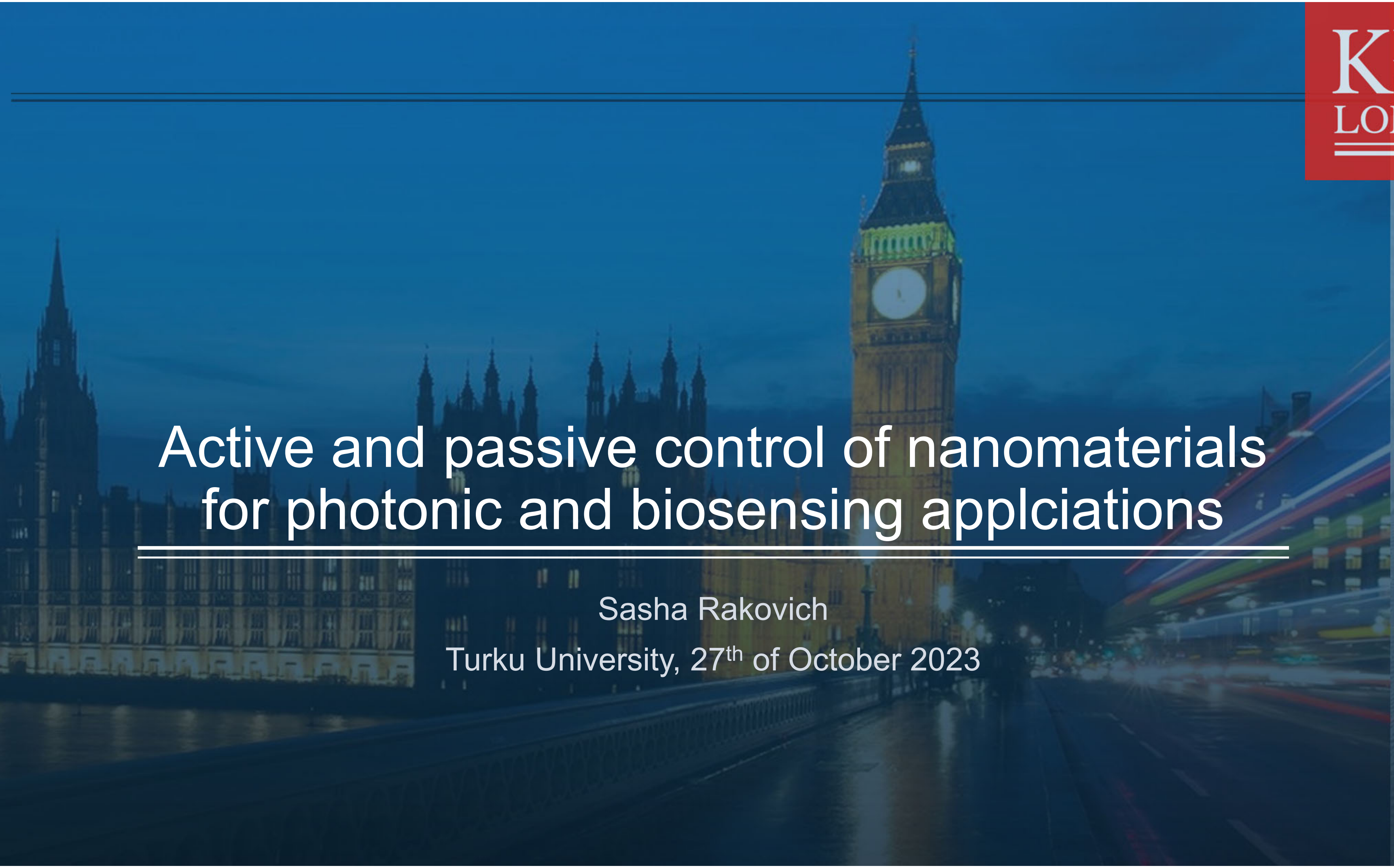


Active and passive control of nanomaterials for photonic and biosensing applciations

Sasha Rakovich

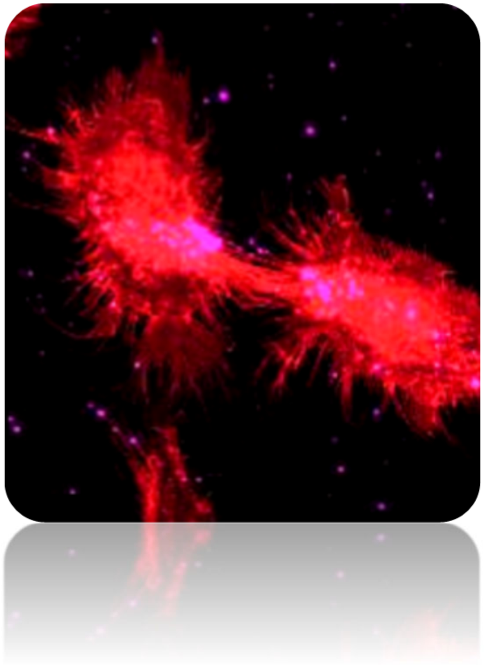
Turku University, 27th of October 2023

Physics@King’s College London

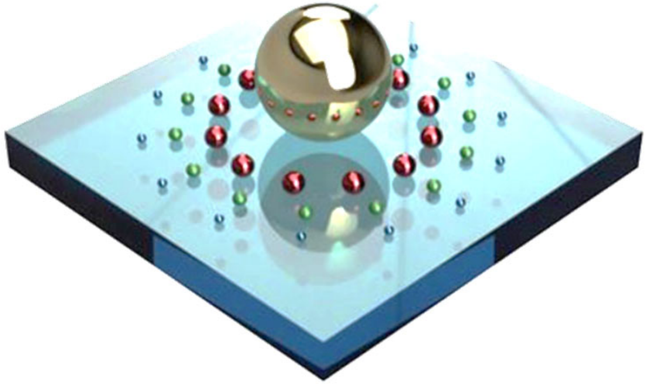
- **Photonics & Nanotechnology**
- **Biological Physics & Soft Matter**
- **Theory & Simulation of Soft Matter**
- **Theoretical Particle Physics & Cosmology**
- **Experimental Particle & AstroPhysics**

NanoBioPhotonics @ KCL-Physics

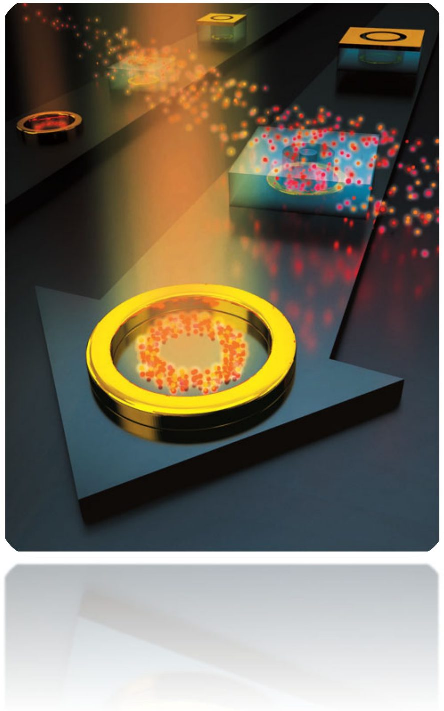
Nanophotonics for bioapplications



Nanophotonics for clean energy and sustainability

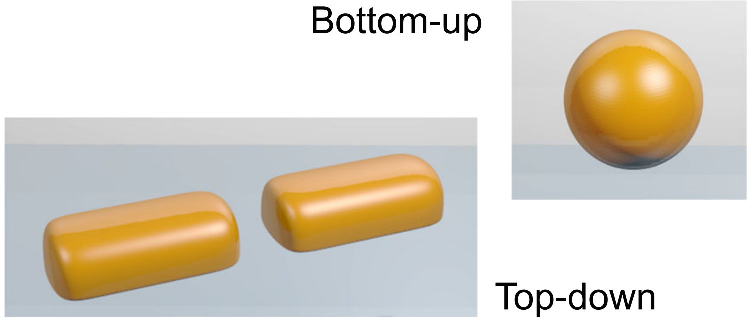


Nanomaterials assembly and control



Why colloidal nanomaterials?

Fabrication of nanomaterials

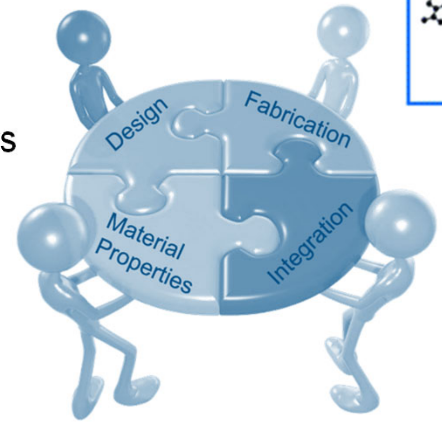


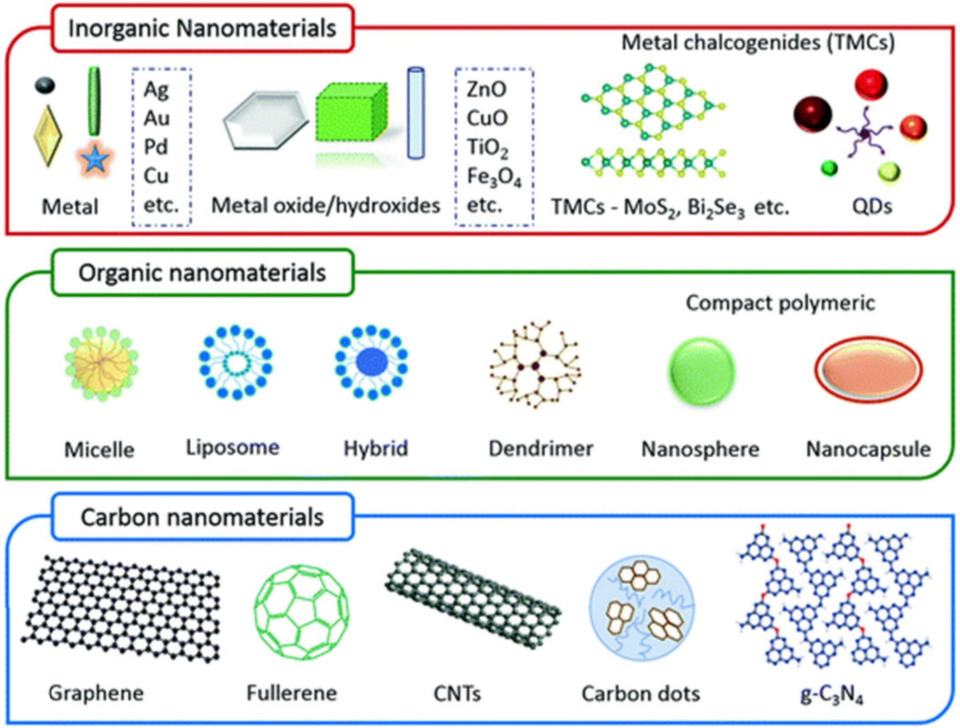
Bottom-up

Top-down

Considerations

- Material systems / sizes
- Scalability of fabrication
- Cost of fabrication & precursors
- Reproducibility
- Pre-determined localization
- Compatibility with pre-existing structures





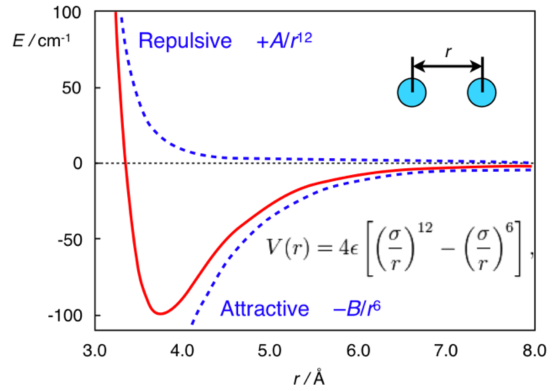
Applications:

- Renewable energy
- Environment
- Electronics
- Biomedical
- Textiles
- Industrial
- Food
- Agriculture
- Materials for sport

“Synthesis and Functionalization of Nanomaterials”, N. Kumar, S. S. Ray, Springer

Material immobilization toolbox

Long-range attractive forces

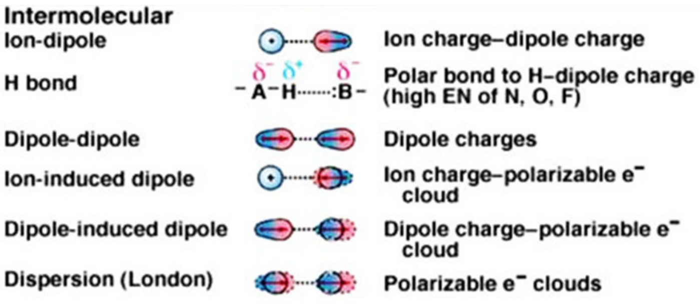


Delivery

+

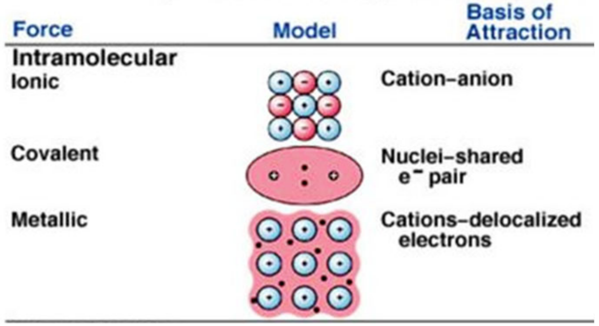
Fixation

Intermolecular forces



Intermolecular		
Ion-dipole		**Ion charge–dipole charge**
H bond	δ⁻ δ⁺ δ⁻ −A−H·······:B−	**Polar bond to H–dipole charge (high EN of N, O, F)**
Dipole-dipole		**Dipole charges**
Ion-induced dipole		**Ion charge–polarizable e⁻ cloud**
Dipole-induced dipole		**Dipole charge–polarizable e⁻ cloud**
Dispersion (London)		**Polarizable e⁻ clouds**

Intramolecular forces



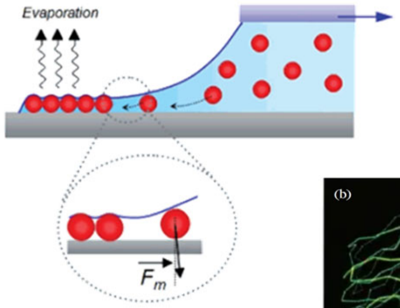
Force	Model	Basis of Attraction
Intramolecular		
Ionic		**Cation–anion**
Covalent		**Nuclei–shared e⁻ pair**
Metallic		**Cations–delocalized electrons**

cscsdashaicechem.weebly.com

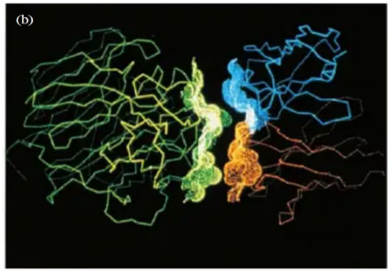
Other driving forces

- Electrostatic
- (Di-)electrophoretic
- Brownian motion
- Gravity
- Optical
- Convective
- Capillary

Typically more than type contributes



Malaquin, Langmuir 23, 11513 (2007)



Kuby Immunology. Ed. J.A. Owen, J. Punt, S.A. Stranford. 7th edition, W. H. Freeman and company, New York (2013)

Outline

Introduction
    Control of nanomaterials for applications

Self-assembled systems
    Nano-bio hybrids
    Plasmonic superclusters

Deterministic localization of NPs
    QDs coupling to plasmonic structures
    Large area localization of metallic NPs

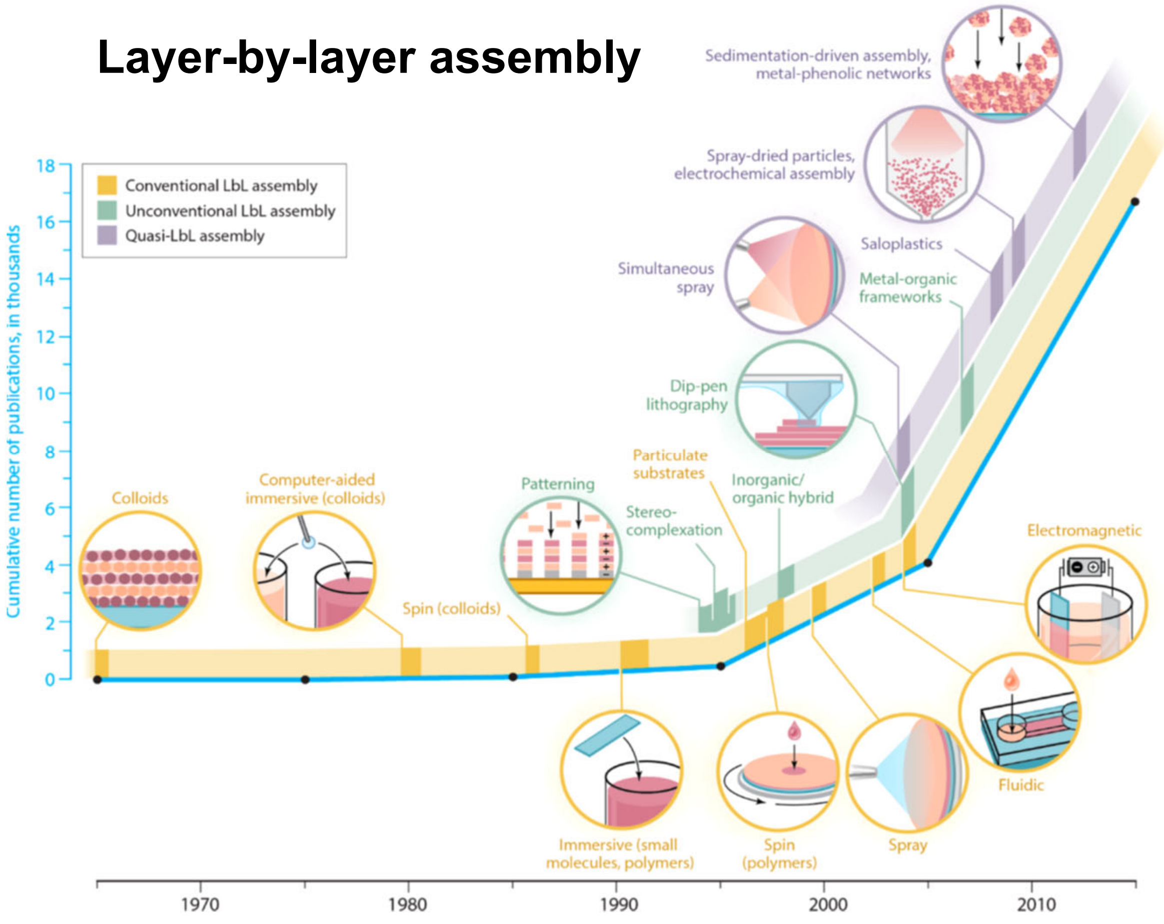
Active control of NPs
    Exploiting Brownian motion for long range transport

Conclusions & future outlook

KING'S College LONDON
Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

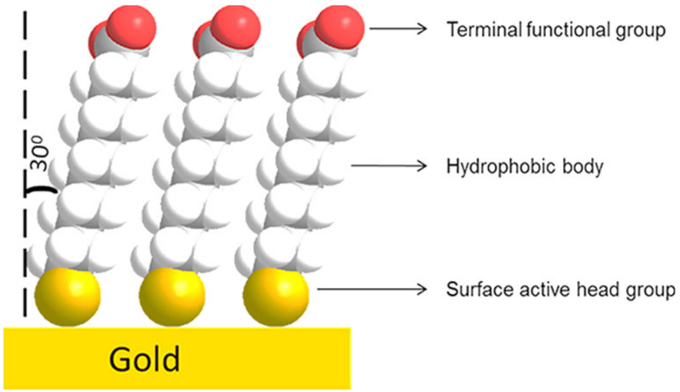
Self-assembly

Layer-by-layer assembly



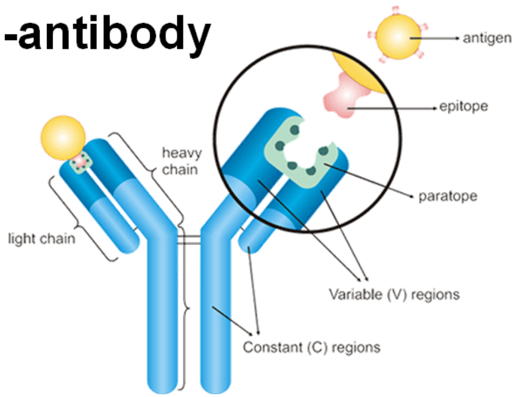
DOI: 10.1021/acs.chemrev.6b00627
Chem. Rev. 2016, 116, 14828−14867

SAM formation



https://www.intechopen.com/books/carbohydrate/self-assembled-monolayers-of-carbohydrate-derivatives-on-gold-surfaces

