Plasmon enhanced fluorescence characteristics government by selecting the right objective function

Mária Csete

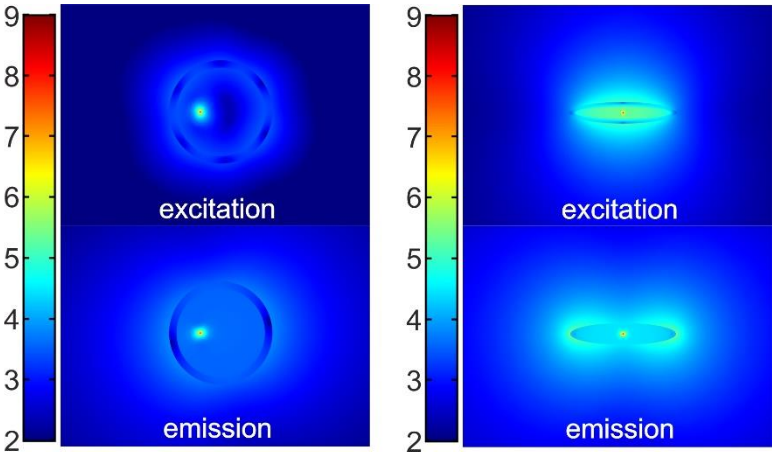
Dávid Vass, András Szenes, Balázs Bánhelyi, Tibor Csendes, Gábor Szabó

Department of Optics and Quantum Electronics
Department of Computational Optimization

University of Szeged

COMSOL 2018

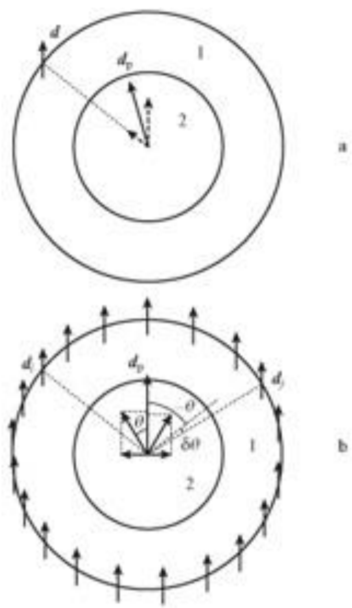
Localized surface plasmon resonance



excitation enhancement via plasmonic resonance
emission improvement via Purcell & antenna effect

metal nanoshells as plasmonic nanoresonators
->smaller metal volume
->resonant frequency tuning via GAR
->ellipsoid: non-degenerated trans. and long. modes

Dicke effect



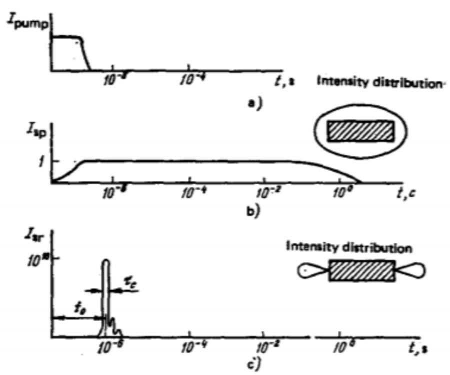


FIG. 2. Comparison of superradiance and noncoherent spontaneous emission.[24] The time scale is logarithmic. a) Pump pulse which creates a population inversion for the working transition, $a \to b$; b) emission intensity in the case of noncoherent spontaneous decay ($T_1 \sim 1s$): a slow exponential decay with an isotropic directional distribution of the intensity; c) the observed highly directional superradiance signal (in gaseous HF; Ref. 24). The peak intensity I_{sr} is roughly 10^{10} times I_{sp}.

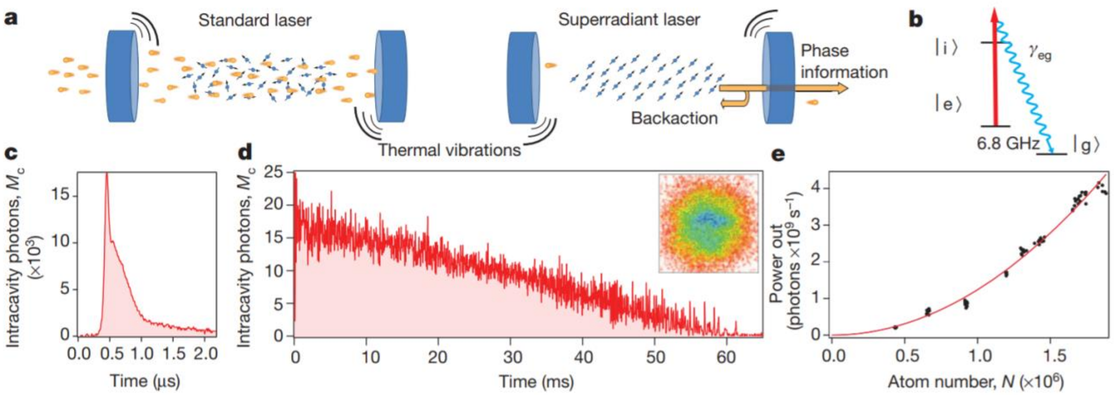
emitters can radiate cooperatively

N-times shorter radiative decay:
-> N-times shorter pulse
-> emission intensity proportional to N^2

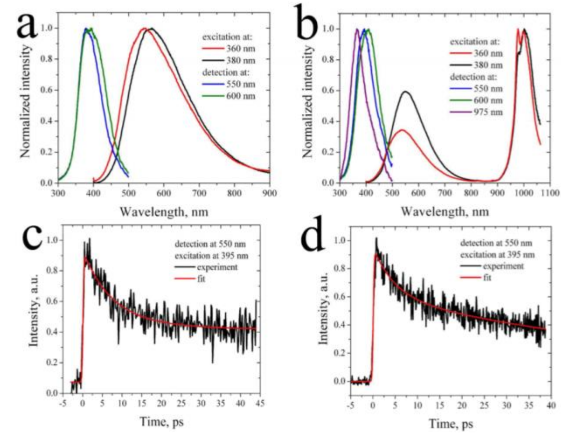
indistinguishability & ensemble volume smaller than the wavelength

A. Szenes *et al* Scientific Reports 7, 13845 (2017)
I. E. Protsenko and A. V. Uskov Quantum Electron. 45 561 (2015)
A. V. Andreev *et al* Sov. Phys. Usp. 23 493 (1980)

Dicke effect applications



superradiant lasers with ultra-narrow lines (non-plasmonic)



generation of ps pulses in Ag nanoclusters

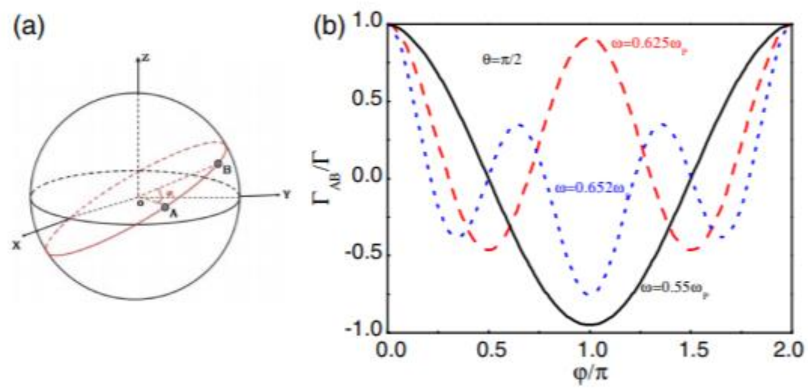
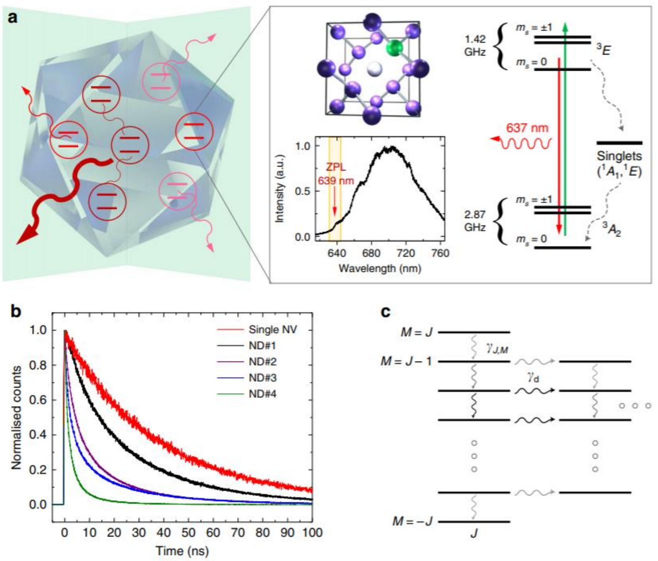


Fig. 3. (a) Positions of two emitters (A and B) near a metal nanoparticle. (b) Γ_{AB}/Γ as a function of the angle between two emitters around the sphere. The solid, dashed, and dotted lines correspond to the cases with $\omega = 0.55\omega_p$, $0.625\omega_p$, and $0.652\omega_p$, respectively. The other parameters are identical with those in Fig. 2.

multi-qubit deterministic quantum phase gate with ordered radial arrangement



superradiance of NV centers

J. G. Bohnet Nature 484(7392), 78-81 (2012).
J. Ren *et al* J. Opt. Soc. Am. B 31(2), 229-236 (2014).
M. V. Shestakov J. Phys. Chem. C 119(34), 20051-20056 (2015).
C. Bradac *et al* Nat. Commun. 8(1), 1205 (2017).

