Fluorescence enhancement with optical antennas

how to enlarge the reported enhancement without changing the antenna design

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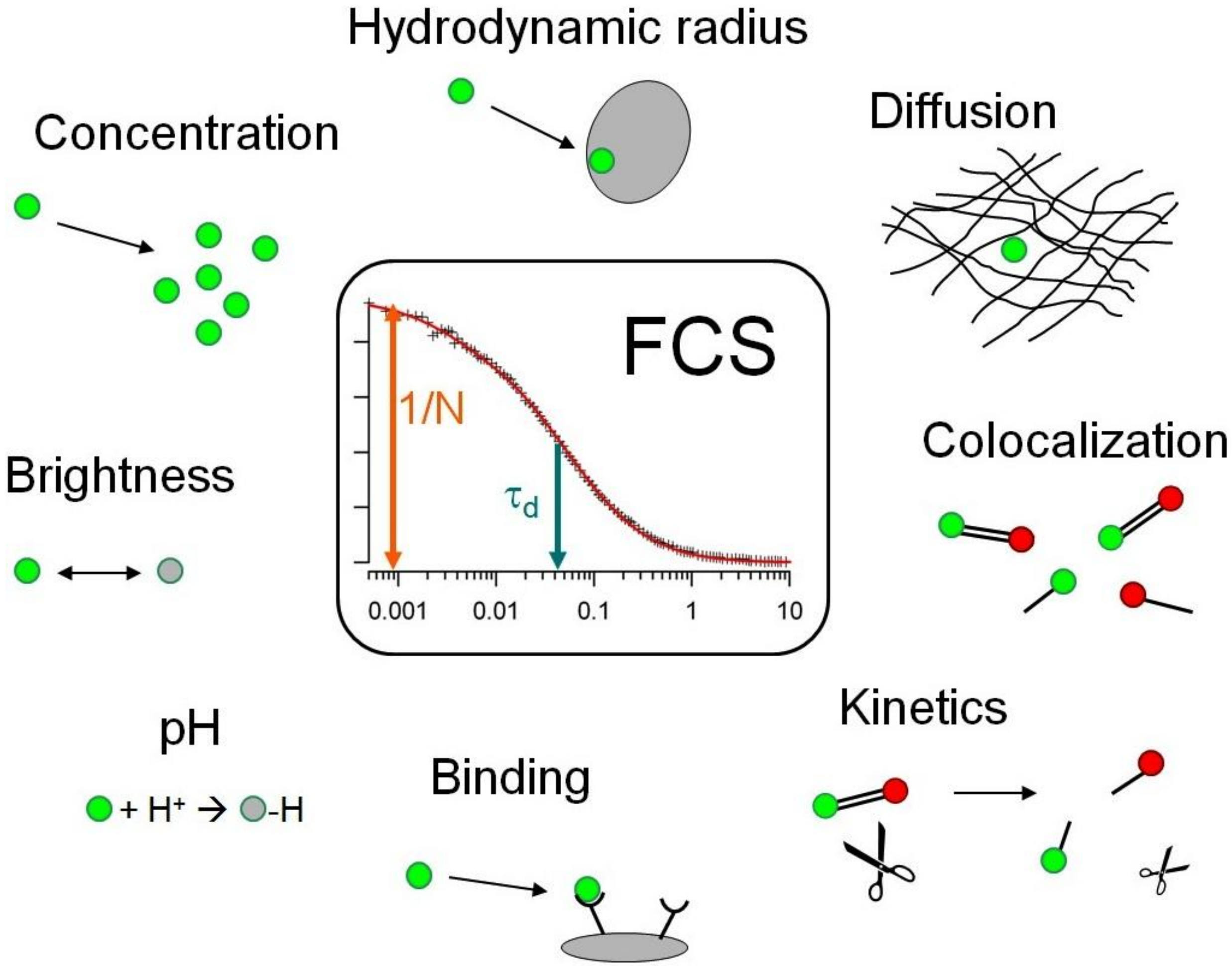
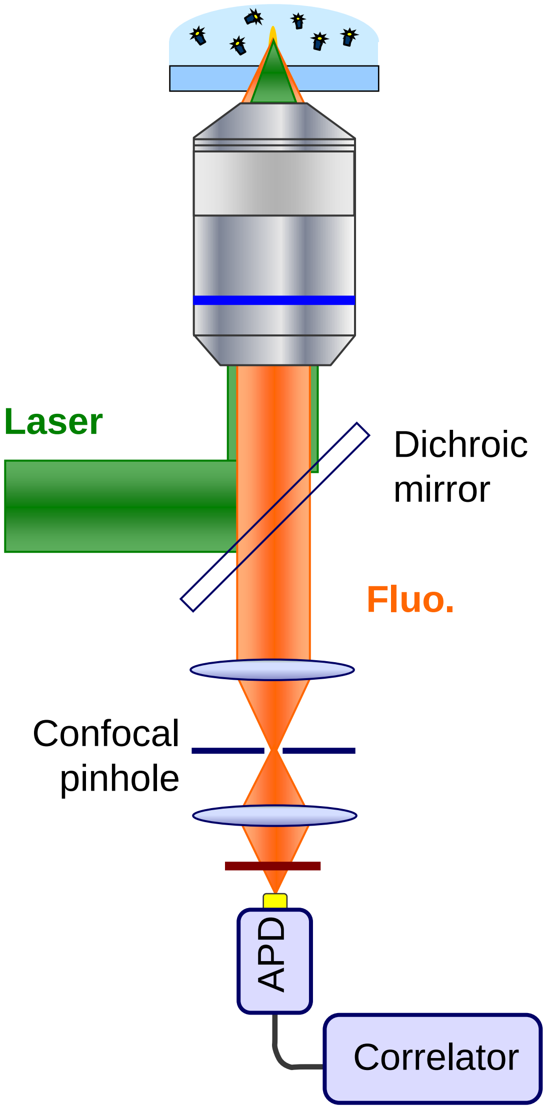
FCS: Fluorescence Correlation Spectroscopy



FCS: Fluorescence Correlation Spectroscopy



Laser

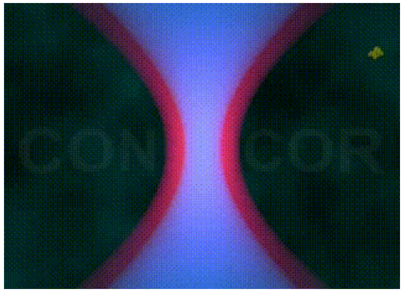
Dichroic
mirror

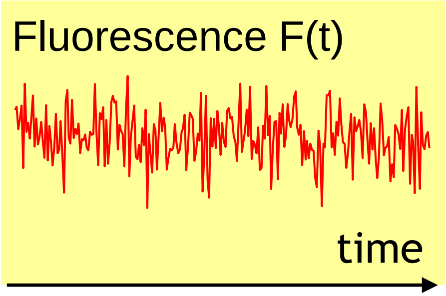
Fluo.