Antigen-antibody binding

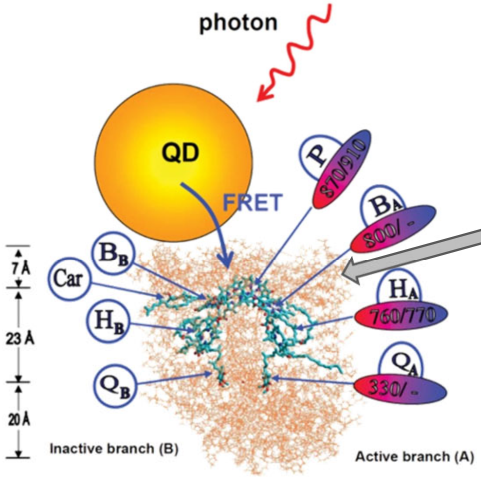


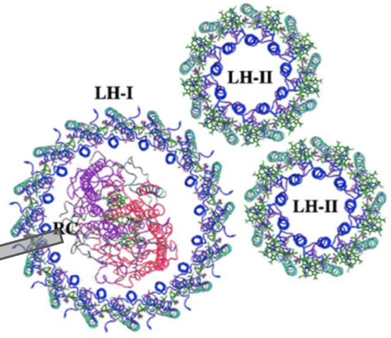
https://www.cusabio.com/c-21045.html

Self-assembly of nano-bio hybrids

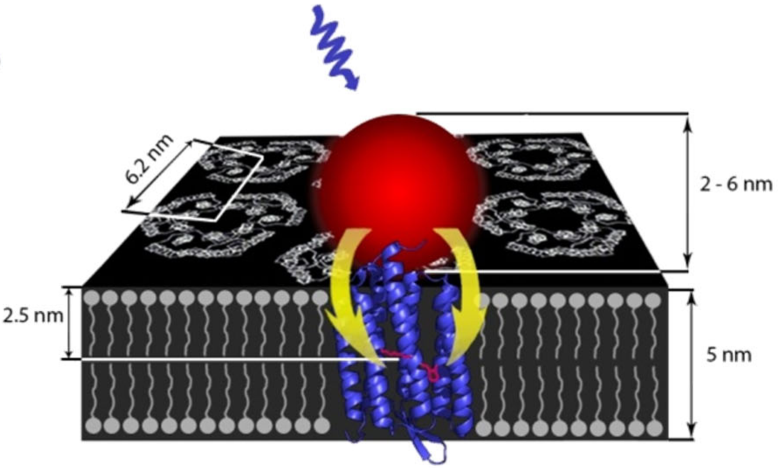
Biomaterials:

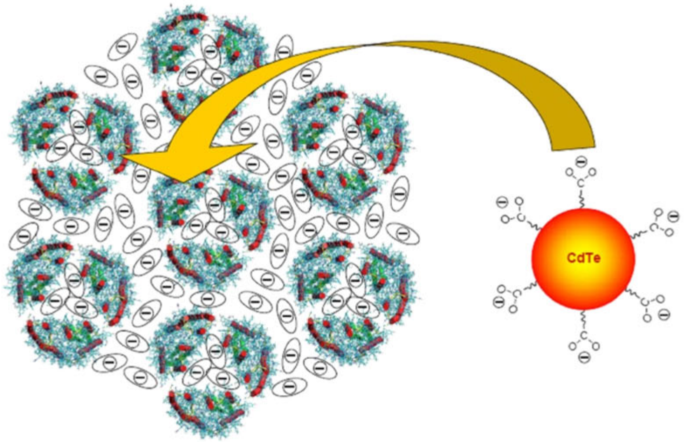
- Typically have many amino acids
- In solutions, some of end groups can be charged
- In many cases, electrostatic self-assembly with colloidal NPs is possible





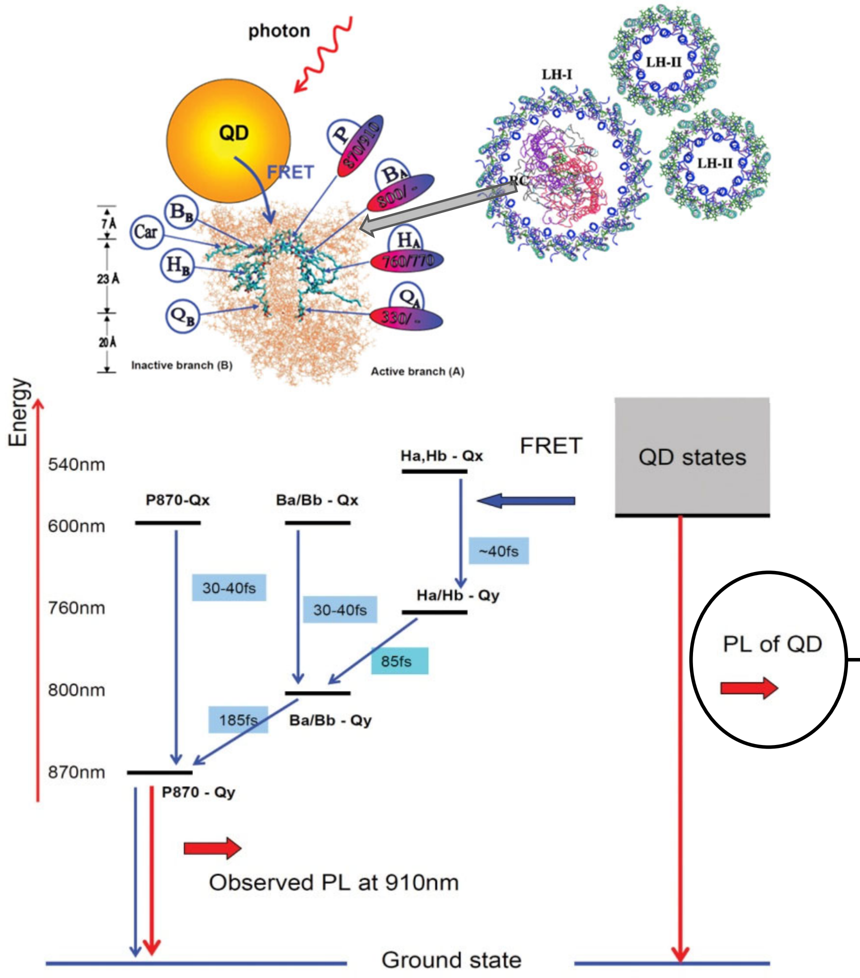
Assembly of QDs with bacterial reaction centres





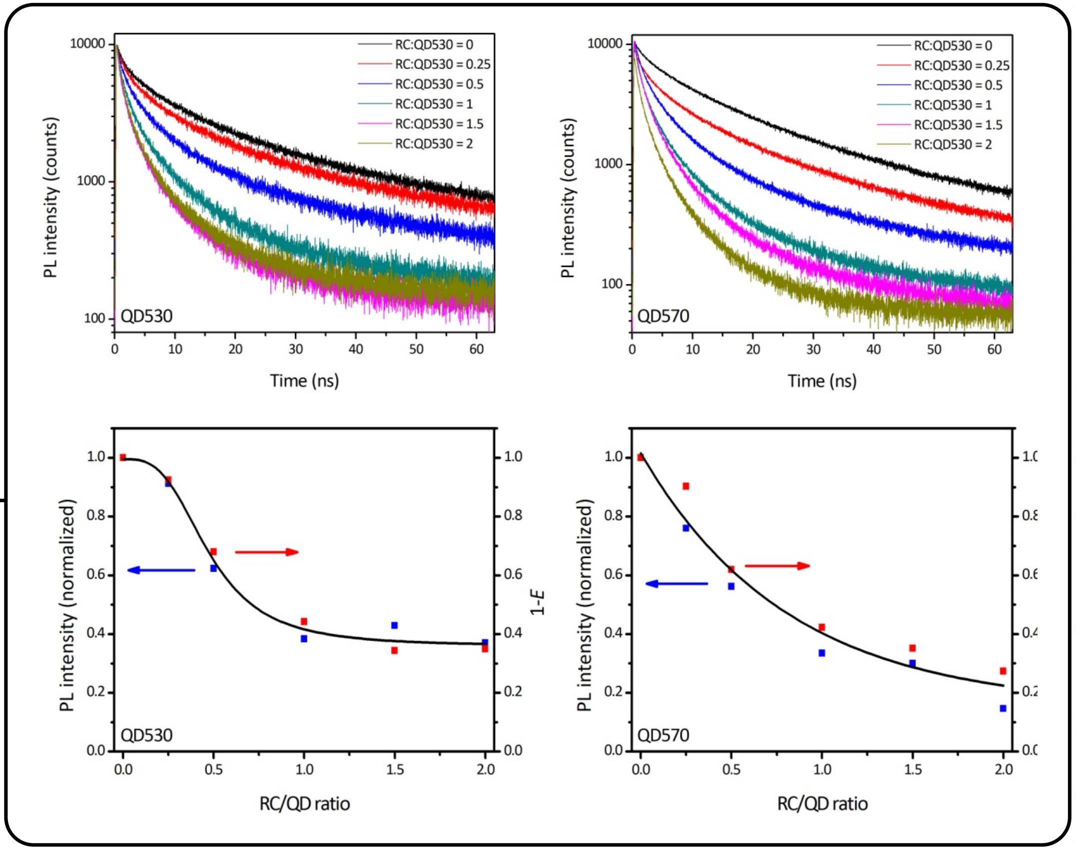
Assembly of QDs on Purple Membranes containing bR protein

QDs as artificial antenna for bacterial reaction centres



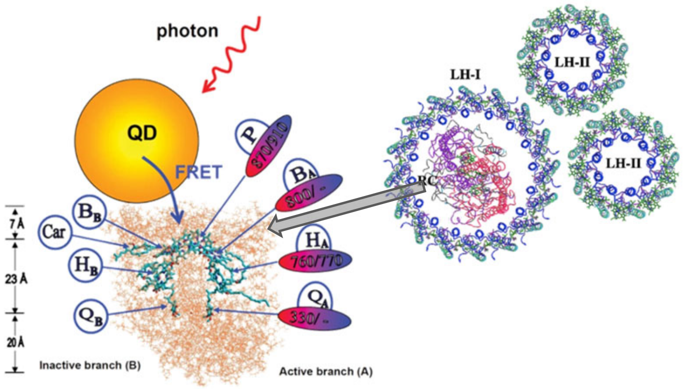
FRET signatures:

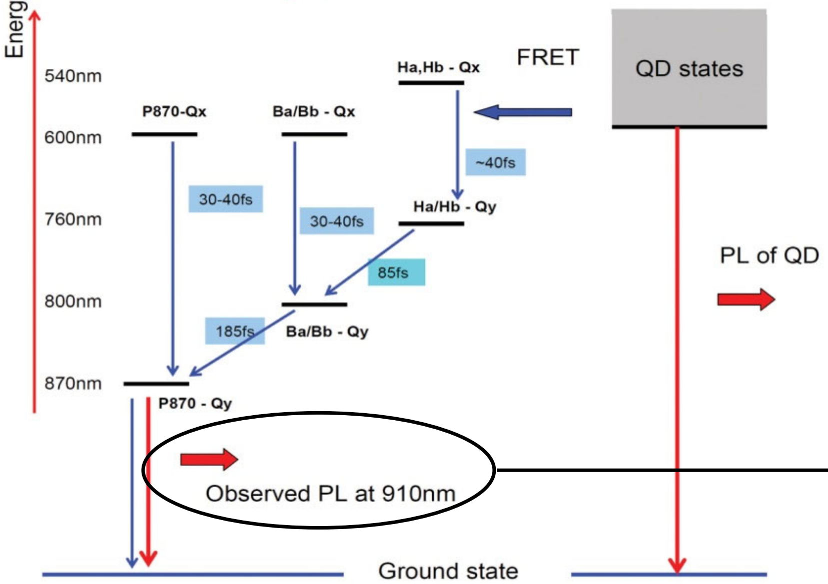
- PL intensity reduction of donor
- Reduction of fluorescence lifetime of donor



Angew. Chem. Int. Ed. **49**, 7217 (2010)

QDs as artificial antenna for bacterial reaction centres



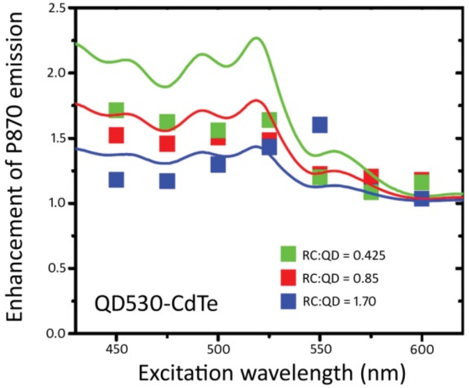


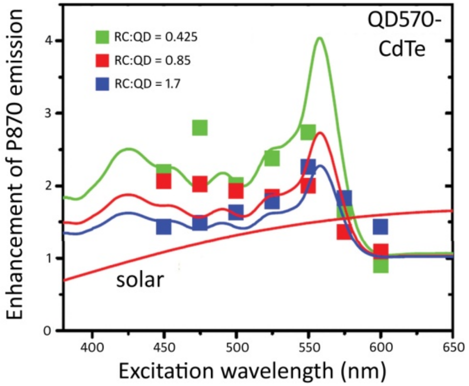
FRET signatures:

- PL intensity enhancement for the acceptor
- Should be proportional to FRET efficiency

$$A_{920\,nm} = \frac{I_{RC+QD}}{I_{RC}} = \frac{\int (PL_{RC+QD} - PL_{QD})\,d\lambda}{\int PL_{RC}\,d\lambda} =$$

$$= 1 + E \cdot \frac{A_{QD}(\lambda_{exc})}{A_{RC}(\lambda_{exc})} = 1 + E \cdot x \cdot \frac{\varepsilon_{QD}(\lambda_{exc})}{\varepsilon_{RC}(\lambda_{exc})}$$





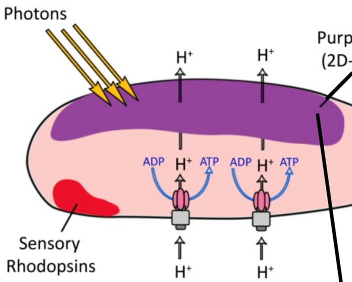
- Emission from Special Pair @920 nm is a measure of photosynthetic efficiency of complex

Angew. Chem. Int. Ed. **49**, 7217 (2010)

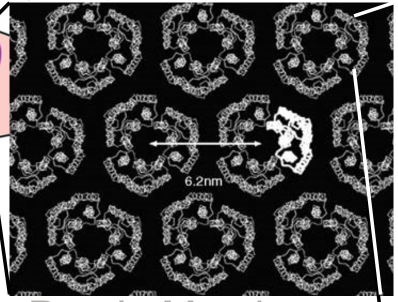
QDs as artificial antenna for bacteriorhodopsin protein

Membrane protein with:

- Photoelectric properties
- Photochromic properties
- Charge transport properties

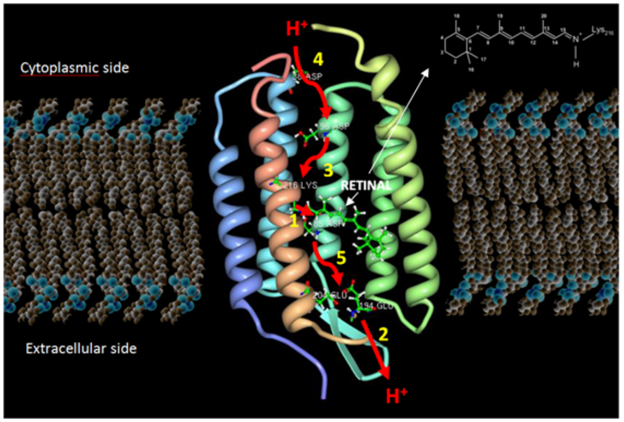


Halobacteria



Purple Membrane
(2D crystal of PM)

Bacteriorhodopsin protein
(light-activated proton pump)



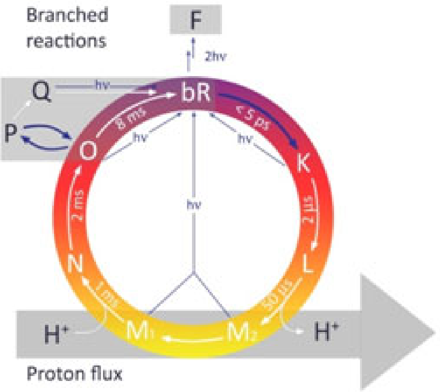
Performance optimised by evolution:

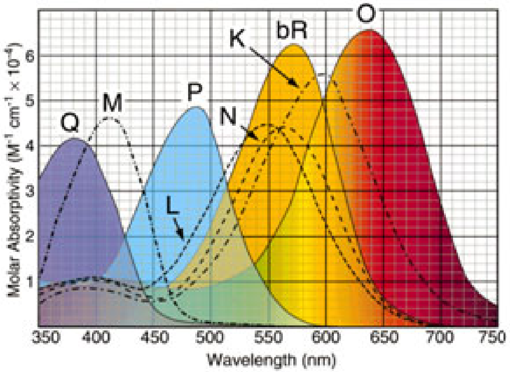
- High photo- chemical and thermal stability
- High fatigue resistance

Not able to deal with UV-photons:

- Can destroy light-absorbing molecule
- Utilizes only 0.1-0.5% of solar light

Use QDs as artificial down-converting LH antenna

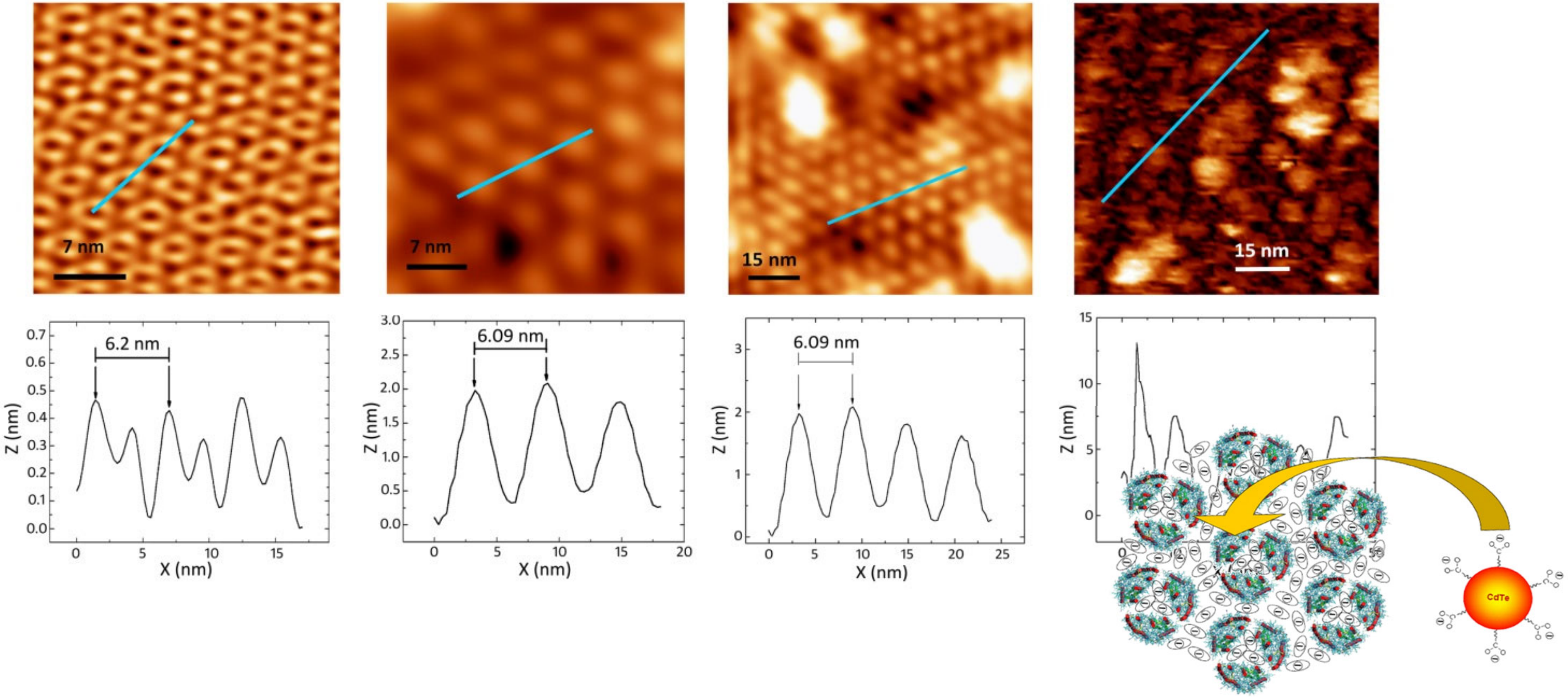




Adapted from Birge et al. J. Phys. Chem. B 103, 10746 (1999)

QDs as artificial antenna for bacteriorhodopsin protein

Electrostatic self-assembly of QDs on Purple and White Membranes



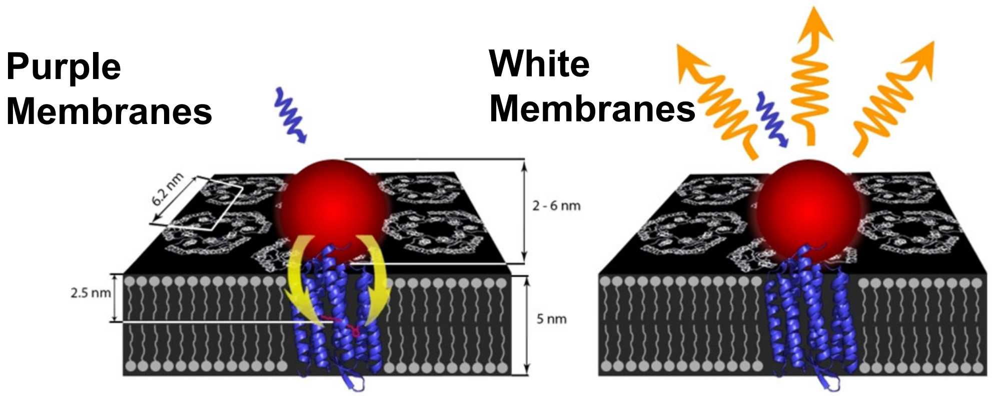
bR membrane

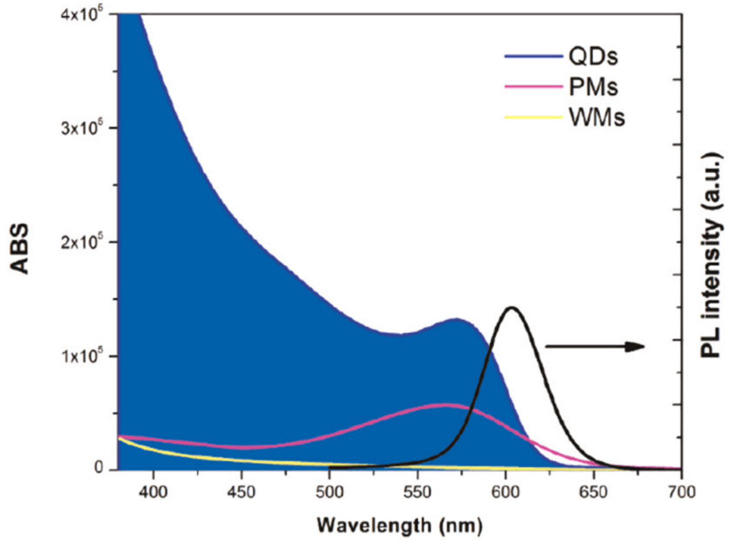
6 nm hydrodynamic radius QDs

Typical, high density

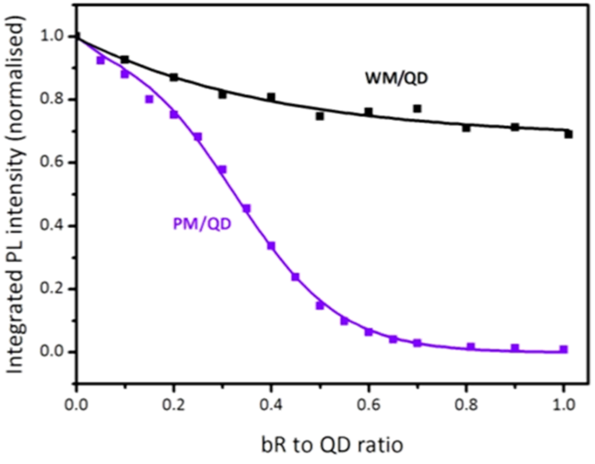
NanoLetters **10**, 2640 (2010)