Plasmonic Dicke effect

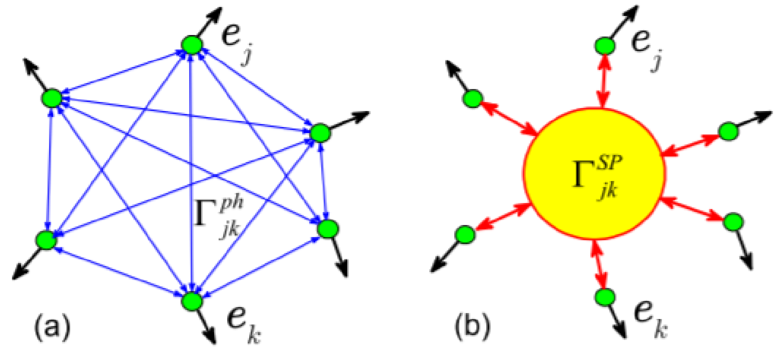


FIG. 1 (color online). (a) Radiative coupling of emitters in free space and (b) plasmonic coupling of emitters near a NP.

direct coupling through radiation
indirect coupling through plasmons

dipoles around solid NP or in concave resonator:
random phase, uniform orientation
random or CX configuration

plasmonic coupling overrides radiative coupling:
total radiative rate ~N/3, total energy 3x

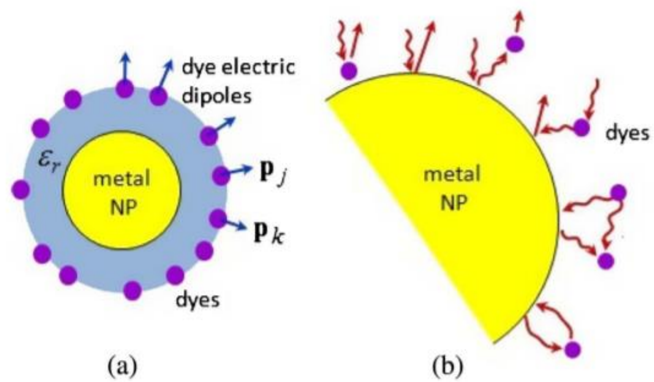


Fig. 1. (a) Aggregate made by one nanoplasmonic sphere and a layer of N dyes. (b) Some radiative and nonradiative coupling mechanisms among dyes and nanosphere are considered.

cooperative plasmon mediated coupling
in metal NP covered by gain medium

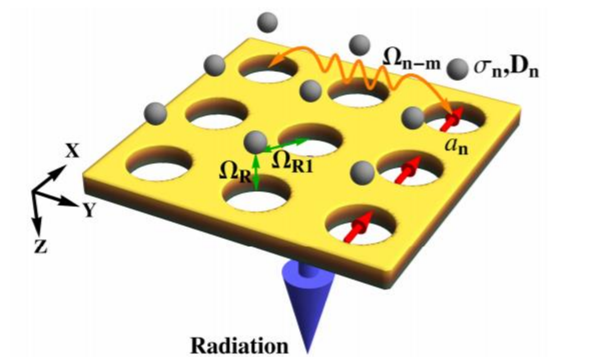


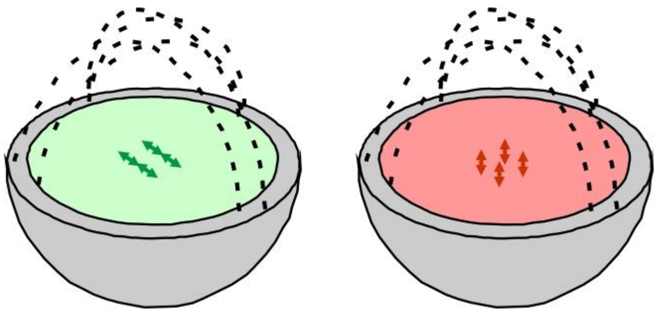
Fig. 1. Phase distribution of the plasmon oscillations in spaser arrays of (a) 5 × 5 and (b) 100 × 100 spasers. In all calculations, we use $\Delta = \lambda/20$, where λ is the free space wavelength.

CW plasmonic SR from gain molecules
coupled through plasmons on nanohole array

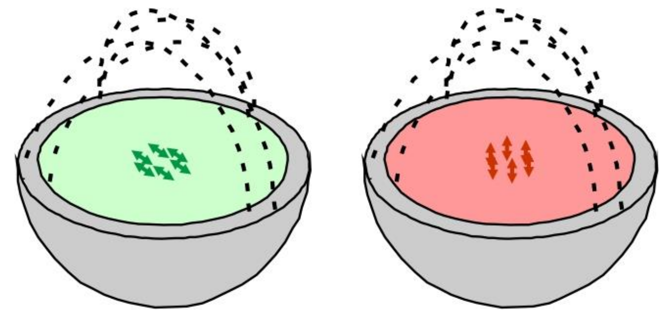
V. N. Pustovit *et al* Phys. Rev. Lett. 102(7), 077401 (2009).
J. T. Manassah Laser Phys. 22(4), 738-744 (2012).
A. V. Dorofeenko Opt. Express 21(12), 14539-14547 (2013).
V. N. Pustovit *et al* J. Opt. Soc. Am. B 32(2), 188-193 (2015).

Nanoresonator types and geometries

4iCS



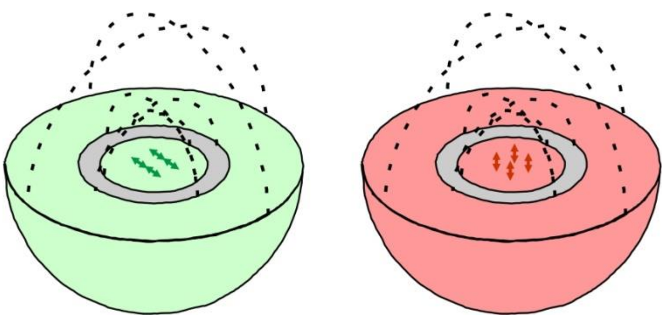
6iCS



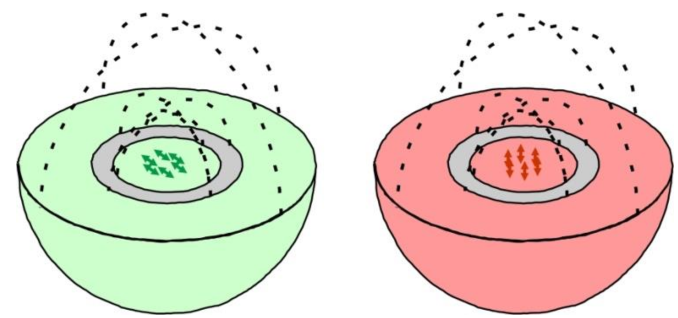
SCS-type

diamond-silver
core-shell

4iCSS



6iCSS



SCSS-type

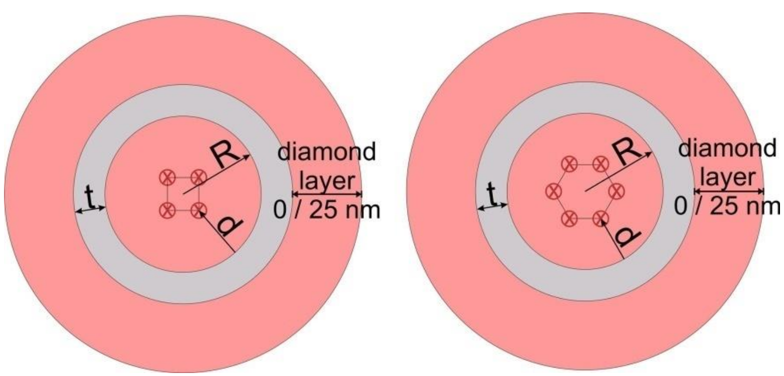
diamond-silver-diamond
core-shell-shell

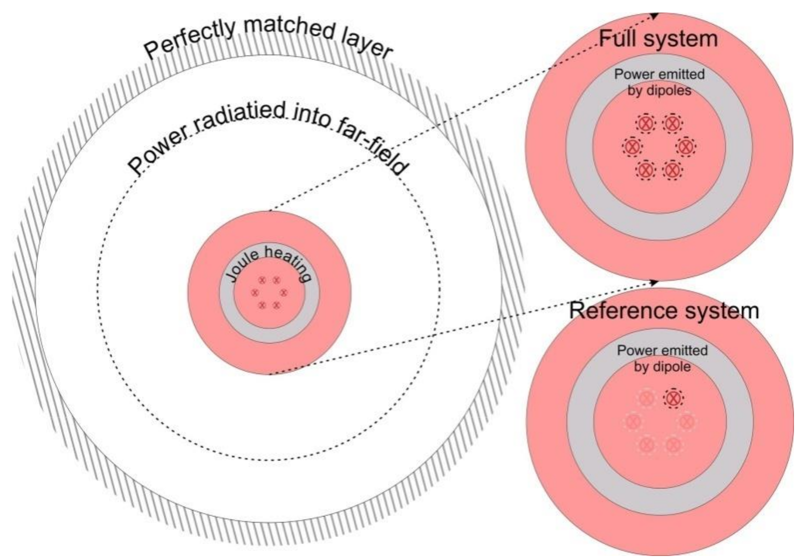
Optimization-> cooperative fluorescence

- **Objective**: enhancement of excitation & emission simultaneously
- **Method**: configuration optimization (geometry and illumination condition)
- Type of concave core-shell nanoresonators:
  - diamond-silver core-shell (CS) and diamond-silver-diamond core-shell-shell (CSS)
- Geometry of concave core-shell nanoresonators:
  - spherical (SCS & SCSS) as a special kind of ellipsoidal
- Varied parameters
  - 2r, t, GAR, φ, θ
- Type of fluorescent dipoles:
  - SiV center

coupled fluorescence qualification:

δR_{exc}=$Purcell_{exc}$*QE & δR_{em}=$Purcell_{em}$*cQE





evaluation of superradiance:
comparison with the reference system

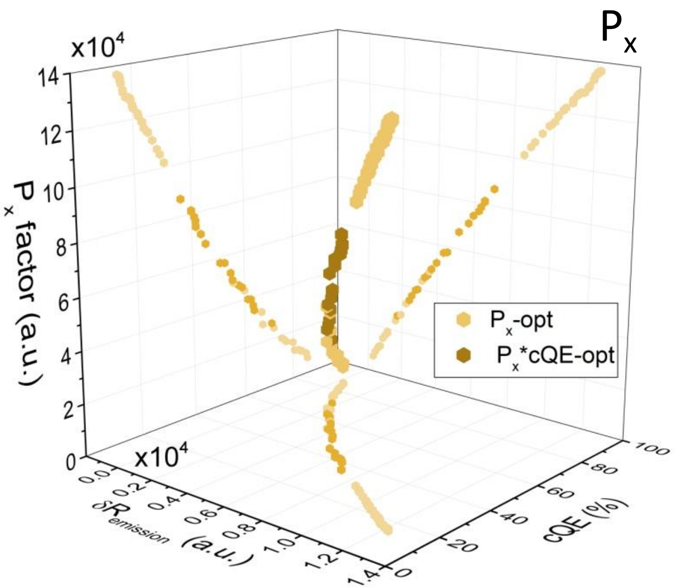
Conditional optimization

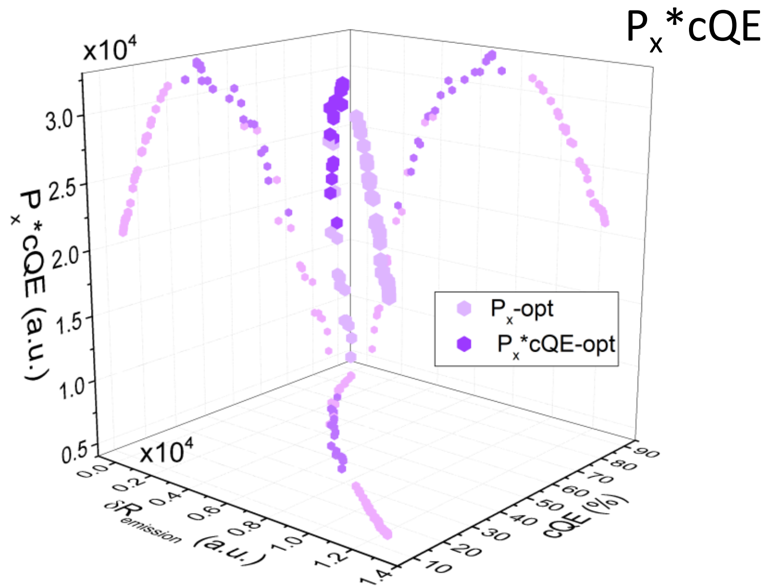
$P_x = \delta R_{exc} * \delta R_{em}$: total fluorescence rate enhancement optimization

$P_x * cQE = \delta R_{exc} * \delta R_{em} * cQE$: weighted composite objective function optimization

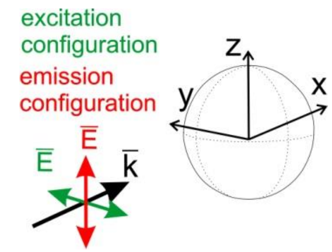
radiative rate enhancement & corrected cQE criteria ->
excitation improvement & multiple cQE mapped

GLOBAL implemented via LiveLink for MATLAB: Sampling (Monte Carlo), Clustering (Single-link), Local searching (UNIRANDI, Random walk, BFGS)
T. Csendes et al.: The GLOBAL Optimization Method Revisited, Optimization Letters 2 (2008) 445-454
B. Bánhelyi et al.: The GLOBAL optimization algorithm. Newly Updated with Java Implementation and Parallelization. Springer Briefs on Optimization, accepted (2018)





Optimization-> cooperative fluorescence



Extracted quantities

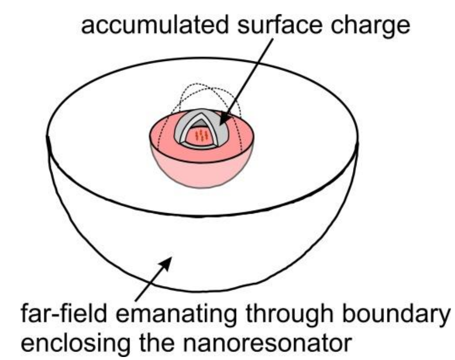
nanoresonator qualification: ecs, scs & ecs, scs

coupled fluorescence qualification: δR_{exc}=$Purcell_{exc}$*QE & δR_{em}=$Purcell_{em}$*cQE

accompanying nanophotonical phenomena: charge, far-field (□ y) & charge, far-field (□ z)

evaluation of nanoresonators: ecs, scs -> FWHM -> Q,

evaluation of coupled systems: Purcell, δR -> FWHM -> Q; $\Delta\lambda$ & Δf



evaluation of superradiance: comparison with the reference system

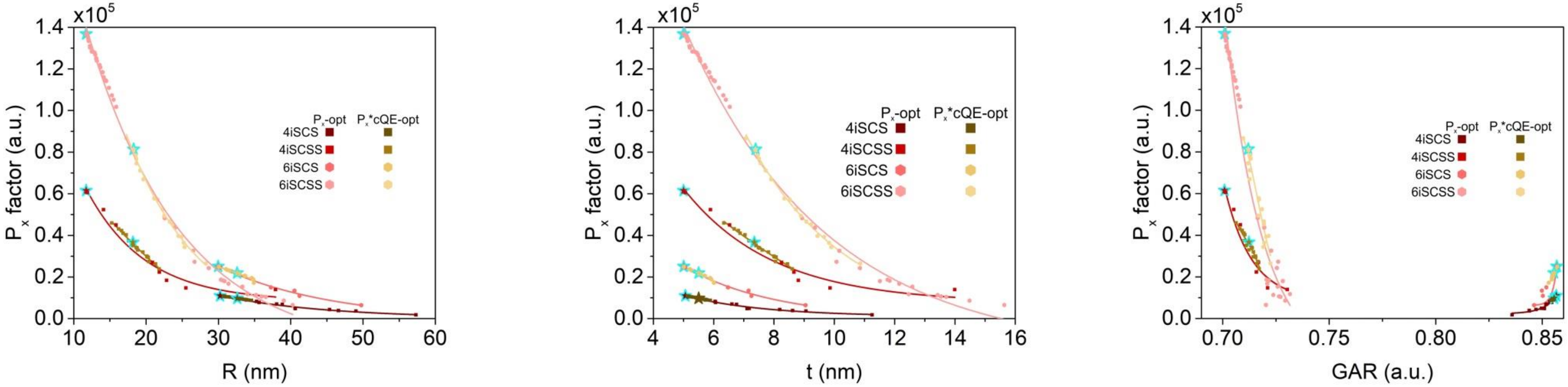
$r\delta R_{exc}$, $r\delta R_{em}$, rcQE, rP_x, rP_x*cQE ⇔ N^2, => **rX_average**

ranking of nanoresonators taking into account P_x, P_x*cQE, cQE, rX_average, Q_Purcell, $\Delta\lambda$

FOM evaluation:

dependency of P_x and P_x*cQE on geometrical parameters, P_x(cQE), P_x*cQE(P_x), P_x*cQE(cQE)

