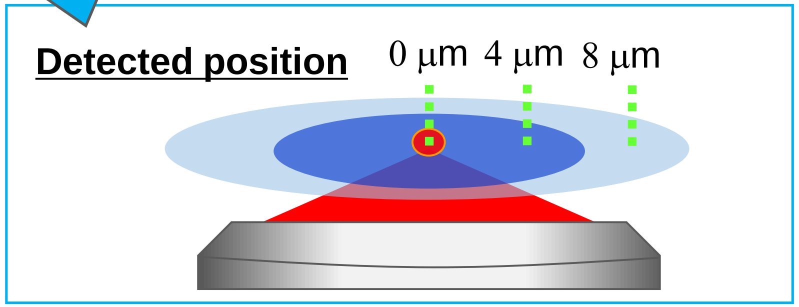
Wang, Yuyama, Kudo, Sugiyama, Masuhara
J. Phys. Chem. C, 2016, 120, 15578-15585
Wang, Yuyama, Kudo, Sugiyama, Masuhara
Langmuir, 2016, in press

Mr. Shun-Fa WANG, Ph. D. student getting the degree this autumn.



Experimental Setup





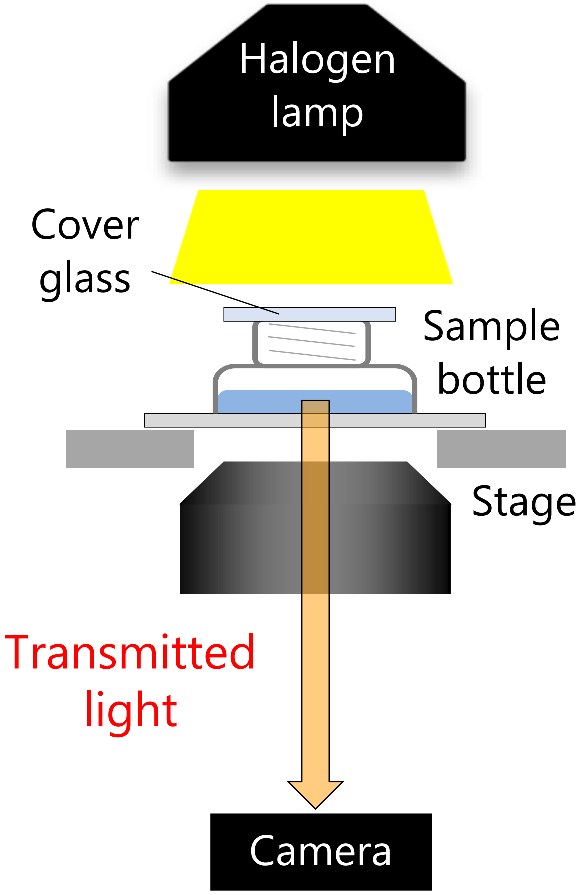
Laser power: 1.4 W

Sample:
208 nm Polystyrene beads in D_2O solution

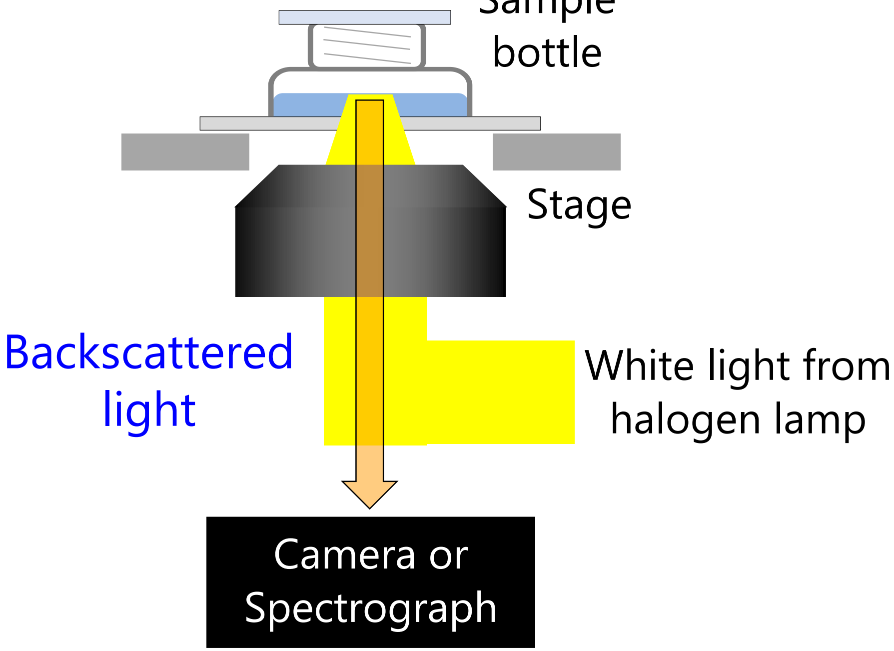
Particle concentration:
2.0×10^{11} particles/ml
(0.20 particles/μm^3)

Observation Methods of Trapping Dynamics

Transmission imaging



Imaging and spectroscopic analysis of backscattered light



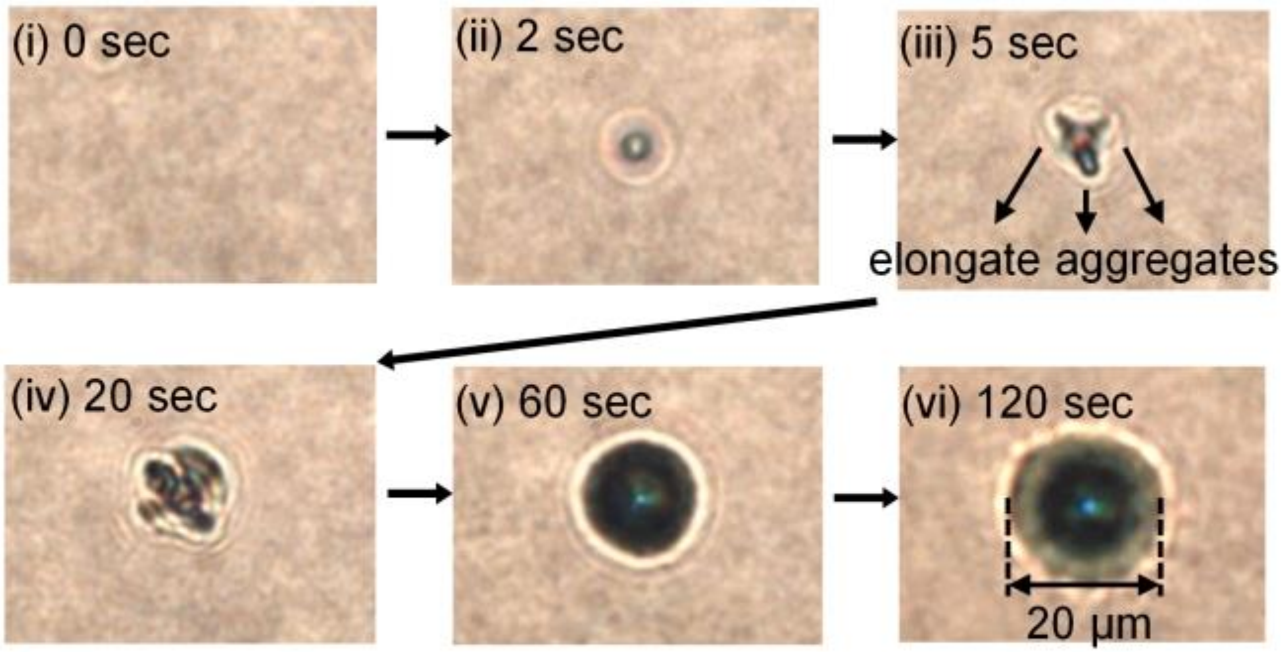
Transmission Imaging of Nanoparticle Assembly Formation

2X Speed

Halogen lamp illumination from top side

20 μm

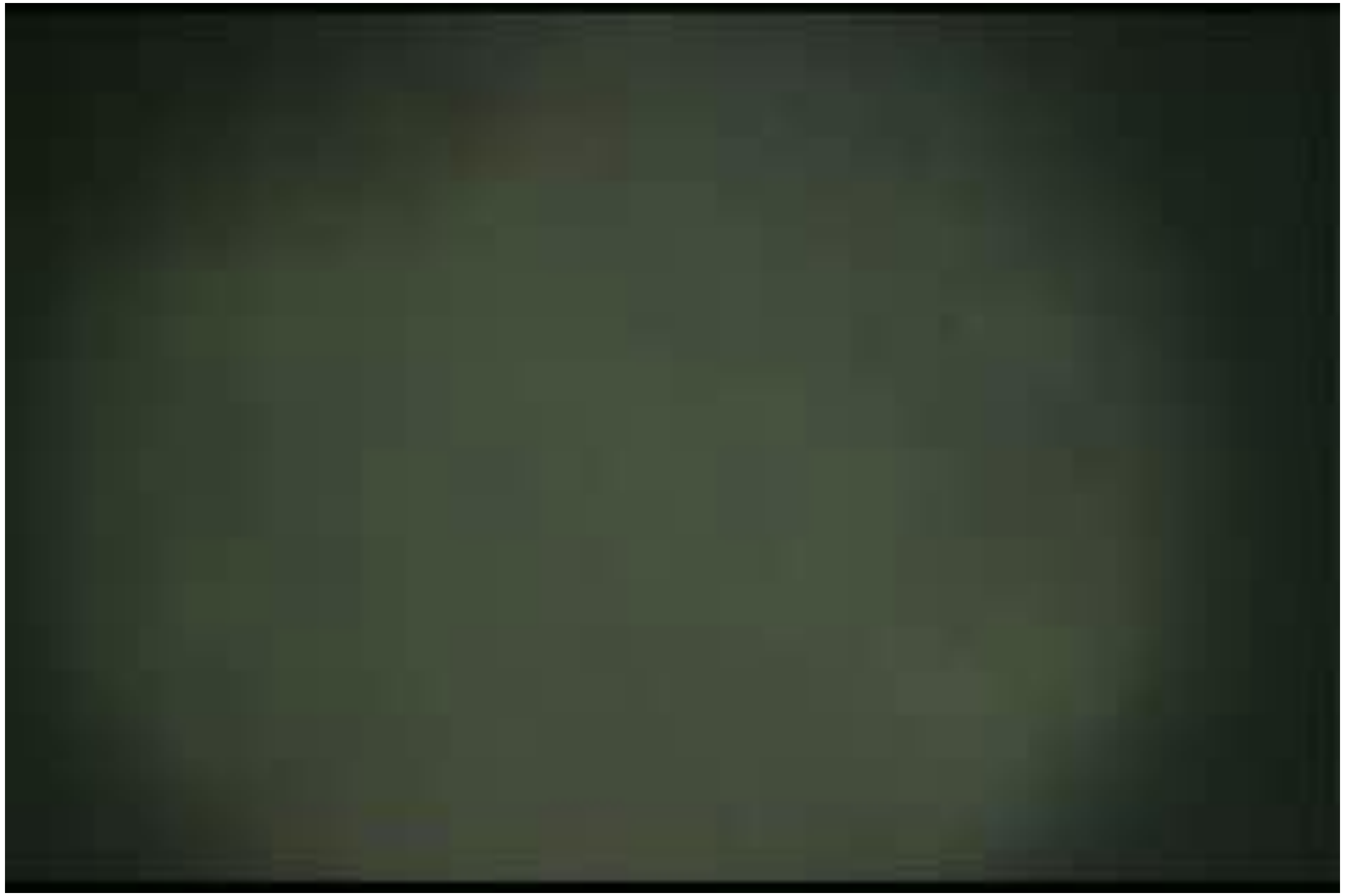
Transmission Images of Nanoparticle Assembly Formation



- Nanoparticle assembly showed coloration, although polystyrene nanoparticles have less absorption in visible region.

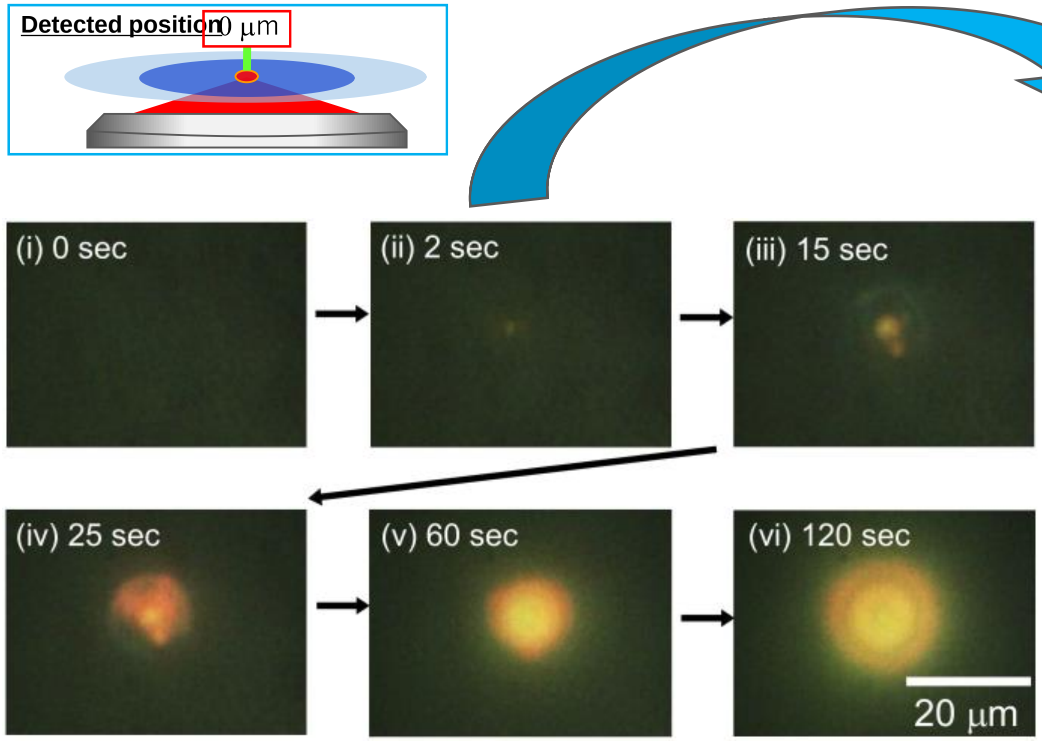
➡ Coloration on the assembly may be <u>structural color</u>.

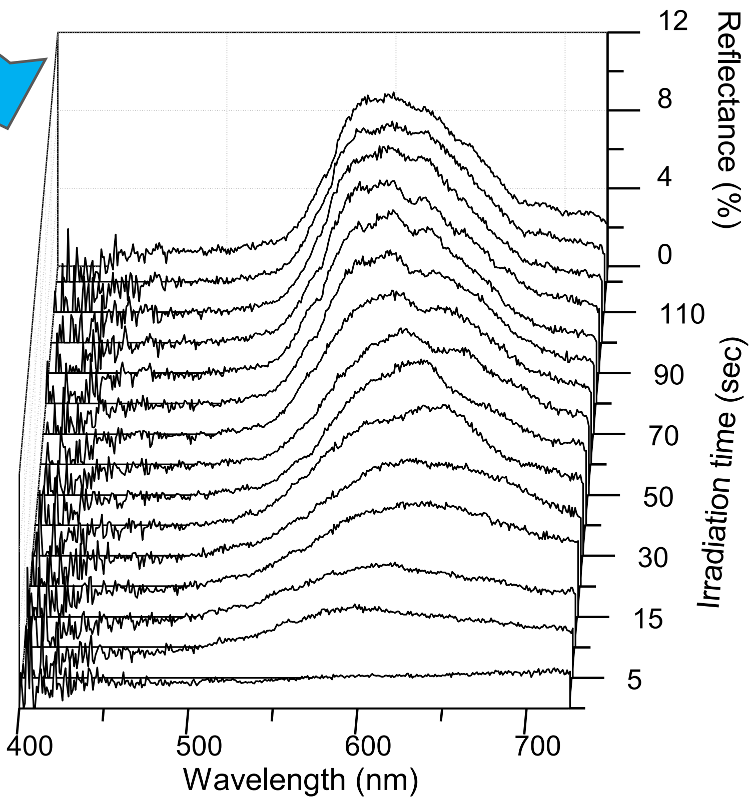
Backscattering Imaging of Nanoparticle Assembly Formation



Halogen lamp illumination from back side (through objective lens)

Backscattering Images and Reflection Spectra of Nanoparticle Assembly Formation

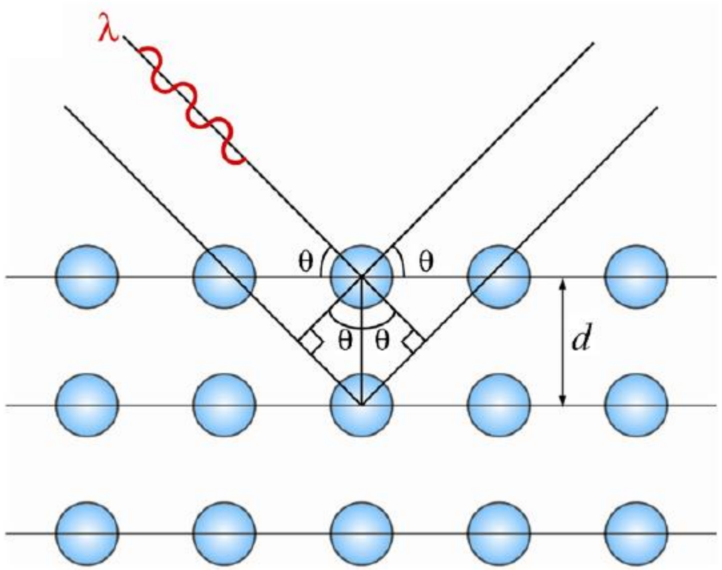




- **Reflectance band appeared at 600 nm.**

It implies that an ordered structure like a colloidal crystal was formed in the assembly.