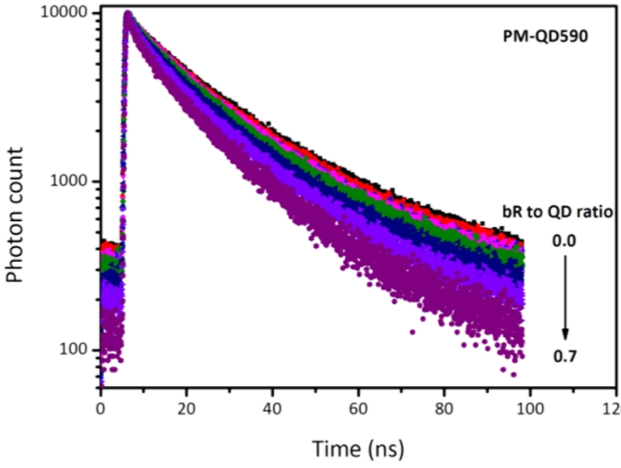
QDs as artificial antenna for bacteriorhodopsin protein

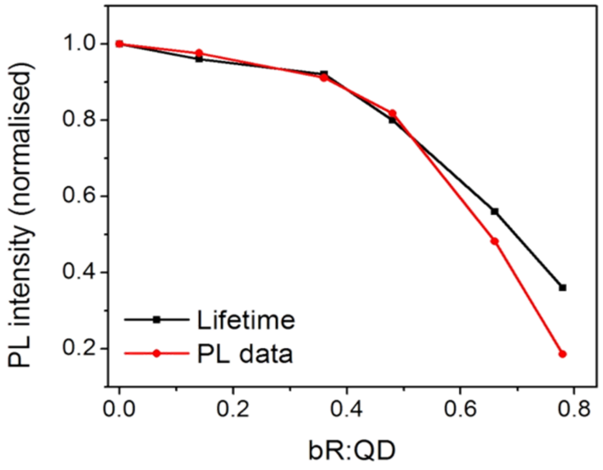




Energy transfer in QD-PM complexes



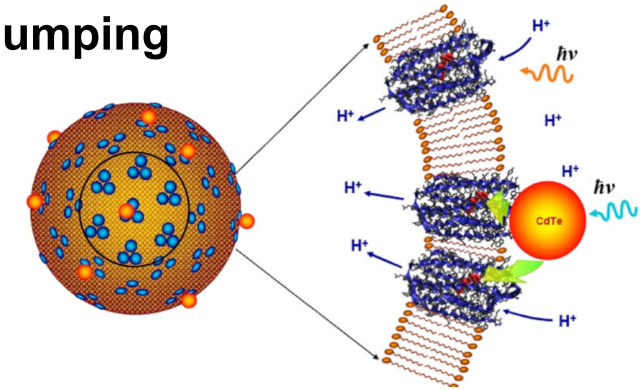


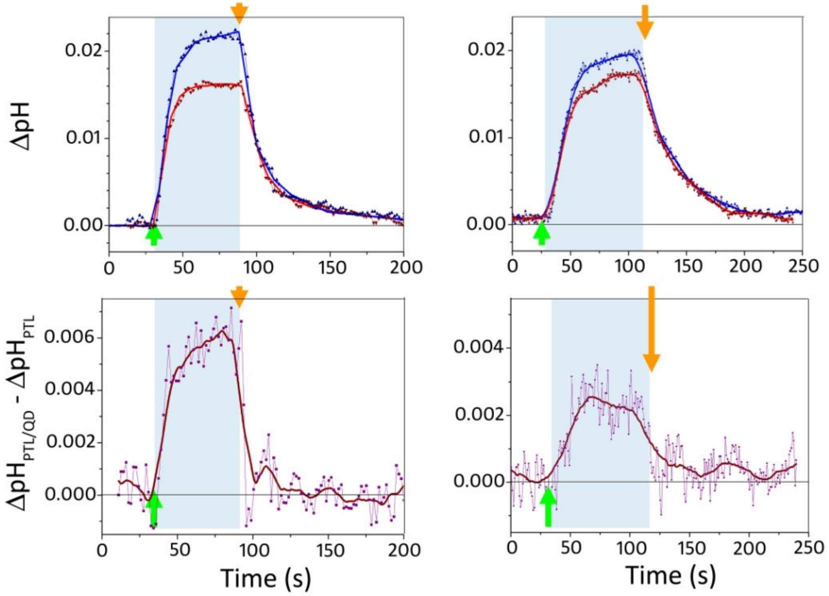


NanoLetters 10, 2640 (2010)

QDs as artificial antenna for bacteriorhodopsin protein

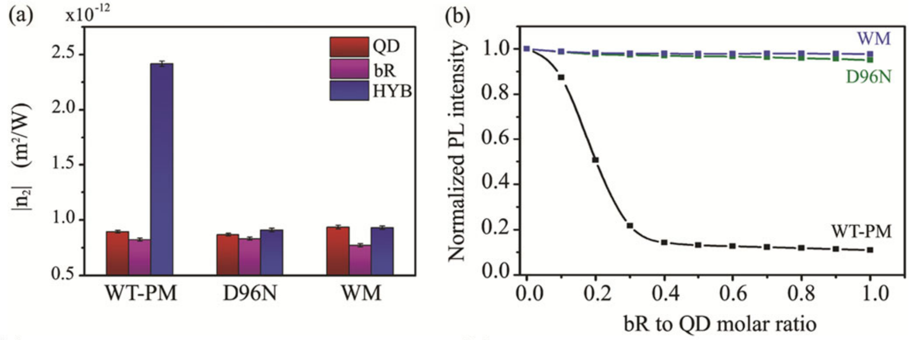
bR proton pumping efficiency

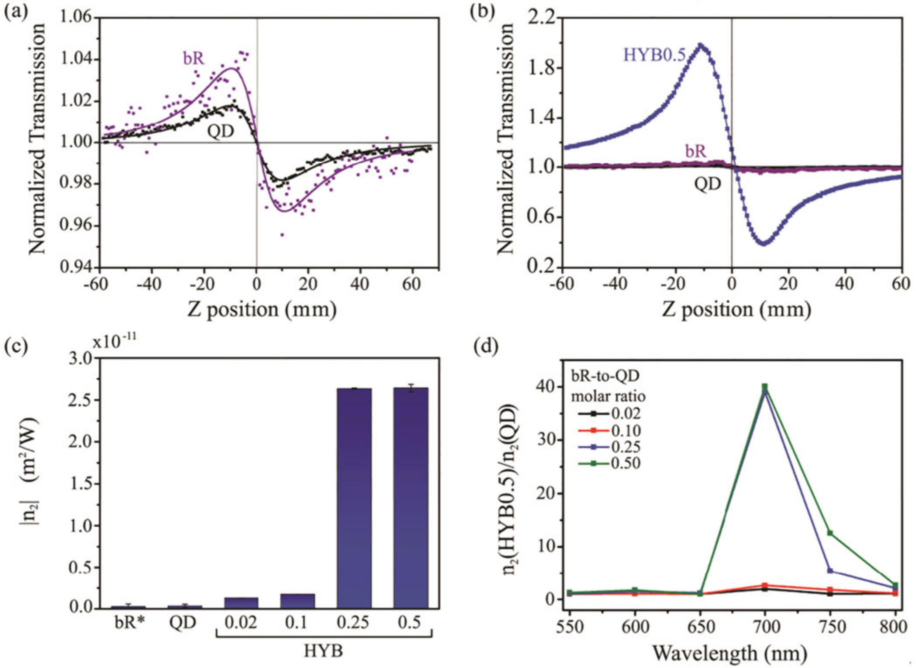




A. Rakovich et al., NanoLetters **10**, 2640 (2010)

Nonlinear refractive index

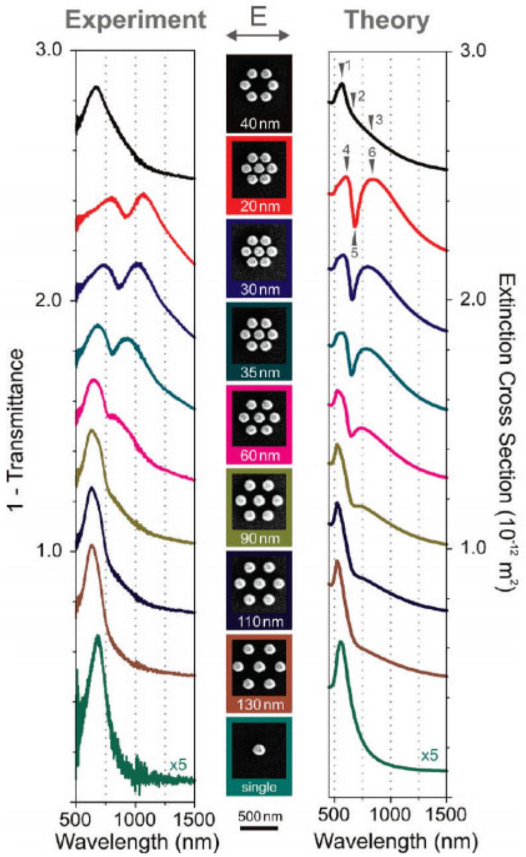




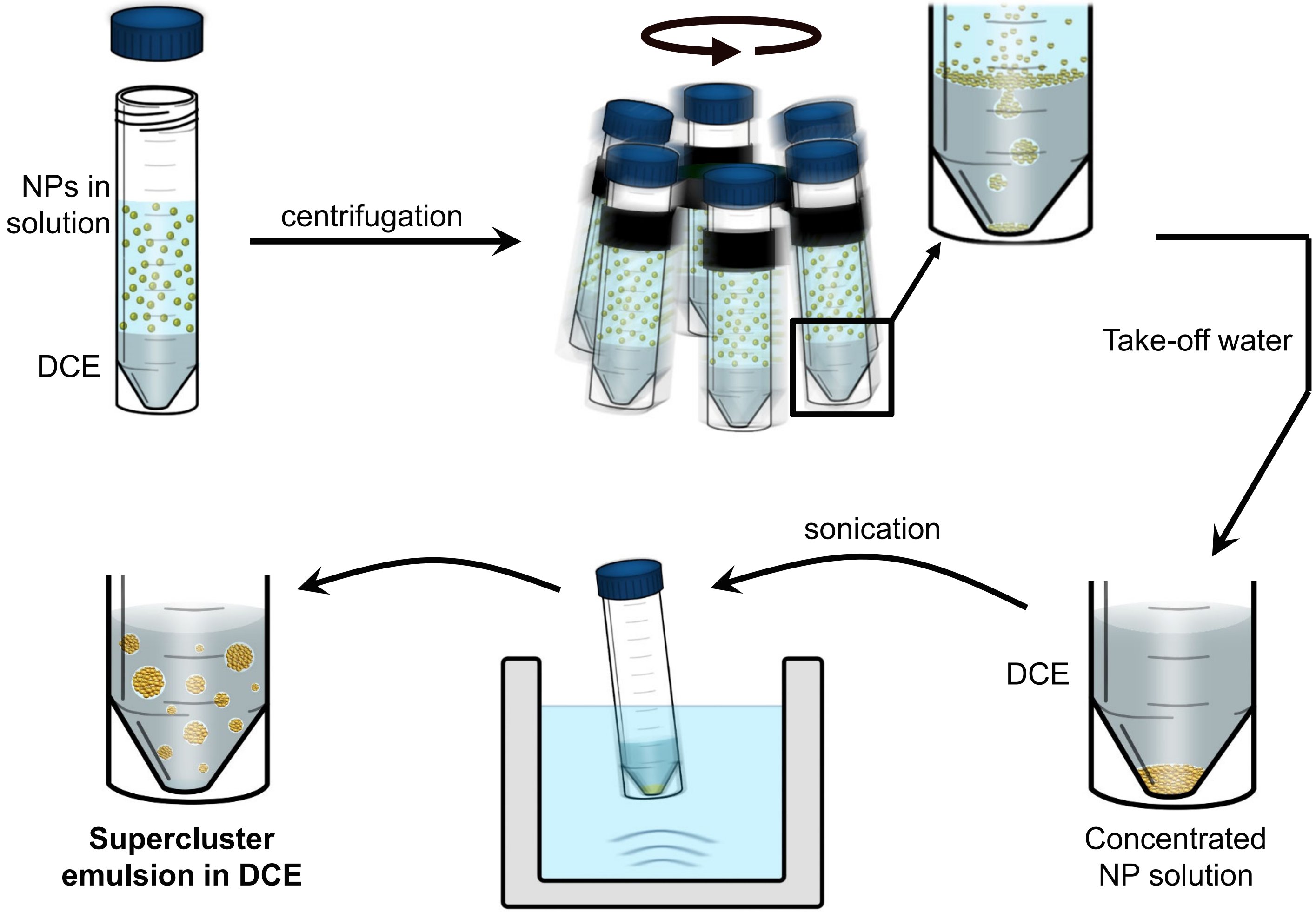
A. Rakovich et al., ACS Nano 7, 2154-2160 (2013)

Self-assembly of metallic superclusters

Based on hydrophobic effect



NanoLetters 10, 2721 (2010)



NPs in solution

DCE

centrifugation

Take-off water

sonication

DCE

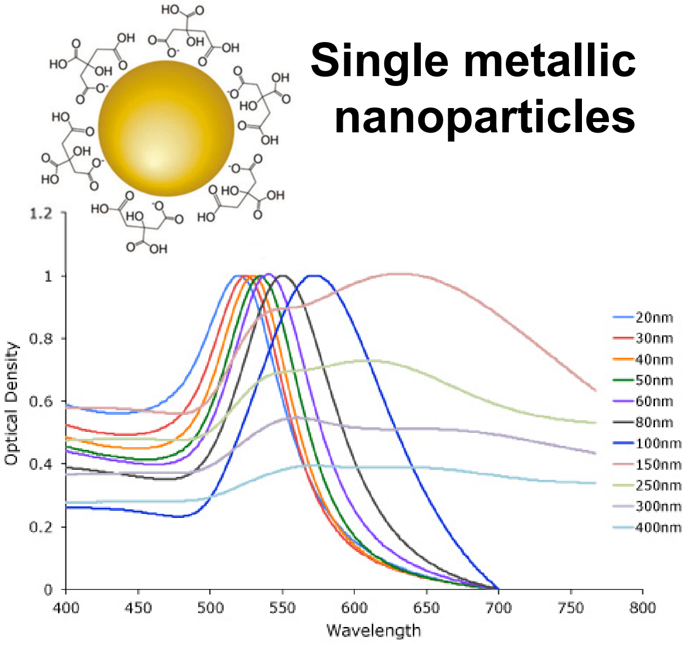
Concentrated NP solution

Supercluster emulsion in DCE

A. Lauri et al. ACS Photonics 4, 2070-2077 (2017)

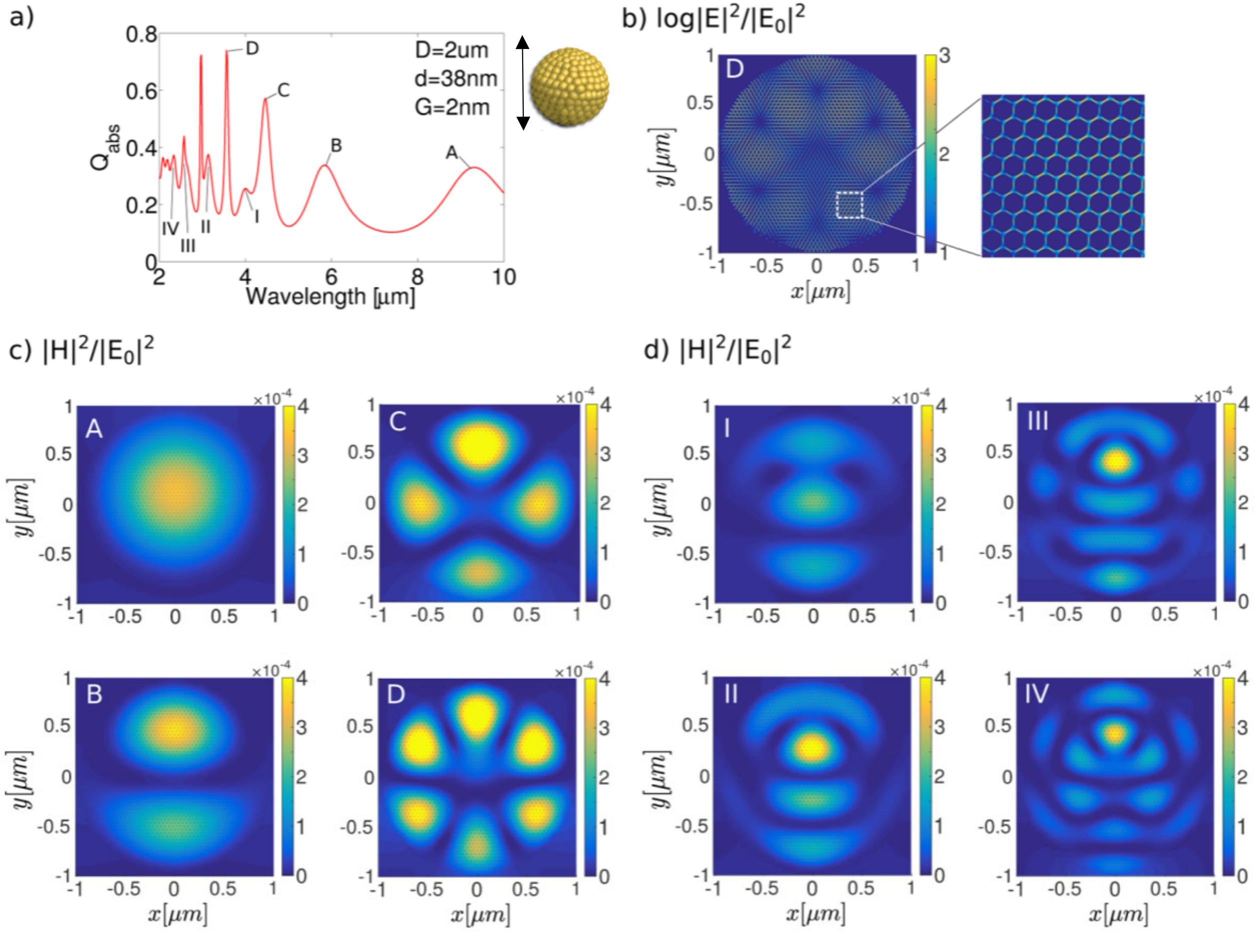
Properties of metallic superclusters

Single metallic nanoparticles



http://www.cytodiagnostics.com

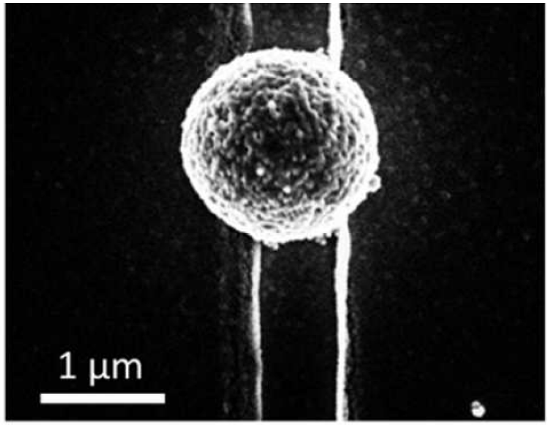
Superclusters of metallic nanoparticles



V. A. Turek et al. ACS Photonics 3, 35-42 (2016)

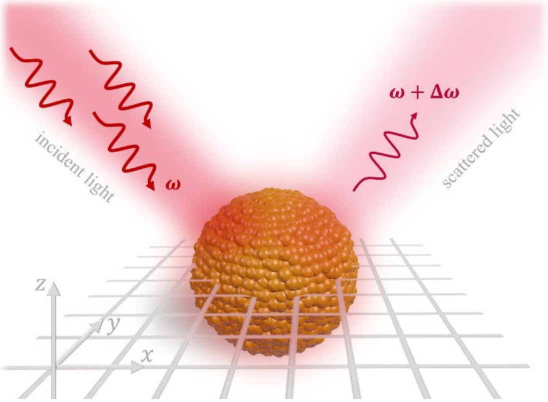
Experimental verification of collective modes