Dependence of the P_x FOM on geometry

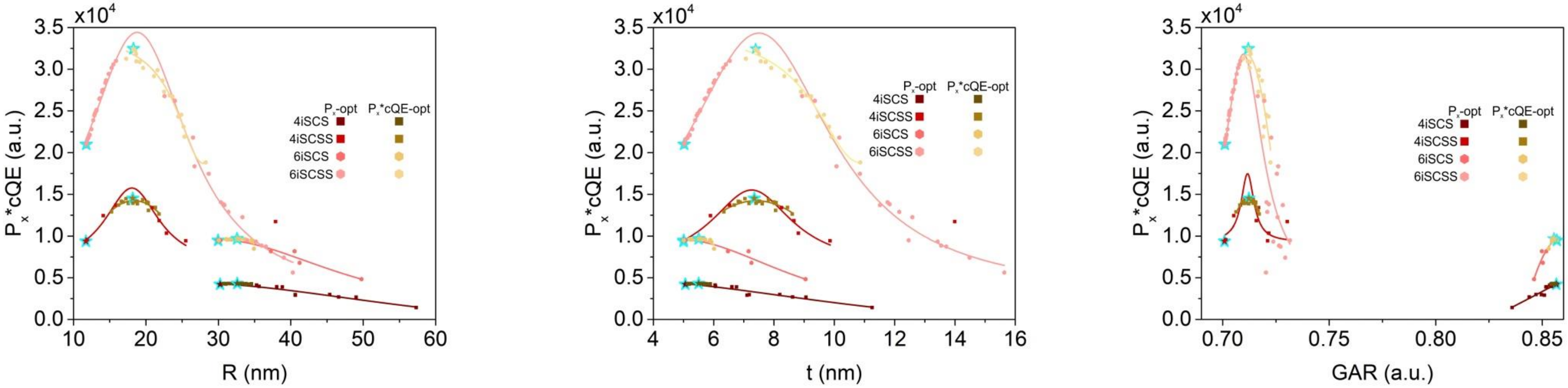


fitting for nanoresonators determined via different FOMs independently
fitted curves overlap

P_x monotonously modifies

P_x⇔P_x*cQE, **,** 4⇔ **6**, SCS ⇔***SCSS***
fitted function takes on larger values

Dependence of the P_x*cQE FOM on the geometry



fitting for nanoresonators determined via different FOMs independently

fitted curves overlap

P_x*cQE ⇔ P_x

fitted functions take on larger values

*-P_x*cQE nanoresonators:*

maximum as a function of all nanoresonator parameters (R, t, GAR) (e: 6iSCSS, outside)

-P_x nanoresonators:

-inside interval in 4iSCSS and 6iSCSS,

-outside interval for R, t, GAR in 6iSCS & for R dependency in 4iSCS,

no maximum for t and GAR dependency in 4iSCS

4⇔**6**

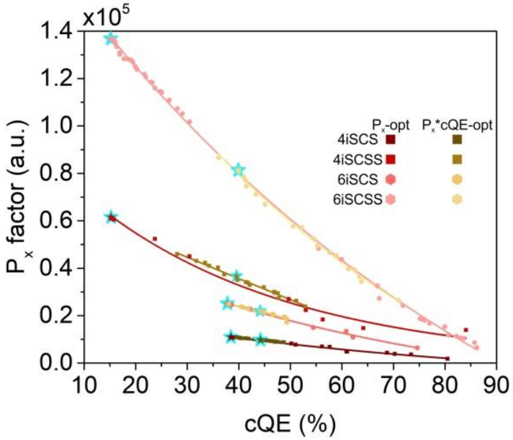
fitted functions take on larger values

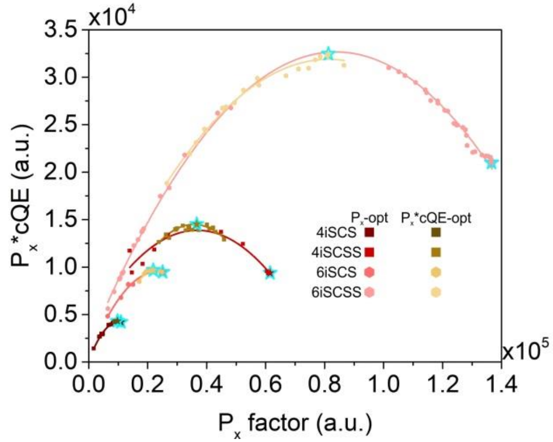
SCS⇔**SCSS**

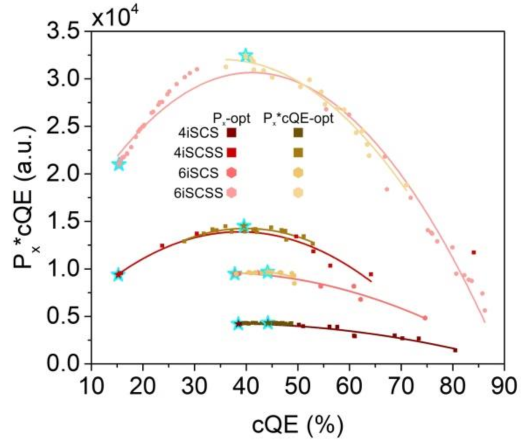
fitted functions take on larger values

parameter intervals of maxima in R / t / GAR are bounding / overlapping / different

Dependence of the FOMs on P_x & cQE/cQE







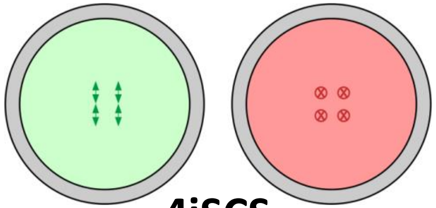
P_x
exponential decay as a function of cQE

P_x*cQE

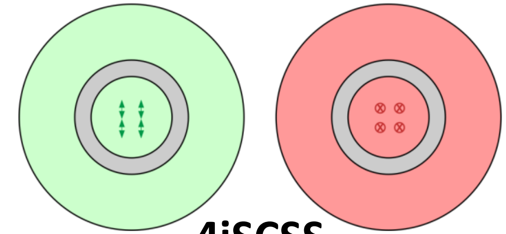
*-P_x*cQE nanoresonators*
P_x*cQE exhibits a maximum as a function of P_x & cQE
(*exception* 6iSCSS, outside the cQE interval)

-P_x nanoresonators
4iSCSS and 6iSCSS exhibit a maximum as a function of P_x & cQE
4iSCS and 6iSCS as a function of cQE outside interval of representative points

$P_x \Leftrightarrow P_x$*cQE: right FOM

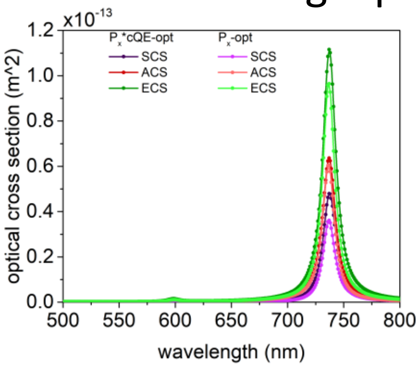


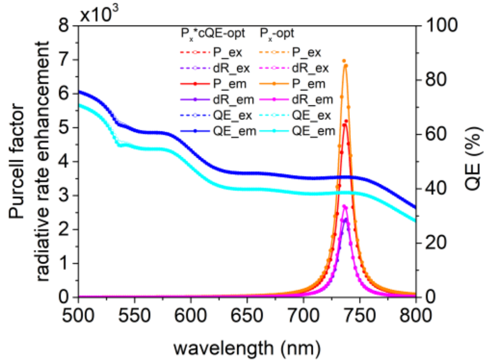
4iSCS

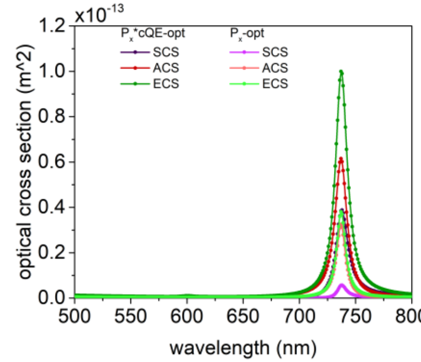


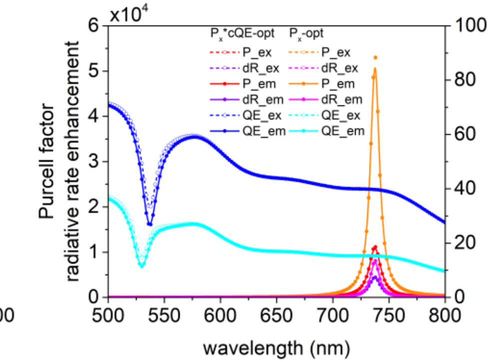
4iSCSS

Single peak on the ecs, scs, Purcell, δR at the emission wavelength









(l_{min}) l_{max} on QE at (exc) emission

*(g_{min}) plateau/decrease on QE at (exc) emission for Px /Px*cQE*

$P_x \Leftrightarrow$ **P_x*cQE - geometry**

larger core, thicker shell, similar GAR,

larger dipole distance

$P_x \Leftrightarrow$ **P_x*cQE - optical response**

-QE larger

-Purcell smaller: weaker resonance

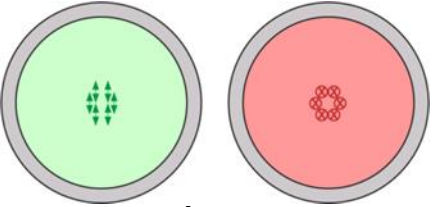
–δR_{exc} larger (δR_{em} smaller): less efficient in emission enhancement