Bragg's Law for Colloidal Crystal



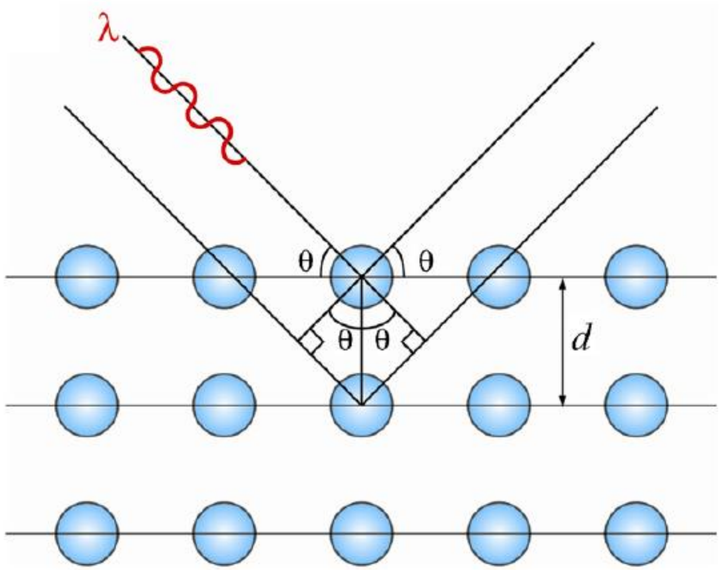
Sensors and Actuators B 125 (2007) 589–595

Bragg's law:

$$m\lambda = 2nd\sin\theta$$

m: diffraction order
λ: wavelength of diffracted light
n: refractive index of the colloidal crystal
d: inter-particle distance
θ: incident angle of light

Bragg's Law for Colloidal Crystal



Sensors and Actuators B 125 (2007) 589–595

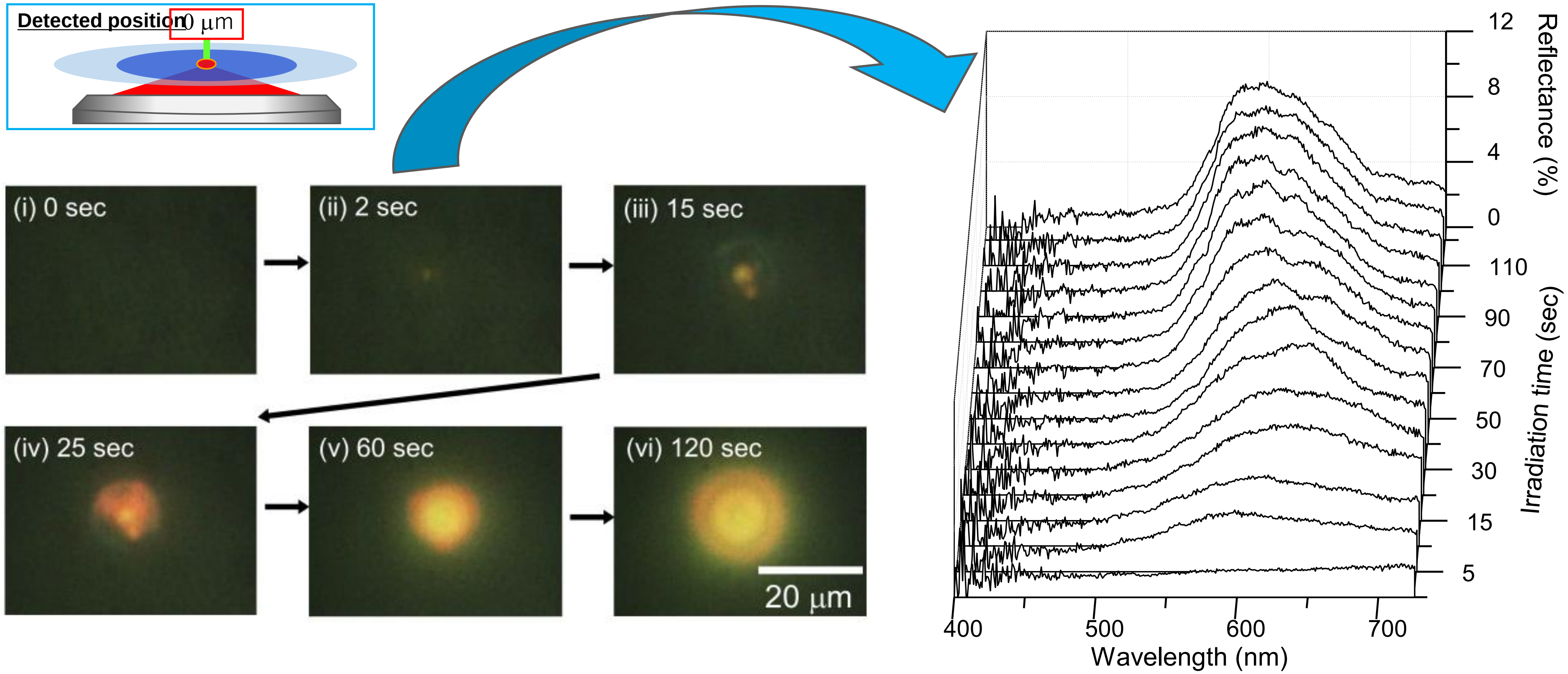
Bragg's law:

$$m\lambda = 2nd\sin\theta$$

~~*m*: diffraction order~~
λ: wavelength of diffracted light
~~*n:* refractive index of the colloidal crystal~~
d: inter-particle distance
~~*θ*: incident angle of light~~

In colloidal crystal, the wavelength of reflected light is shifted to shorter wavelength with the decrease in particle distance.

Backscattering Images and Reflection Spectra of Nanoparticle Assembly Formation



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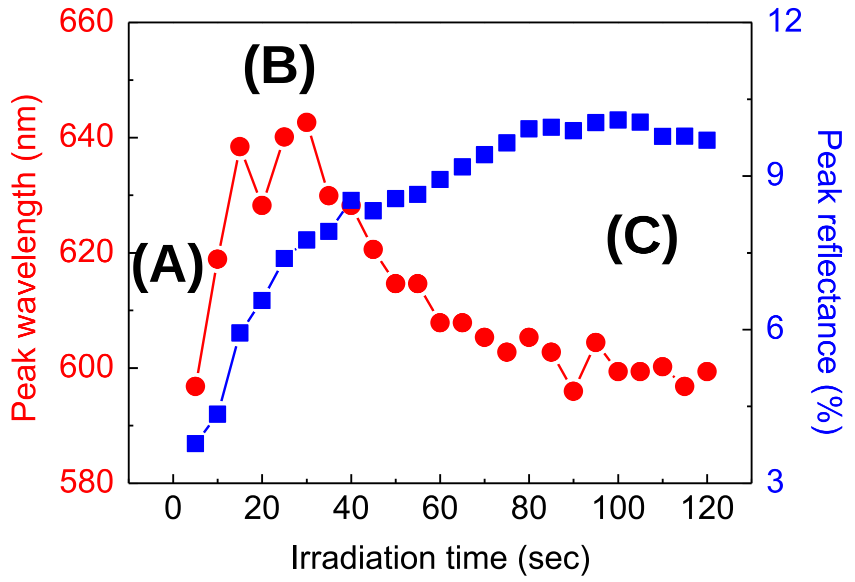
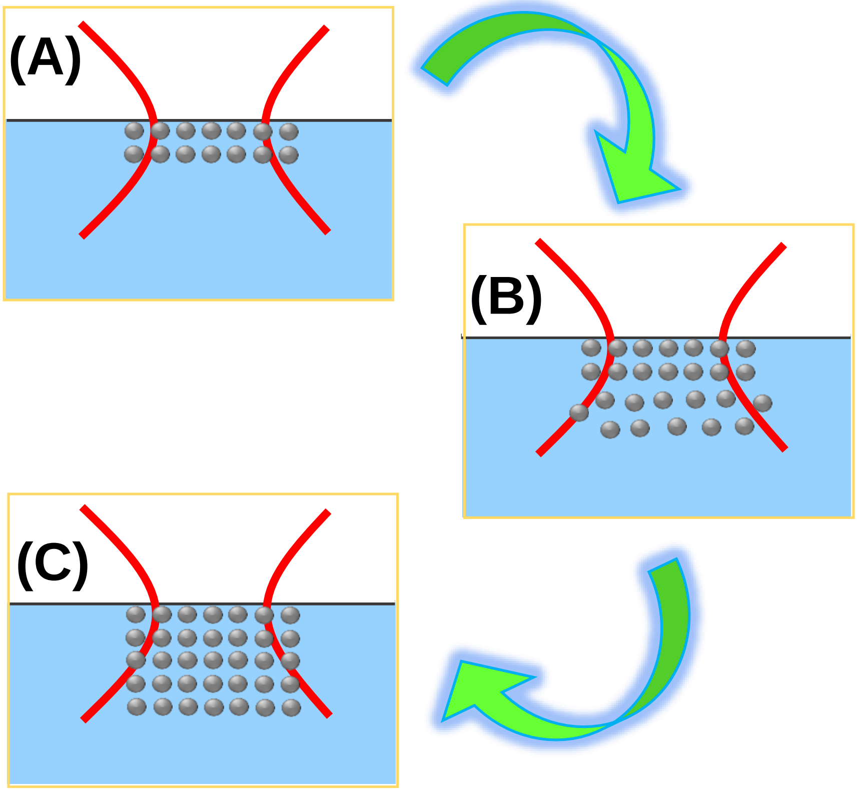
It implies that an ordered structure like a colloidal crystal was formed in the assembly.

Analysis of Time Evolution of Reflection Spectra

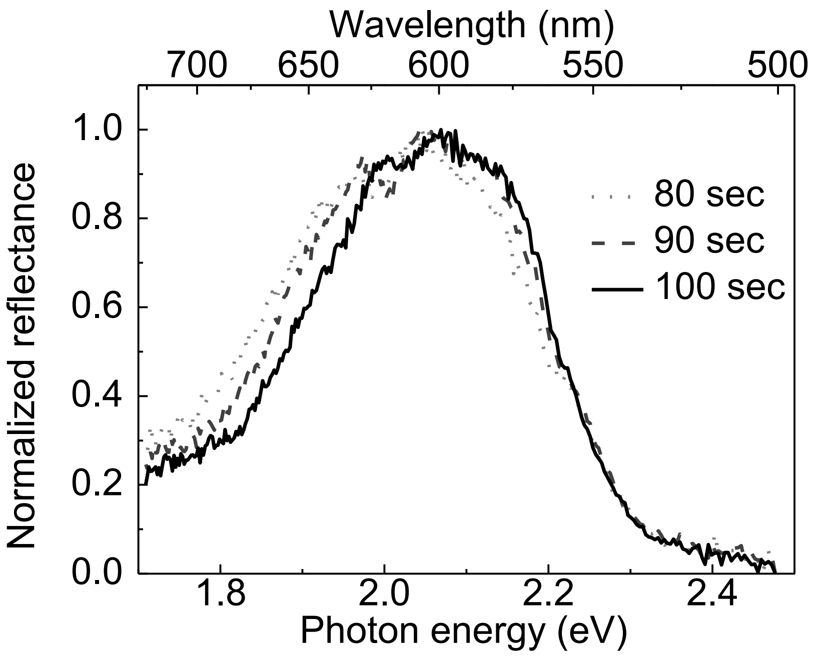


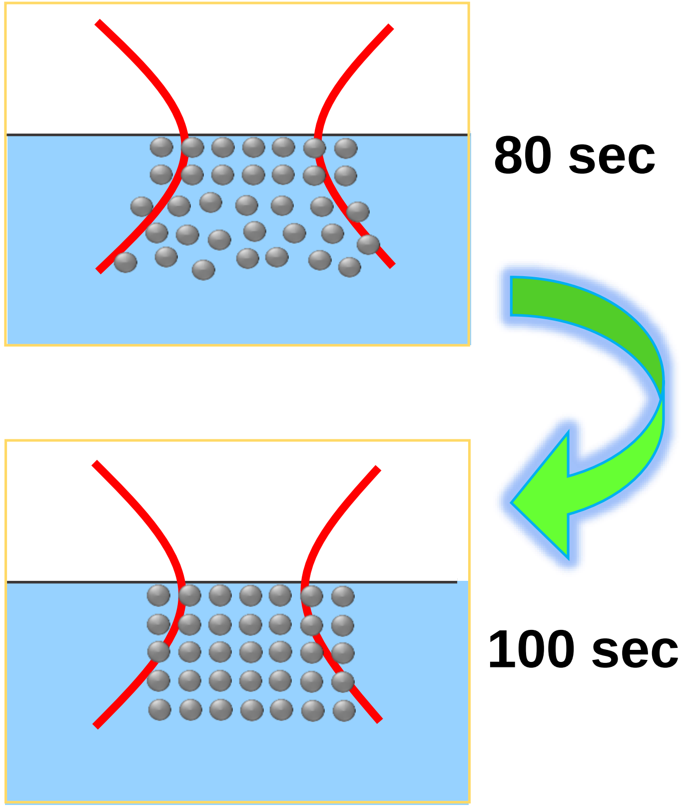


- ➢ **Increase in peak reflectance**
- ➢ **Blue shift of peak wavelength**

- **Increase in assembly thickness**
- **Decrease in particle distance**

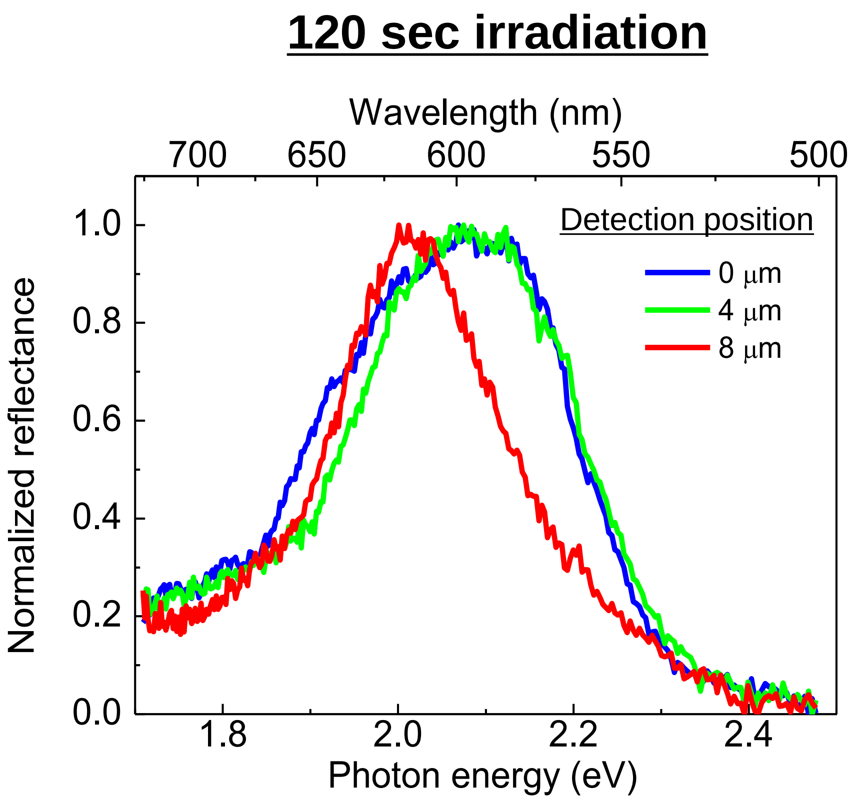
Analysis of Time Evolution of Reflection Spectra

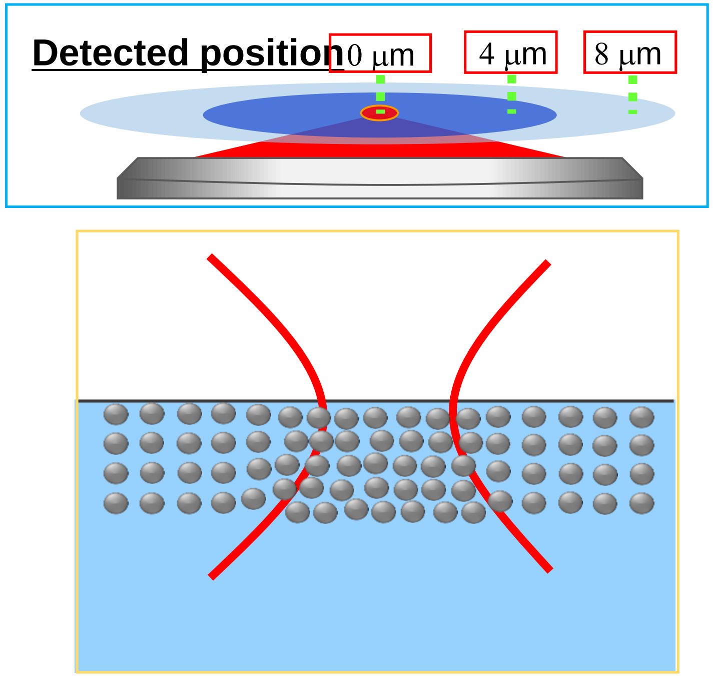




- **Narrowing of band width** → **Increase in homogeneity of particle packing structure**