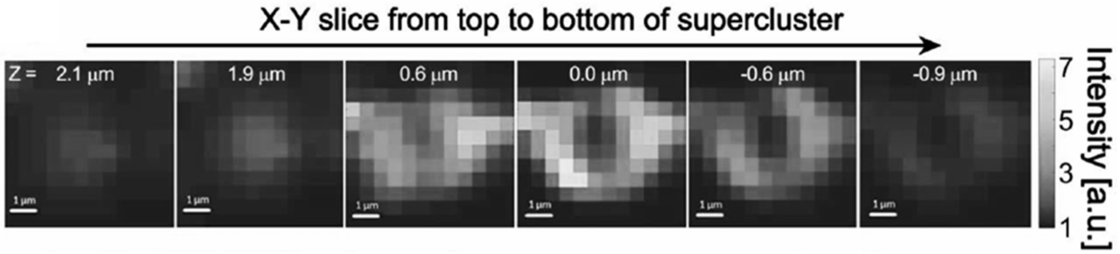
TEM: cluster size

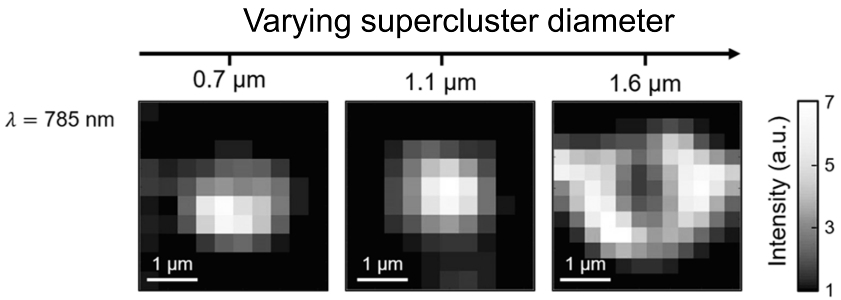


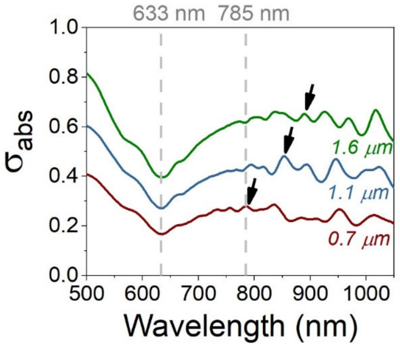
Raman: modal map

4-MBA self-assembled onto Au NPs prior to supercluster formation

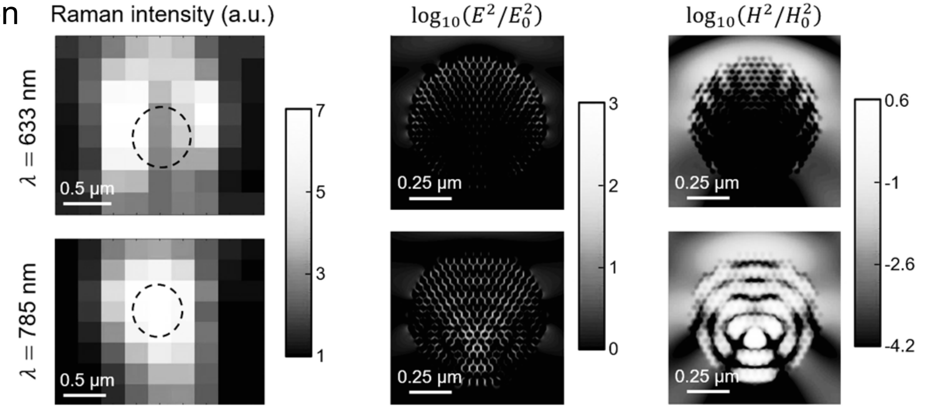








Varying excitation wavelengths
D = 0.7 μm:

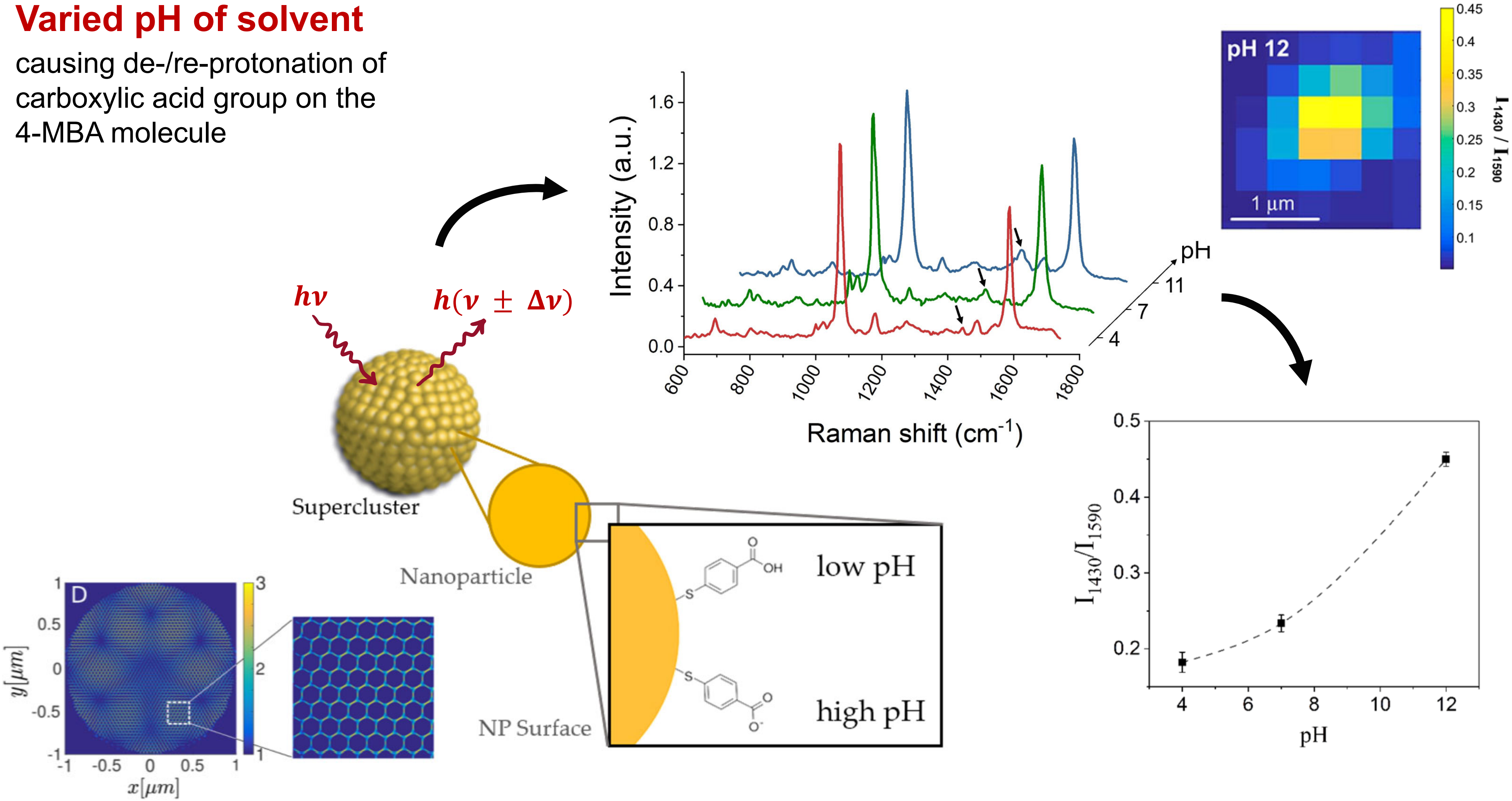


V. A. Turek et al. ACS Photonics 3, 35-42 (2016); *A. Lauri et al.* ACS Photonics 4, 2070-2077 (2017)

Sensing with metallic superclusters

Varied pH of solvent

causing de-/re-protonation of carboxylic acid group on the 4-MBA molecule



A. Lauri et al. ACS Photonics 4, 2070-2077 (2017)

Selective localization for as-designed fabrication

Tendency towards interdisciplinary science

- Exploit properties of different materials

Drive for device minimisation & integration

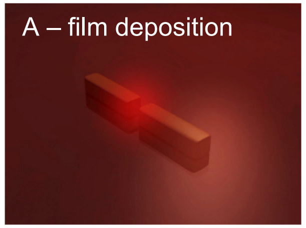
- Avoid cross-talk of different components
- Nanoscale control of materials

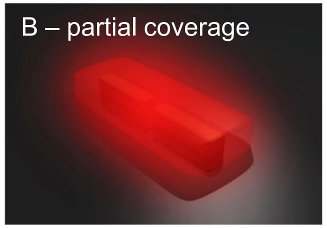
Independent design of components

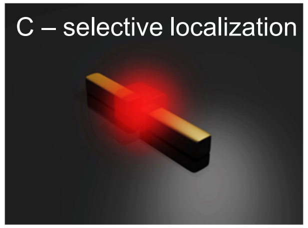
- Time-efficiency
- Collaborative efforts

Reproducibility of performance

- Chemo- & photo- stability of components
- Reproducible characteristics





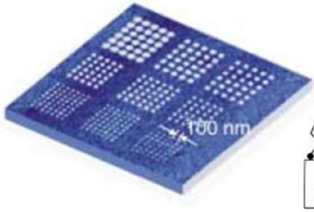


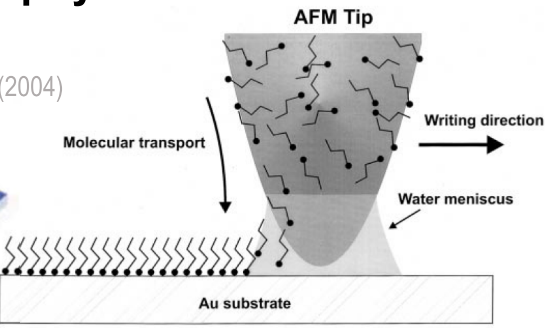
Selective localization methods

Technique	Advantages	Disadvantages
Directed self-assembly	Fast Large area coverage Works on almost any substrate	Weak adhesion Use of non-removable masks
SAM patterning	Good precision	SAM covers entire substrate Slow due to large area exposure
MACE-ID	Good control over amount deposited OK precision	Precursor in EBL chamber Use of additional material as scaffolding (no functional purpose)
Multi-step EBL	OK precision Very flexible	Use of masks (can leave residues)
AFM-based techniques	High precision	Slow and labour intensive SAM cover entire substrate Difficult to do on samples with pre-existing structures
Localised polymerization	High precision No mask	Deposition of additional material (polymer matrix) Only works with resonator structures
LAMI-based approach	Very high precision "In-built" localisation No mask	Low yield No mask: non-specific attachment can be an issue Only works with plasmonic structures
Hot-carrier driven chemistry	High precision "In-built" localisation No mask	Chemistry difficult to control Localisation not only in hotspot Only works with plasmonic structures
Optical printing	Moderate precision No mask Very strong attachment	Labour intensive Difficult to do with pre-existing structures Functionalisation of entire substrate

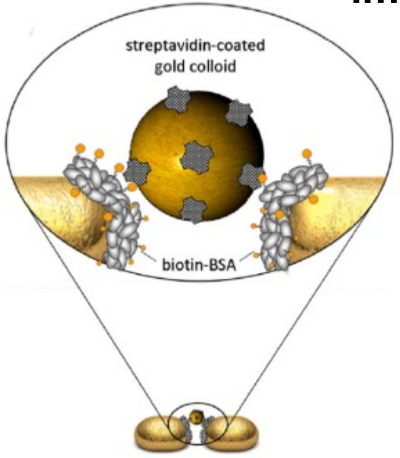
Dip-pen lithography

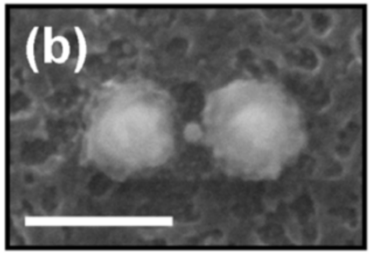
D. S. Ginger *et al.*
Ang Chem Int Ed 43, 30-45 (2004)





Light-activated molecular immobilization (LAMI)-based approach



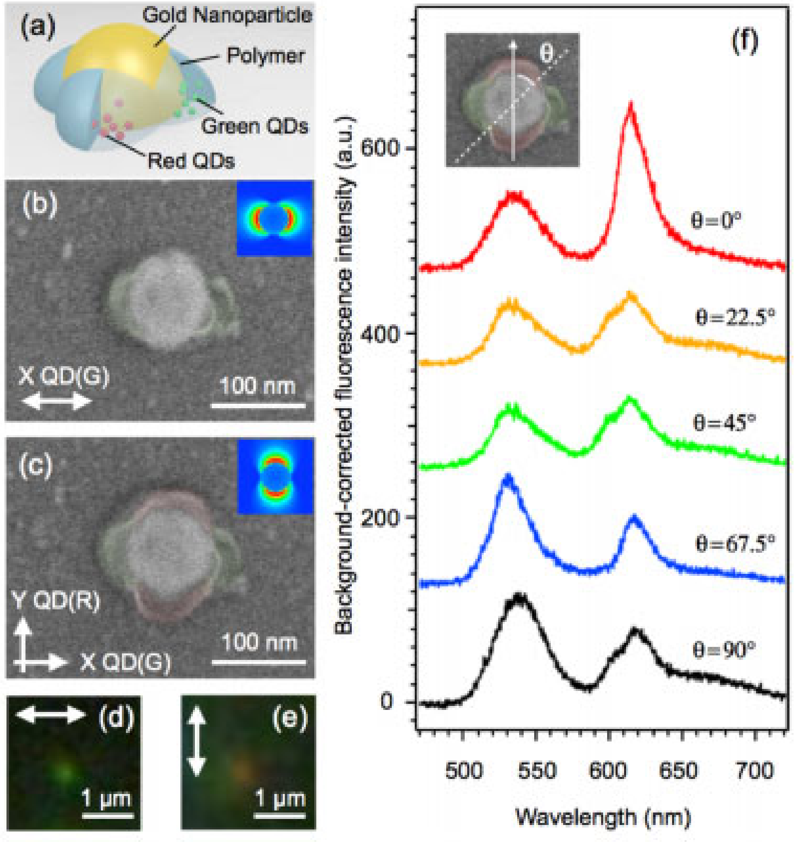


C.M. Galloway *et al.*
NanoLetters 13, 4299 (2013)

Deterministic localization methods

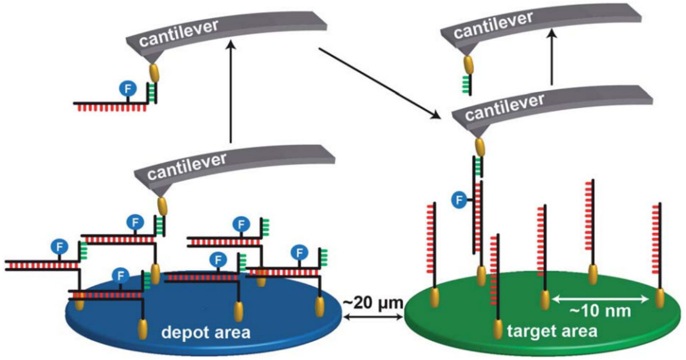
Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

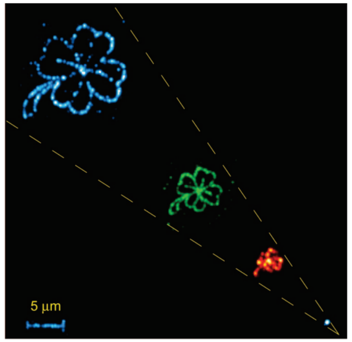
Photopolymerization



Zhou, Nano Lett. 15, 7458-7466 (2015)

Cut and Paste

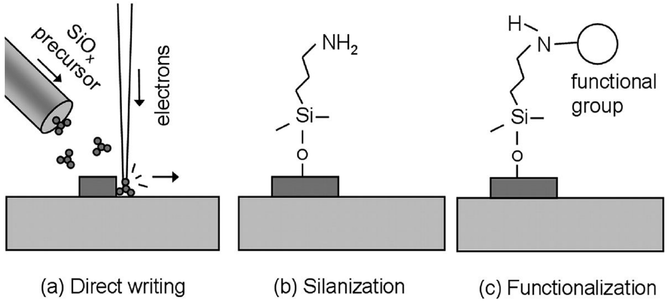


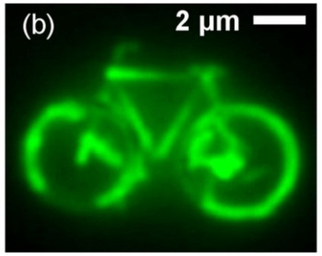


Jacobs, Chem. Sci. 5, 1680 (2014)

Puchner, NanoLetters 8, 3692-3695 (2008)

MACE-ID



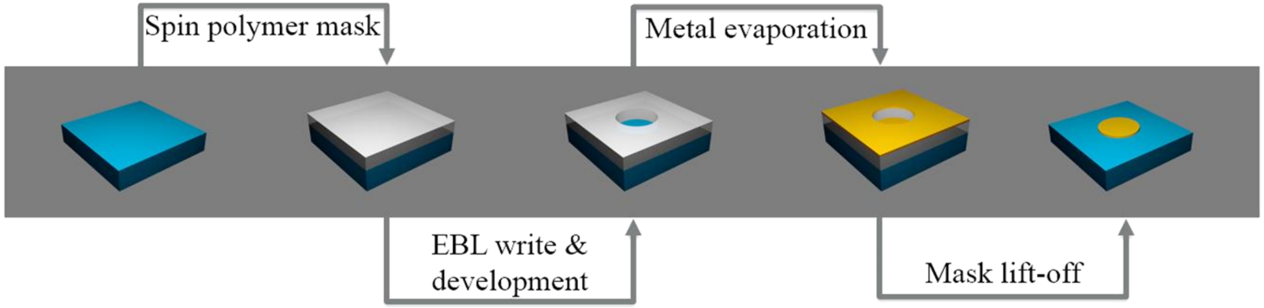


W. Slingenbergh, ACS Nano 6, 9214 (2012)

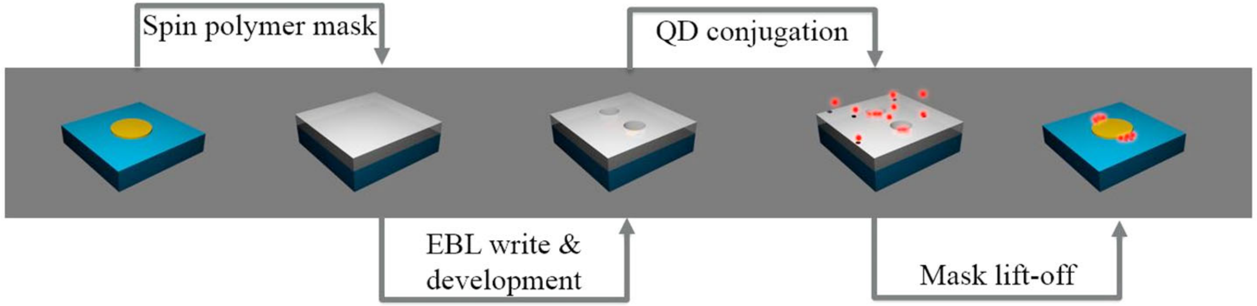
2-step EBL method

For localization of QDs in regions of interest near pre-existing structures

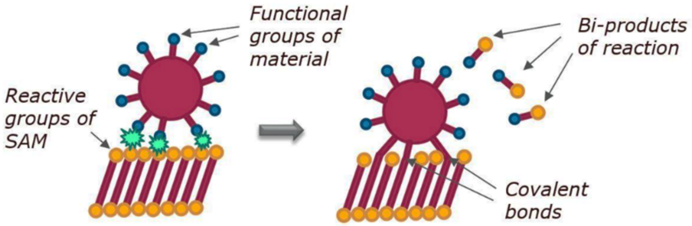
Step 1: fabrication of nanoantenna



Step 2: selective localisation of NPs



QD attachment step



SAM formation:

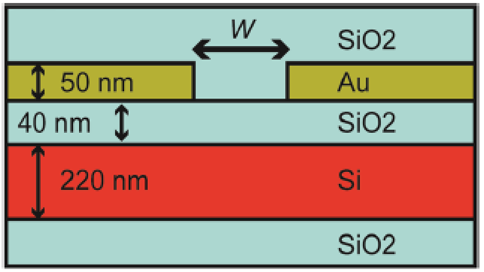
- Alkane-thiols and derivatives (e.g. 1-amino undecanethiol) for metals, some semiconductors
- Ethoxysilanes and derivatives (e.g. APTES) for oxygen- or silicon terminated surfaces

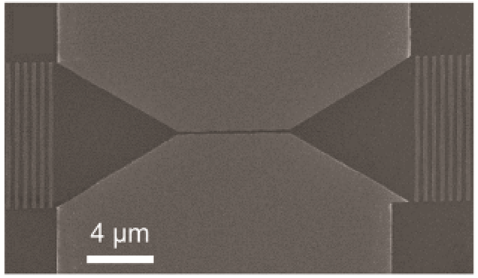
QD conjugation to SAMs

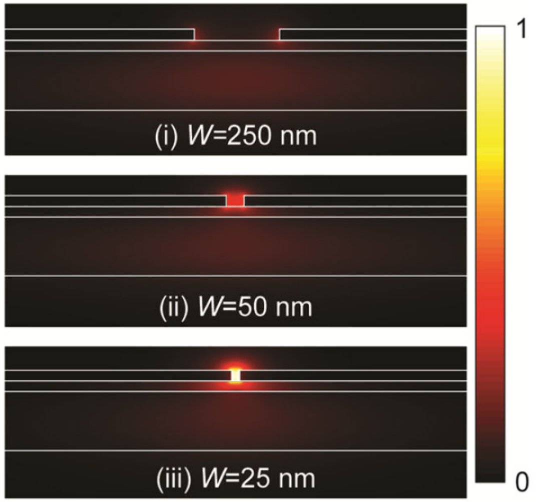
- Covalent conjugation, e.g. via EDC-coupling reaction
- Antigen-antibody linkage

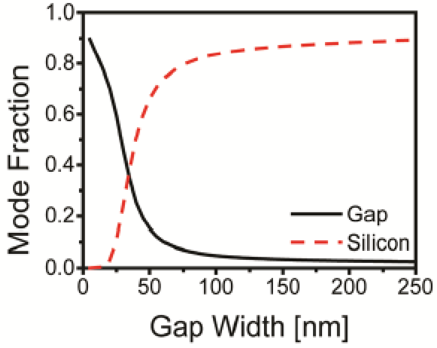
Application of the 2-step EBL method

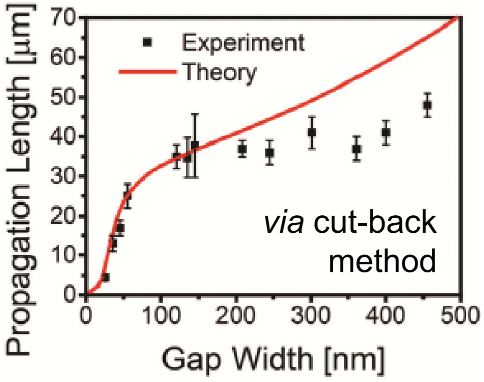
For characterization of SOI gap plasmon waveguides







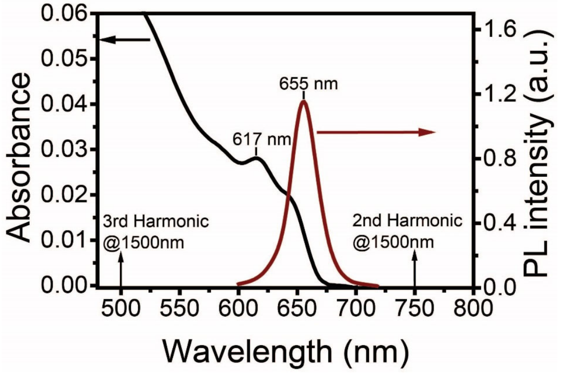


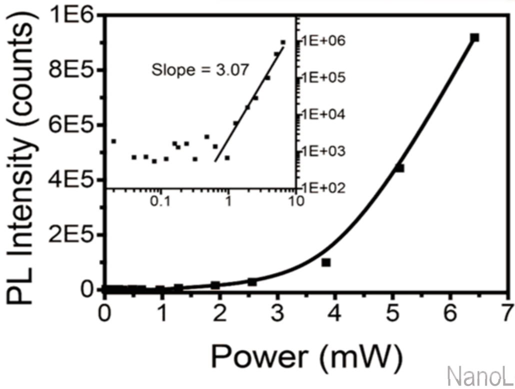


Cut-back method:

- ➢ Requires many sacrificial structures
- ➢ Measures propagation length
- ➢ Does not reveal mode location

Use selectively deposited SQDs!