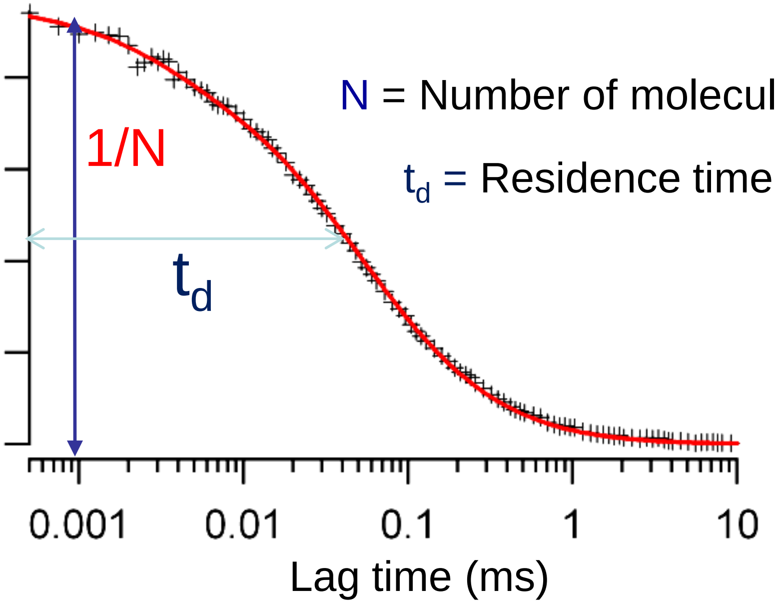
Confocal
pinhole

APD

Correlator







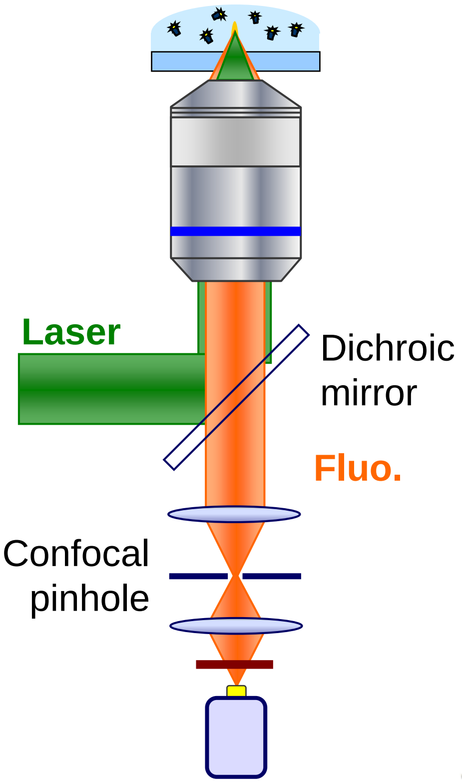
N = Number of molecules

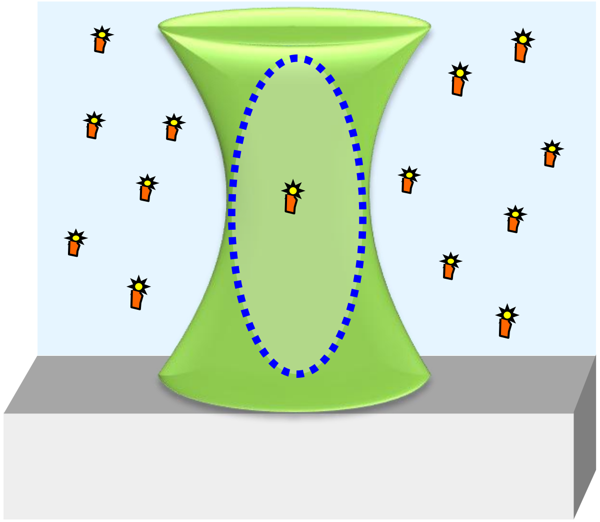
t_d = Residence time

Fluorescence Autocorrelation $g(\tau)=\dfrac{\langle F(t)\cdot F(t+\tau)\rangle}{\langle F(t)\rangle^2}$

Fluorescence sensing with confocal microscopy

Limited by optical diffraction: signal & concentration range

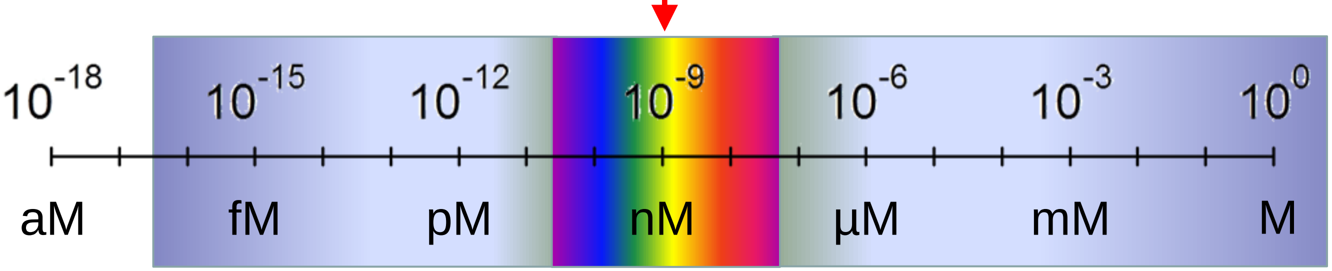




Detection volume
~ 1 femtolitre (1 µm^3)