-smaller P_x & larger P_x*cQE

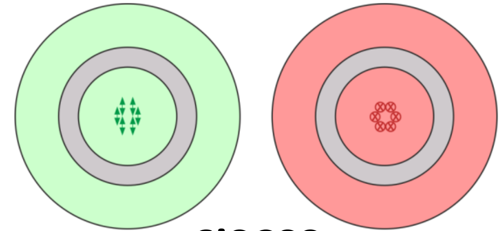
larger difference for 4iSCSS

		P_{exc} (a.u.)	QE (%)	δR_{exc} (a.u.)	P_{em} (a.u.)	cQE(%)	δR_{em} (a.u.)	P_x (a.u.)	P_x*cQE (a.u.)	R (nm)	t (nm)	d (nm)	GAR (a.u.)
4iSCS	P_x	6.8	59.7	4.1	7027.8	38.5	2703.2	10954.3	4213.5	30.2	5.1	26.9	0.8566
	P_x*cQE	6.4	66.3	4.2	5241.3	44.2	2316.1	9151.5	4309.6	**32.6**	**5.5**	**29.4**	0.8556
4iSCSS	P_x	46.7	16.1	7.5	53584.1	15.2	8156.6	61470.1	9357	11.7	5	9.1	0.7009
	P_x*cQE	19.4	42.7	8.3	11208.9	39.6	4435.6	36641.8	14499.8	**18.2**	**7.4**	**13.6**	**0.7123**

$P_x \Leftrightarrow P_x$*cQE: right FOM

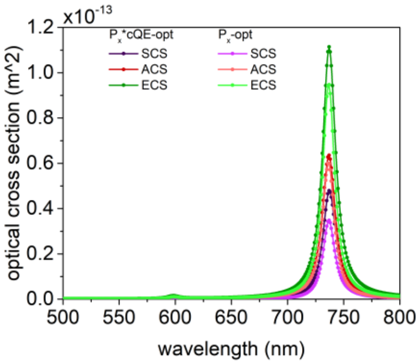


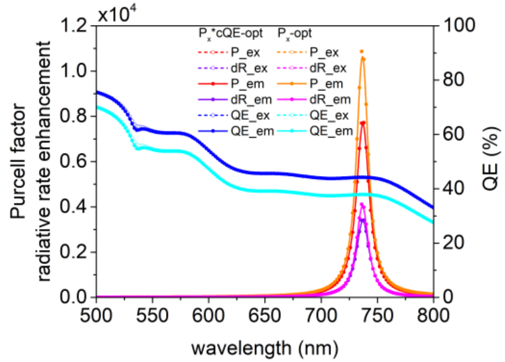
6iSCS

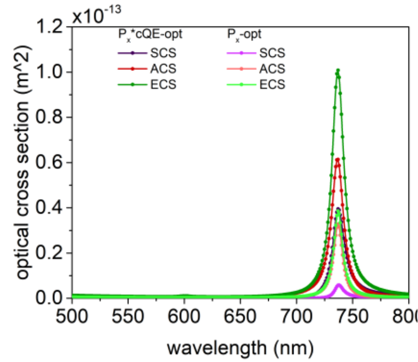


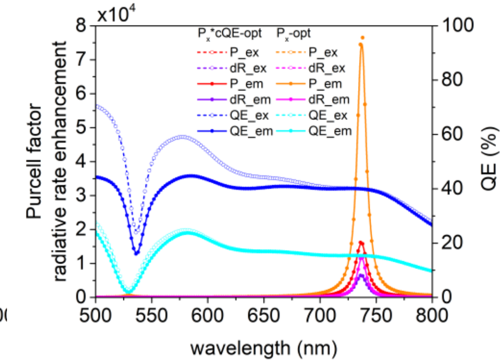
6iSCSS

Single peak on the ecs, scs, Purcell, δR at the emission wavelength









(l_{min}) l_{max} on QE at (exc) emission

*(g_{min}) plateau/l_{max} on QE at (exc) emission for P_x/P_x*cQE*

$P_x \Leftrightarrow$ **P_x*cQE - geometry**

larger core, thicker shell, similar GAR,

larger dipole distance

$P_x \Leftrightarrow$ **P_x*cQE - optical response**

-QE larger

-Purcell smaller: weaker resonance

–δR_{exc} larger (δR_{em} smaller): less efficient in emission enhancement

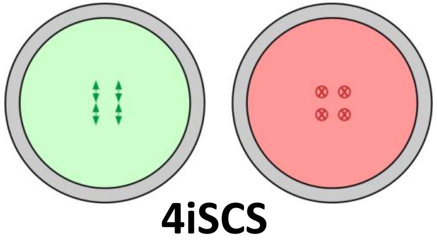
-smaller P_x & larger P_x*cQE

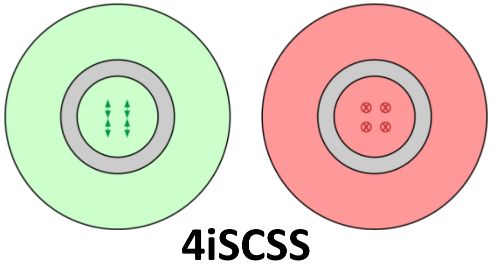
larger difference for 6iSCSS

6iSCSS larger cQE at emission than at excitation

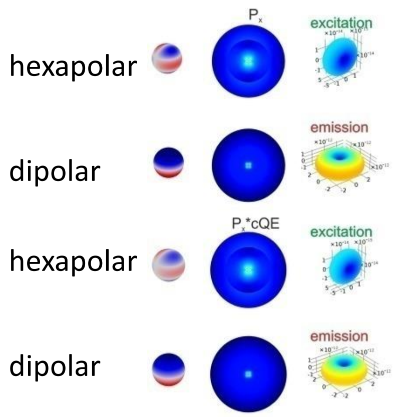
		P_{exc} (a.u.)	QE (%)	δR_{exc} (a.u.)	P_{em} (a.u.)	cQE(%)	δR_{em} (a.u.)	P_x (a.u.)	P_x*cQE (a.u.)	R (nm)	t (nm)	d (nm)	GAR (a.u.)
6iSCS	P_x	10.3	58.8	6	10984.7	37.8	4151.7	25087.4	9481.8	30	5	26.5	**0.8568**
	P_x*cQE	9.7	65	6.3	7871.1	44.2	3474.8	21989.5	9667.3	**32.6**	**5.5**	**28.9**	0.8555
6iSCSS	P_x	324.3	3.5	11.3	78999.7	15.4	12136.7	136649.7	20993.5	11.8	5	7.3	0.701
	P_x*cQE	38	32.7	12.4	16386	39.9	6539.9	81311.4	32452.4	**18.3**	**7.4**	**13**	**0.712**

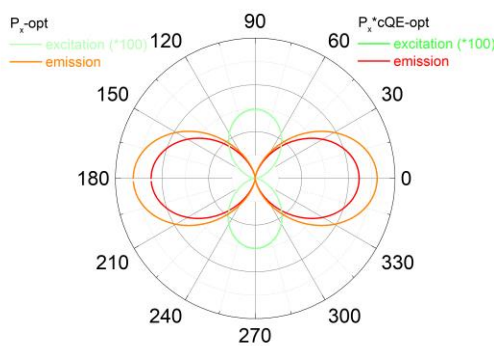
$P_x \Leftrightarrow P_x$*cQE: right FOM

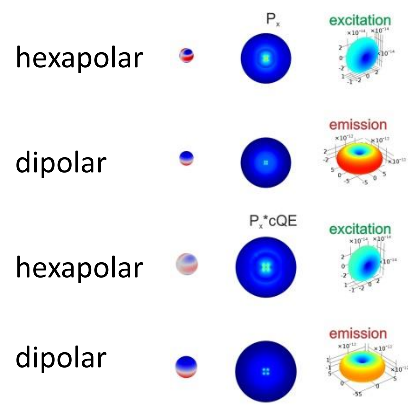


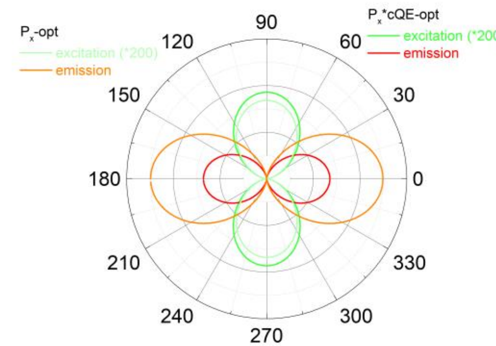


*exc ⇔ **em** ~10^2 *charge, Purcell factor, stronger resonance - > larger emission enhancement*









$P_x \Leftrightarrow P_x$*cQE – near- & far-field response

-smaller amount of accumulated charges according to weaker resonance

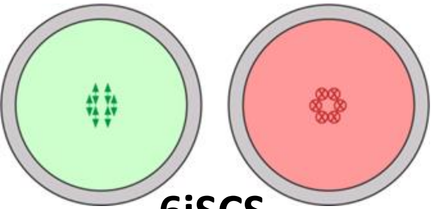
-larger (smaller) lobes at excitation (emission)