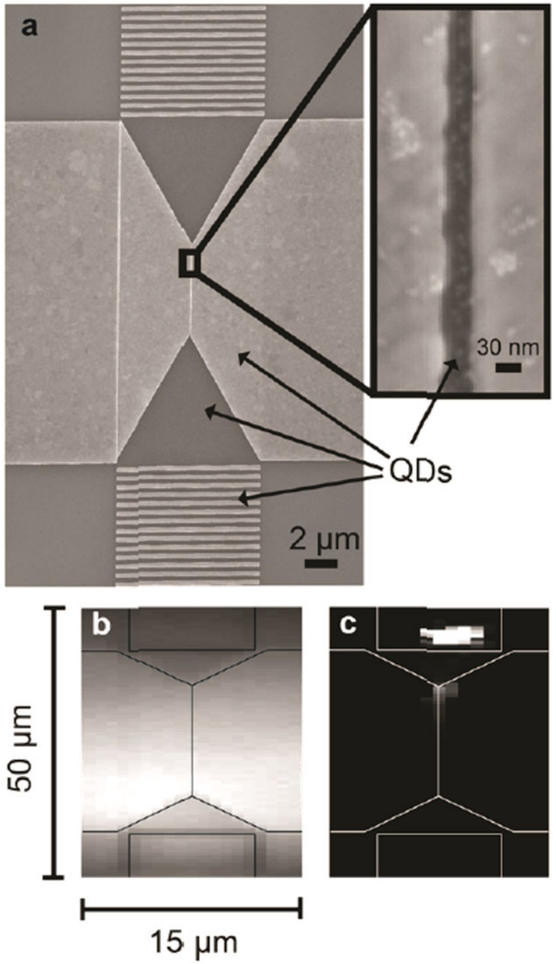




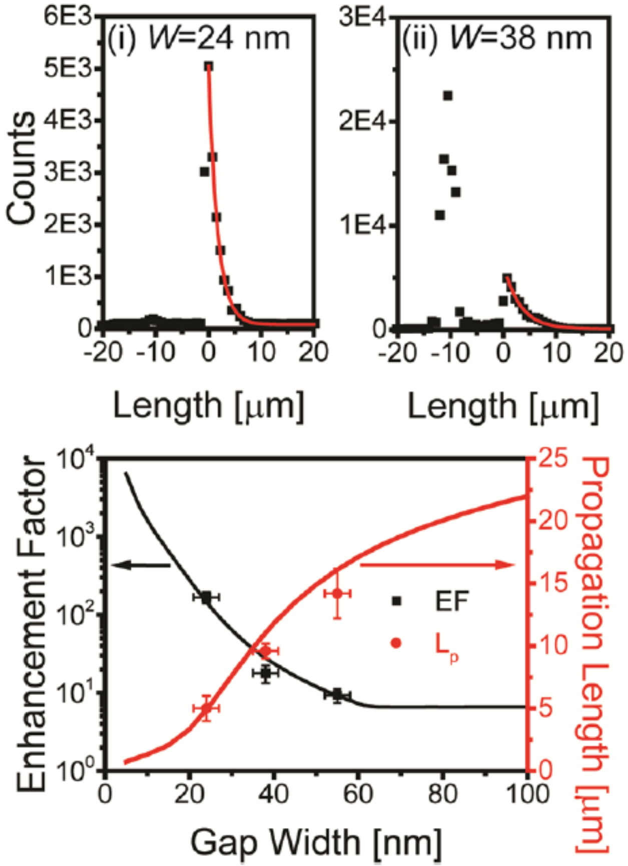
NanoLett **16**, 1410-1414 (2016)

Application of the 2-step EBL method

For characterization of SOI gap plasmon waveguides

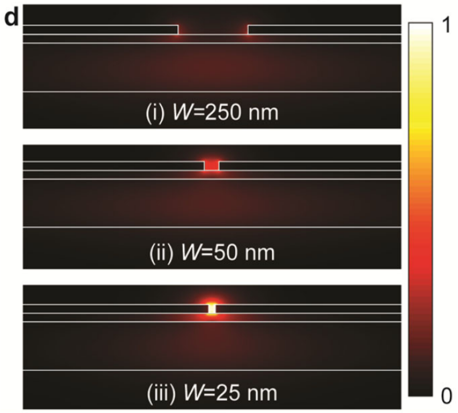


QDs' TPE mapping



Characterization of a single sacrificial structure:

- Direct measurement of propagation length from TPE data
- Direct confirmation of "nano-squeezing" of light



$$\mathrm{EF} = \left|\frac{I}{I_o}\right| = \frac{\left(\frac{C}{C_o}\,\frac{W_{\mathrm{pixel}}}{W}\right)^{1/3}\left(\frac{\rho_{\mathrm{QD}}(W)}{\rho_{\mathrm{QD}}(W_o)}\right)}{\eta_{\mathrm{grating}}}$$

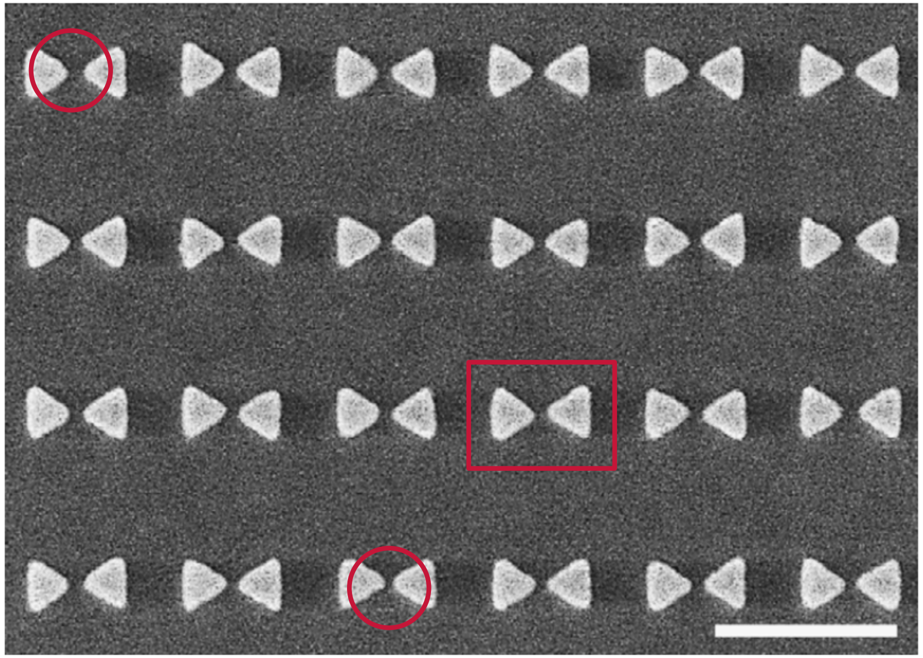
M.Nielsen et al. NanoLett **16**, 1410-1414 (2016)

Application of the 2-step EBL method

For deterministic control of radiative properties of QDs via exciton-plasmon coupling

Plasmonic nanoantennas' performance depends on:

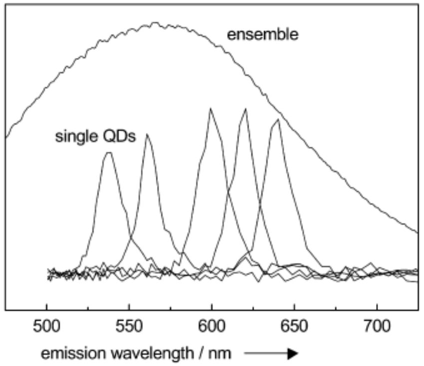
- Antenna shape & size
- Material from which it is made
- Dimension of gaps (if present)

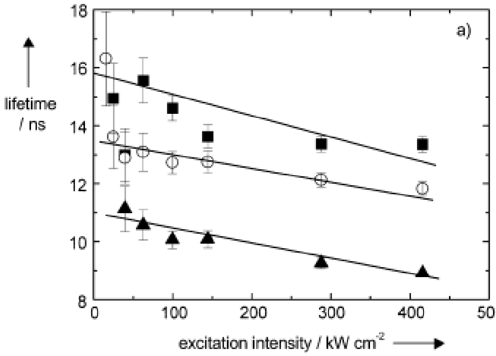


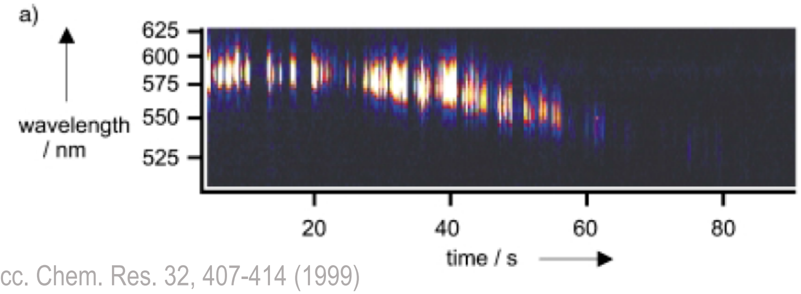
Nature Comm. 5, 4427(2014)

Colloidal QDs:

- Distribution of sizes (=λ_{em}) in a sample
- Blinking behaviour on a few/single QD level
- Blue-shifts and shortening of lifetime at high excitation intensities



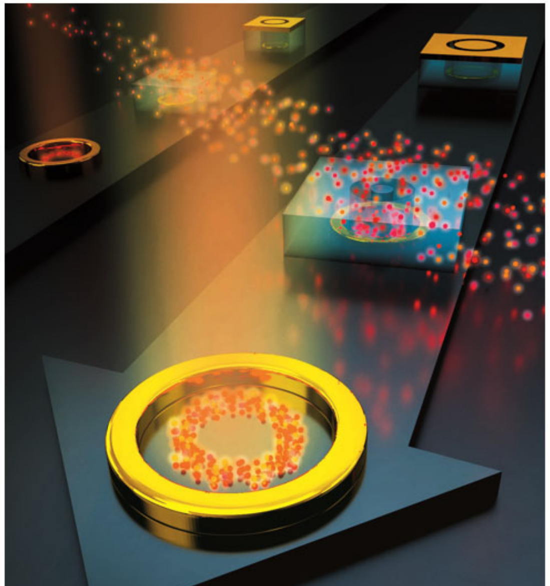




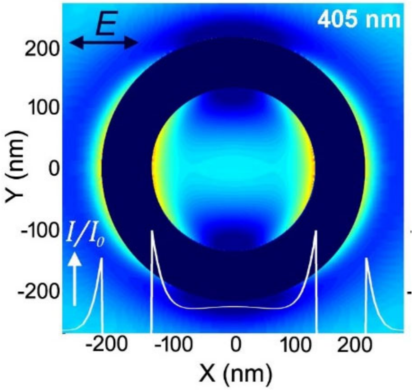
Acc. Chem. Res. 32, 407-414 (1999)
ChemPhysChem 3, 871-879 (2002)

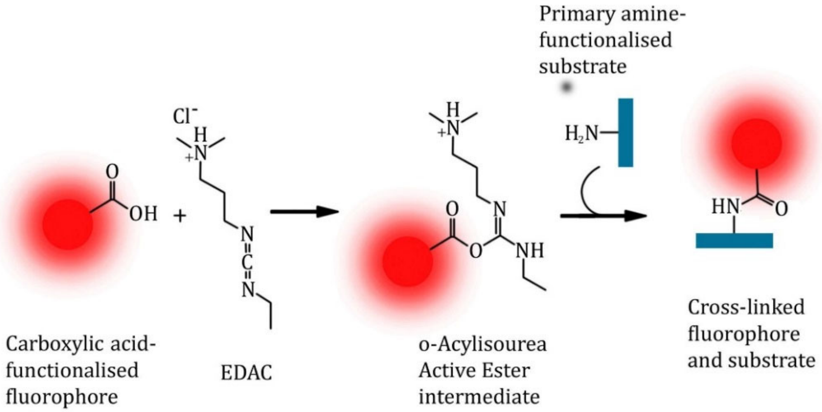
Application of the 2-step EBL method

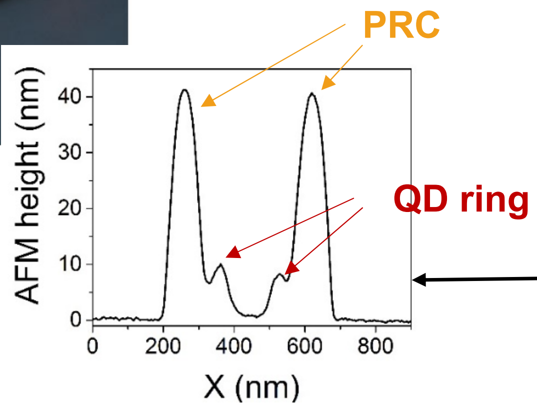
For deterministic control of radiative properties of QDs via exciton-plasmon coupling

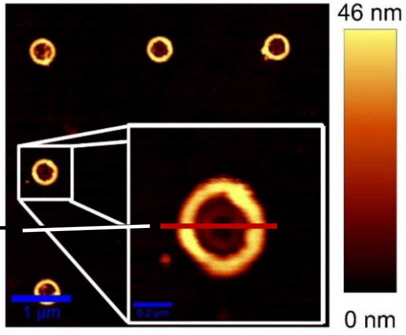


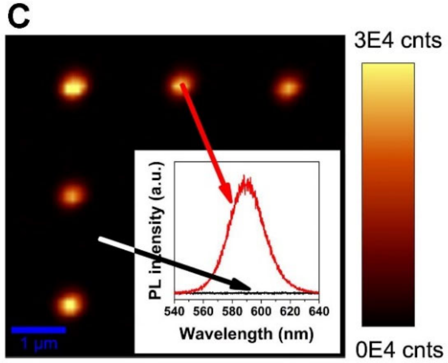
Selectively deposited colloidal QDs inside plasmonic ring cavities











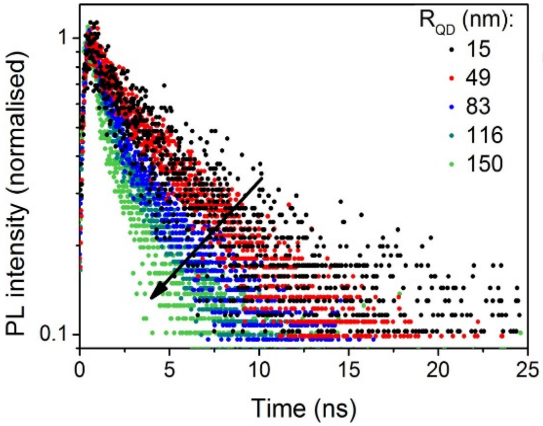
A. Rakovich et al. ACS Nano **9**, 2648-2658 (2015)

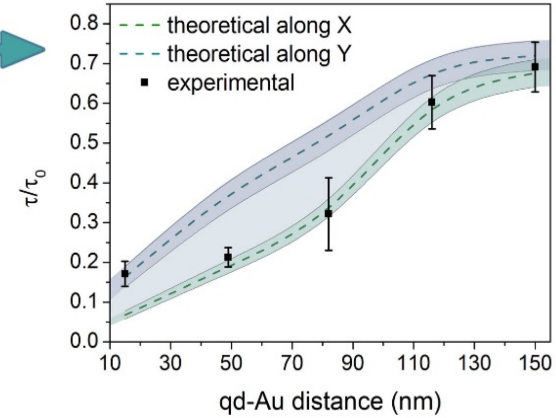
Application of the 2-step EBL method

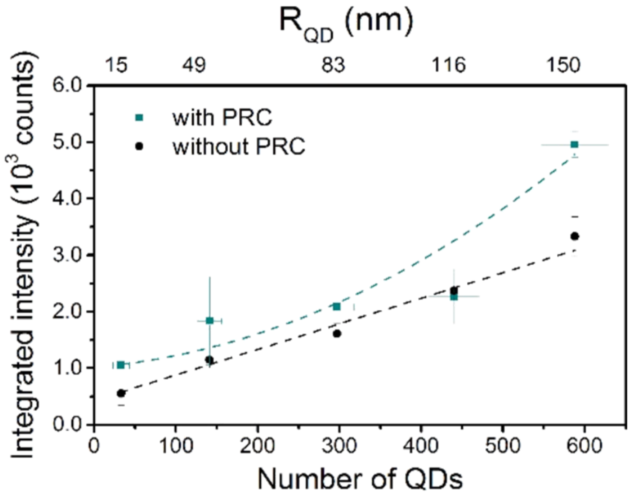
For deterministic control of radiative properties of QDs via exciton-plasmon coupling

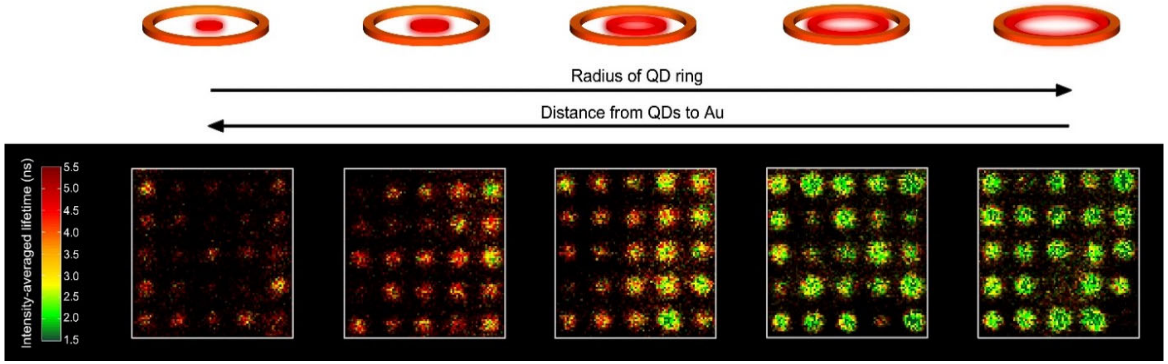
QD-PRC coupling

- Varied QD-PRC separation by increasing radius of QD ring
- Dimensions of PRC kept constant (D440t60)
- Strong change in radiative rates
- Good agreement with FDTD calculations







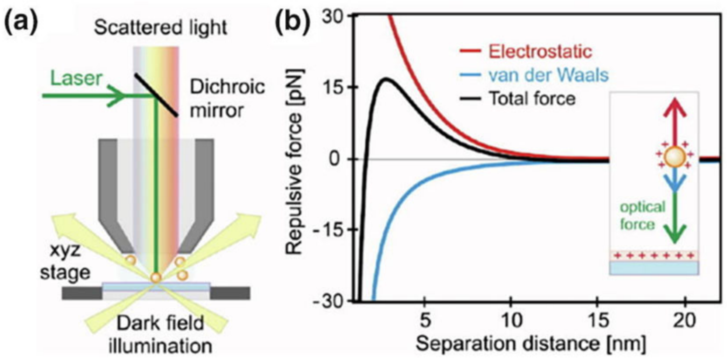


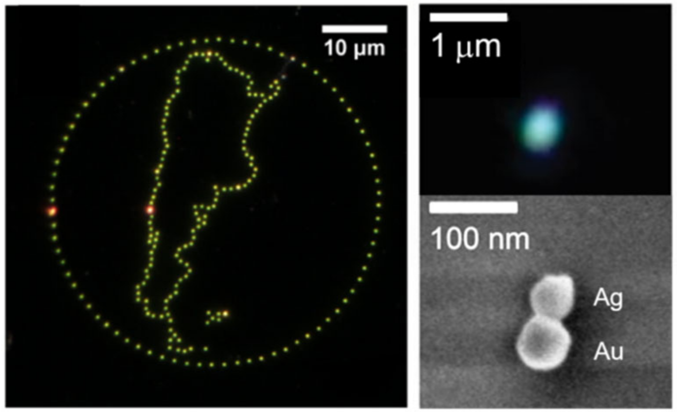
A. Rakovich et al. ACS Nano **9**, 2648-2658 (2015)

Going big!