Reflection Spectra at Different Positions

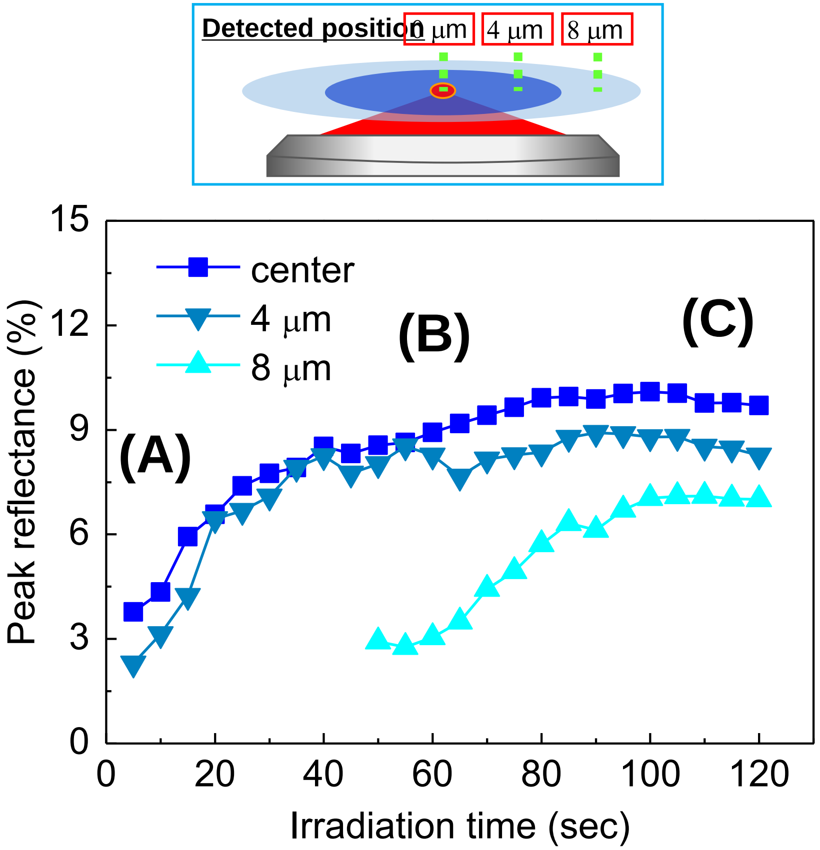


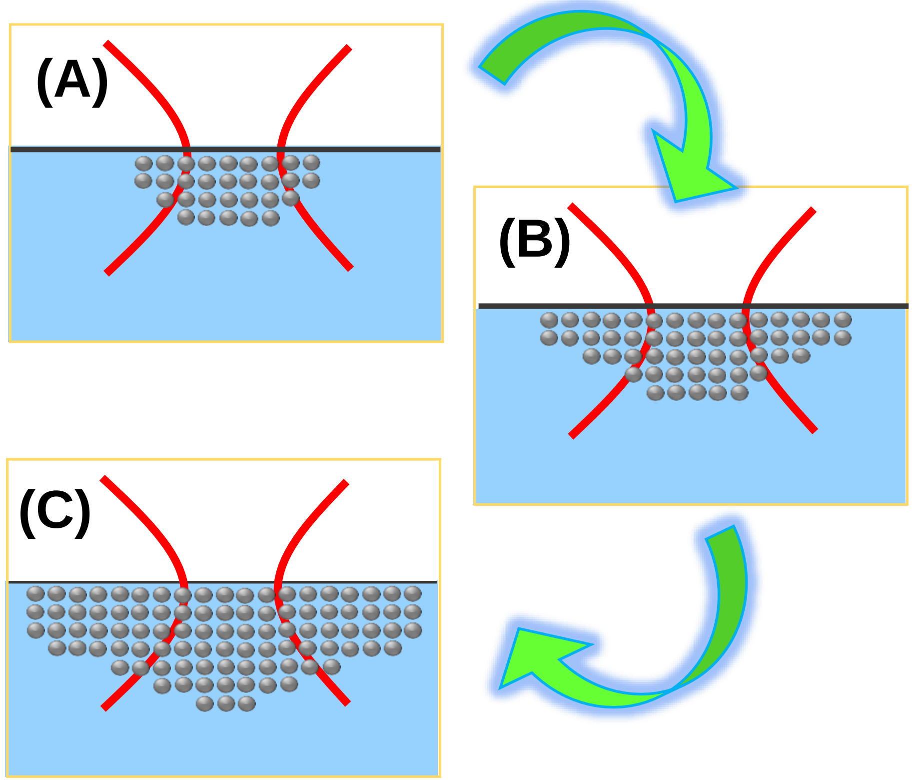


- **In normalized spectra, reflection band at the boundary of the assembly was narrower compared to that of the assembly center.**

Homogeneity of the assembly structure becomes better toward the assembly boundary.

Reflection Spectra at Different Positions

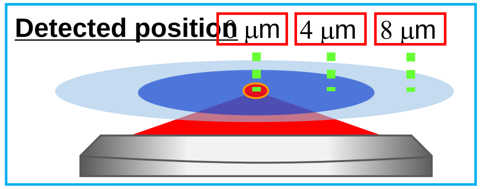


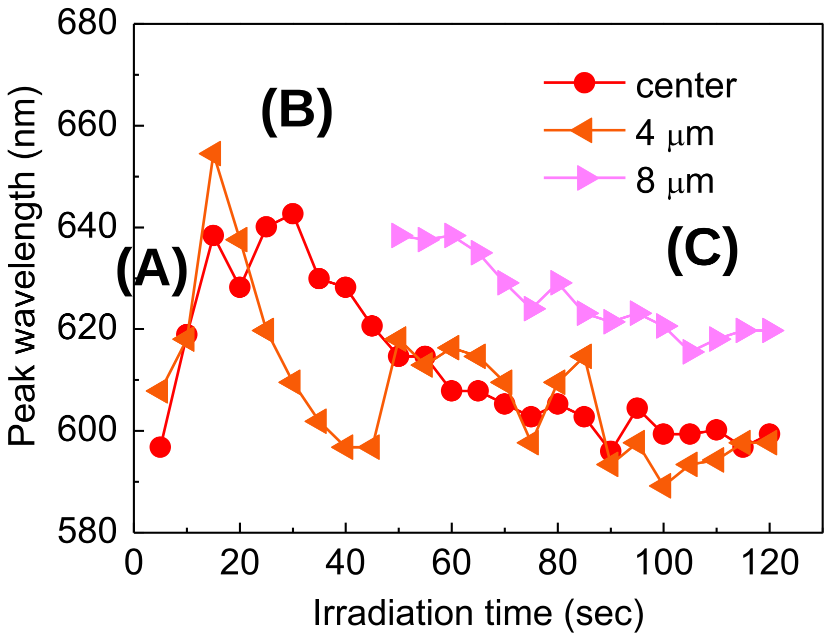


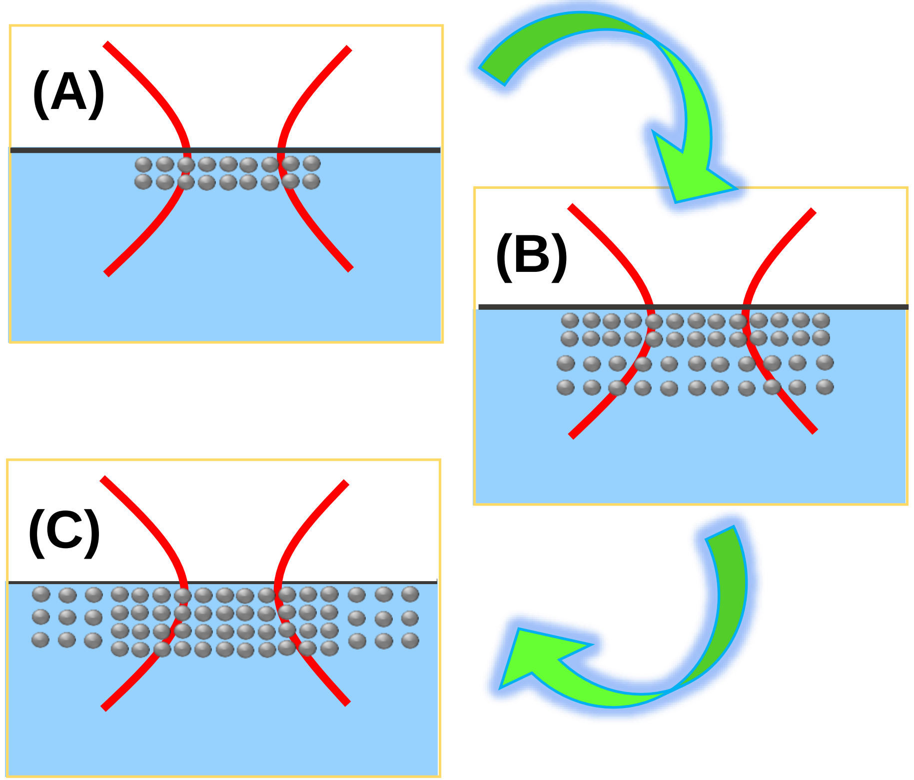
➢ **Peak reflectance decreased along the assembly center to the boundary.**

The assembly becomes thicker and it has thickness distribution.

Reflection Spectra at Different Positions



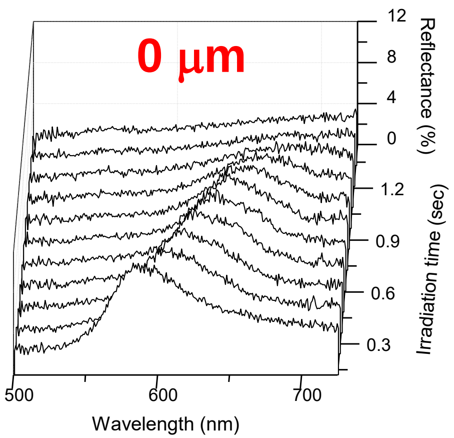


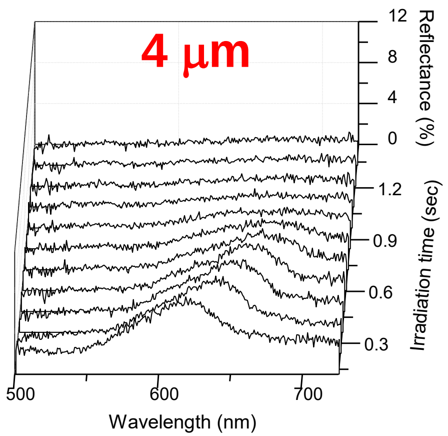


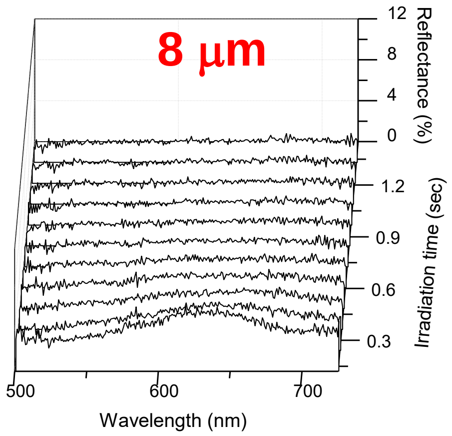
➢ **In the assembly boundary, the peak wavelength was located in long position.**

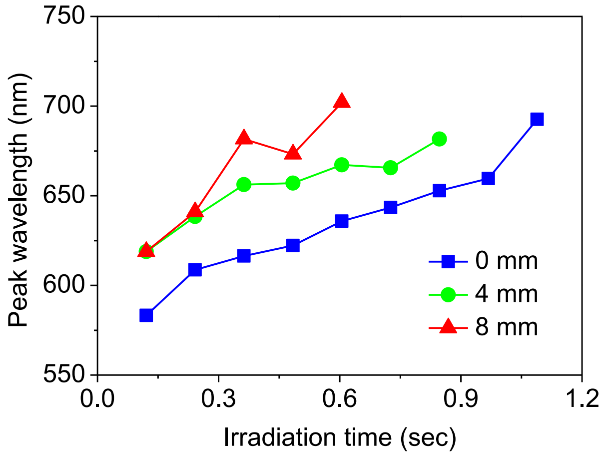
The assembly structure is tighter in the center while looser in the boundary.

Spectral Change after Turning off Laser









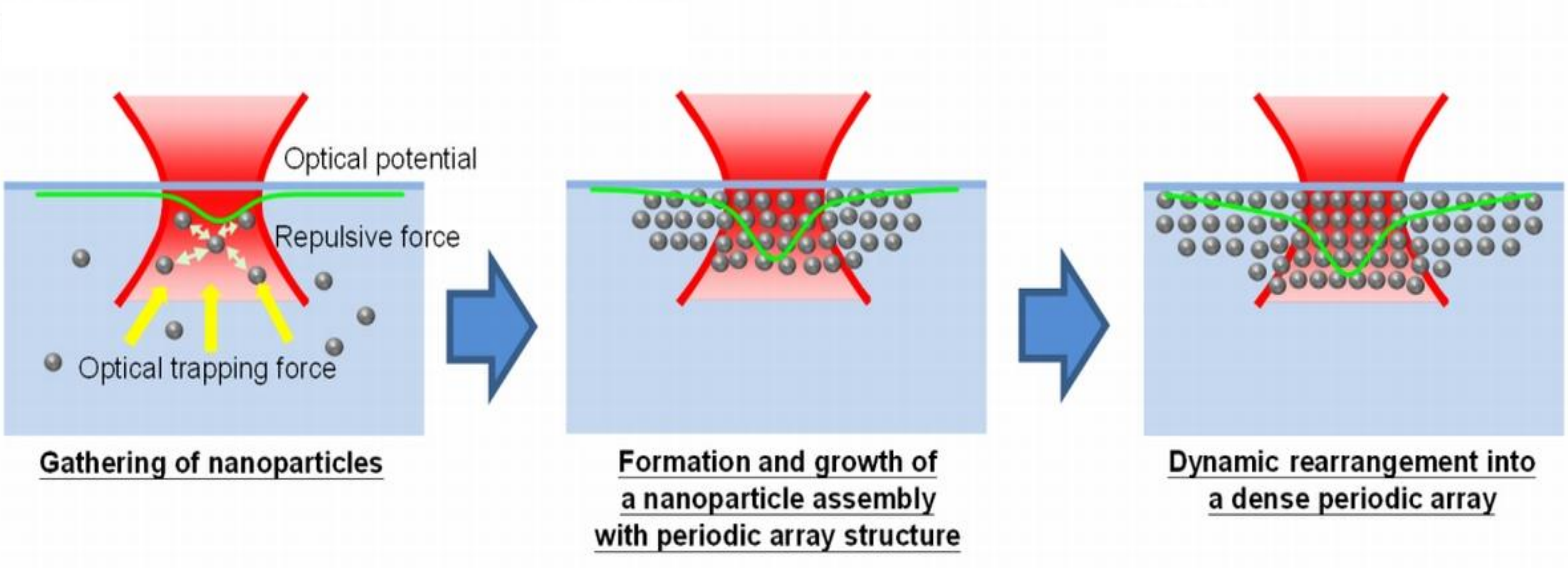
Laser off after 120 sec irradiation

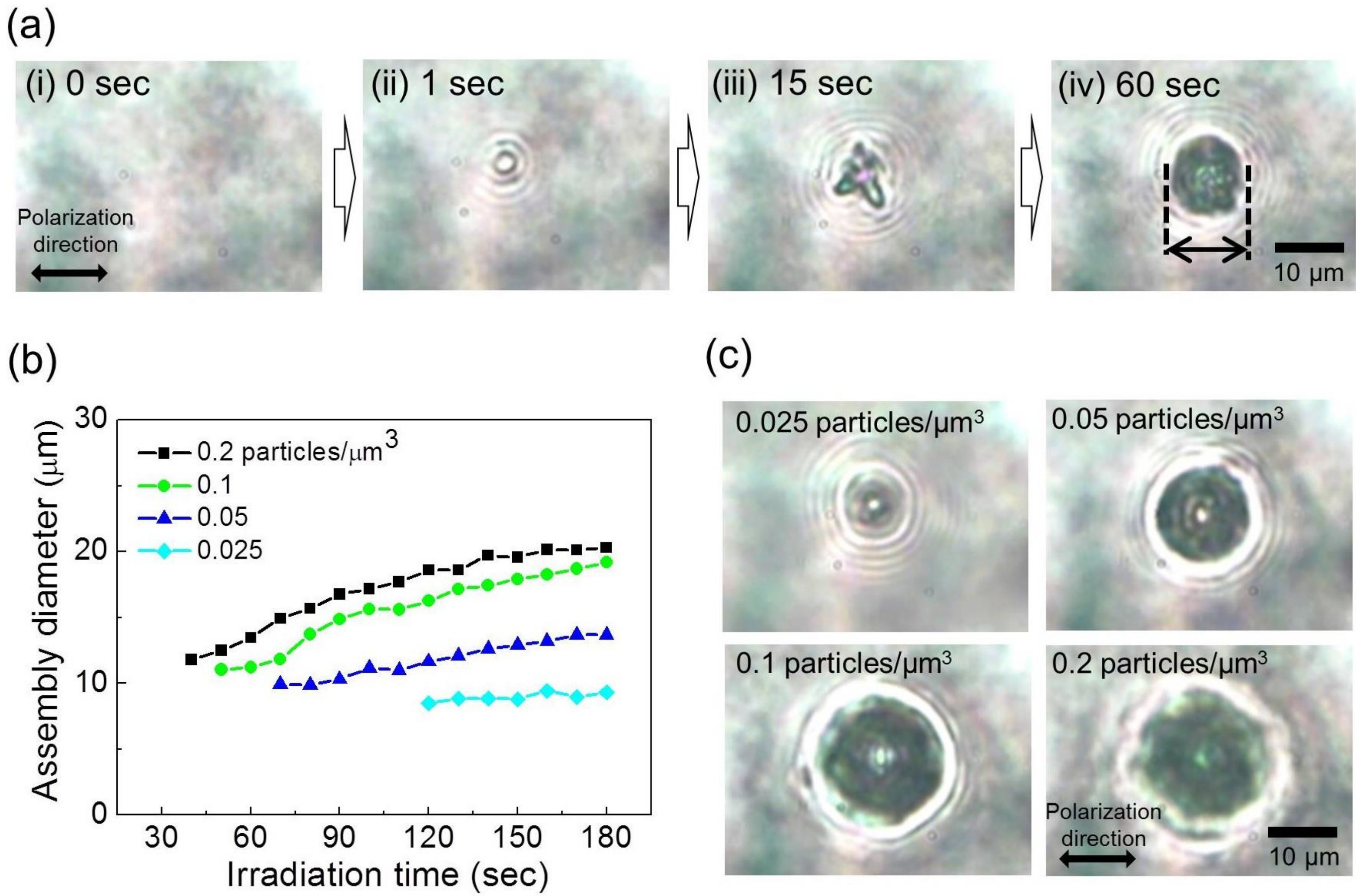
- **Peak wavelength was shifted to longer wavelength, accompanying with reflectance decrease in all positions.**