-FWHM larger -> Q factor smaller

-bad cavity more well defined in 4iSCS | **in 4iSCSS**

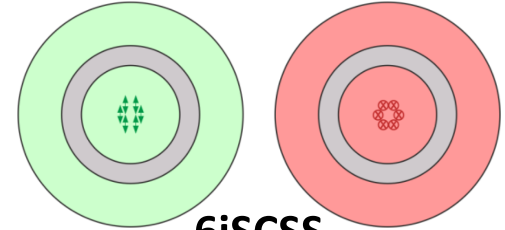
-detuning smaller in ecs | *-detuning smaller in Purcell & δR & scs*

		charge (C)		FWHM (nm)				detuning (nm)				Q-factor (a.u.)	
		excitation	emission	Purcell	δR	ecs	scs	Purcell	δR	ecs	scs	Purcell	ecs
4iSCS	P_x	3.00E-16	5.25E-14	12.89	12.48	12.89	12.98	-0.21	-0.21	**-0.34**	0.60	**58.71**	**57.13**
	P_x*cQE	2.29E-16	4.55E-14	**14.04**	**13.62**	**14.04**	**14.13**	**0.27**	**0.26**	0.22	**0.65**	53.89	52.49
4iSCSS	P_x	5.96E-15	3.40E-13	9.41	9.09	9.41	9.10	**0.78**	**0.46**	0.19	**1.29**	**80.90**	**78.37**
	P_x*cQE	3.63E-15	1.57E-13	**12.97**	**12.25**	**12.67**	**12.58**	0.46	0.42	**0.44**	1.23	59.91	58.13



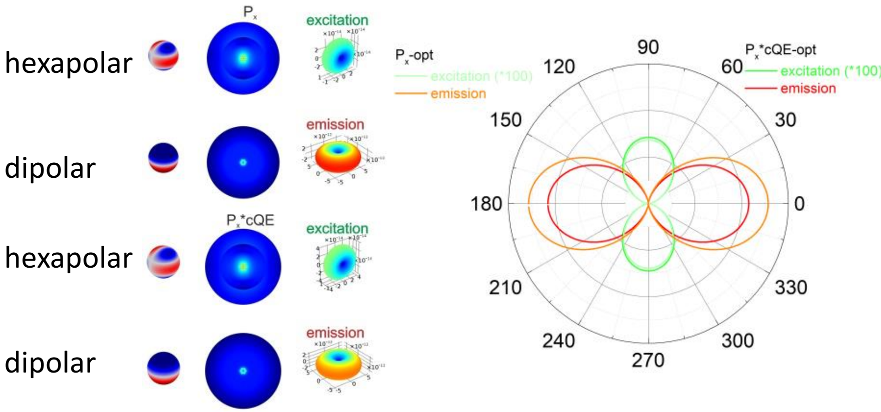
6iSCS

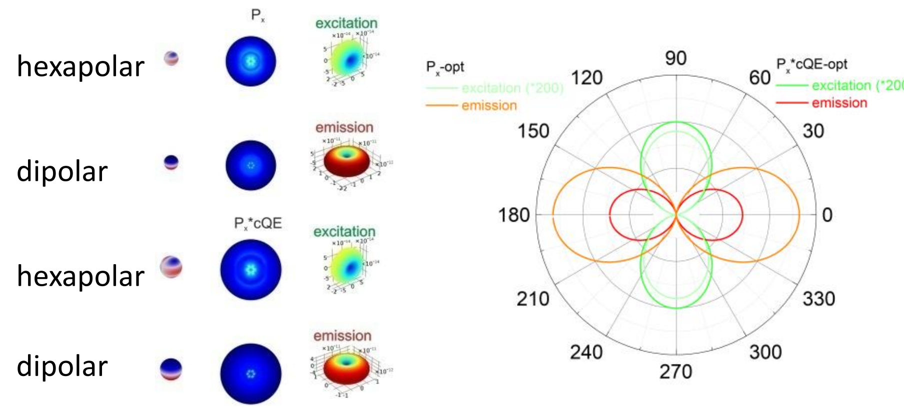
$P_x \Leftrightarrow P_x$*cQE: right FOM



6iSCSS

*exc ⬄em~10^2 *charge (except 6iSCSS_P_x), Purcell factor, stronger resonance - > larger emission enhancement*





P_x ⬄P_x*cQE near- & far-field response

***exception**: 6iSCS at excitation*

-smaller amount of accumulated charges according to weaker resonance

-larger (smaller) lobes at excitation (emission)

-FWHM larger -> Q factor smaller

-bad cavity more well defined in 6iSCS

-detuning smaller in Purcell, δR, ecs

6iSCSS

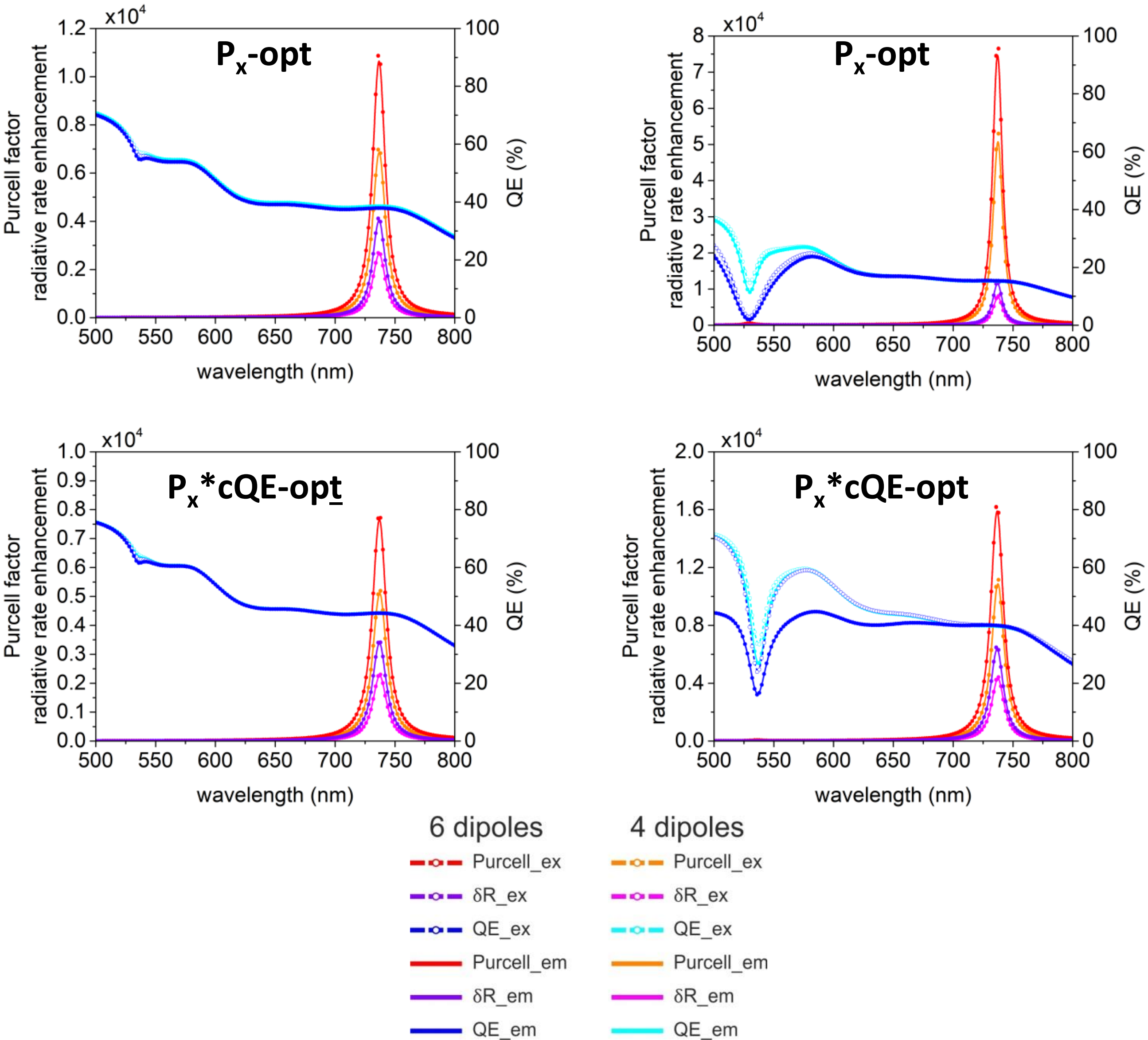
-detuning smaller in ecs

		charge (C)		FWHM (nm)				detuning (nm)				Q-factor (a.u.)	
		excitation	emission	Purcell	δR	ecs	scs	Purcell	δR	ecs	scs	Purcell	ecs
6iSCS	P_x	4.65E-16	8.06E-14	12.43	12.36	12.77	12.86	**-0.03**	**-0.33**	**-0.39**	0.01	**59.29**	**57.66**
	P_x*cQE	4.83E-16	6.82E-14	**13.68**	**13.62**	**14.04**	**14.14**	0.02	0.01	0.03	**0.46**	53.88	52.48
6iSCSS	P_x	2.58E-14	5.07E-13	9.12	9.10	9.42	9.13	0.14	0.13	**0.15**	0.75	**80.83**	**78.23**
	P_x*cQE	7.48E-15	2.32E-13	**12.56**	**12.50**	**12.78**	**12.69**	**0.46**	**0.43**	-0.05	**1.24**	58.71	57.68

4⇔6 dipoles

6 ⇔4

CS nanoresonator | **CSS nanoresonator**



-core radius, shell thickness, GAR ~same (for same optimization), distance smaller