↓

Concentration for single molecule ~ 1 nM

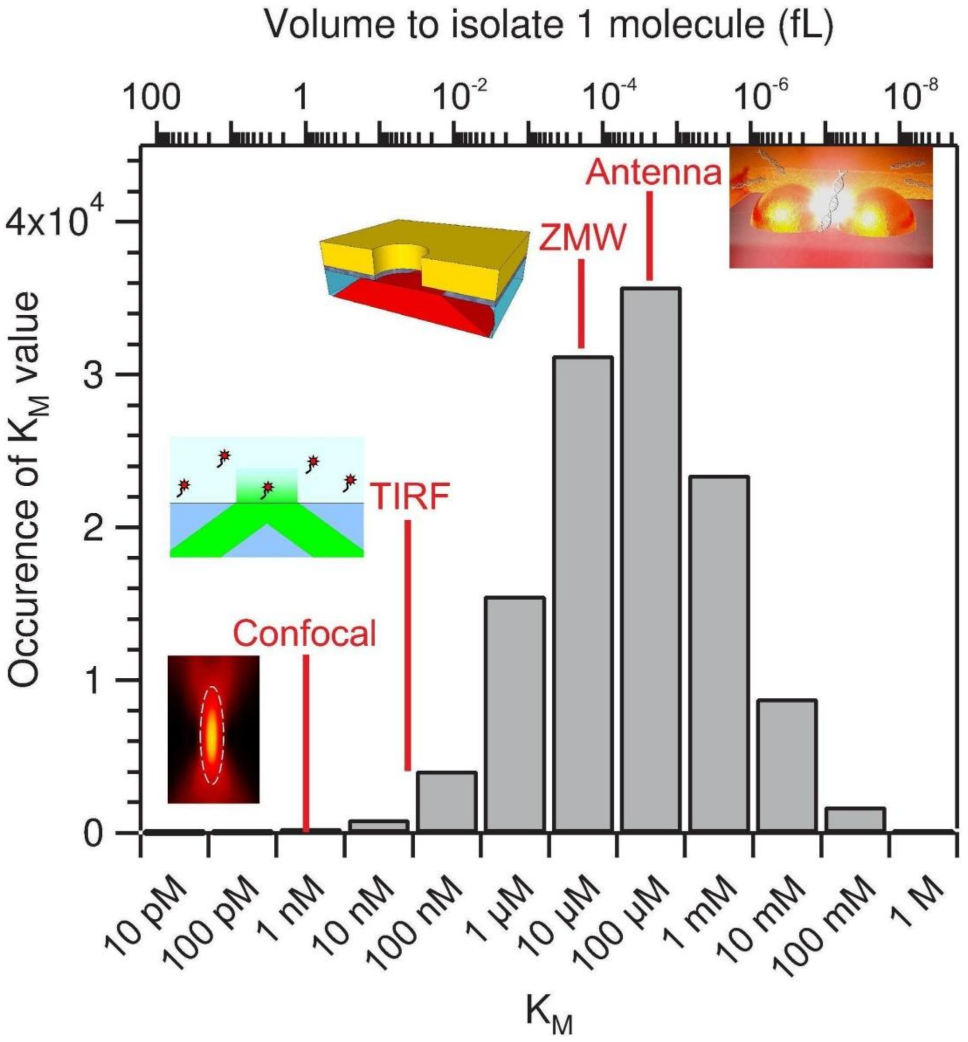


Sensing
SPR

Available for confocal microscopy

Ensemble
(cuvette)
spectroscopy

Limitations of Diffraction:

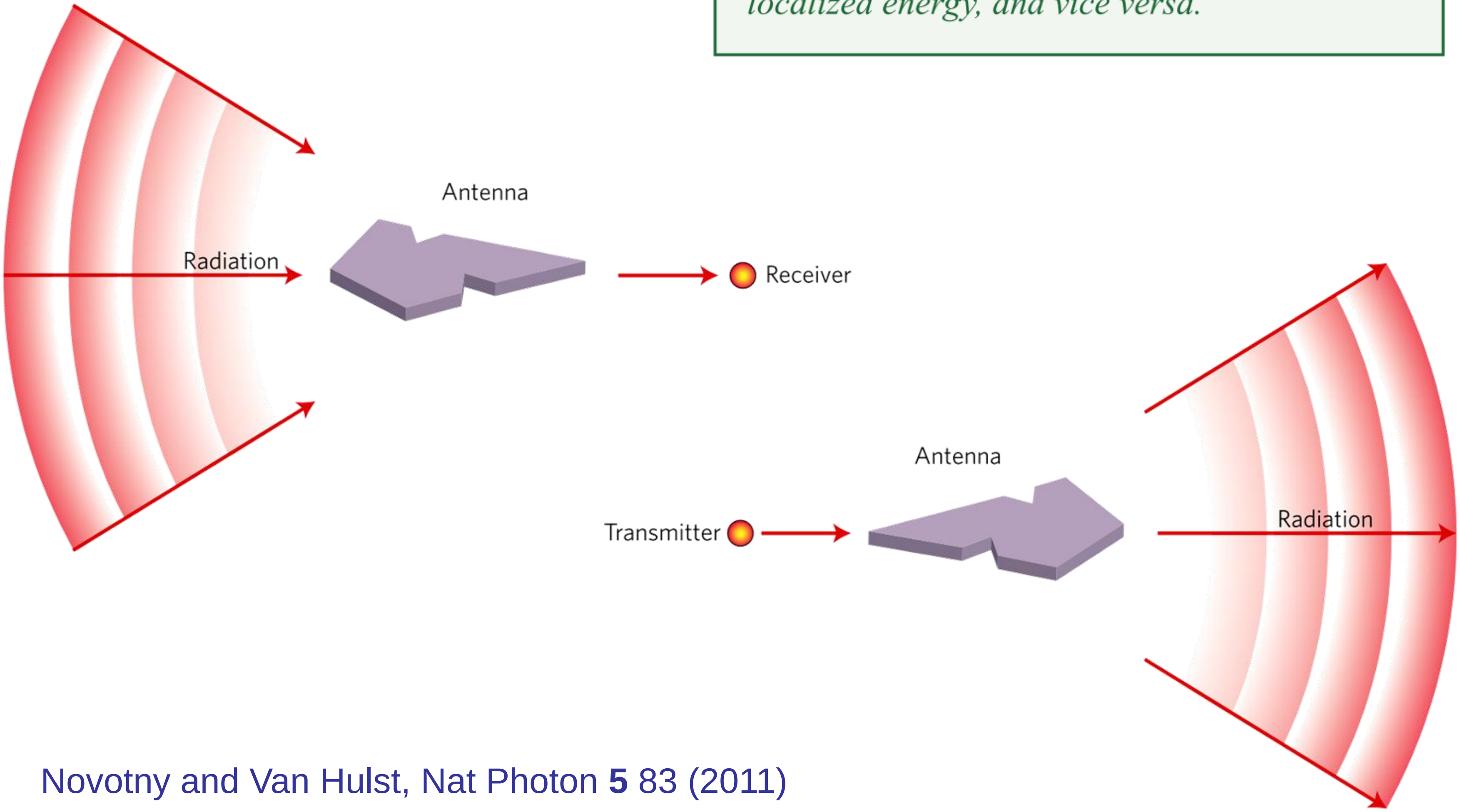


Punj *et al*, WIREs Nanomed Nanobiotechnol. 2014. doi: 10.1002/wnan.1261

ArXiv 1403.1390

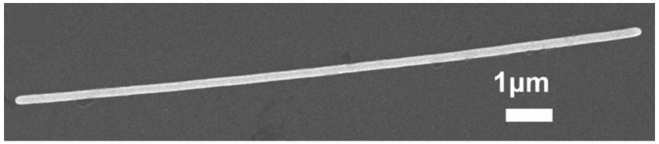
Plasmonic optical antennas

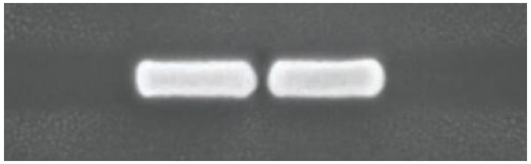
Optical antenna: a device designed to efficiently convert free-propagating optical radiation to localized energy, and vice versa.

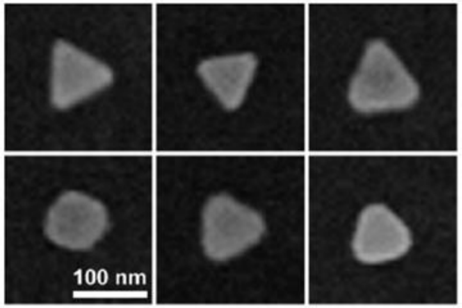


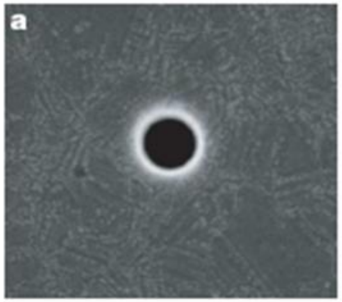
Novotny and Van Hulst, Nat Photon **5** 83 (2011)