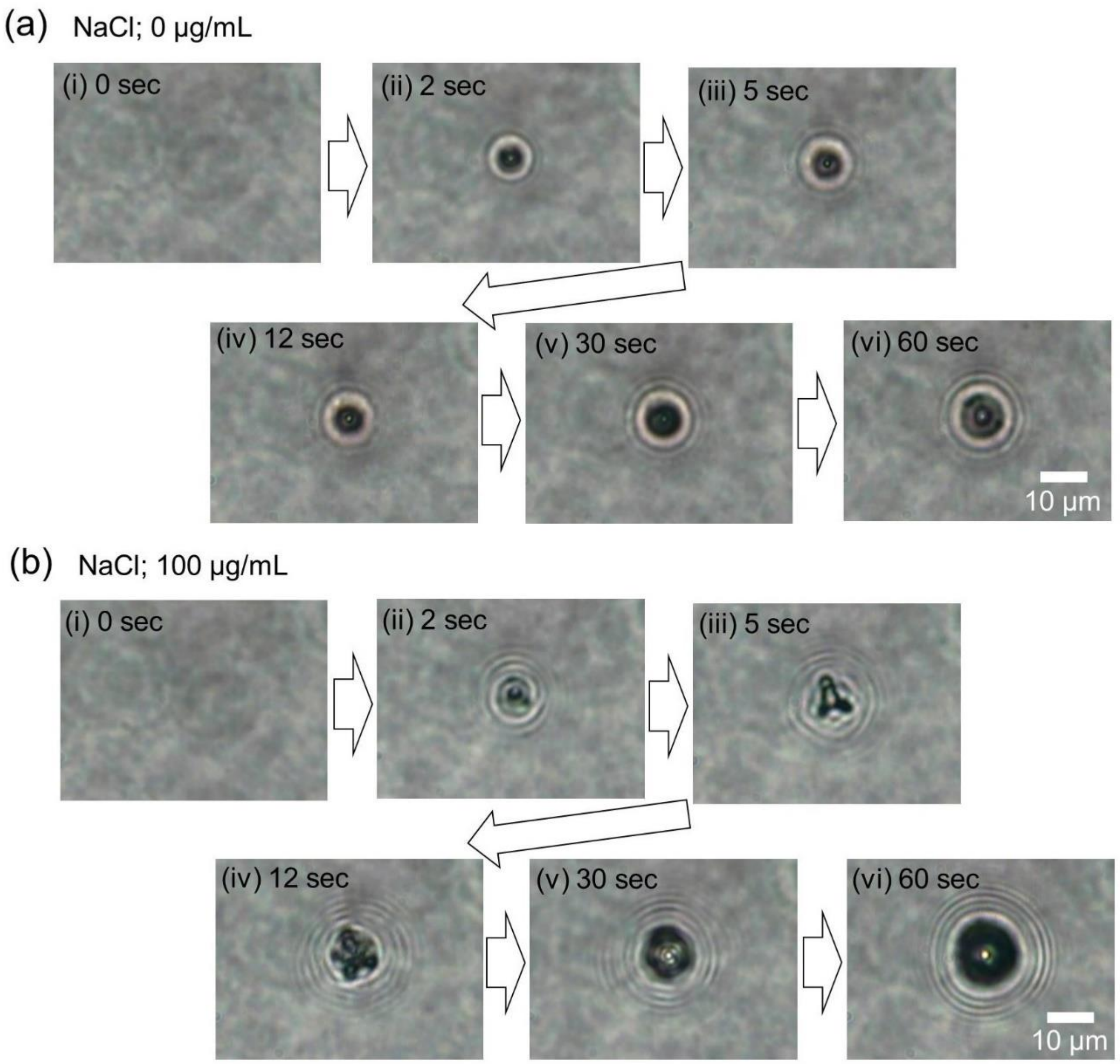
Assembly structure is under dynamical balance between gradient force of trapping laser and repulsive force between particles.

A nanoparticles assembly expands out of the focus!

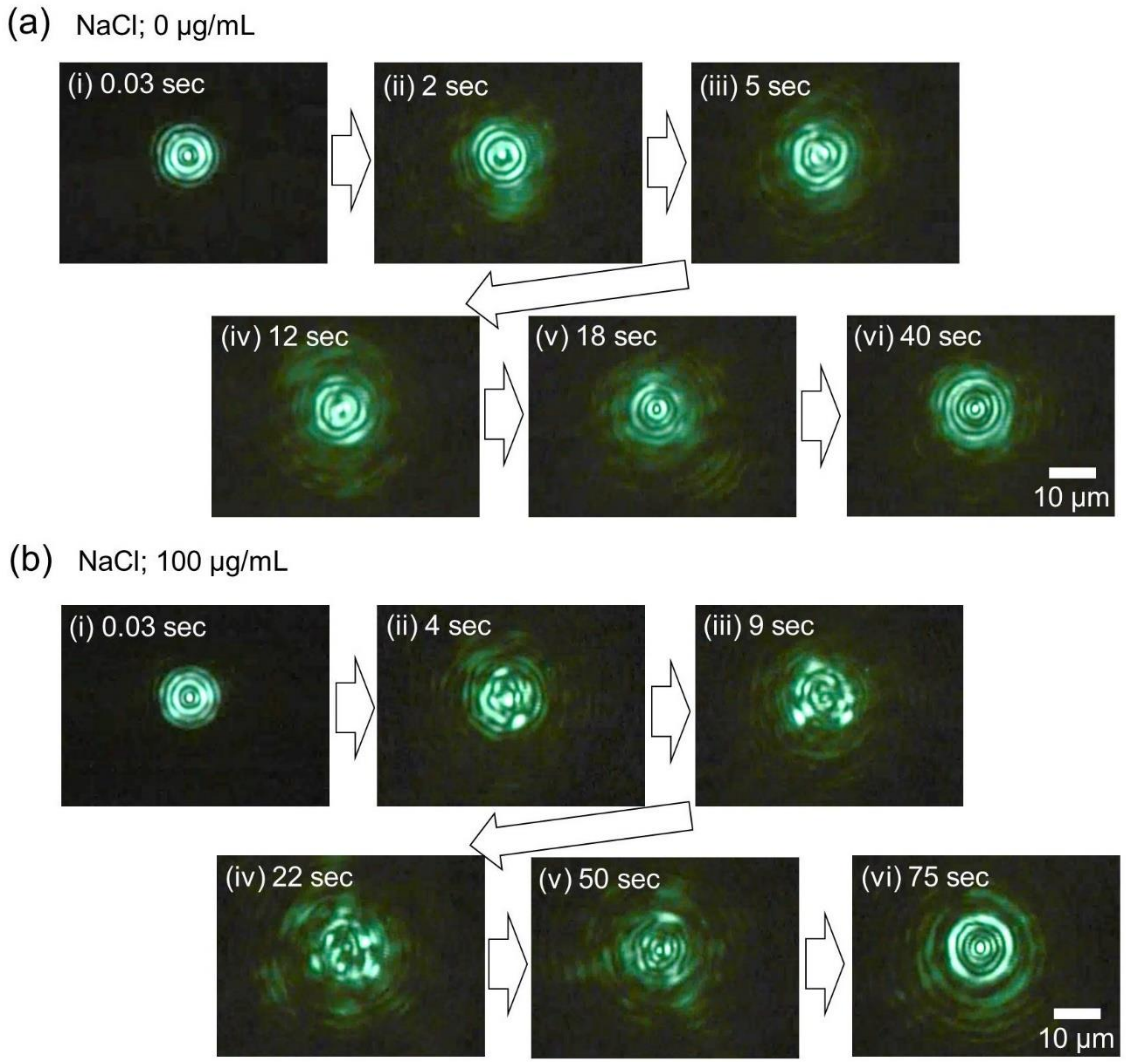
Inhomogeneous structure is confirmed.

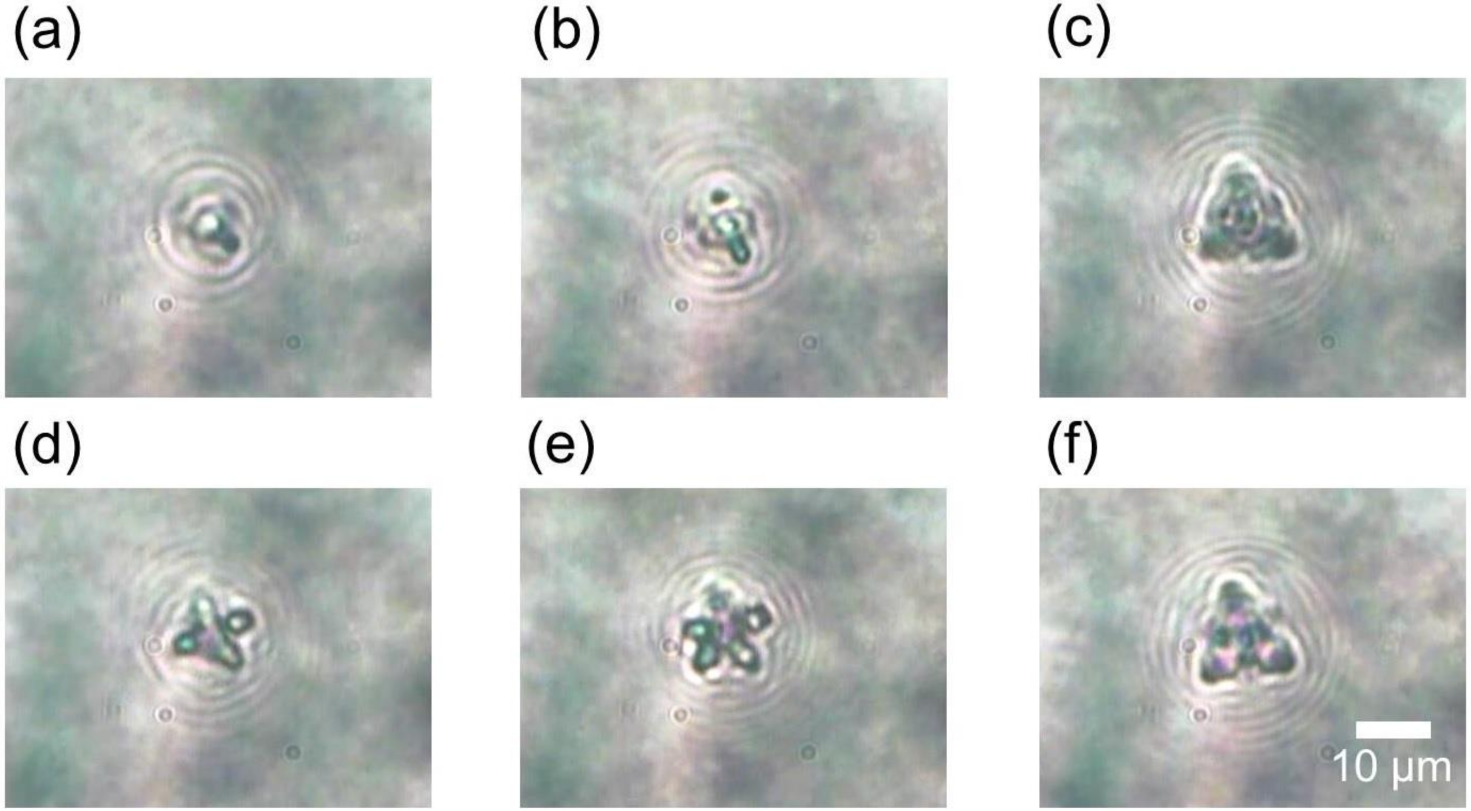


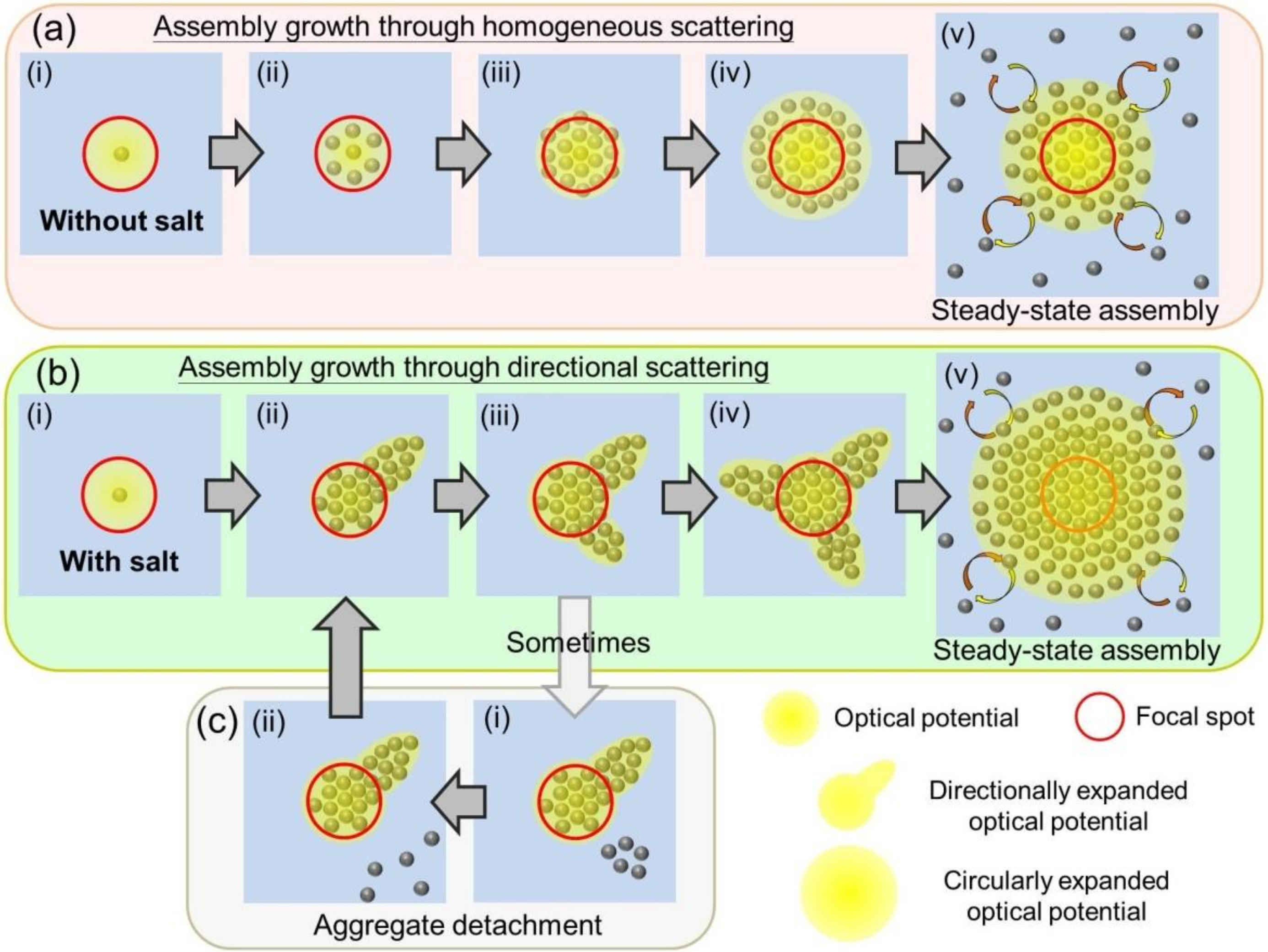

(a)
(i) 0 sec
Polarization direction
(ii) 1 sec
(iii) 15 sec
(iv) 60 sec
10 μm
(b)
Assembly diameter (μm)
Irradiation time (sec)
0.2 particles/μm3
0.1
0.05
0.025
0
10
20
30
30
60
90
120
150
180
(c)
0.025 particles/μm3
0.05 particles/μm3
0.1 particles/μm3
0.2 particles/μm3
Polarization direction
10 μm



(a) NaCl; 0 μg/mL
(i) 0 sec
(ii) 2 sec
(iii) 5 sec
(iv) 12 sec
(v) 30 sec
(vi) 60 sec
10 μm
(b) NaCl; 100 μg/mL
(i) 0 sec
(ii) 2 sec
(iii) 5 sec
(iv) 12 sec
(v) 30 sec
(vi) 60 sec
10 μm


(a) NaCl; 0 μg/mL
(i) 0.03 sec
(ii) 2 sec
(iii) 5 sec
(iv) 12 sec
(v) 18 sec
(vi) 40 sec
10 μm
(b) NaCl; 100 μg/mL
(i) 0.03 sec
(ii) 4 sec
(iii) 9 sec
(iv) 22 sec
(v) 50 sec
(vi) 75 sec
10 μm


(a)
(b)
(c)
(d)
(e)
(f)
10 μm



(a)
Assembly growth through homogeneous scattering
(i)
Without salt
(ii)
(iii)
(iv)
(v)
Steady-state assembly
(b)
Assembly growth through directional scattering
(i)
With salt
(ii)
(iii)
(iv)
(v)
Steady-state assembly
Sometimes
(c)
(ii)
(i)
Aggregate detachment
Optical potential
Focal spot
Directionally expanded optical potential
Circularly expanded optical potential