-QE smaller&same near λ_{exc} & λ_{em} except in SCSS at λ_{em}
-larger Purcell factor & δR independently of the optimization
-larger P_x and P_x*cQE

-larger amount of accumulated charges
-larger far-field lobes

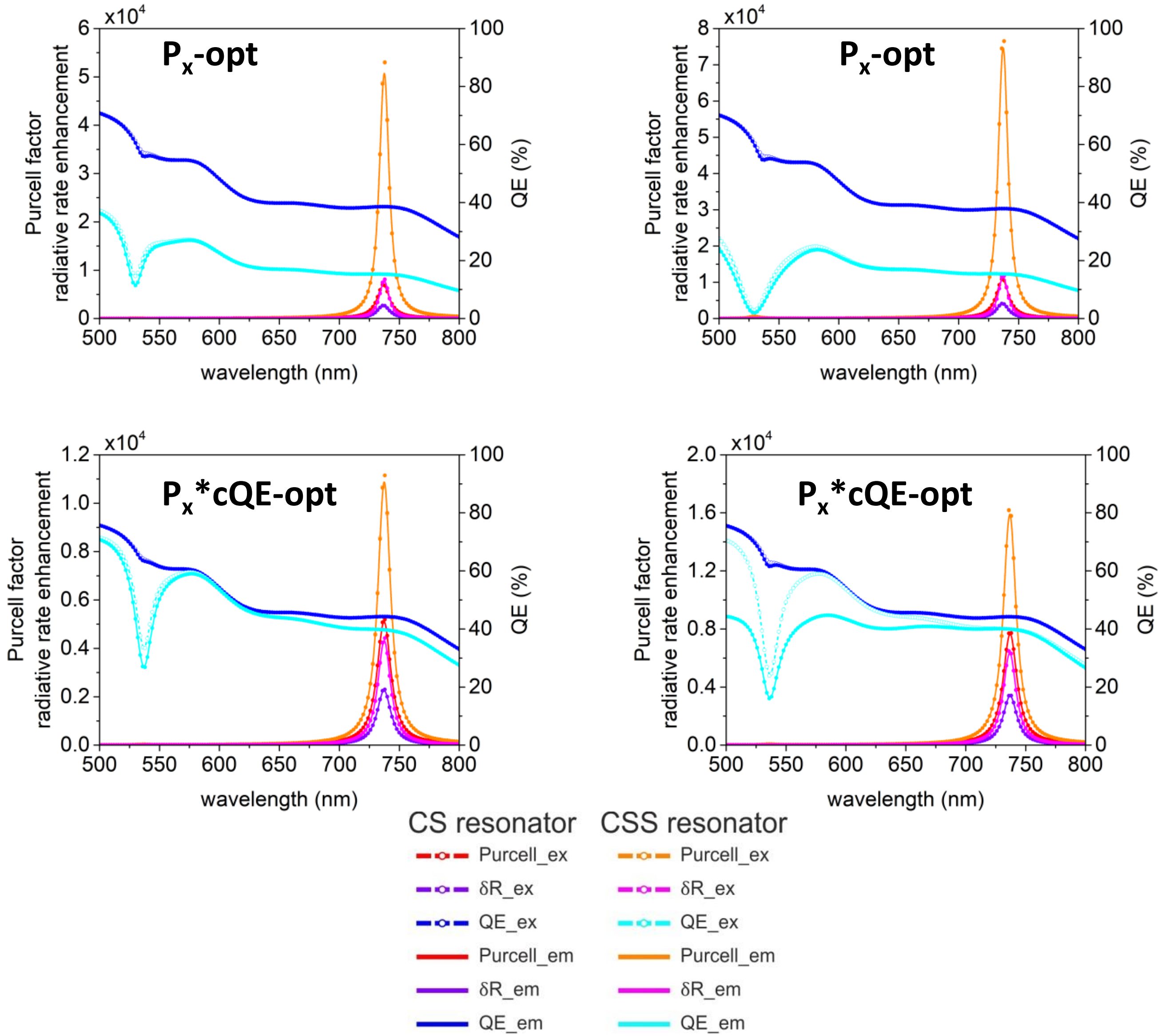
-larger FWHM (9 exceptions)
-smaller Q (2 exceptions)
-bad cavity more well defined
-detuning smaller (5 exceptions)
-Δf difference smaller (same) in SCS (SCSS)

CS ⇔ CSS

SCSS ⇔ **SCS**

4 dipoles

6 dipoles



-larger core, thinner shell
(e: 4iCS&CSS_P_x) => larger GAR,
larger distance

-QE larger
(more with P_x objective function)
-smaller Purcell & δR at exc & em
-smaller P_x and P_x*cQE

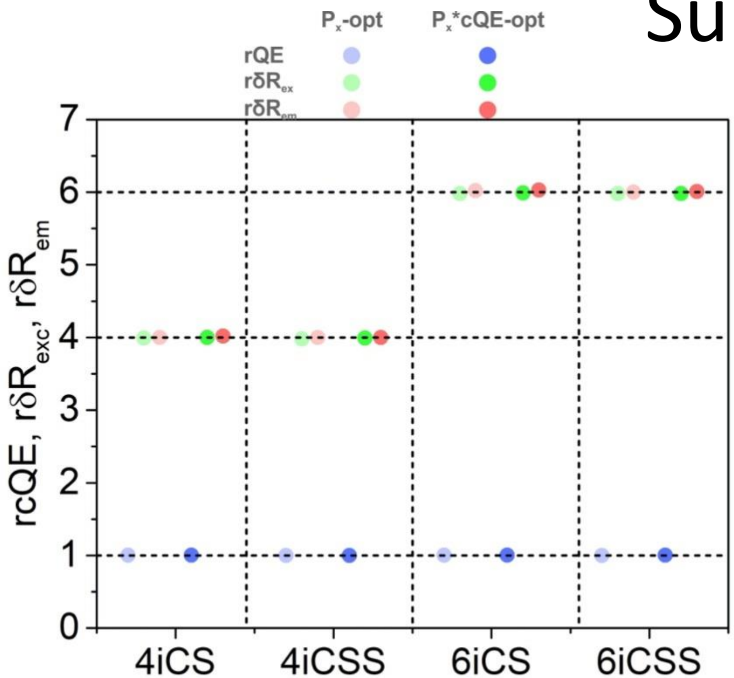
-weaker charge accumulation
-smaller far-field lobes

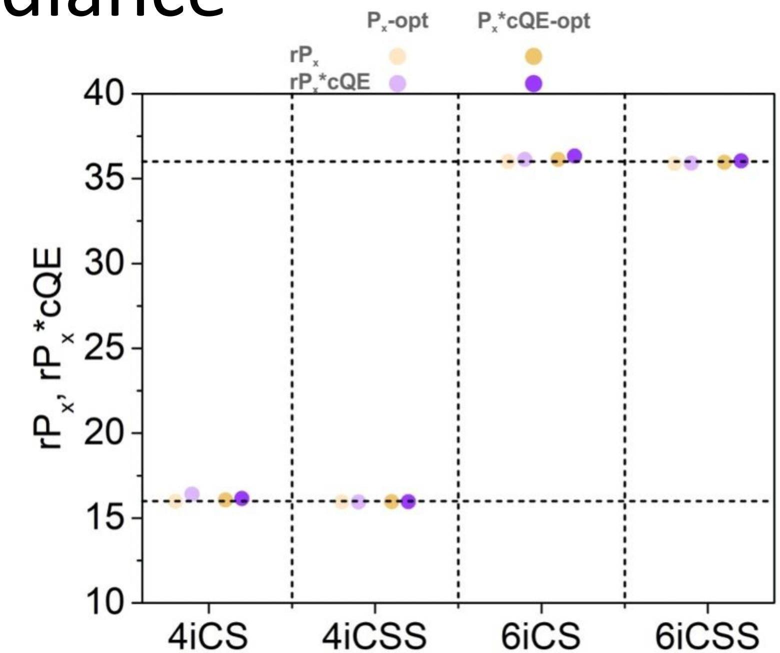
-larger FWHM, smaller Q
-bad cavity better in SCS

-detuning is smaller in SCS
3 exceptions: in ecs for 4iSCS_P_x
in δR and ecs for 6iSCS_P_x

-difference in Δf is
smaller in SCS

Superradiance





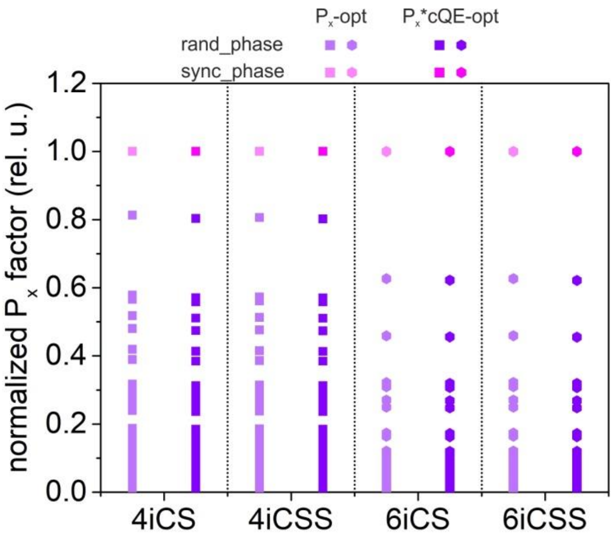
P_x⇔ **P_x*cQE (17/20)**: better for δR_{exc} & δR_{em} & rcQE & P_x & P_x*cQE (e: $r\delta R_{em}$, rcQE in 4iCSS; δR_{exc} in 6iCSS)