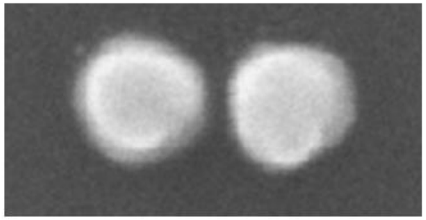
Plasmonic Optical Nanoantennas

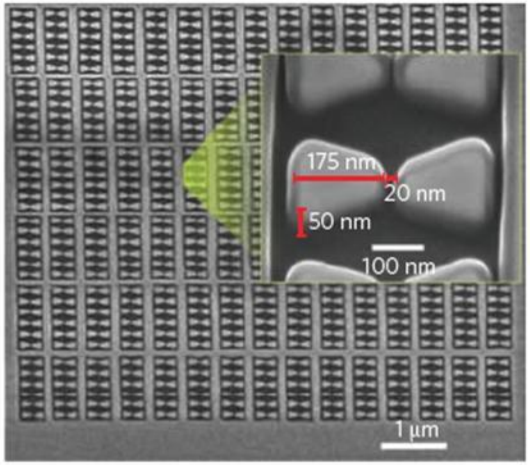


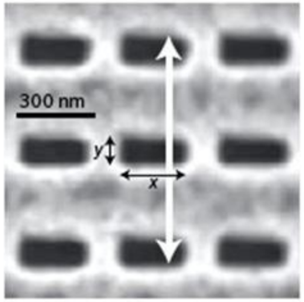


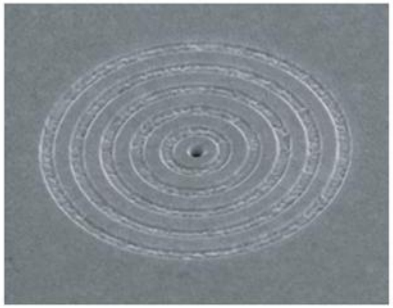


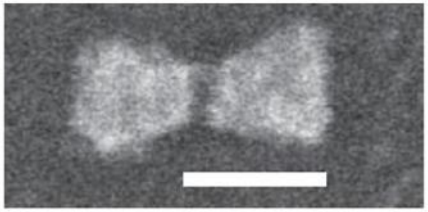


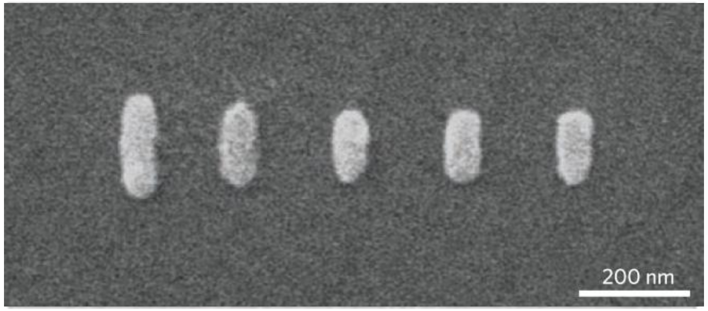


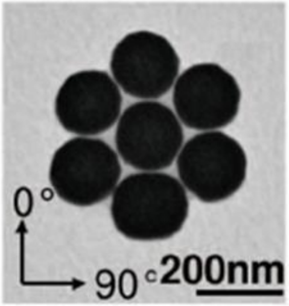


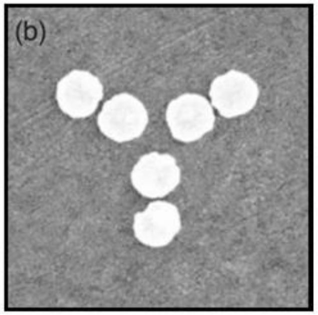


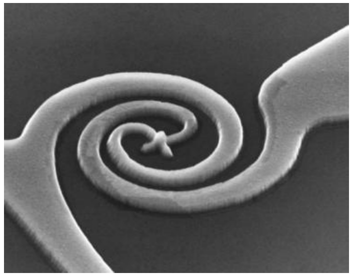


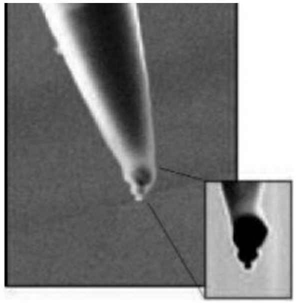


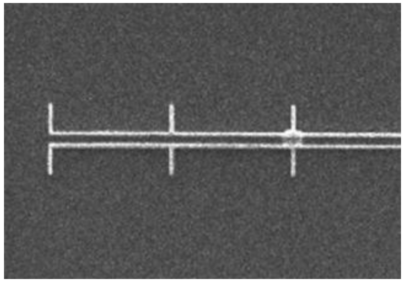


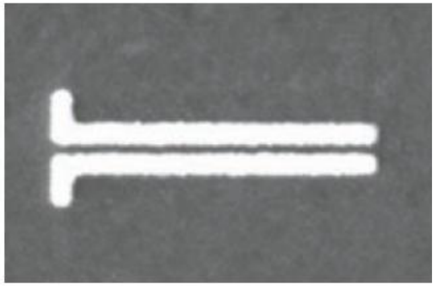


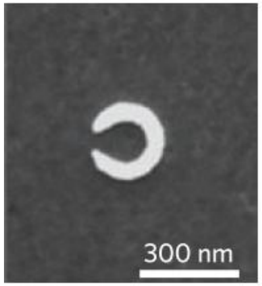




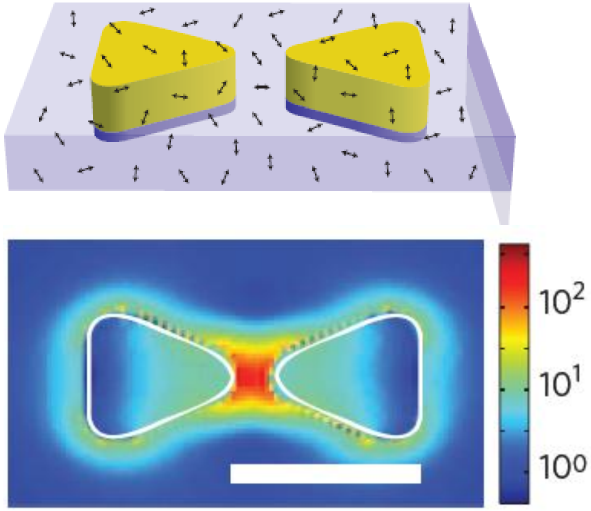


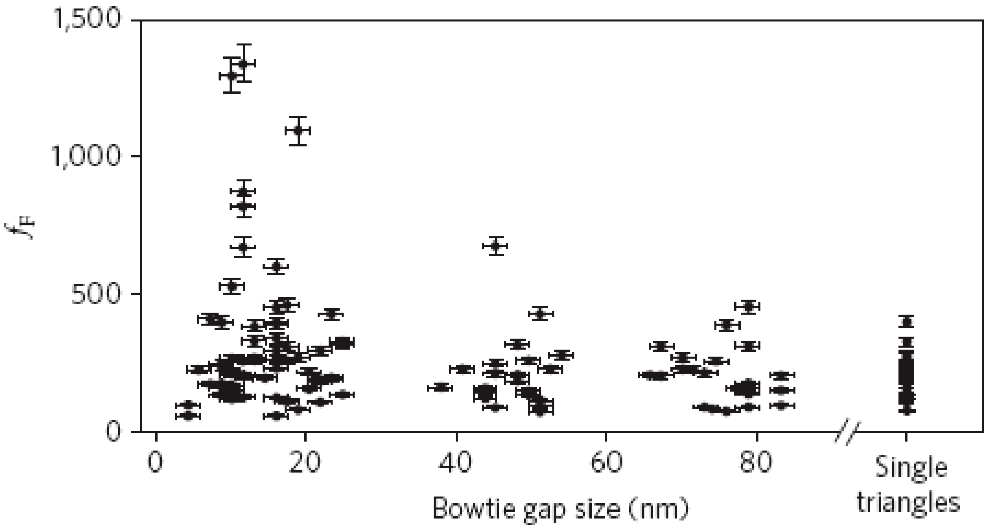






Fluo. enhancement on optical antennas





Kinkhabwala *et al*, Nature Phot. **3**, 654 (2009)

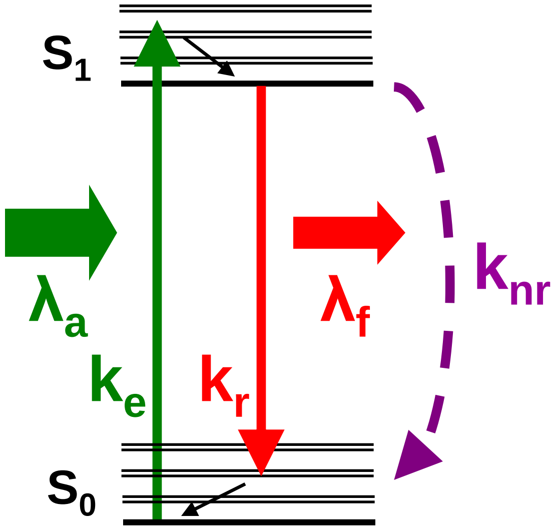
Depends on:

- Gap distance
- Antenna shape
- Emitter's location
- Emitter's orientation
- Metal / adhesion layer
- Excitation / emission wavelength
- Excitation polarisation