Large-area printing & deposition techniques

Optical printing of metallic NPs

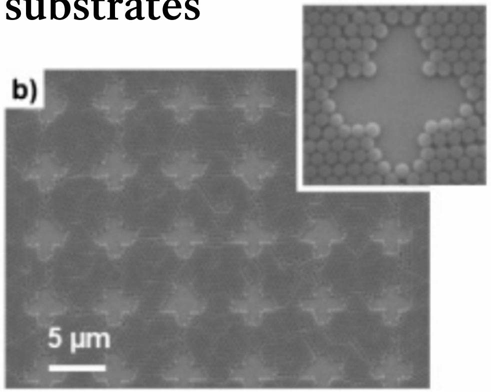


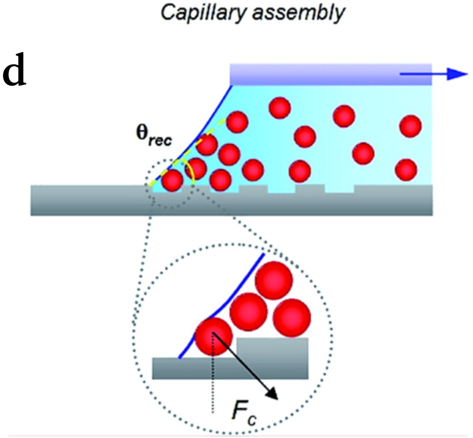


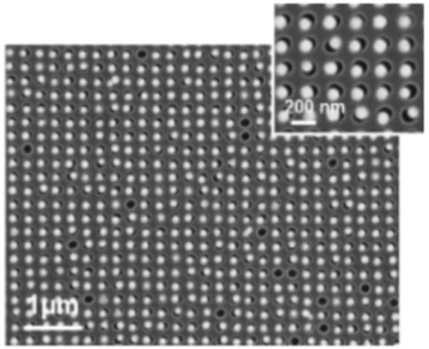
Linhan Lin et al. Materials Today 28, 49-62 (2019)

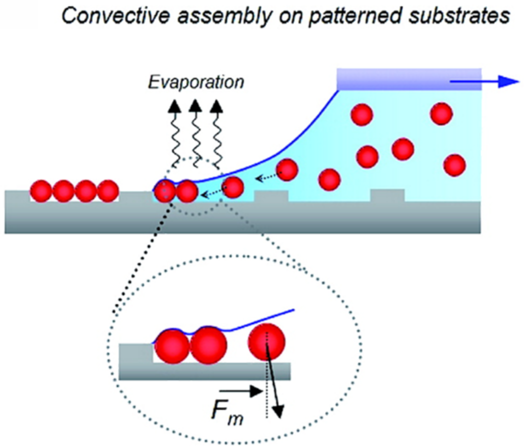
Julian Gargiulo et al. NanoLetters 16, 1224-1229 (2016)

Capillary and convective assembly on pre-patterned substrates





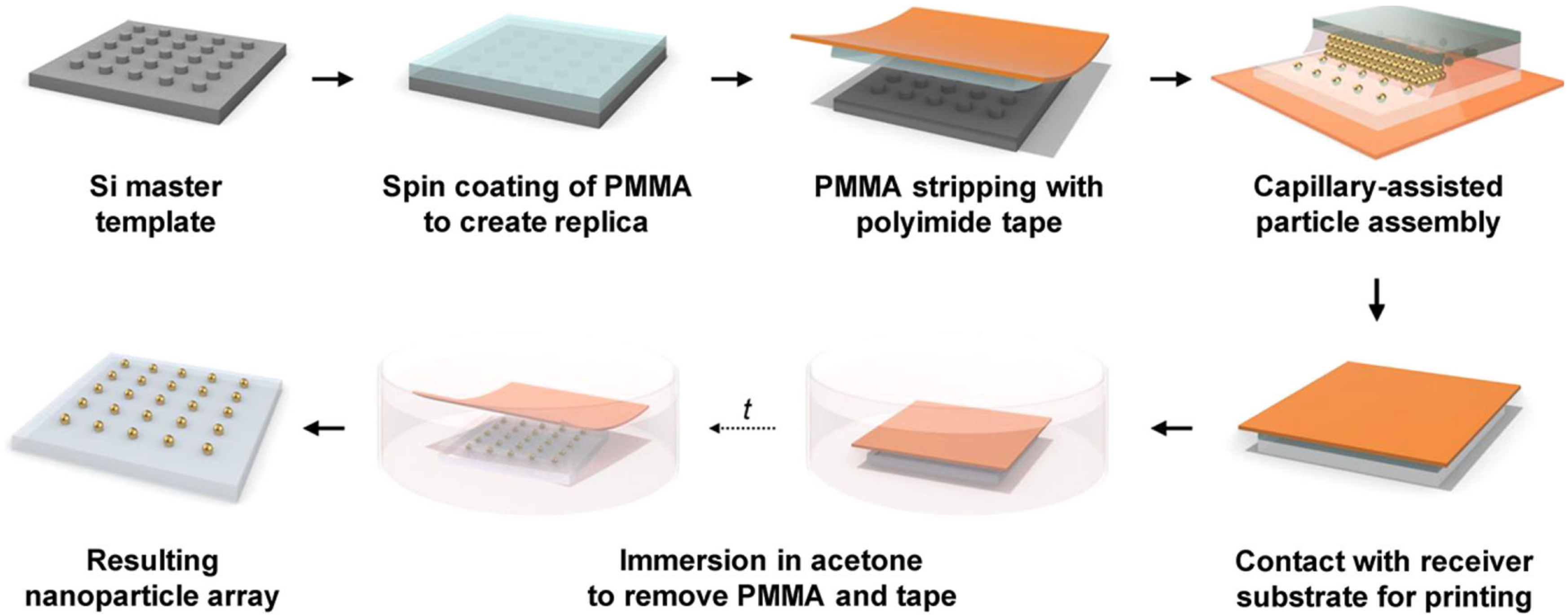




L. Malaquin et al., Langmuir 23, 11513 (2007)

Large-area immobilization of Au NPs arrays

CAPA (Capillary assisted particle assembly) + **Stamping** + **Template-dissolution**



Si master template

Spin coating of PMMA to create replica

PMMA stripping with polyimide tape

Capillary-assisted particle assembly

Contact with receiver substrate for printing

Immersion in acetone to remove PMMA and tape

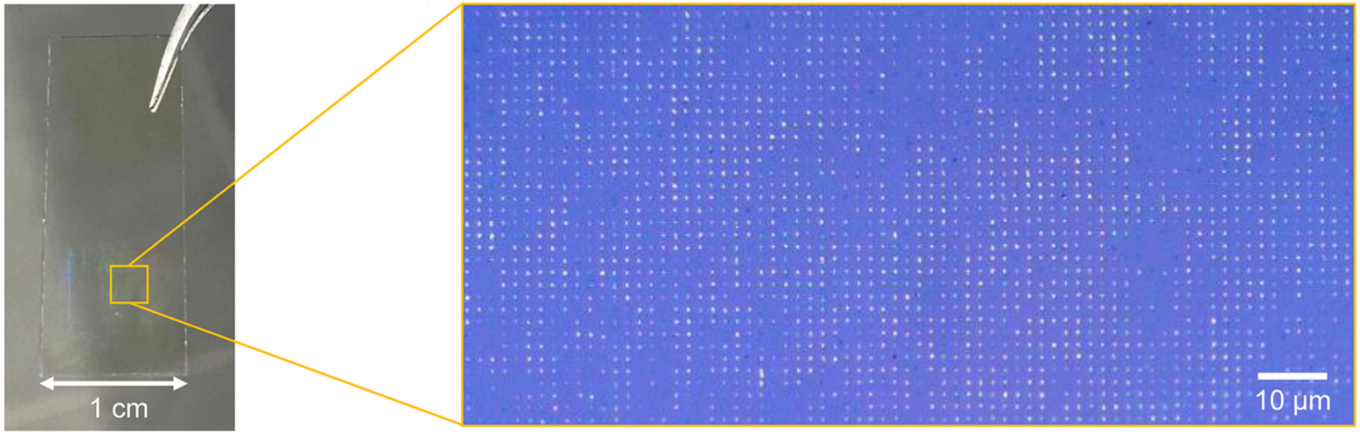
Resulting nanoparticle array

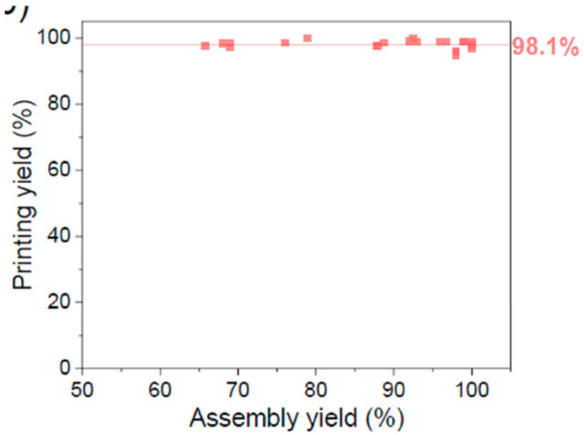
In collaboration with LMU, ICL, KAIST, SUST

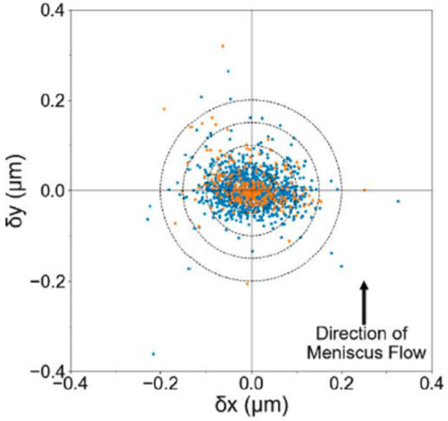
J.B. Lee et al., ACS Nano 2020, 14, 17693

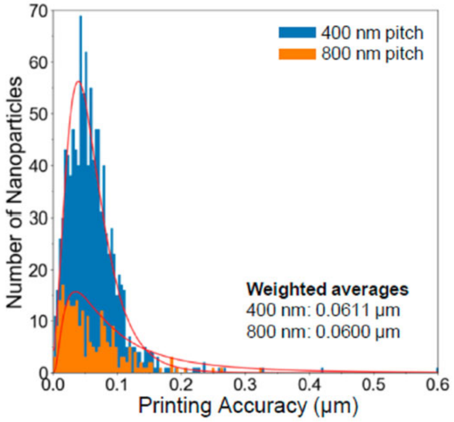
Large-area immobilization of Au NPs arrays

Printing accuracy and yield









In collaboration with LMU, ICL, KAIST, SUST

J.B. Lee et al., ACS Nano 2020, 14, 17693

Introduction
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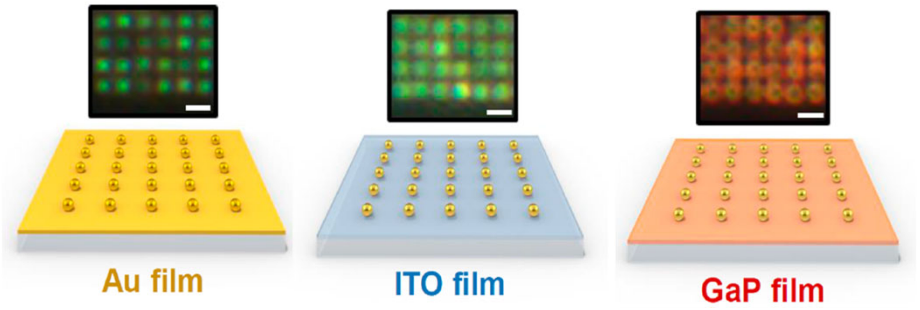
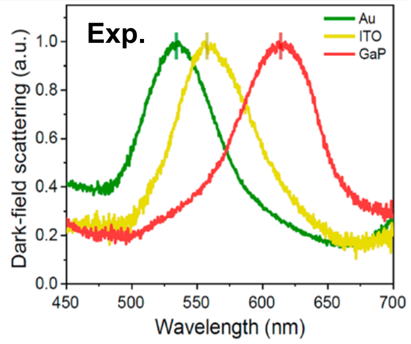
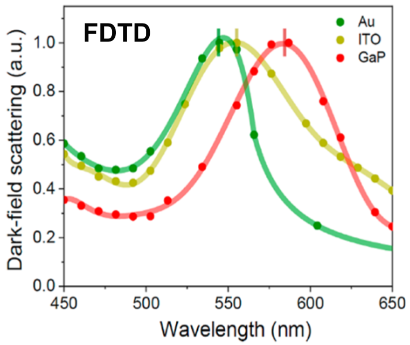
Large-area immobilization of Au NPs arrays

Printing on different substrates

- Assembly conditions depend on NP and substrate type
- Works for any substrate not soluble in acetone
- Can be used with pre-existing structures

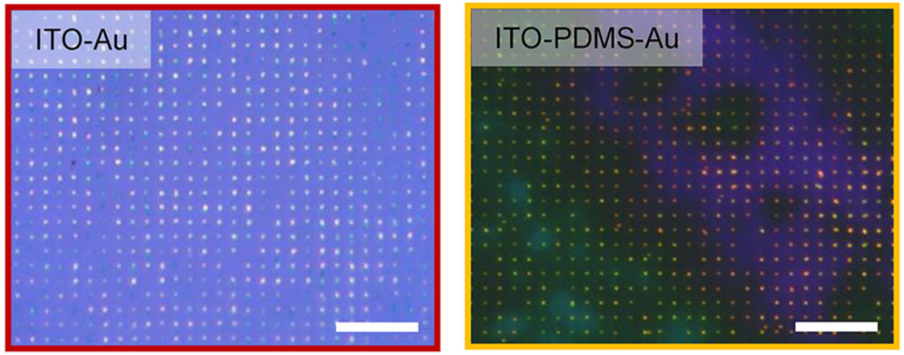


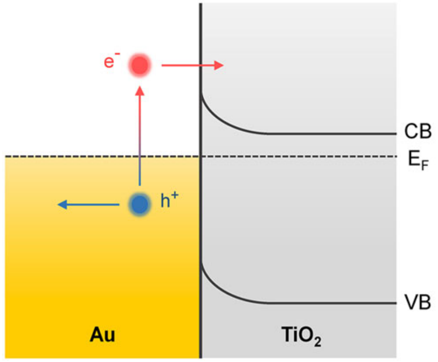


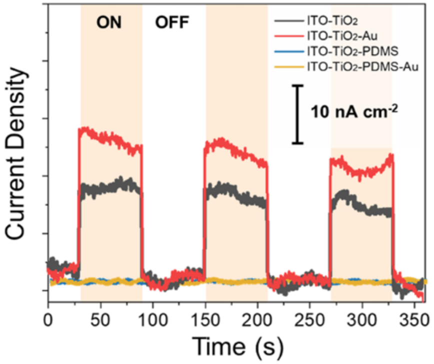


Hot-electron detection

via an introduction of a tunnelling junction







In collaboration with LMU, ICL, KAIST, SUST

J.B. Lee et al., ACS Nano 2020, 14, 17693

Introduction

Self-assembly
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Superclusters

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2-step EBL
Template dissolution

Active control
Brownian ratchets

Conclusions

Active control of colloidal nanoparticles

In aqueous environments

Active control can enable

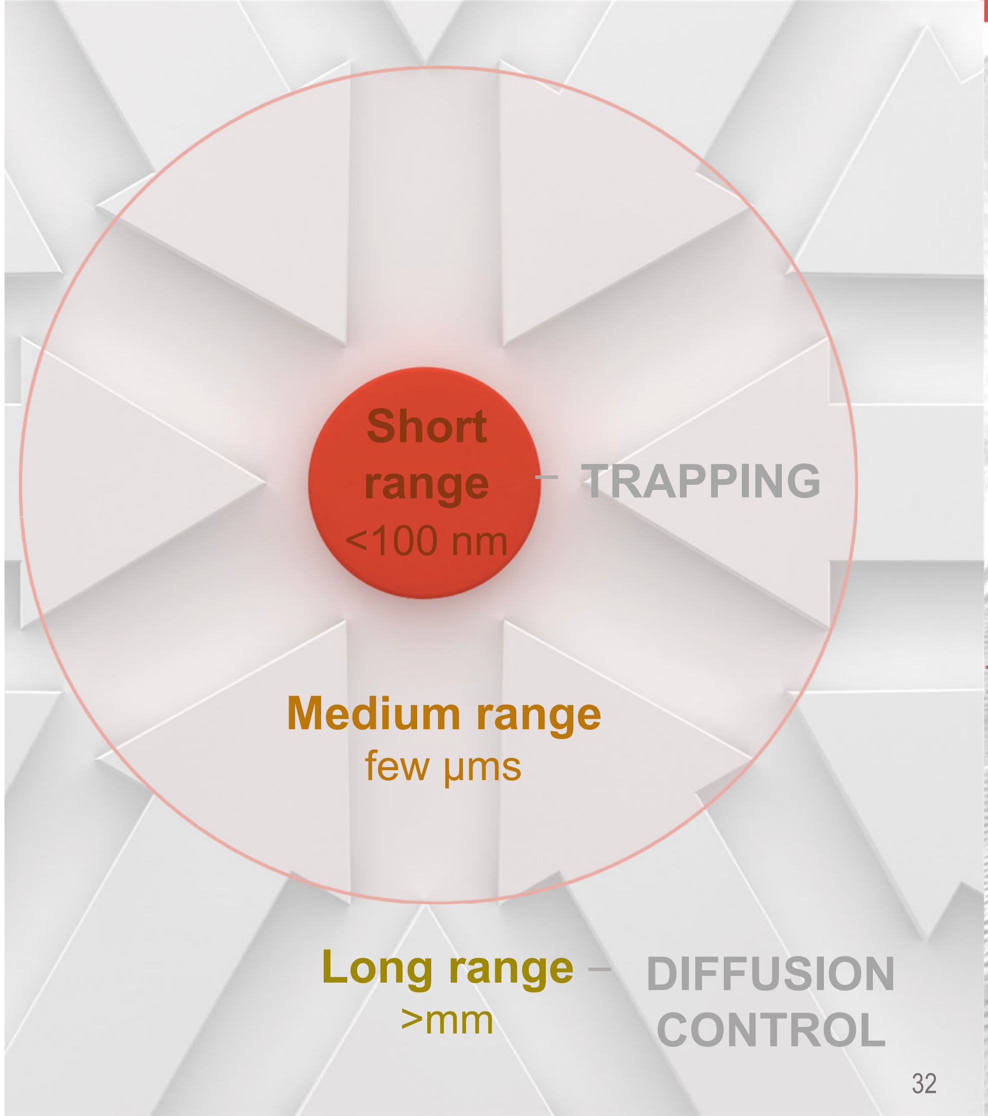
- Particle sorting
- Temporary/permanent concentration of samples
- Delivery of test materials to sensing areas

Allowing

- Lower LODs in sensing schemes
- In-situ measurements ranging from on single-particle level to ensemble level on same sample

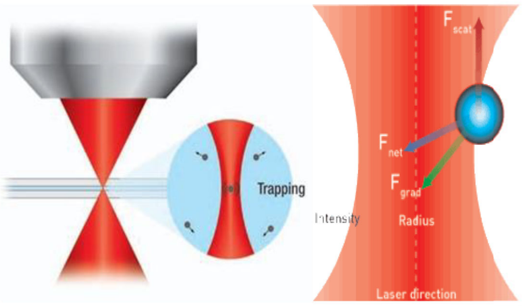
Various forces can be utilized

- Have different action ranges

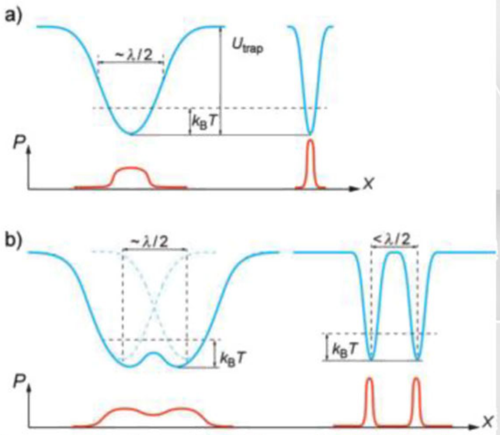


Active control of colloidal nanoparticles

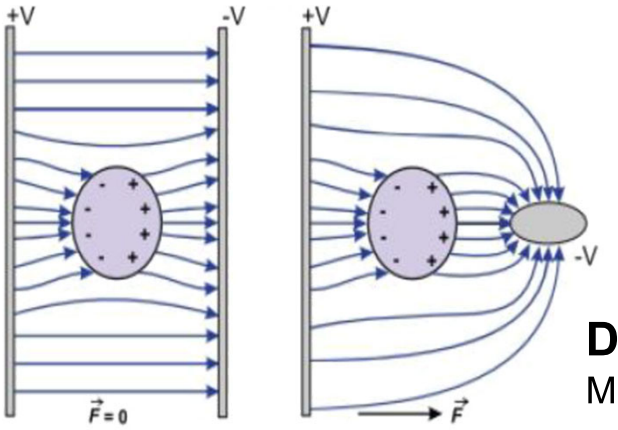
Optical trapping
(Usually) short range



Ashkin, (1986)