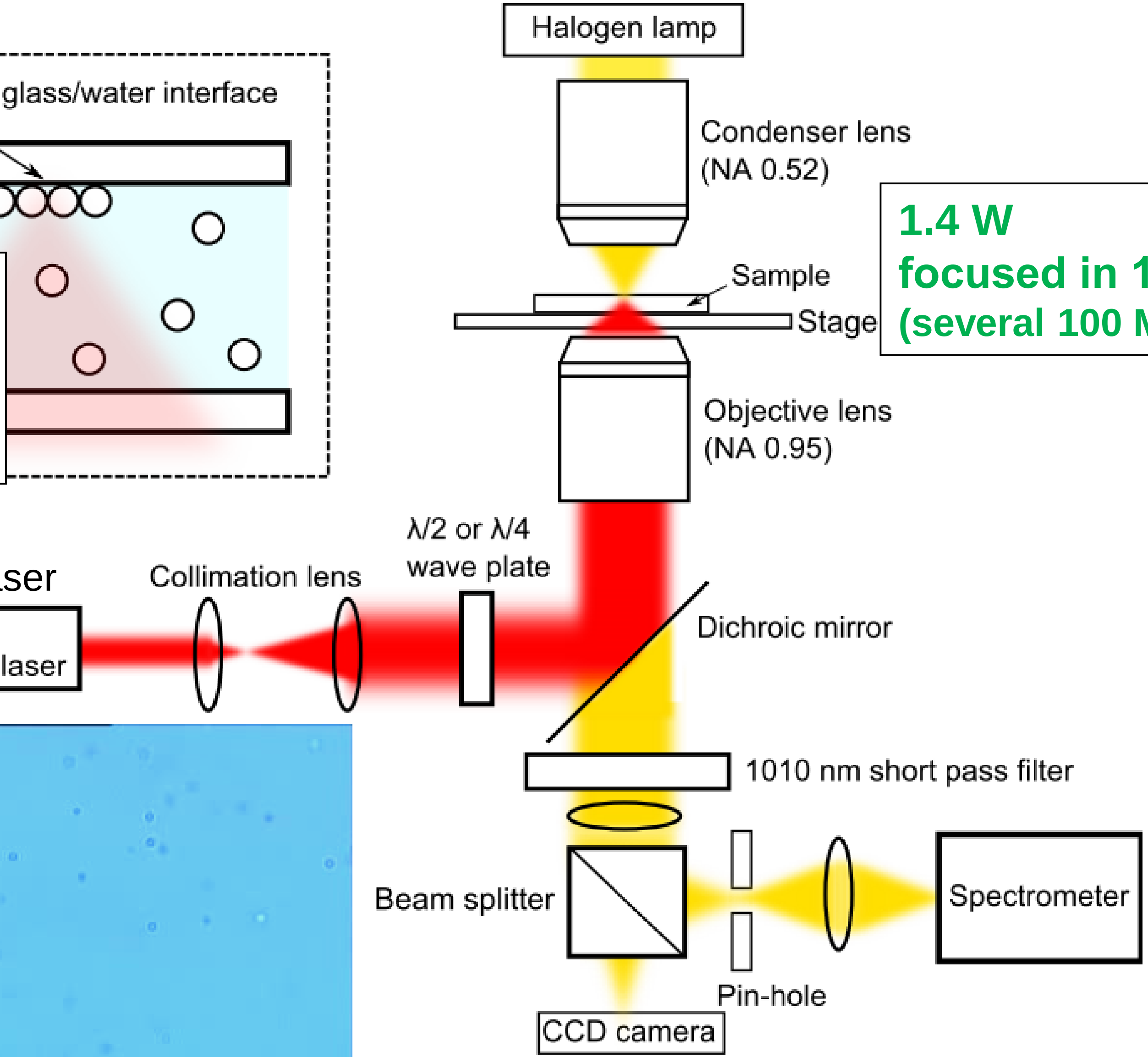
Direct confirmation on light propagation in laser trapping assembling at glass/solution interface

Polystyrene nanoparticles

Wang, Yuyama, Sugiyama, Masuhara
J. Phys. Chem. C, 120, 15578-15585
Kudo, Wang, Yuyama, Masuhara
Nano Lett., 16, 3058-3062 (2016)

Dr. Tetsuhiro KUDO styed with us for several months as a PhD student of Osaka Prefecture Univeristy studying on Optical Properties of Matters. After he obtained his degree, he joined me to start his new career as an experimentalist in NCTU.

Optical setup and sample

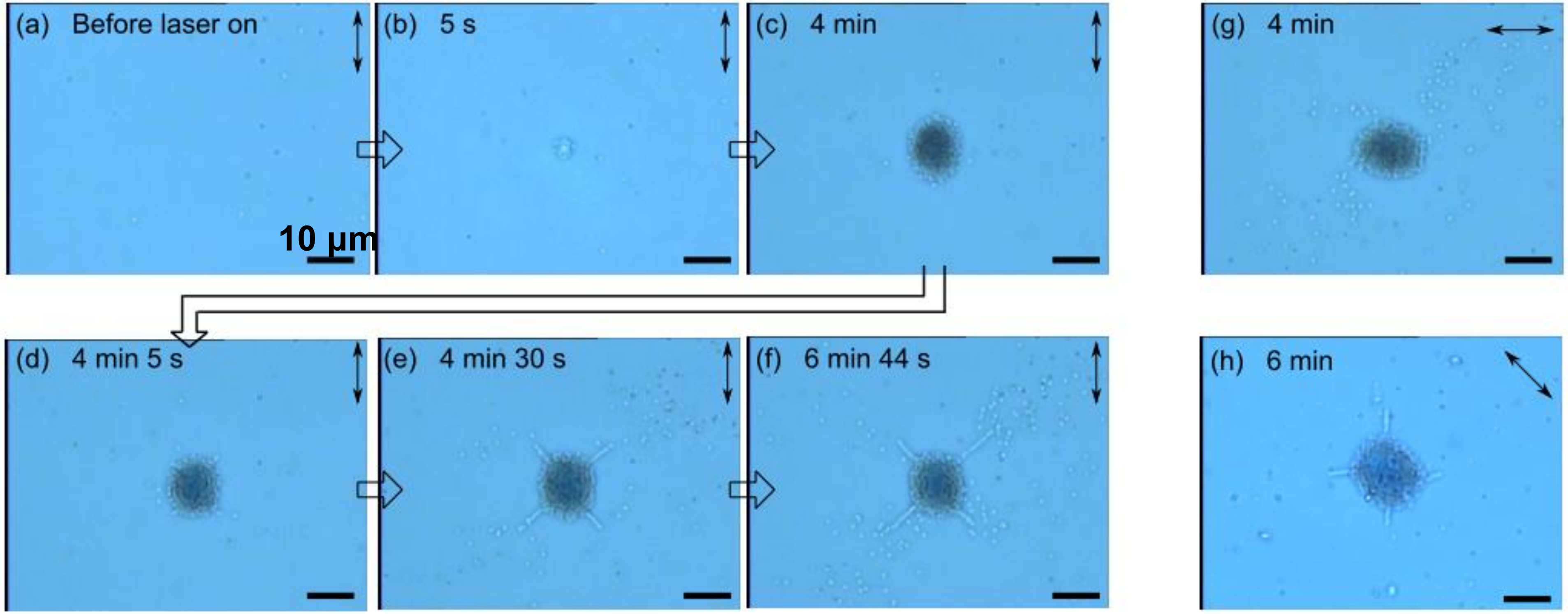


Polystyrene particles (500 nm in diameter)

1.4 W focused in 1 μm^2 (several 100 MW/cm^2)

Transmission images of the colloidal assembly formed by optical trapping at the interface

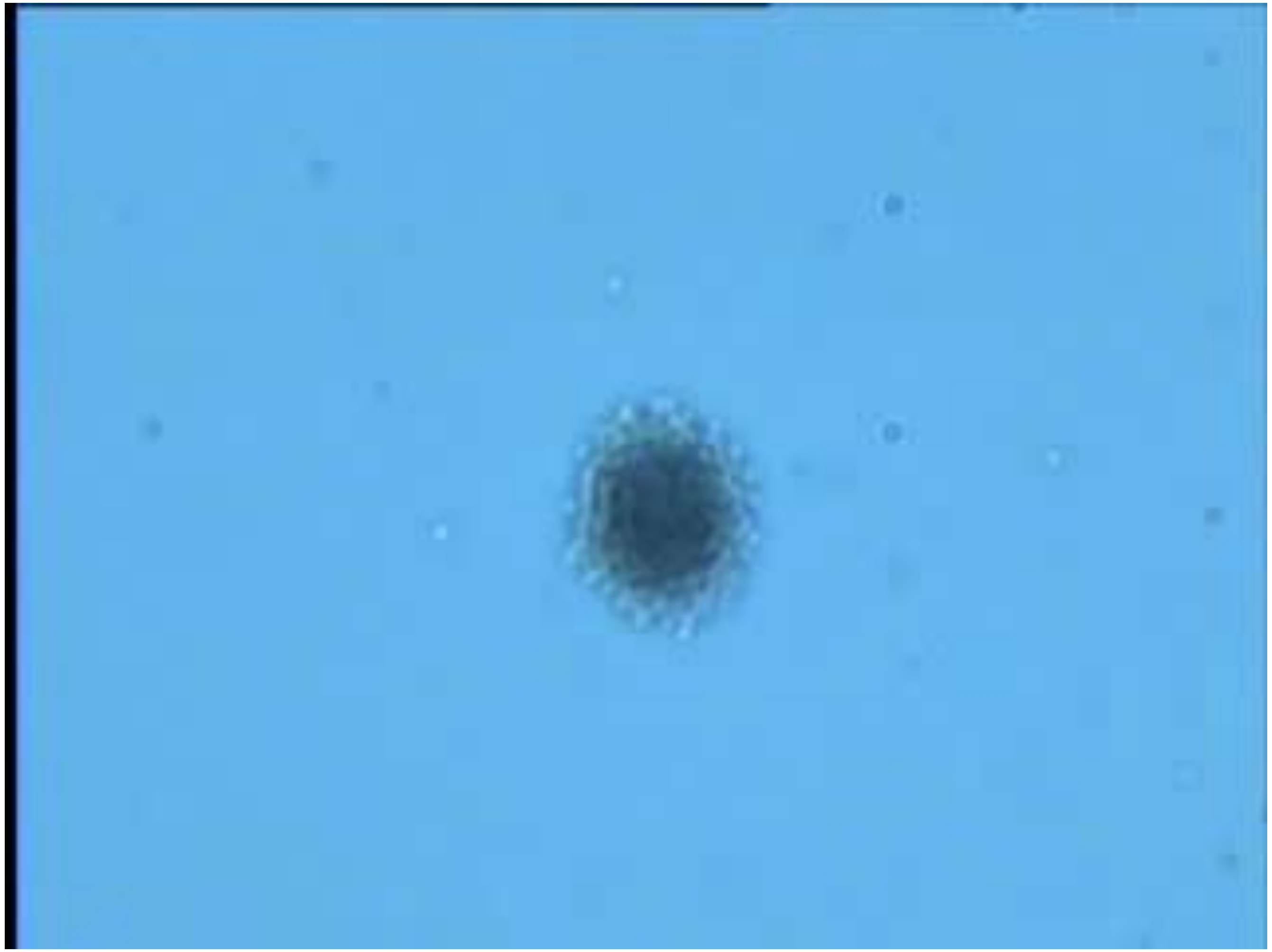
Linearly polarized light, 1.4 W



Transmission images of the colloidal assembly formed by optical trapping at the interface

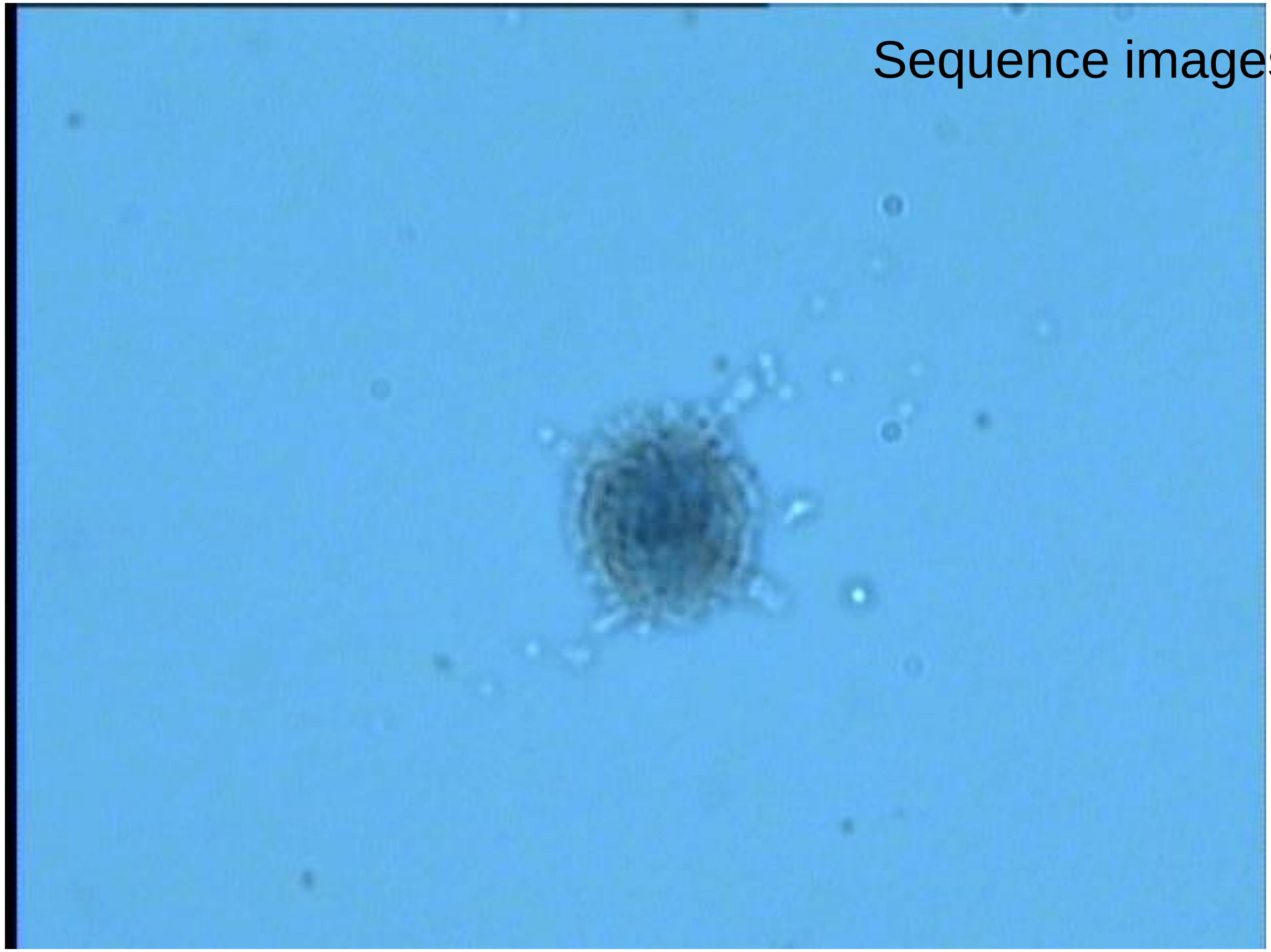
Linearly polarized light, 1.4 W

Movie



Transmission images of the colloidal assembly formed by optical trapping at the interface

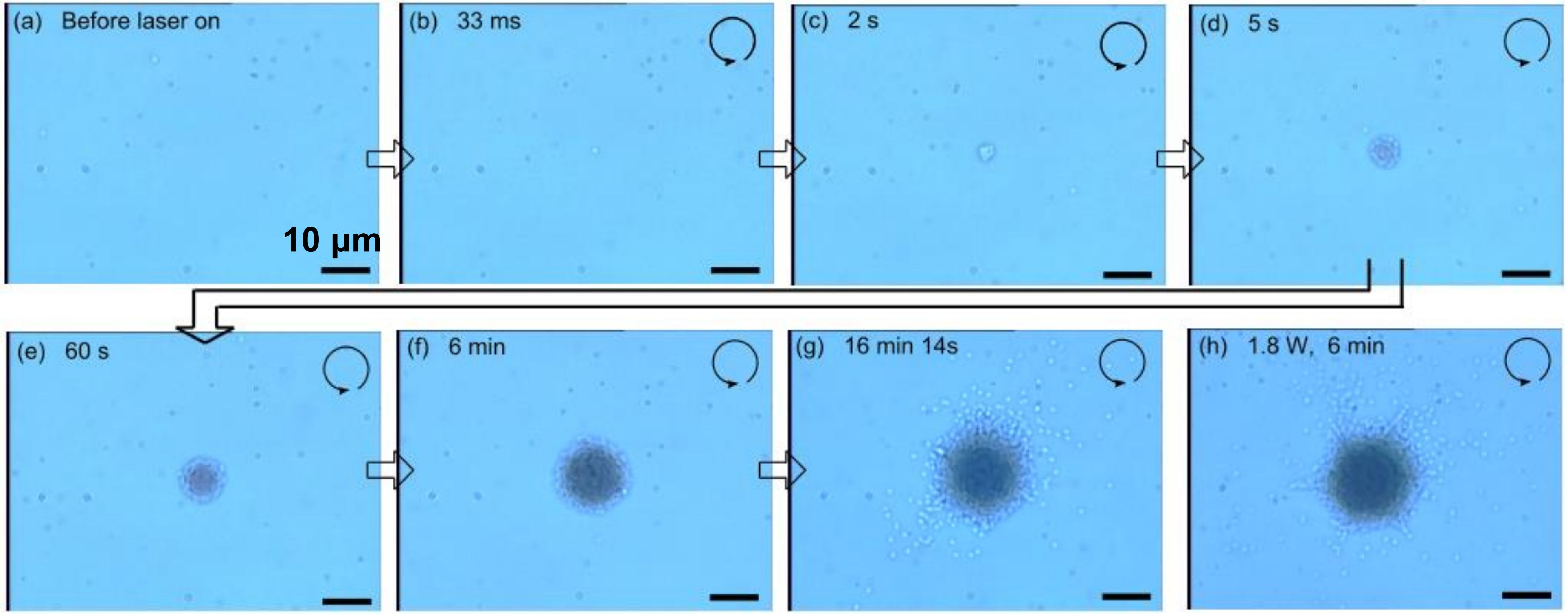
Linearly polarized light, 1.4 W



Sequence images

Transmission images of the colloidal assembly formed by optical trapping at the interface