4⇔**6 (13/30)**: better for $r\delta R_{exc}$ in 6iSCSS_P_x, $r\delta R_{em}$ & rP_x in 6iSCS_P_x, 6iSCSS_P_x*cQE, rP_x*cQE in 6iSCS_P_x, 6iSCSS_P_x&P_x*cQE

CS⇔CSS **(22/30)**: better for $r\delta R_{exc}$ & $r\delta R_{em}$ & rcQE & rP_x & rP_x*cQE (e: $r\delta R_{exc}$ in 6iCS_P_x, $r\delta R_{em}$ in 4iCS_P 6iCS_P_x) on the average for all SCS

	4iCS		4iCSS		6iCS		6iCSS	
	P_x-opt	P_x*cQE-opt	P_x-opt	P_x*cQE-opt	P_x-opt	P_x*cQE-opt	P_x-opt	P_x*cQE-opt
$r\delta R_{exc}$	3.99	4	3.98	3.99	5.98	5.99	5.98	5.98
$r\delta R_{em}$	4.01	4.02	4.01	4	6.02	6.03	6	6.01
rcQE	1.0031	1.005	1	0.9994	1.0033	1.0055	1.0008	1.0025
rP_x	15.99	16.07	15.95	15.97	36	36.13	35.88	35.95
rP_x*cQE	16.04	16.15	15.95	15.96	36.12	36.33	35.91	36.04
∑r_average	5.003	5.018	4.992	4.994	4.996	5.026	4.991	4.999

Comparison of collective and random systems



-larger P_x & P_x *cQE in collectively oscillating systems

-P_x *cQE (P_x) is larger in systems optimized with P_x *cQE (P_x) objective function

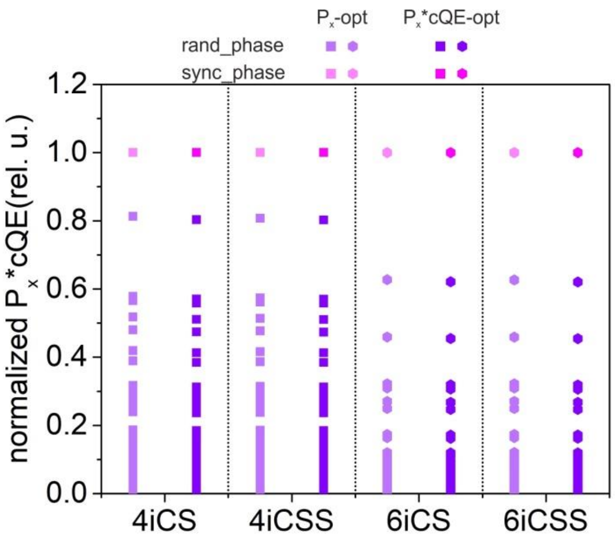
-more significant difference for **6** dipoles (independently of the optimization or the resonator type)

-P_x and P_x*cQE is larger in nanoresonators consisting of **6 dipoles** independently of the optimization

-P_x and P_x*cQE is larger in ***SCSS*** type nanoresonators, independently of the optimization

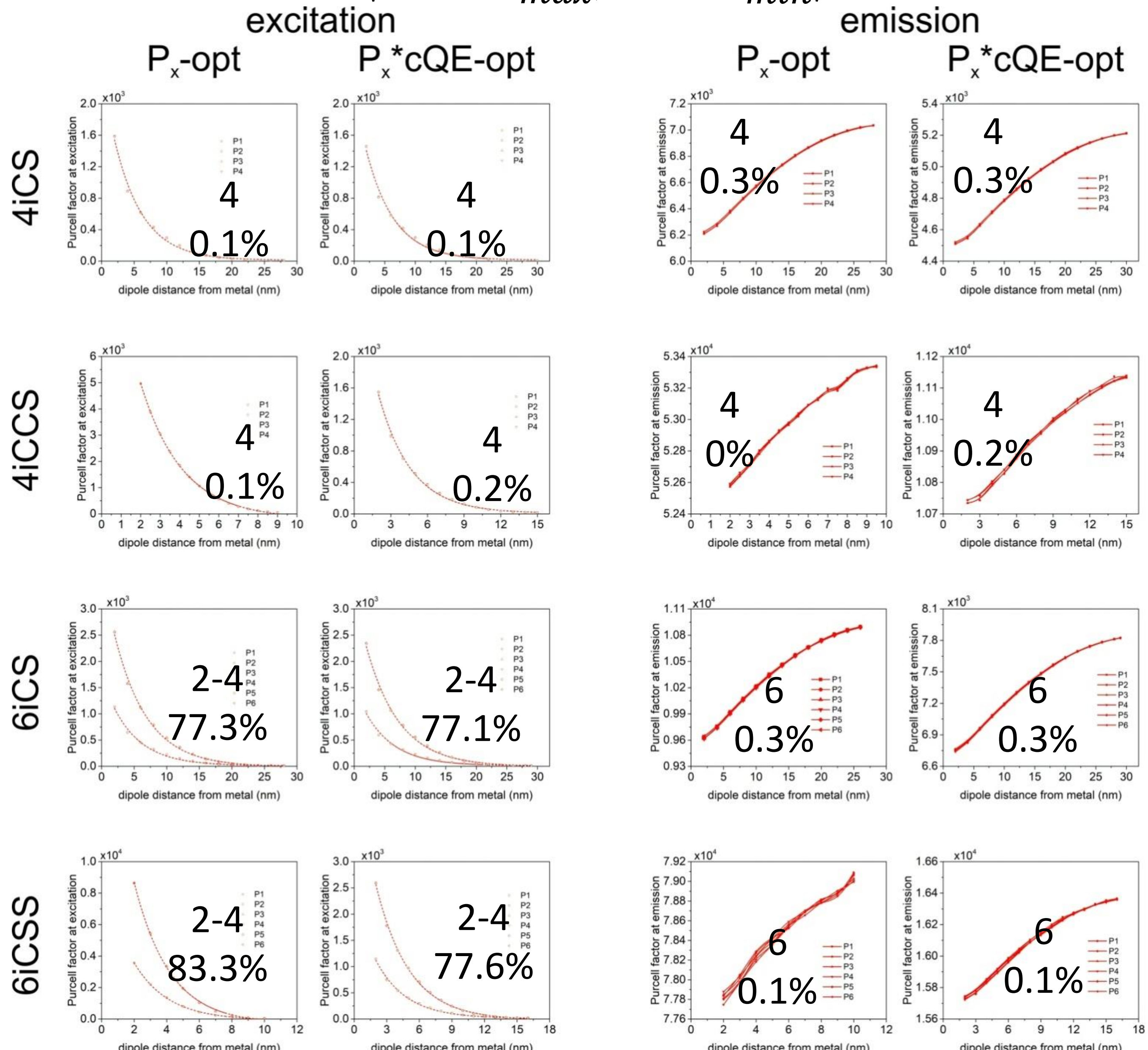
- P_x objective function to improve non-cooperative emission

- **P_x*cQE objective function to improve cooperative emission**



Distance dependency of Purcell factor

$$\frac{splitting_{max}}{\langle Purcell_{max}, Purcell_{min}\rangle}$$



Conclusion

- P_x / **P_x*cQE** efficient to maximize non-cooperative / **cooperative** fluorescence
  P_x & P_x*cQE is larger in case of 6 dipoles and SCSS type resonators
  average ratio larger/smaller for **6** dipoles for SCS & SCSS in case of Px*cQE / Px

- 4 / **6** larger seeding is more suitable to result in **non-cooperative & cooperative** fluorescence
  FWHM is larger-> the Q factor is smaller, and $\Delta\lambda$ is smaller

- SCSS / **SCS** type resonators are more suitable for non-cooperative / **cooperative** fluorescence
  FWHM is larger-> the Q factor is smaller, and $\Delta\lambda$ is smaller in **SCS** type nanoresonators

- line-width narrowing
- indistinguishable: both configurations in case of 4 dipoles (proposed 4iSCS)

- δR & far-field: 4iSCS-4iSCSS-6iSCS-6iSCSS

- ranking of P_x spherical nanoresonators: 4iSCSS < 4iSCS = 6iSCS < 6iSCSS
- ranking of P_x*cQE spherical nanoresonators: **4iSCSS < 4iSCS <6iSCSS<6iSCS**

- **proposed: 6iSCS: larger efficiency, smaller detuning and deviation in frequency pulling**

Acknowledgements

The research was supported by the National Research, Development and Innovation Office-NKFIH through project “Optimized nanoplasmonics” K116362.

The project has been supported by the European Union, co-financed by the European Social fund, EFOP-3.6.2-16-2017-00005.

András Szenes

Dávid Vass

Géza Veszprémi

Lóránt Zsolt Szabó

Dr. Balázs Bánhelyi

Prof. Tibor Csendes

Prof. Gábor Szabó

SZÉCHENYI 2020

HUNGARIAN GOVERNMENT

European Union
European Social Fund

INVESTING IN YOUR FUTURE