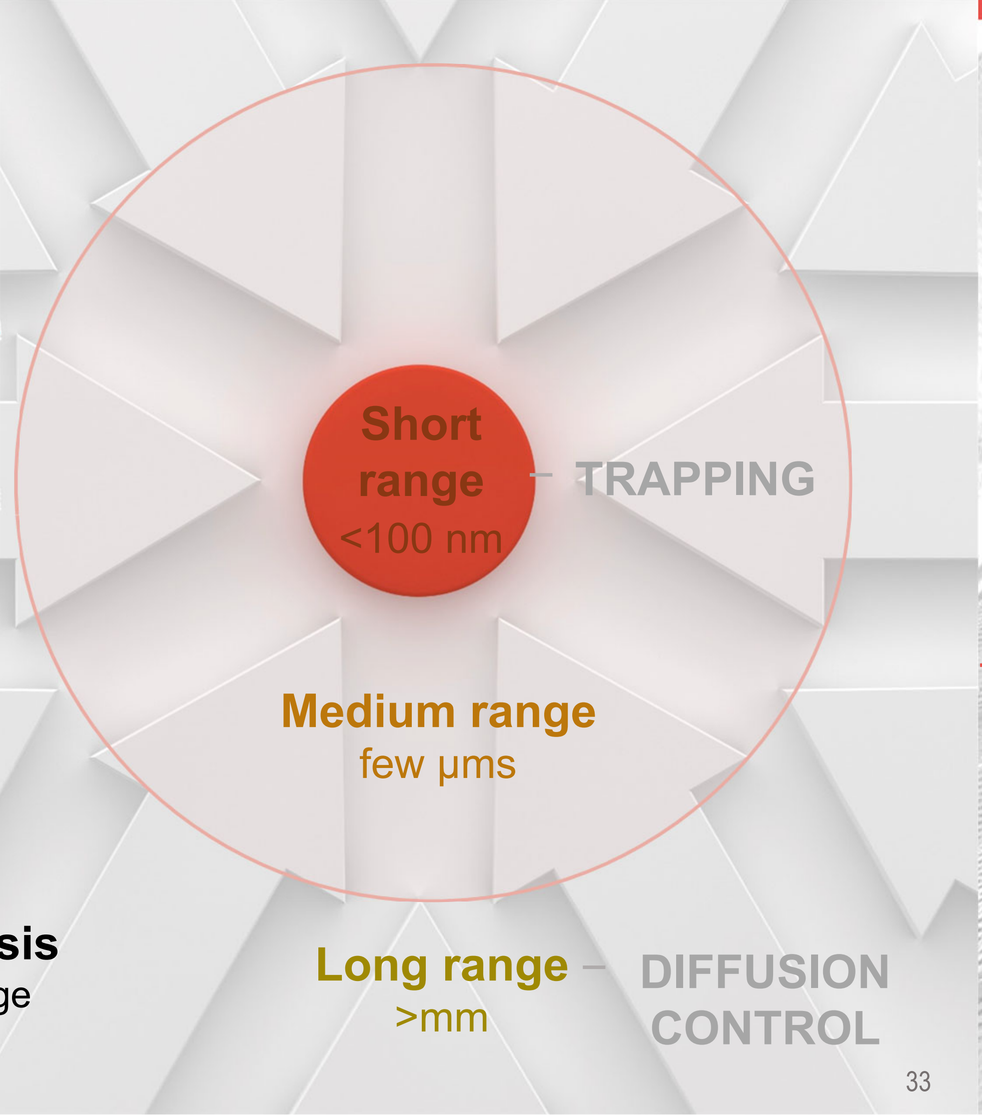


Wang et al., ChemPhysChem 13, 2639 (2012)



Dielectrophoresis
Medium-to-long range

Electrophoresis, 32 2307 (2011)



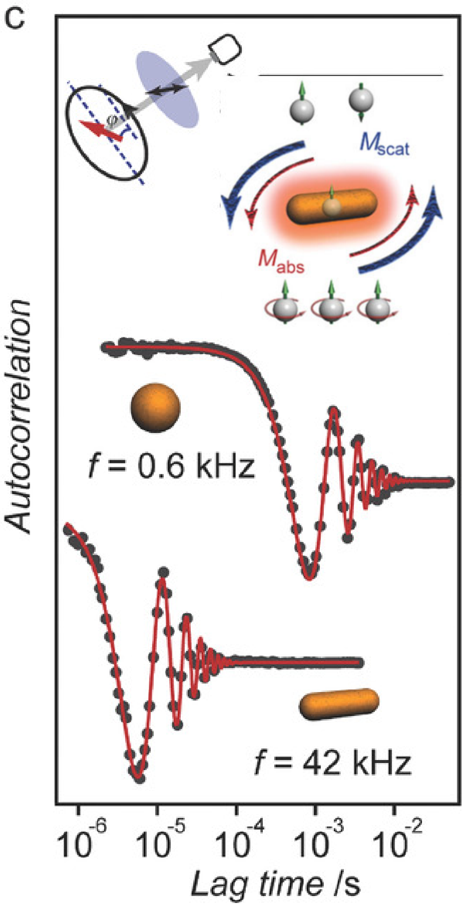
Short range
<100 nm – **TRAPPING**

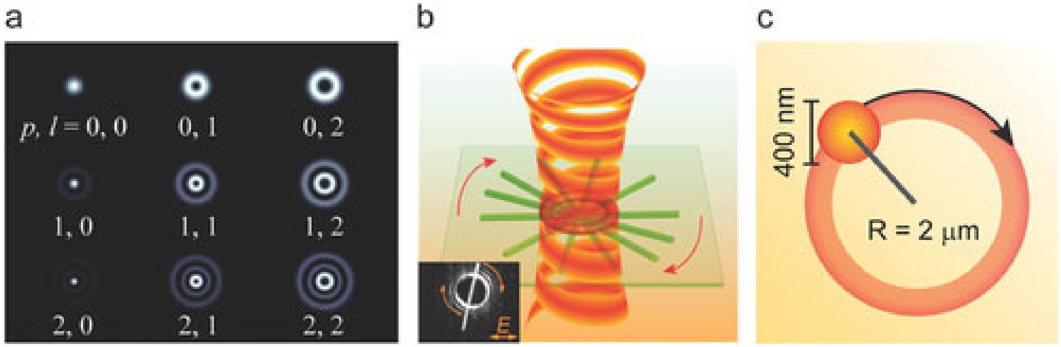
Medium range
few μms

Long range – **DIFFUSION CONTROL**
>mm

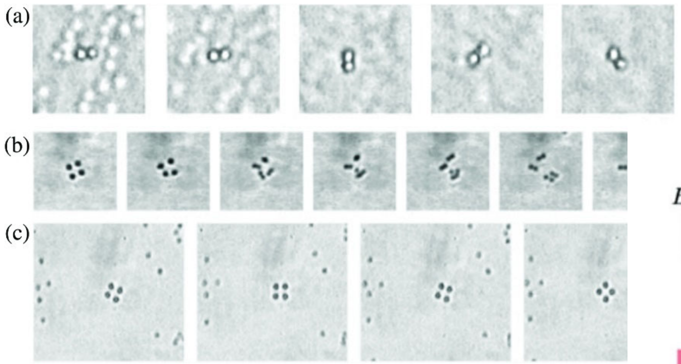
Control of nanoparticle motion in solution using SLMs

doi.org/10.1002/adfm.201706272

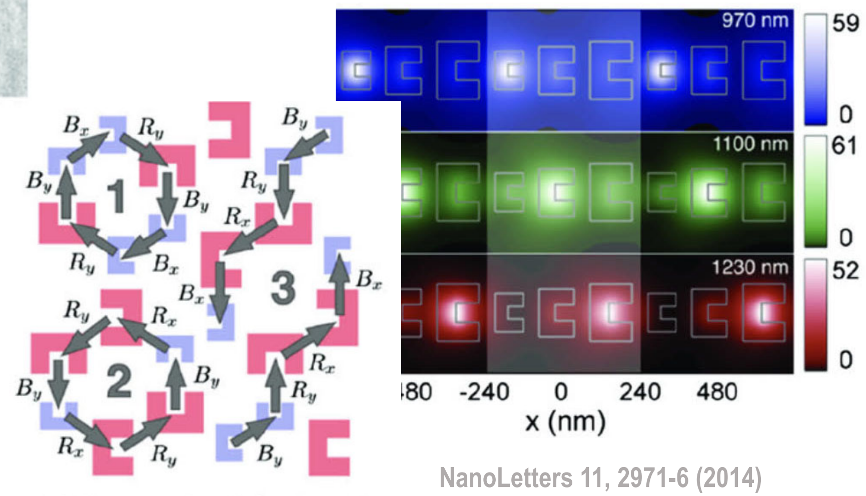




J. Phys. Chem. Lett. 2013, 4, 17, 2937–2942



Science, 296 (5570), 1101 –1103 (2002)



modulating wavelength / polarization

NanoLetters 11, 2971-6 (2014)

Active control of colloidal nanoparticles

In aqueous environments

Active control can enable

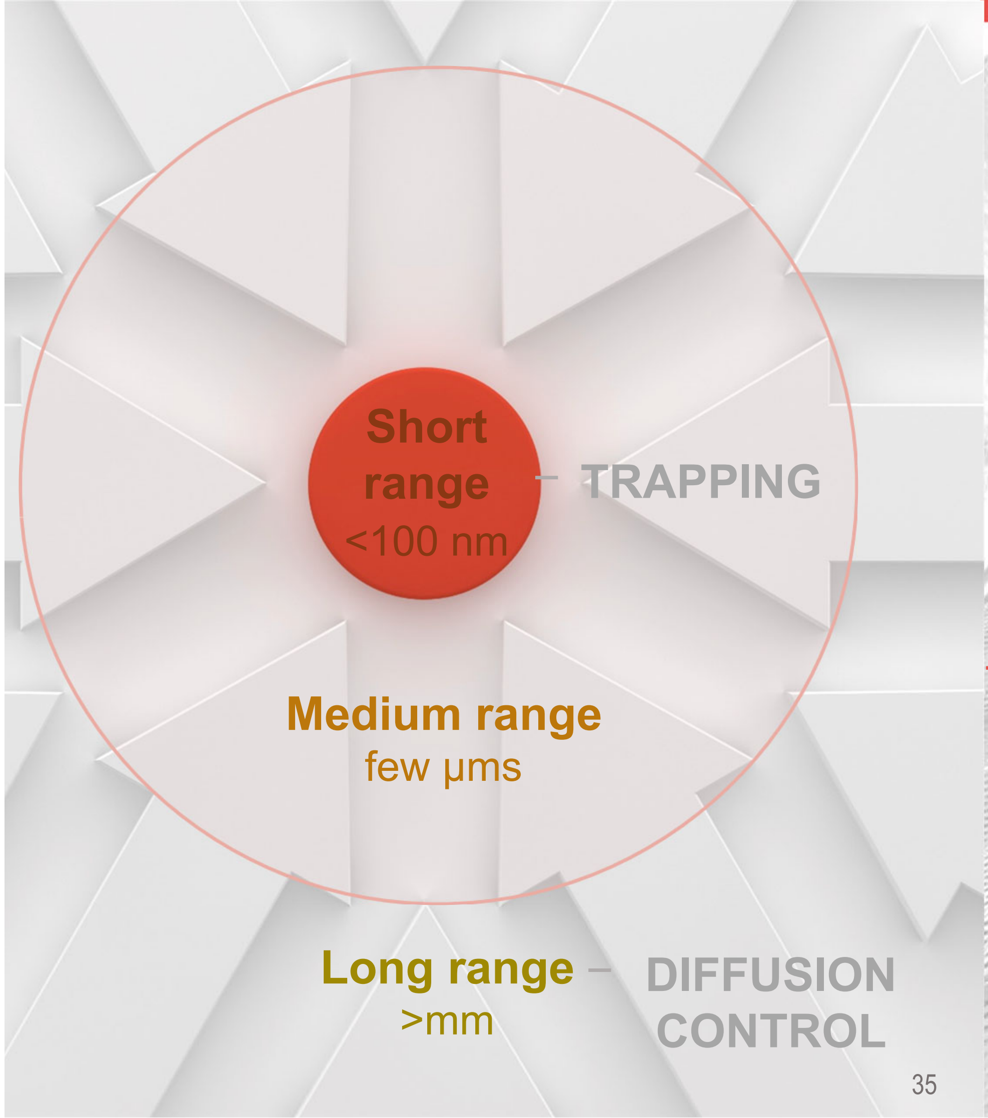
- Particle sorting
- Temporary/permanent concentration of samples
- Delivery of test materials to sensing areas

Allowing

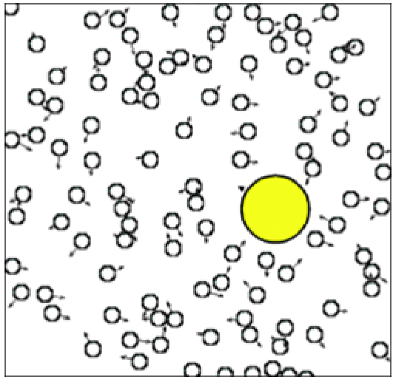
- Lower LODs in sensing schemes
- In-situ measurements ranging from on single-particle level to ensemble level on same sample

Various forces can be utilized

- Have different action ranges



Brownian motion of particles in solutions



Brownian motion

- ➢ Stochastic process resulting in random motion
- ➢ Mean Square displacement for an ensemble:

$$\langle (x_t - x_0)^2 \rangle = 2Dt$$

where D is the diffusion coefficient:

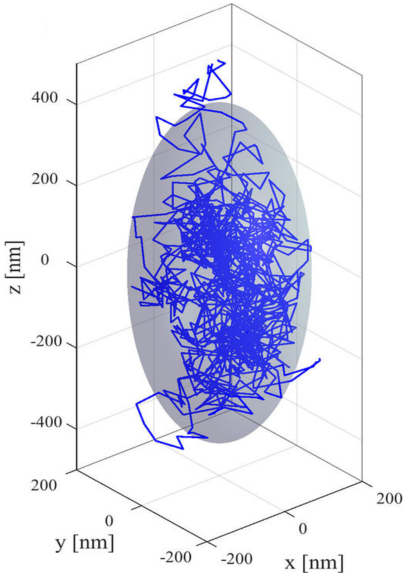
$$D = \frac{k_B T}{\gamma}, \quad \gamma = 6\pi\eta a$$

Particle diffusion in presence of a potential

- ➢ Additional forces are exerted on particles
- ➢ Brownian motion “adds” thermal noise

Can exploit this noise for long range transport!

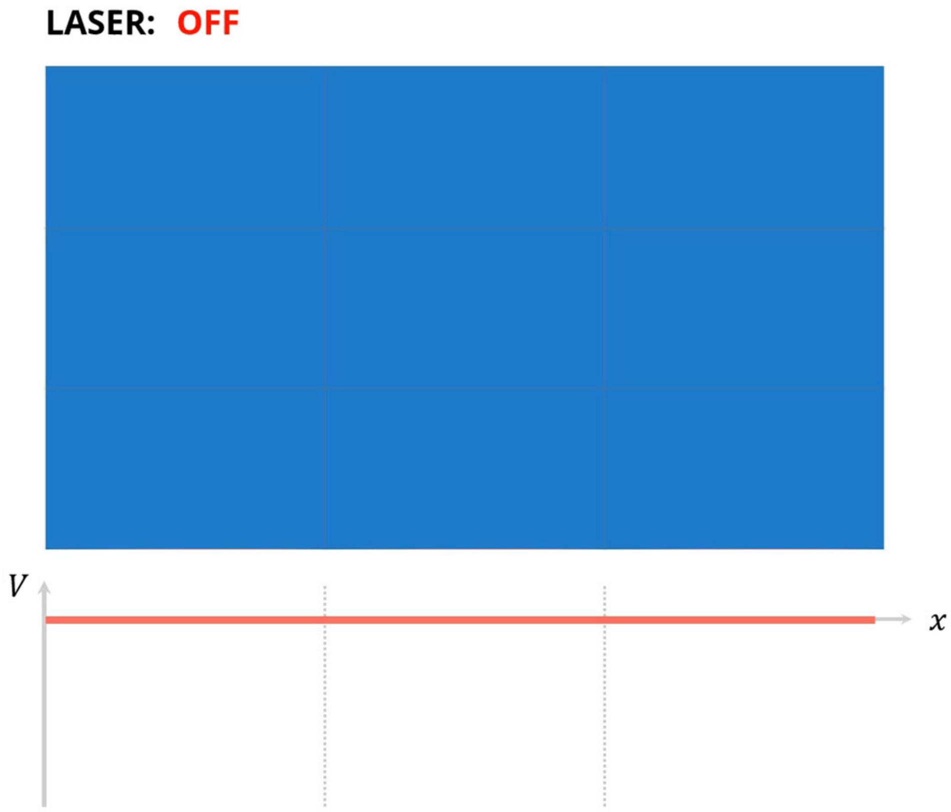
Particle motion in an optical trap



Eur. Phys. J. Plus 135, 949 (2020)

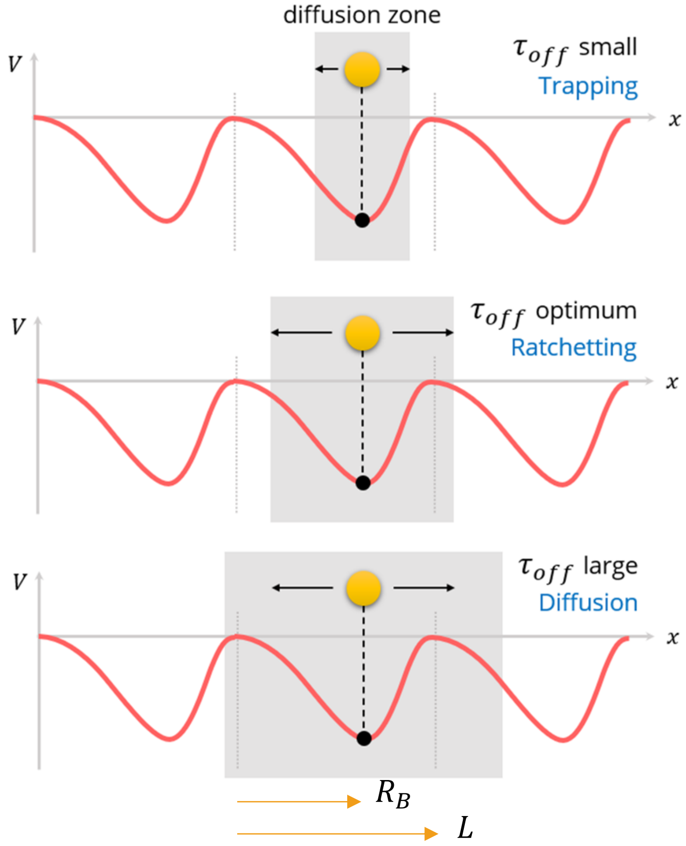
Rectification of Brownian motion

Through application of period & asymmetric potential



Optimum time to keep the potential off:

$$\tau_{,} = \frac{(L - R_B)^2}{2D} < \tau_{off} < \tau_{\#} = \frac{R_B^2}{2D}$$



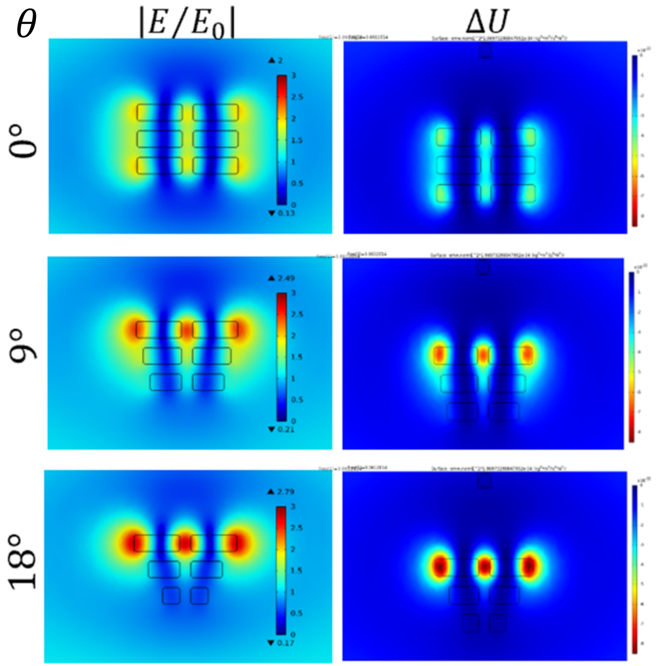
Can use any type of potential as long as it is switchable

In preparation

Plasmonic Brownian ratchets

Advantages

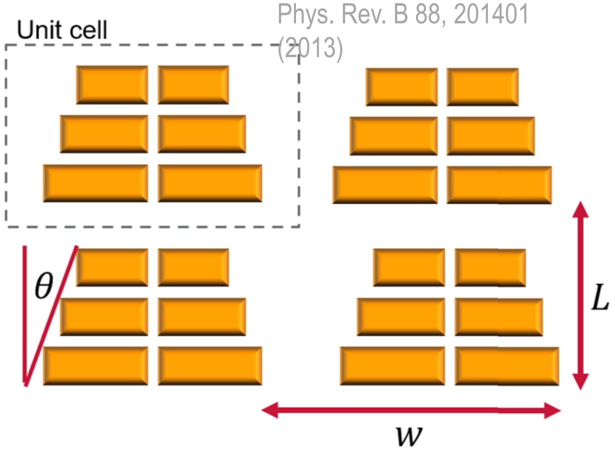
- ➢ Easily designed / fabricated
- ➢ Asymmetries easy to implement
- ➢ Reduced power requirements
- ➢ Simple implementation