NOT
intrinsic to dipole-antenna device

- Excitation power
- Emitter's quantum yield
- Collection optics

Back to fluorescence basics



Detected fluorescence:

$$F = \kappa\, k_r\, N_1$$

$$= \underbrace{\kappa}_{\text{Collection efficiency}}\ \underbrace{\frac{k_r}{k_r + k_{nr}}}_{\text{Quantum yield } \Phi}\ \underbrace{\frac{k_e}{1 + k_e/(k_r + k_{nr})}}_{\text{Excitation intensity } I_e}\ N_{tot}$$

k_e : excitation rate

k_r : radiative emission rate

k_{nr} : non radiative emission rate

For a single emitter:

$$CRM = \kappa\,\phi\,\frac{\sigma I_e}{1 + I_e/I_s}$$

Collection efficiency

Quantum yield

Excitation intensity I_e

Fluorescence enhancement:

$$\eta_F = \frac{CRM^*}{CRM} = f(\kappa,\kappa^*,\phi,\phi^*,I_e,I_e^*)$$

Influence of:

- Collection numerical aperture
- Emitter’s quantum yield
- Excitation intensity

Excitation intensity: weak excitation $(I_e \ll I_s)$

$$CRM = \kappa\,\phi\,\sigma\,I_e$$

$$\eta_F = \frac{CRM^*}{CRM} = \frac{\kappa^*}{\kappa}\,\frac{\phi^*}{\phi}\,\frac{I_e^*}{I_e} = \frac{\kappa^*}{\kappa}\,\frac{k_r^*}{k_r}\,\boxed{\frac{\tau^*}{\tau}}\,\frac{I_e^*}{I_e}$$

Lifetime
reduction

Lifetime reduction
(‘’Purcell factor’’)

$\neq$

Fluorescence
enhancement

Excitation intensity: weak excitation $(I_e \ll I_s)$

$$CRM = \kappa \, \phi \, \sigma \, I_e$$

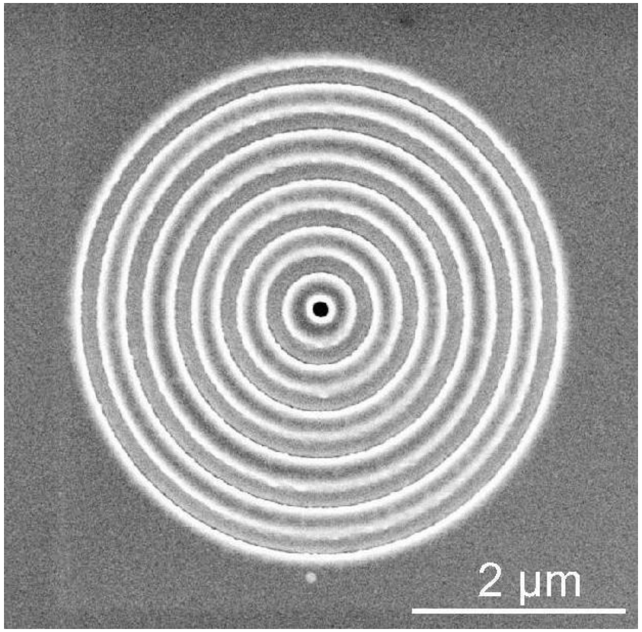
$$\eta_F = \frac{CRM^*}{CRM} = \frac{\kappa^*}{\kappa} \frac{\phi^*}{\phi} \frac{I_e^*}{I_e} = \frac{\kappa^*}{\kappa} \frac{k_r^*}{k_r} \boxed{\frac{\tau^*}{\tau} \frac{I_e^*}{I_e}}$$

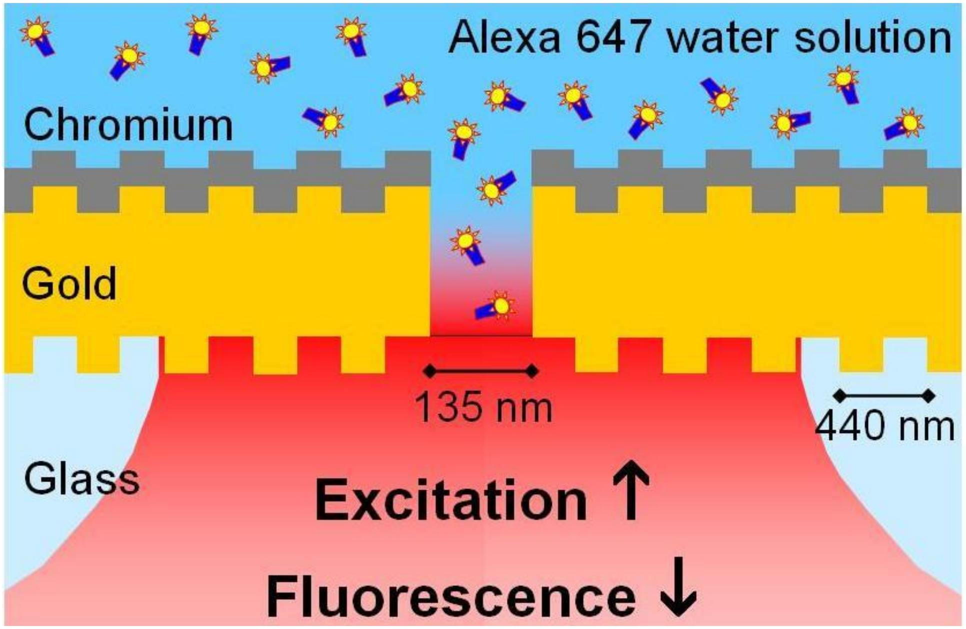
Excitation intensity: saturation $(I_e \gg I_s)$