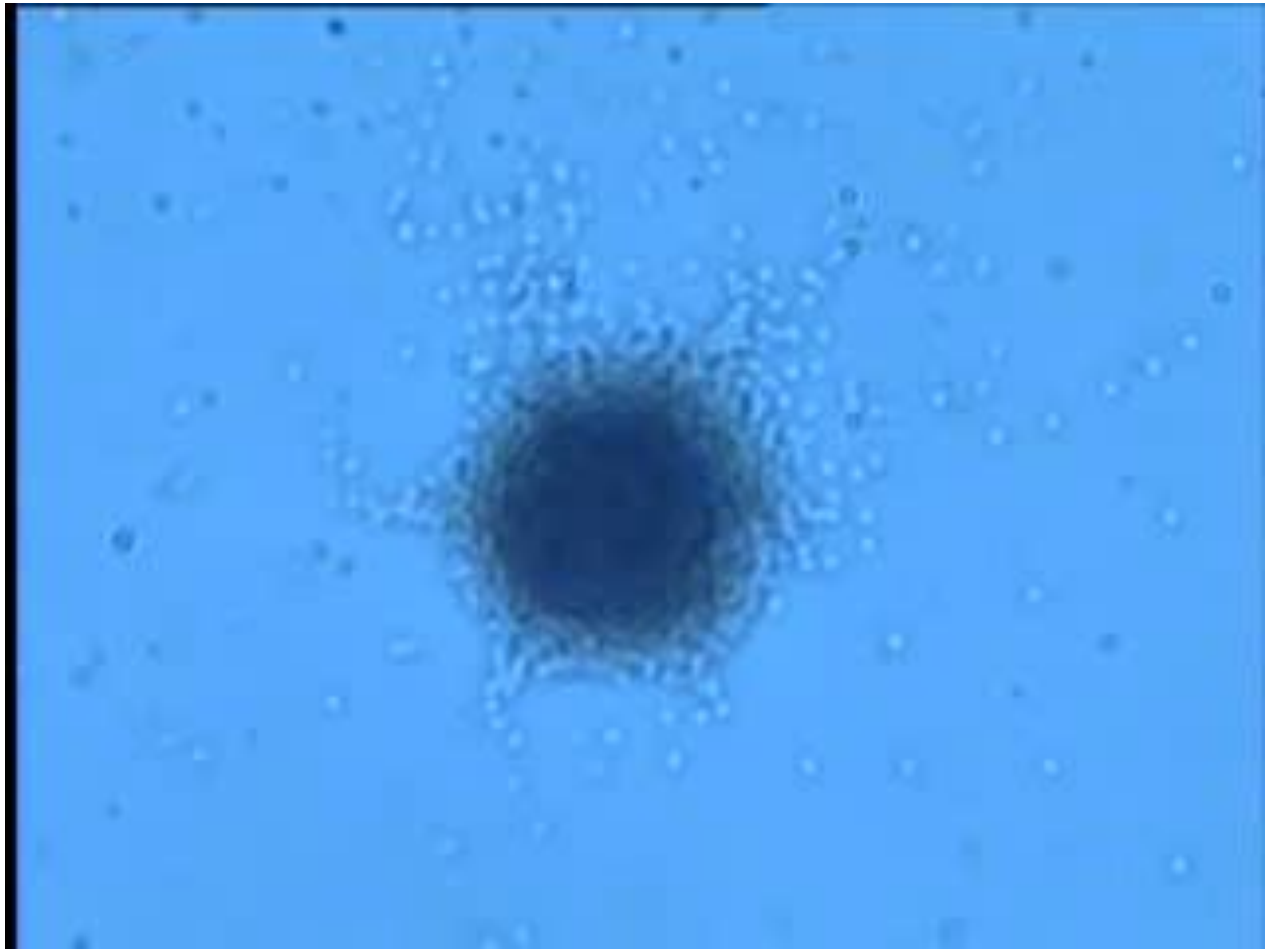
Circularly polarized light, 1.4 W



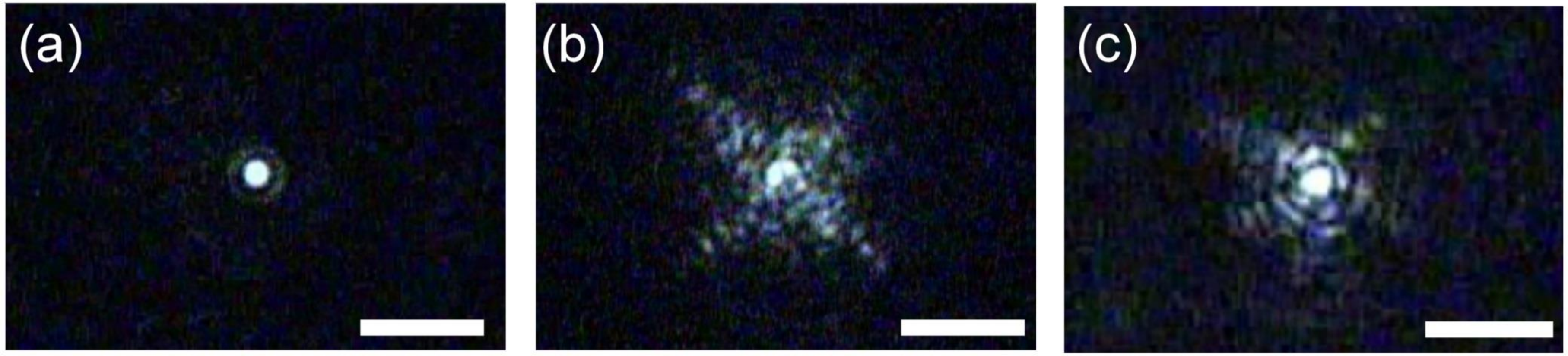
Transmission images of the colloidal assembly formed by optical trapping at the interface

Circularly polarized light, **1.8 W**

Movie



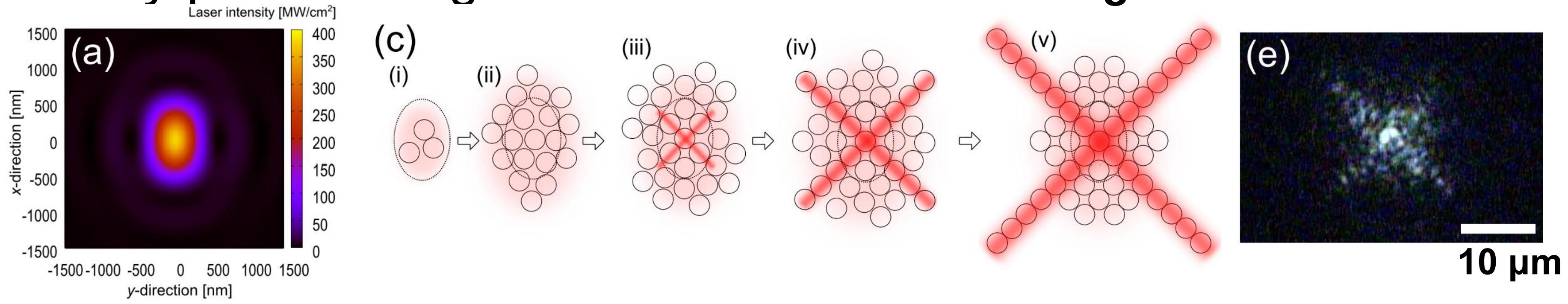
Backscattering image of 1064 nm trapping laser



(a, b) Laser intensity distribution in focal plane
(c, d) Structure of formed assembly
(e, f) Back scattering images of 1064 nm trapping laser

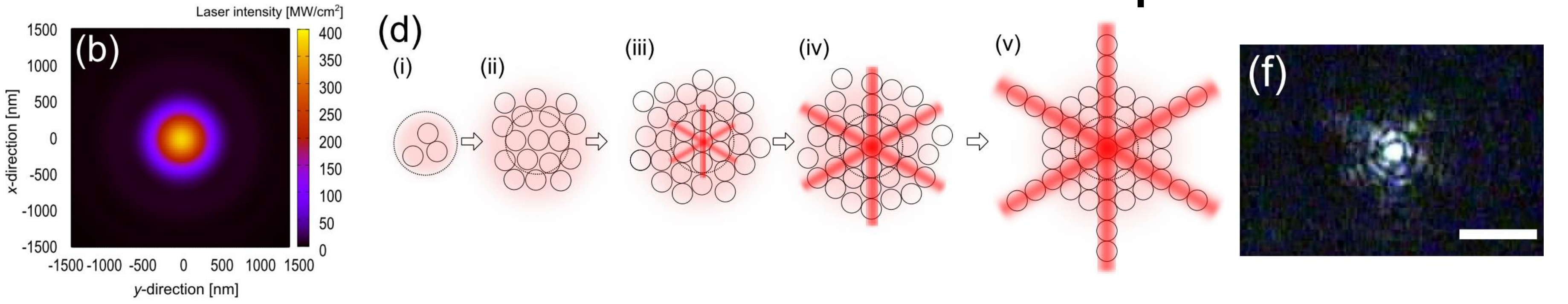
Linearly polarized light

Tetragonal

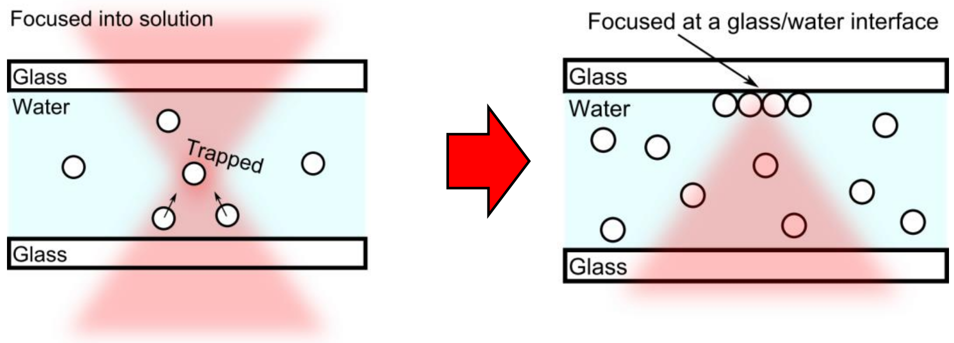


Circularly polarized light

Close-packed



Trapping at the interface

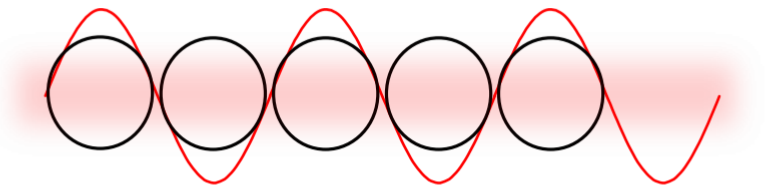


Strong laser intensity

The present laser power of 1.4 W is about **100 times** higher than minimum laser power (15 mW)

Laser wavelength vs. particle size

1064 nm laser
500 nm particle



The horn may serve as one-dimensional photonic waveguide

Our proposals on laser trapping dynamics

A large millimeter-sized domain of liquid like-clusters is formed at solution surface for amino acids, proteins, and supramolecules.

A single crystal and a single assembly are formed at solution surface for amino acids and polystyrene nanoparticles, respectively.

Packing and orientation prepared at the focus propagate to the outside through strong intermolecular interactions..

Optical trapping, scattering, and propagation are coupled, which is named optically evolved assembling.

Mr. Wei-Yi Chiang, Ph. D. student who stayed in KUL and is staying again for 20 October 2016 - 19 July 2017.

Laser Trapping by Femtosecond pulses

Point Dipole (Rayleigh) Approximation

Laser trapping with Pulsed lasers

Lorentz Force

$$\mathbf{F}_{\text{Lorentz}} = [\mathbf{P} \cdot \vec{\nabla}]\mathbf{E} + \frac{1}{c}\partial_t \mathbf{E} \times \mathbf{H}$$

$$\mathbf{F}_{\text{temporal}} = \frac{1}{2}(n_m^3 \varepsilon_0 \alpha / c)\partial_t |E|^2$$

J.P. Gordon, *Phys. Rev. A* 1973, *8*,14;
LG Wang, LG Zhao, *Opt Express* 2007,*15*,16015

$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}\mathbf{E} + \chi^{(3)}\mathbf{E}\mathbf{E}\mathbf{E} + \ldots$$

NLO effects

Pulsed Lasers

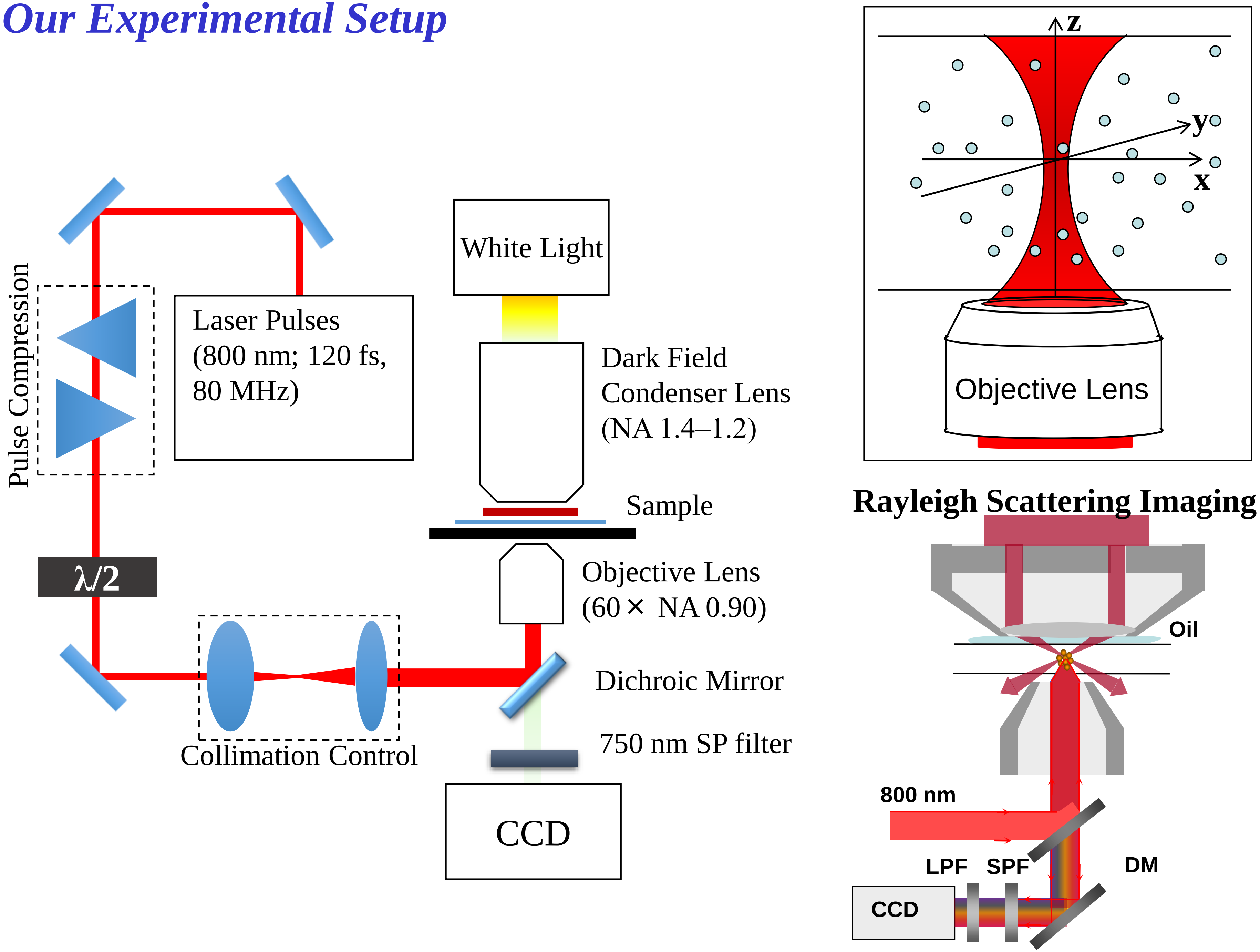
Temporal Force
NLO Effects

Impulsive Peak Powers
Periodical Field; Periodical Optical Forces
Relaxation and diffusion between consecutive pulses.