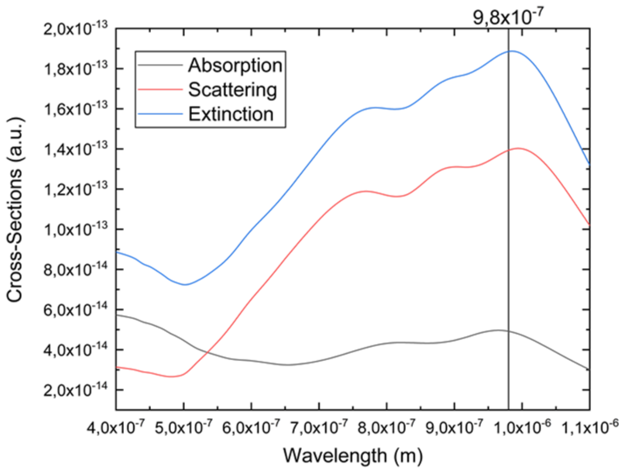
Ratchet design

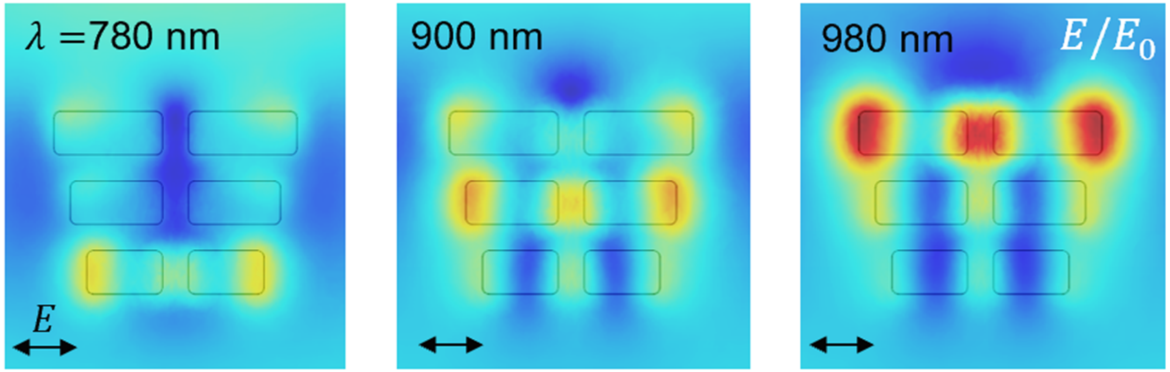
- ➢ Strong resonance at target λ
- ➢ Asymmetric potential profile

⇨



Phys. Rev. B 88, 201401 (2013)



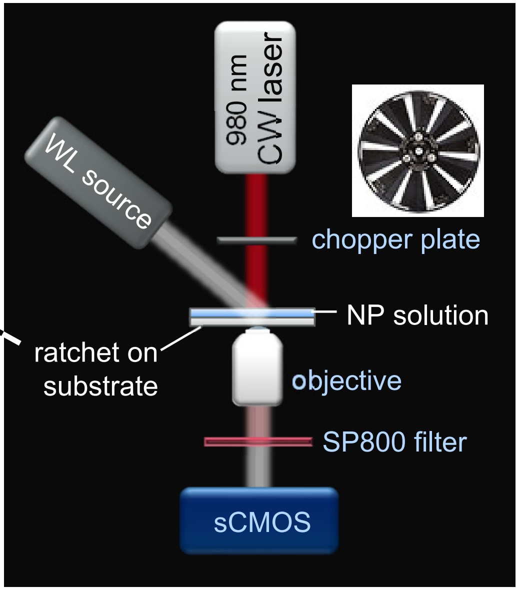


In preparation

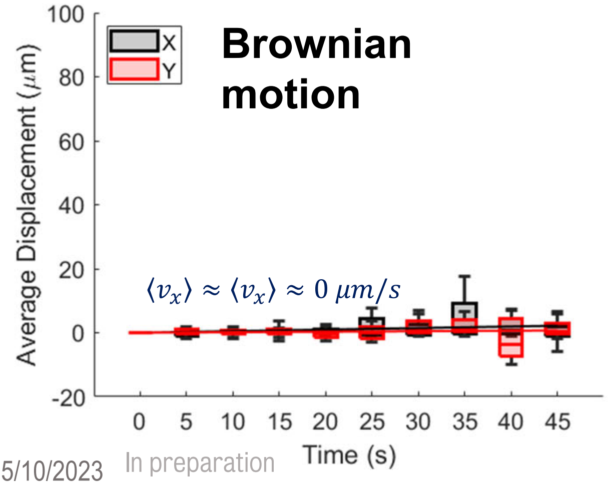
Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

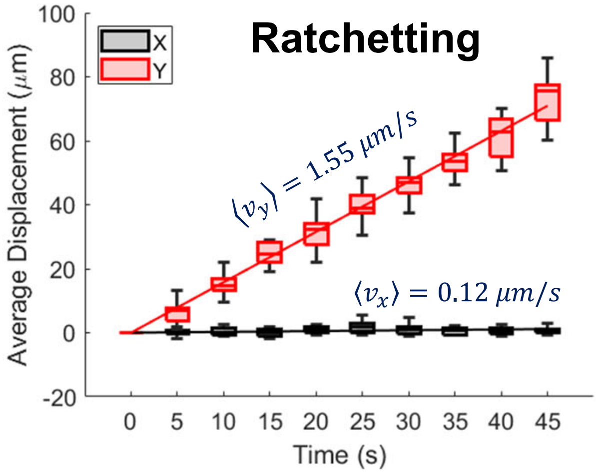
Experimental implementation of plasmonic Brownian ratchets

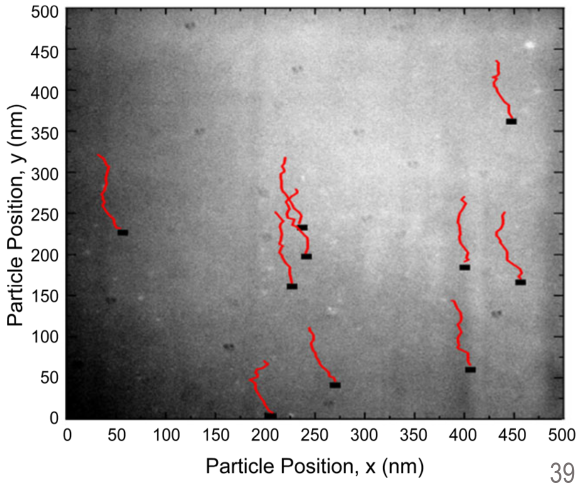
- Chopped 980 nm CW excitation
- Max power used 2.5 kW/cm^2
- Chopping: 50/50 duty cycle
- Adjustable frequency
- Aqueous solutions of various NPs



	Polystyrene (40 nm)	Polystyrene (200 nm)	PTB7 (180 nm)
$\langle v_x \rangle$	0.14 $\mu\mathrm{m/s}$	0.12 $\mu\mathrm{m/s}$	0.15 $\mu\mathrm{m/s}$
$\langle v_y \rangle$	2.37 $\mu\mathrm{m/s}$	1.55 $\mu\mathrm{m/s}$	1.84 $\mu\mathrm{m/s}$



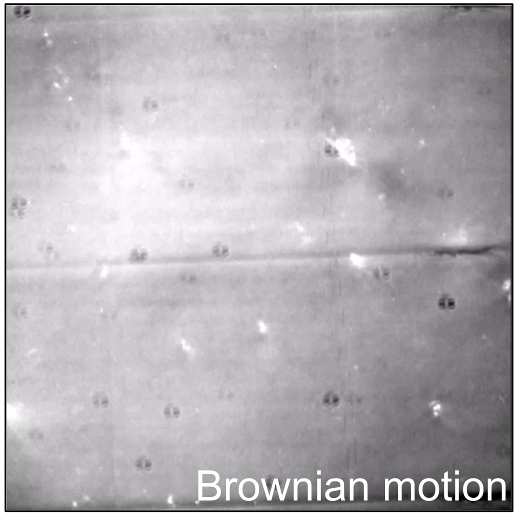


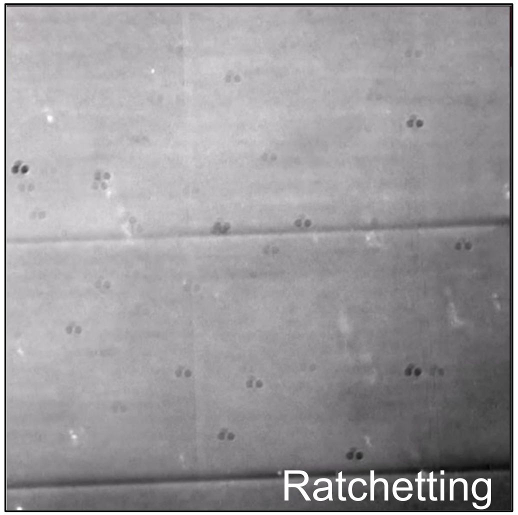


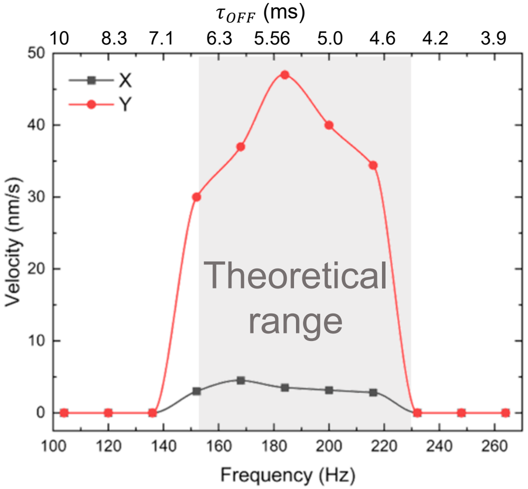
In preparation

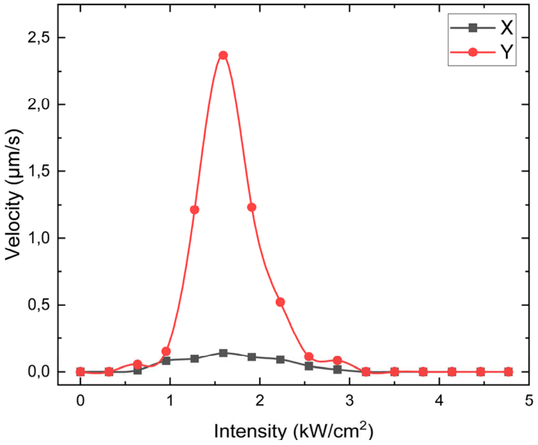
Experimental implementation of plasmonic Brownian ratchets

Polystyrene spheres, 40 nm diameter



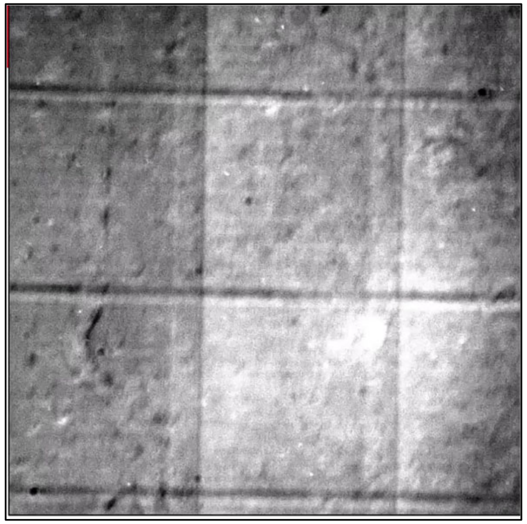




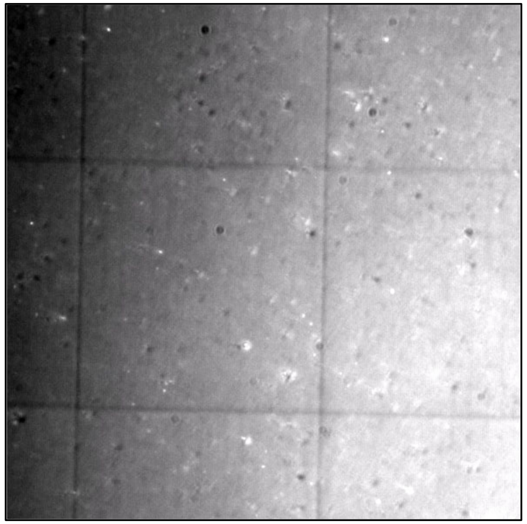


Other sizes/materials

PS spheres, 200 nm



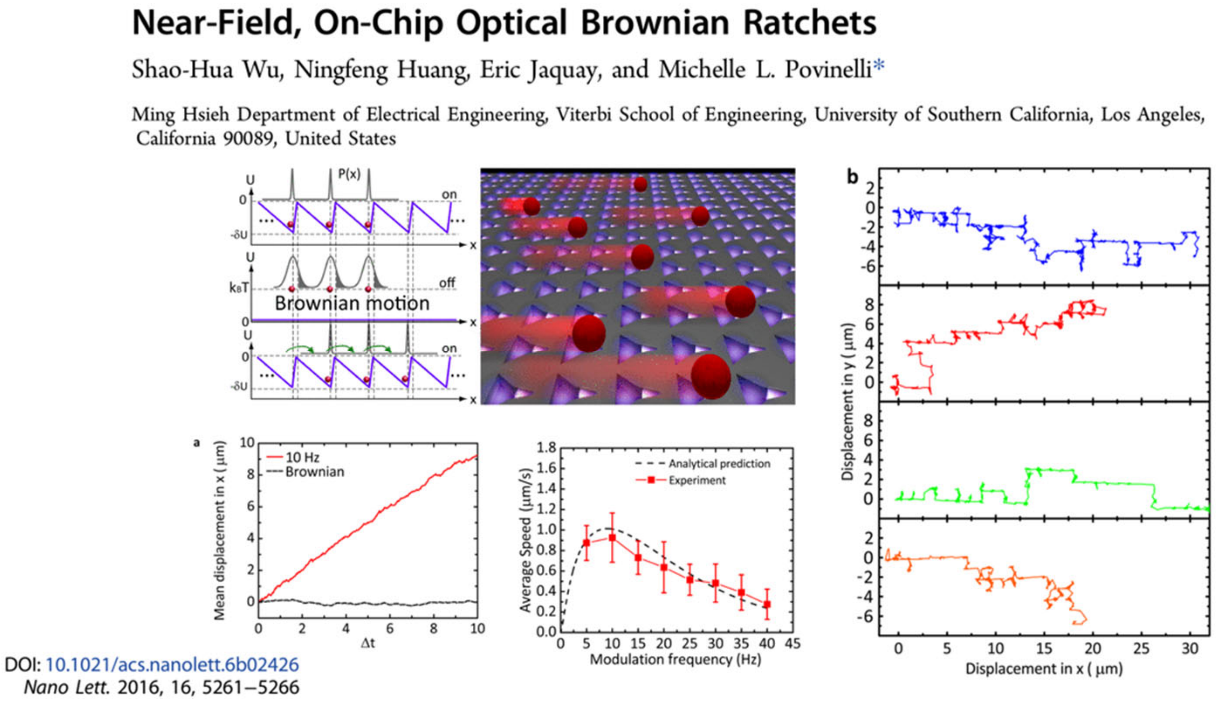
PTB7 CPNs, 180 nm



In preparation

Comparison to other optically-driven Brownian ratchets

Optical ratchets



Near-Field, On-Chip Optical Brownian Ratchets

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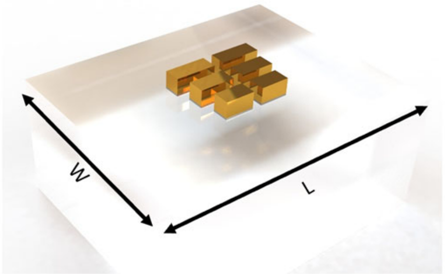
DOI: 10.1021/acs.nanolett.6b02426
Nano Lett. 2016, 16, 5261−5266

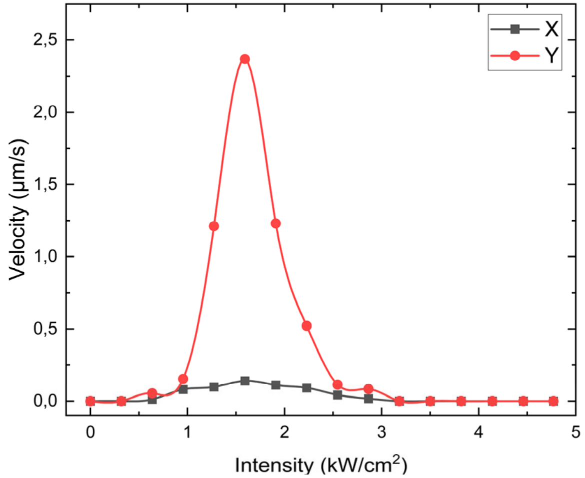
Average speed = 1 μm/s

Coupled power = 100 μW/μm^2 = 10^8 W/m^2

Analyte = ⌀520 nm polystyrene spheres

Our plasmonic ratchets





Average speed ~ 2.5 μm/s

Incident power ~2 kW/cm^2 = 0.2 W/m^2

Analytes = ⌀40-200 nm polymer spheres

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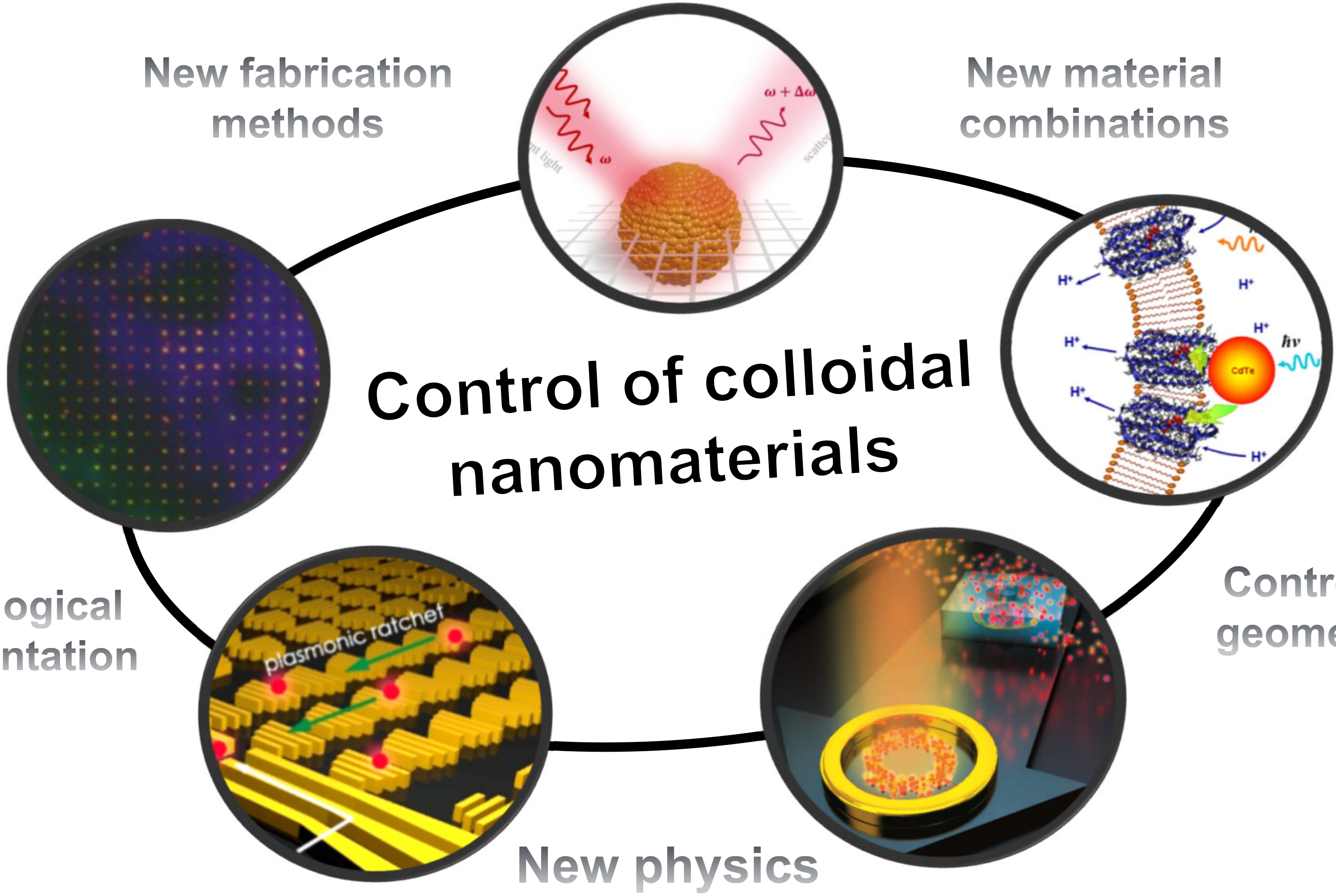
Conclusions



New fabrication methods

New material combinations

Control of colloidal nanomaterials

Technological implementation

Controlled geometries

New physics

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NanoLett. 16, 1410-1414 (2016)

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ACS Nano 9, 2648-2658 (2015)

Template dissolution method

ACS Nano 14, 17693 (2020)

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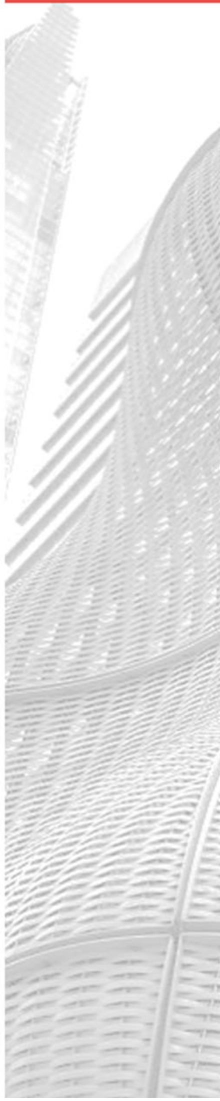
http://nanobiophotonics-group.com/



Thank you for your attention!