$$CRM = \kappa \, \phi \, \sigma \, I_s = \kappa \, k_r$$

$$\eta_F = \frac{\kappa^*}{\kappa} \frac{k_r^*}{k_r}$$

Example: Corrugated aperture antenna

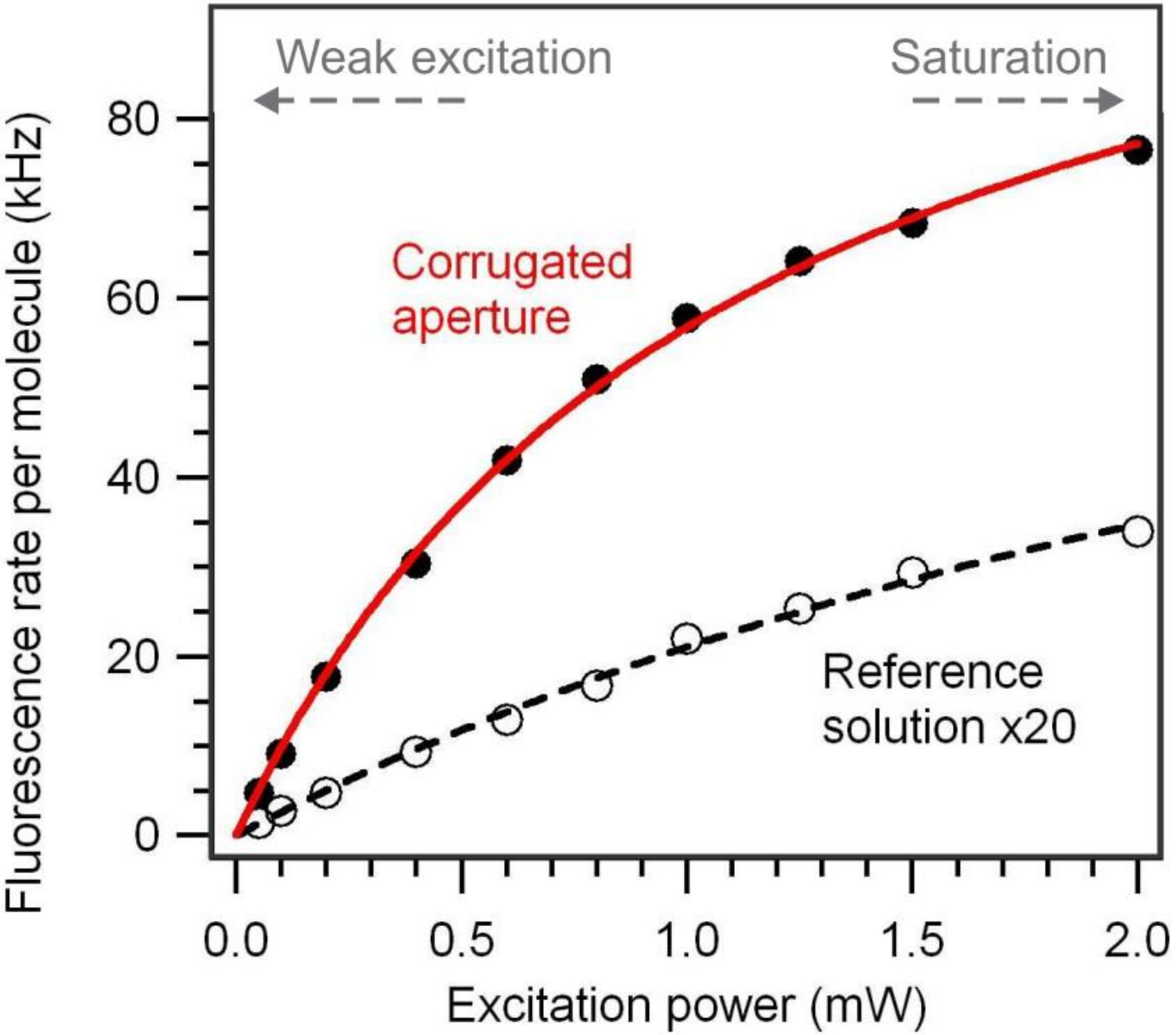




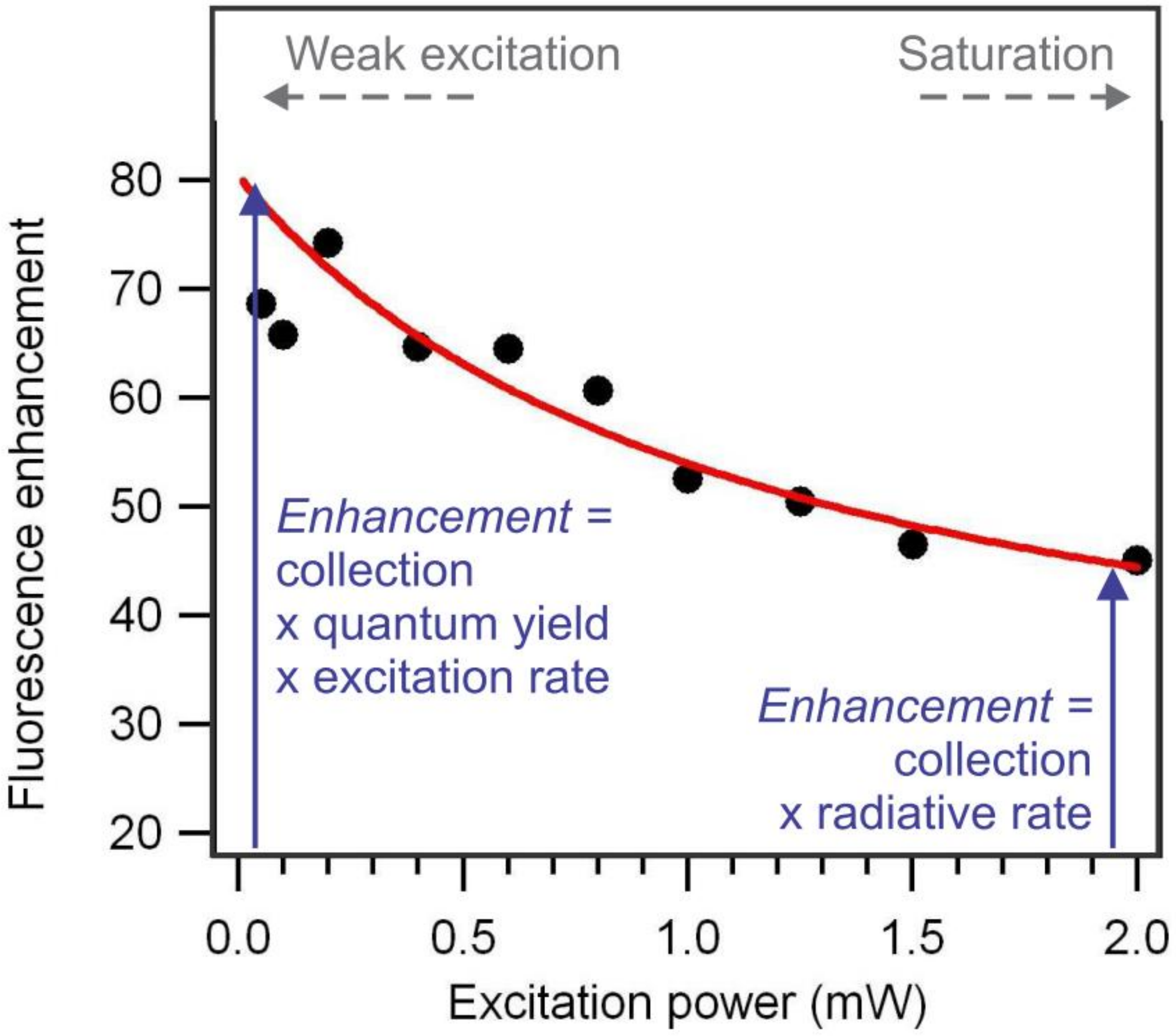
Aouani *et al*, Nano Lett. **11**, 637 (2011)