CW

Constant Field,
Constant Optical Forces,
Suppressed Diffusion,
Steady Trap

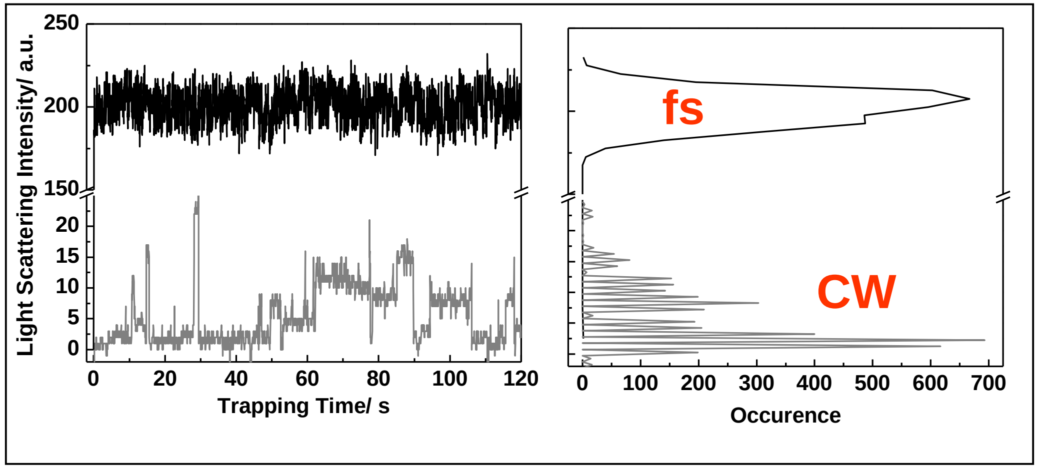
Our Experimental Setup



Optical Trapping and Directional Ejections of Polystyrene NPs

Anwar Usman*, Wei-Yi Chiang, Hiroshi Masuhara*

J. Photochem. Photobiol. A: Chemistry 2012, *234*, 83

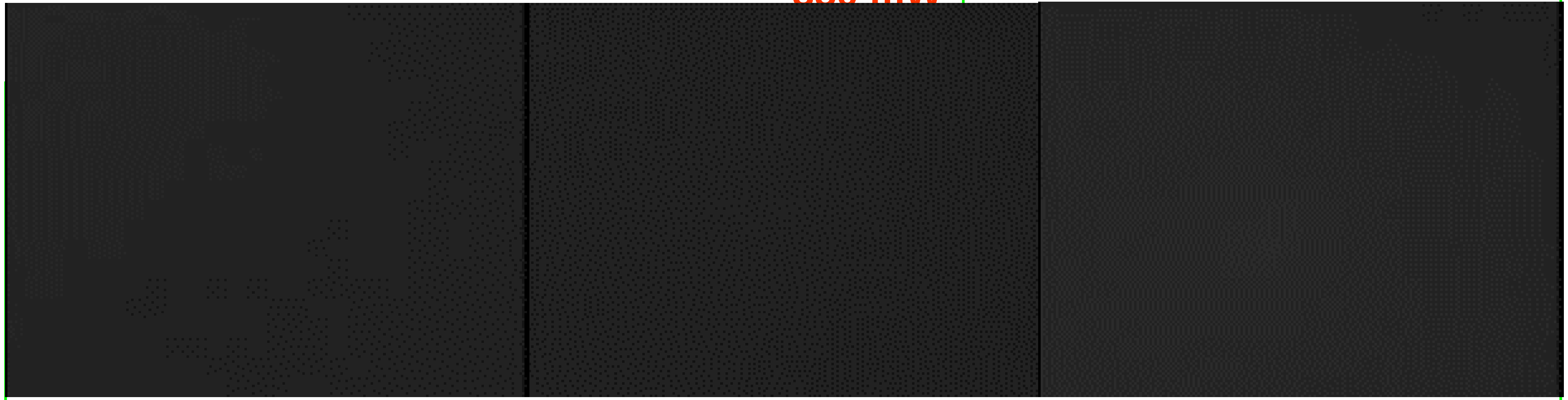


CW

E

20 μm

350 mW

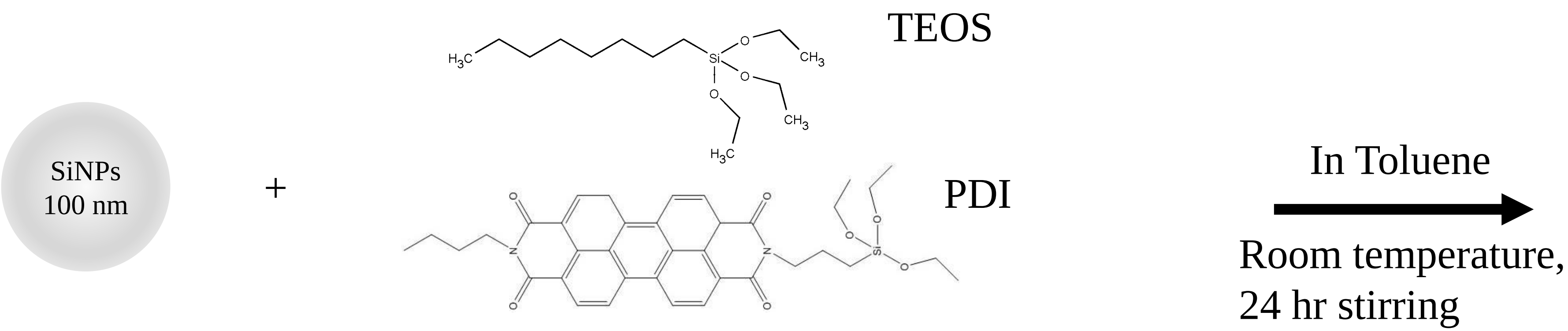


E

E

E

We have prepared silica NPs covered with TEOS and PDI.



Controlling different concentration ratio of alkysilane and PDI to obtain varied dye coverage on SiNPs and avoid PDI aggregations on particle surface.

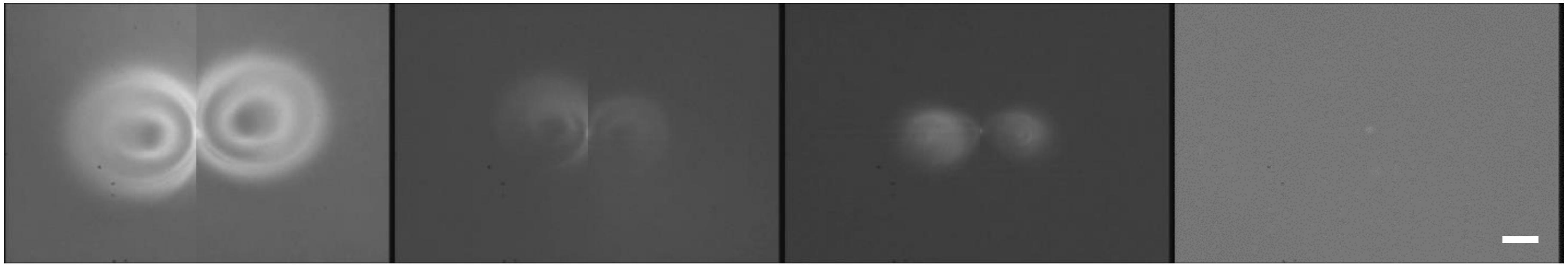
Ejection behavior is observed now for silica NPs covered with TEOS and PDI!

(In preparation for J. Phys. Chem. C)

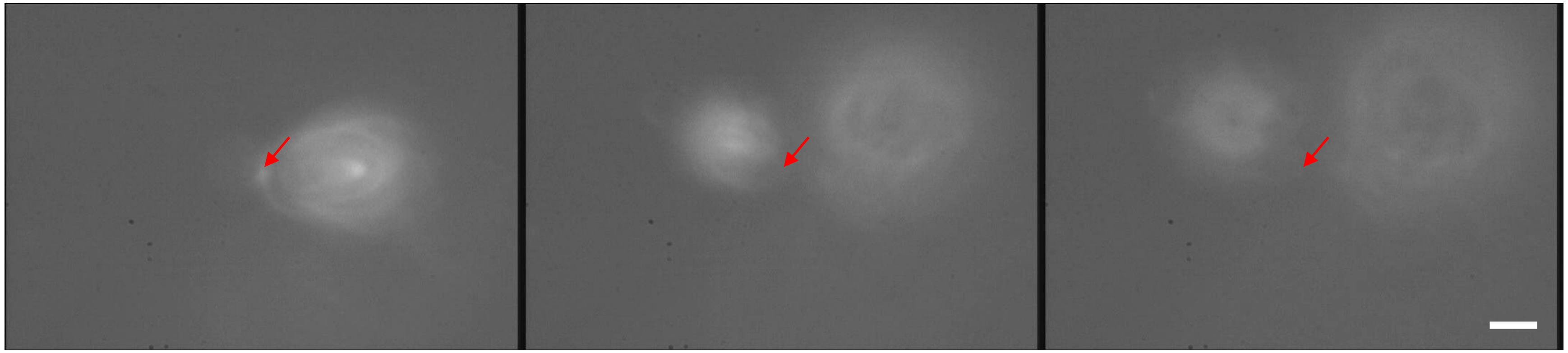
Femtosecond Laser Trapping, Assembling, and Ejection Dynamics of Hydrophobic Nanoparticles in Aqueous Solution

Wei-Yi Chiang,[1,3] Anwar Usman,[2,*] Teruki Sugiyama,[1] Johan Hofkens,[3,*] Hiroshi Masuhara[1,*]

450 nm 150 nm 128 nm 100 nm

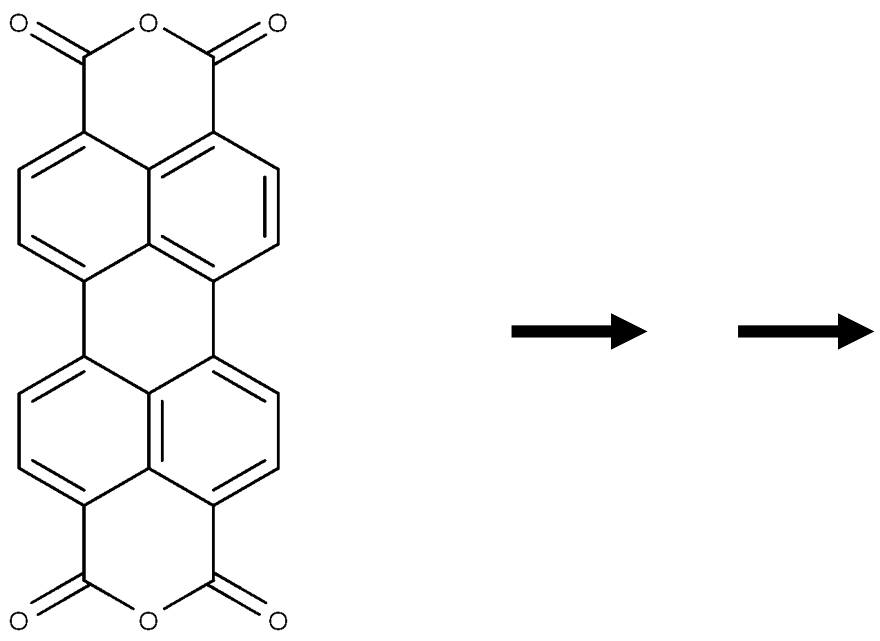


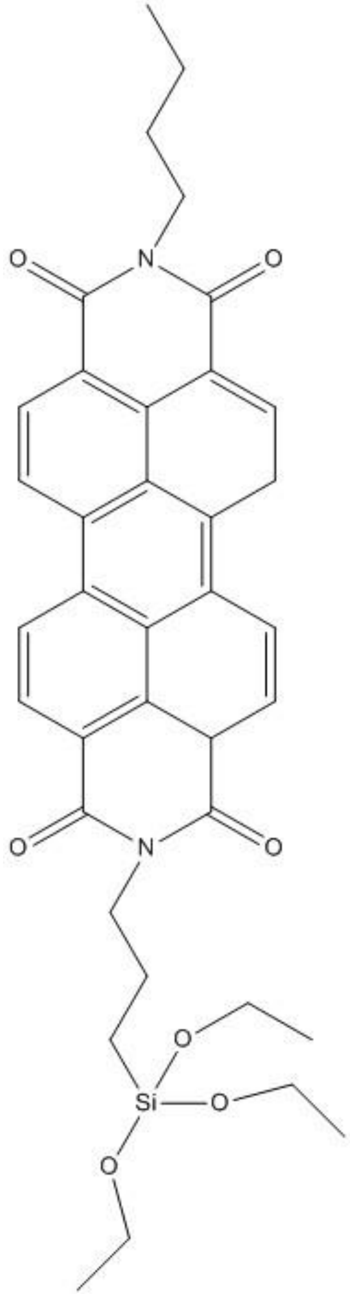
450 nm



when we used the sample modified by low concentration silane solution, which means the coverage on surface of silice was low, the ejection from ball shape changed to fan shape again as what polystyrene beads showed.

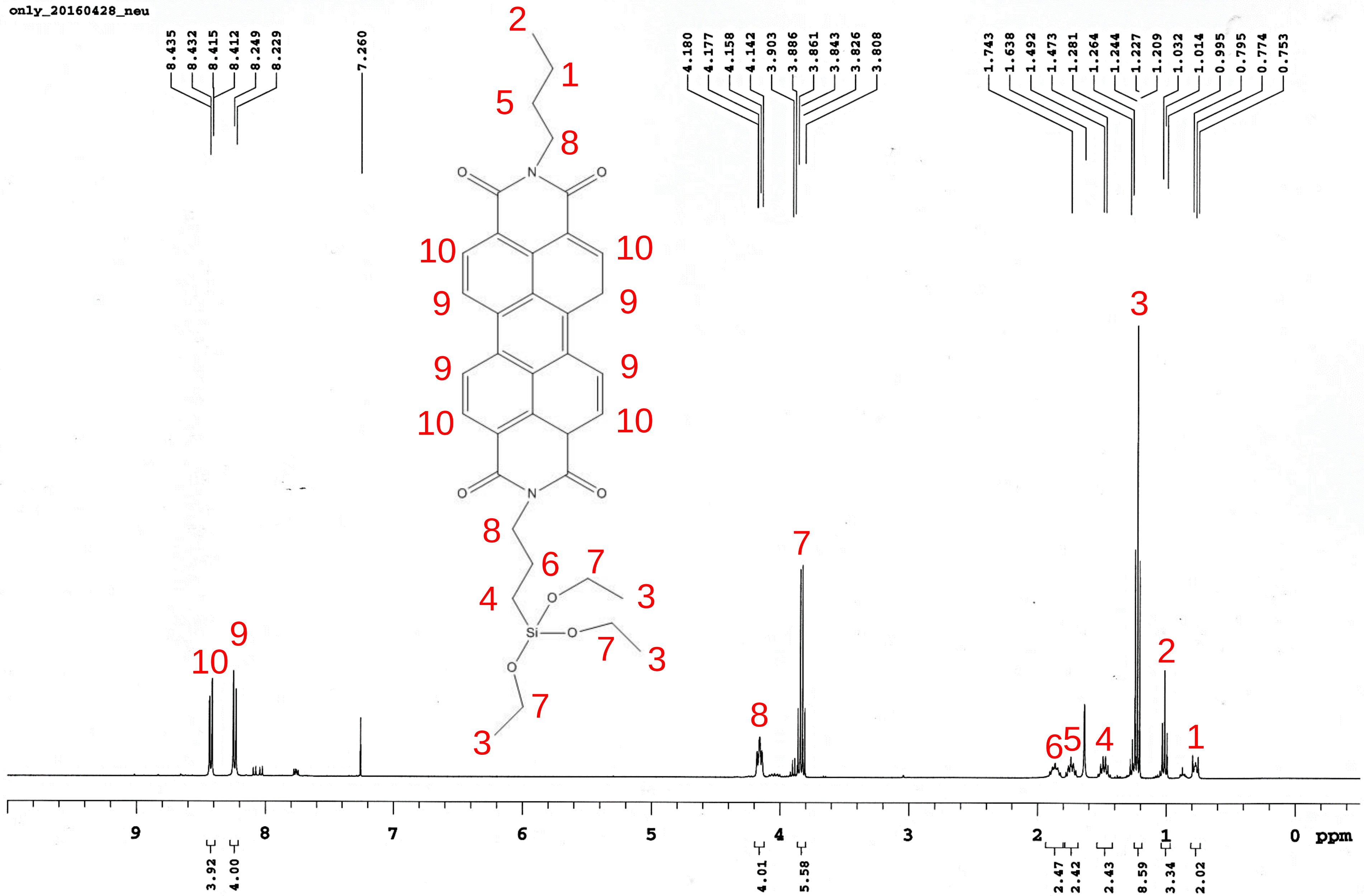
Dyes synthesis



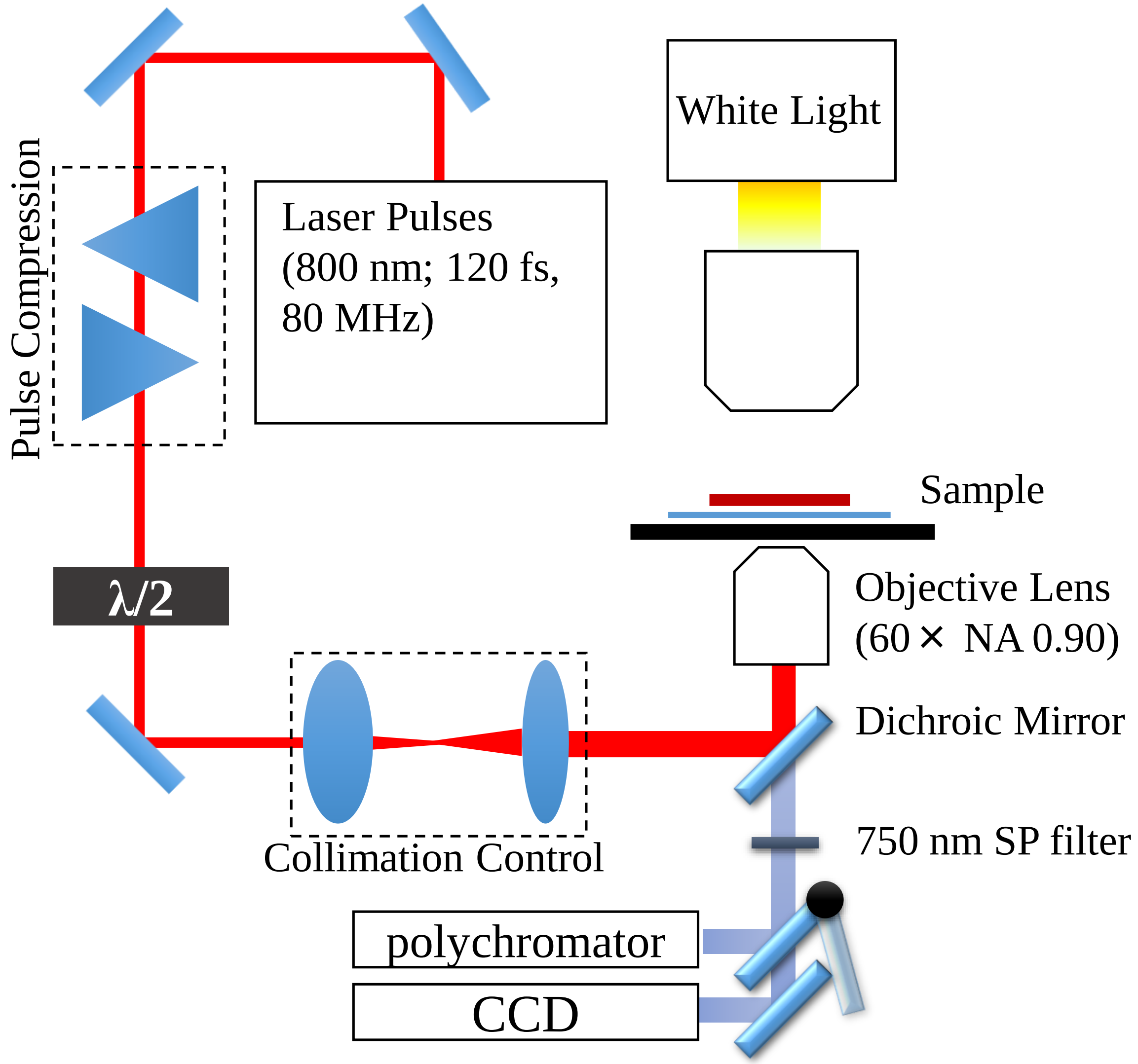


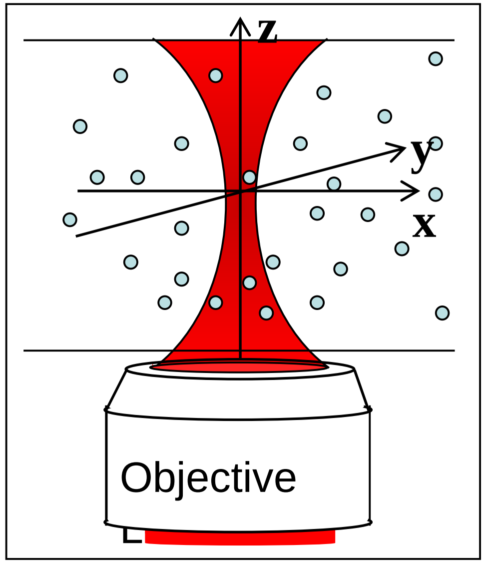
Synthesizing unsymmetrical perylene dye (PDI) which
has ethoxysilane groups that can react on the silica surface.

H-NMR measurement



Experimental setup



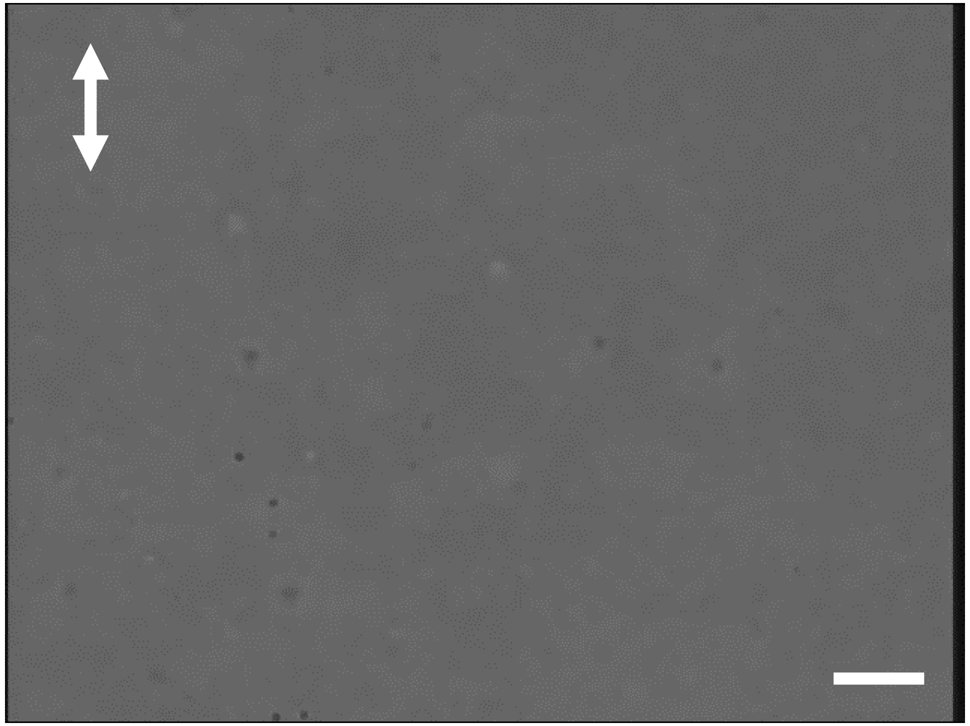


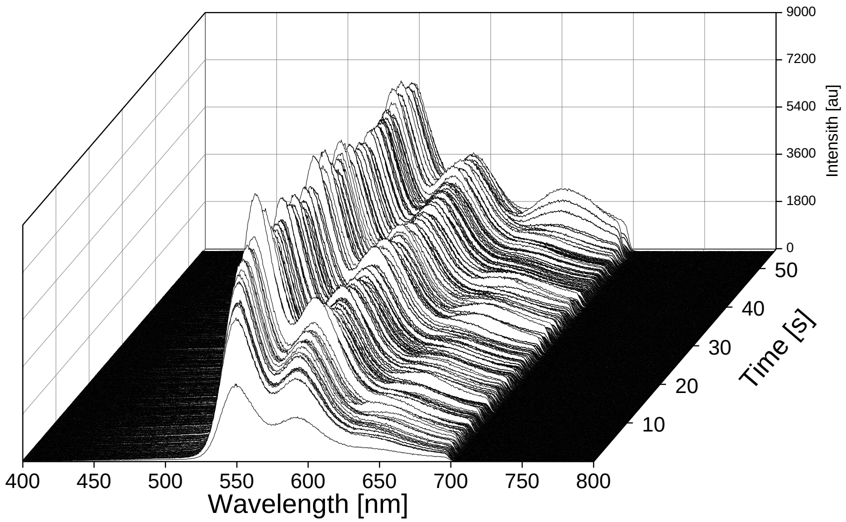
Sample:
100-nm-sized SiNPs
Suspended in water
C = 3.9 × 10^{13} particles/mL

Laser power : 300 mW

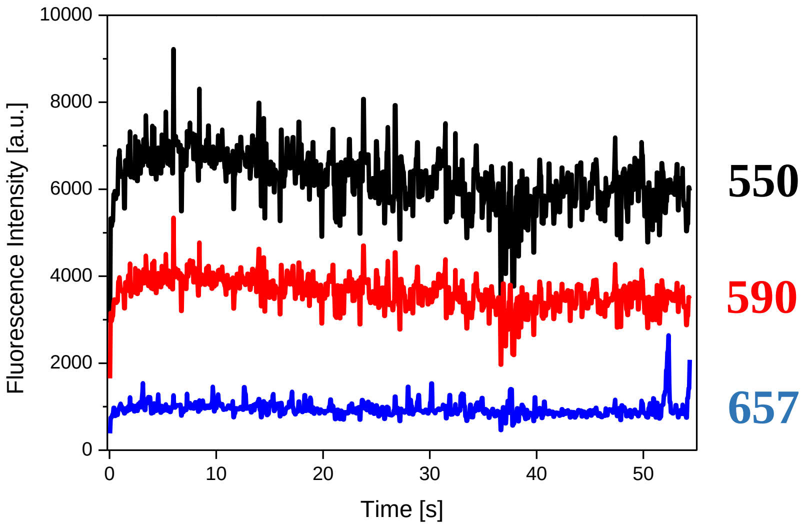
Spectra exposure time = 0.033 s

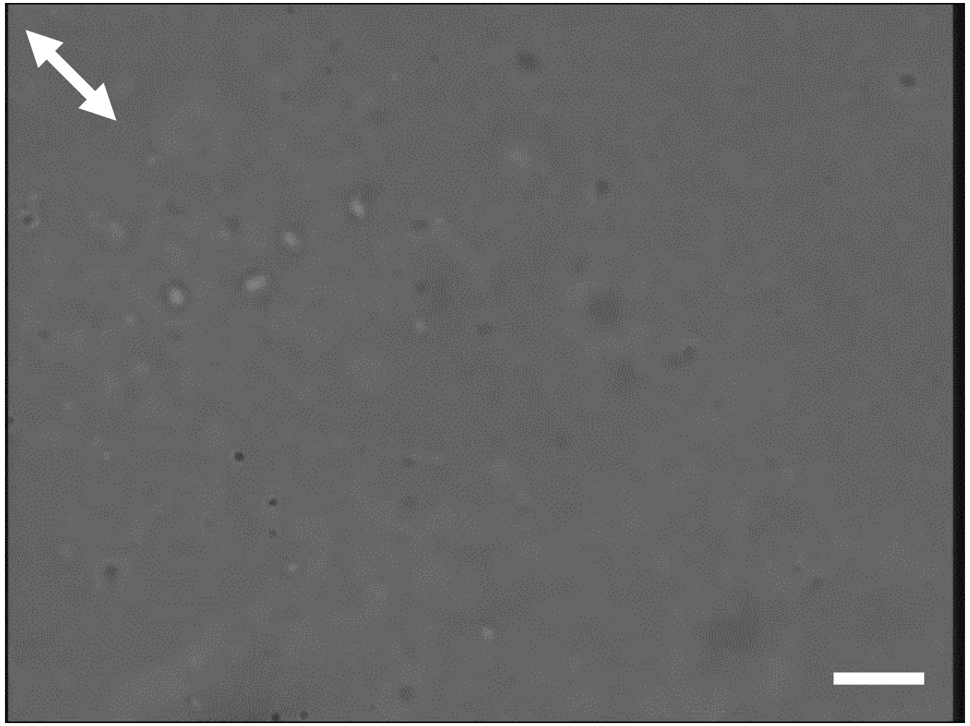
Introducing fs pulsed laser into sample chamber which contain particle solution.
Taking advantage of polychromator to measure fluorescence spectra.

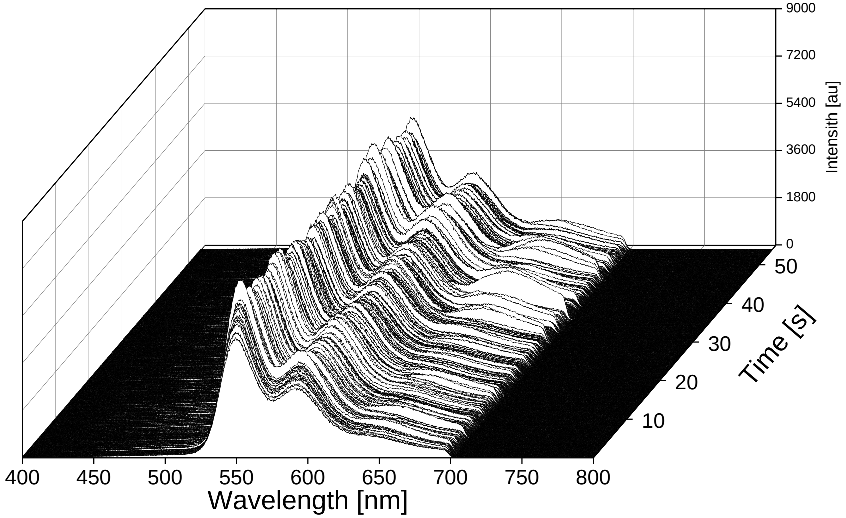




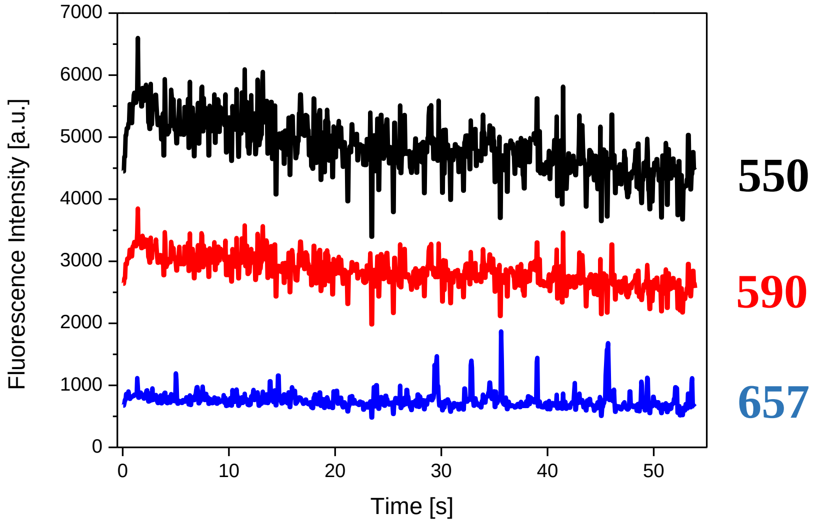
Video and spectra are different measurement!

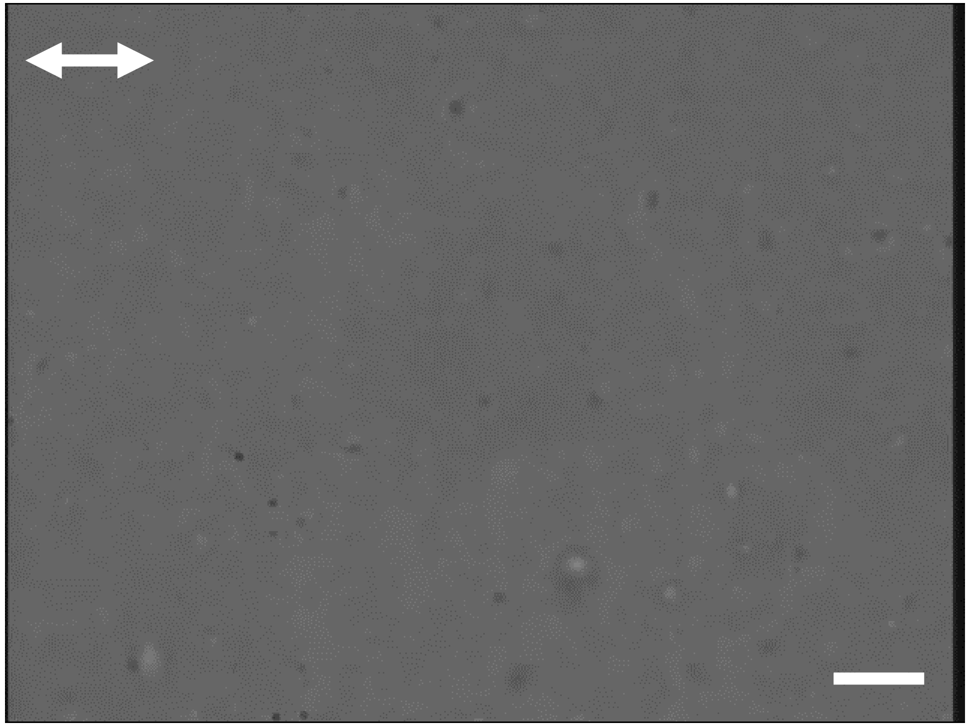


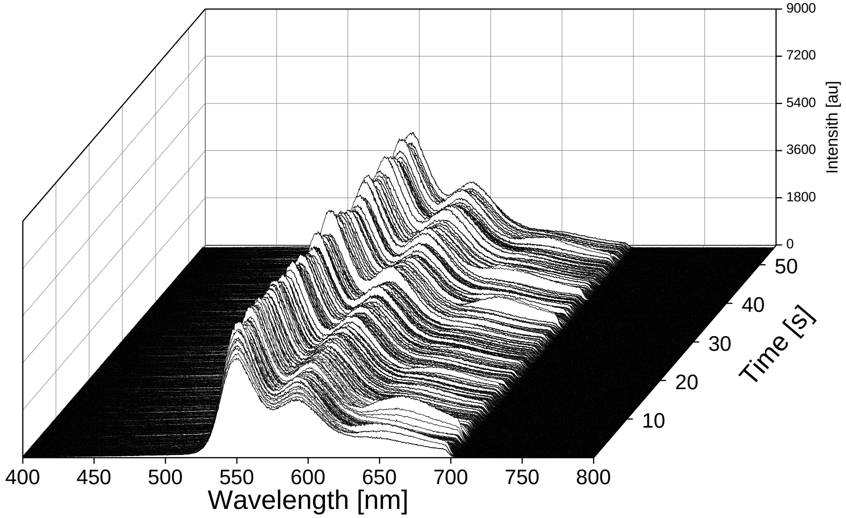




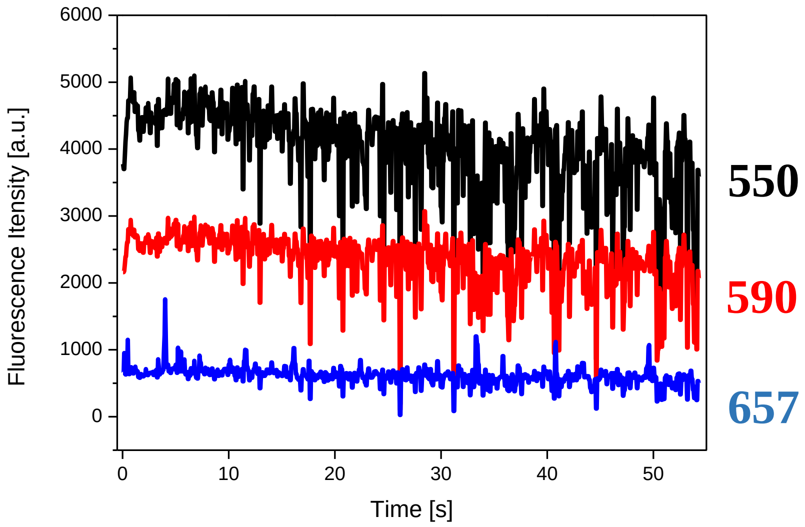
Video and spectra are different measurement!







Video and spectra are different measurement!



増原スタイル：　深謀遠慮

研究成果は人生の全積分

情勢分析は必要不可欠

Pimentel Report　（1970年代）
レーザー、コンピューター、シンクロトロン

又賀コメント　（1968年）
「あらゆる光はレーザーに取って代わられる」

物理化学者は方法論で、有機化学者は合成で、理論化学者は数学（計算機ではない）で勝負。

レーザー、光学顕微鏡・・・・・・・・光と物質の相互作用
STM, AFM, SEM・・・・・・・・・・電子と物質の相互作用

これらの間を乗り換えてはいけない、自分を失くす

Thank you very much for your kind attention !!
All of you are welcome to Hsinchu Taiwan !!