Excitation power dependence

$$CRM = \kappa\,\phi\,\frac{\sigma I_e}{1 + I_e/I_s}$$



A figure makes it easier…



Initial quantum yield

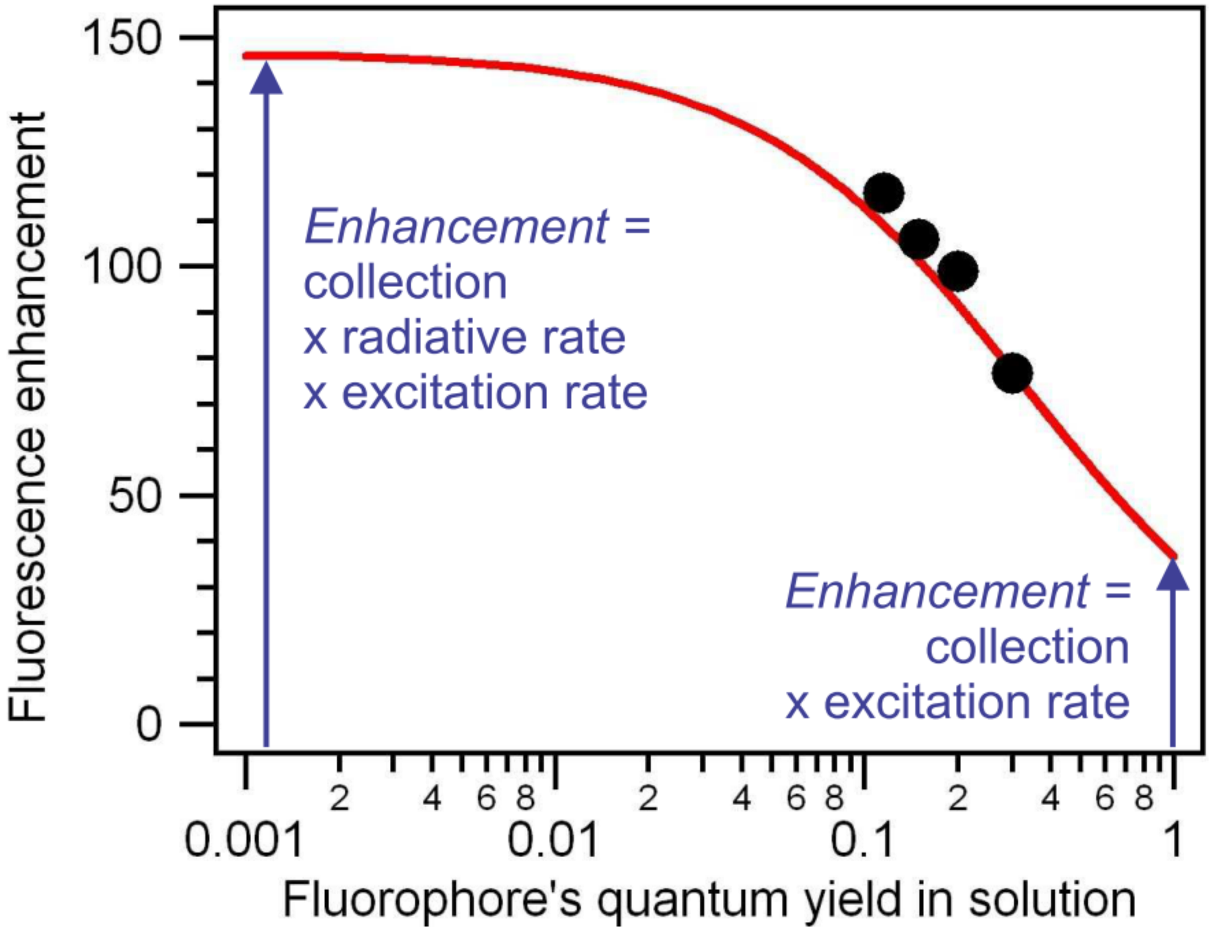
$$\eta_F = \frac{\kappa^*}{\kappa}\frac{k_r^*}{k_r}\frac{I_e^*}{I_e}\frac{1}{(1-\phi)+\phi\zeta} \qquad \text{with } \zeta = (k_r^* + k_{abs}^*)/k_r$$

'Poor' emitter limit: $$\eta_F = \frac{\kappa^*}{\kappa}\boxed{\frac{k_r^*}{k_r}}\frac{I_e^*}{I_e} \qquad (\phi \ll 1)$$

'Perfect' emitter limit: $$\eta_F = \frac{\kappa^*}{\kappa}\frac{I_e^*}{I_e} \qquad (\phi \simeq 1)$$

For efficient antennas, enhancement better with low QY emitters

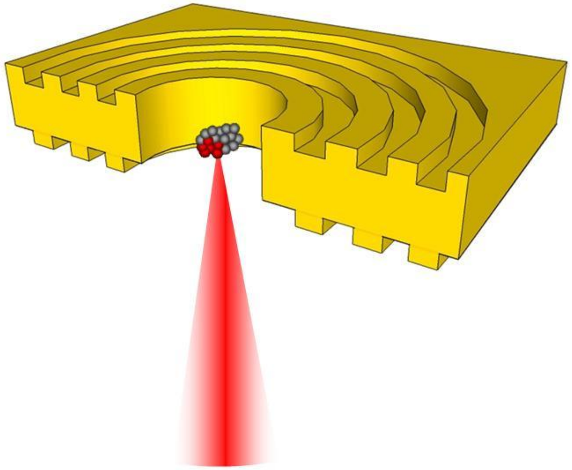
Initial quantum yield

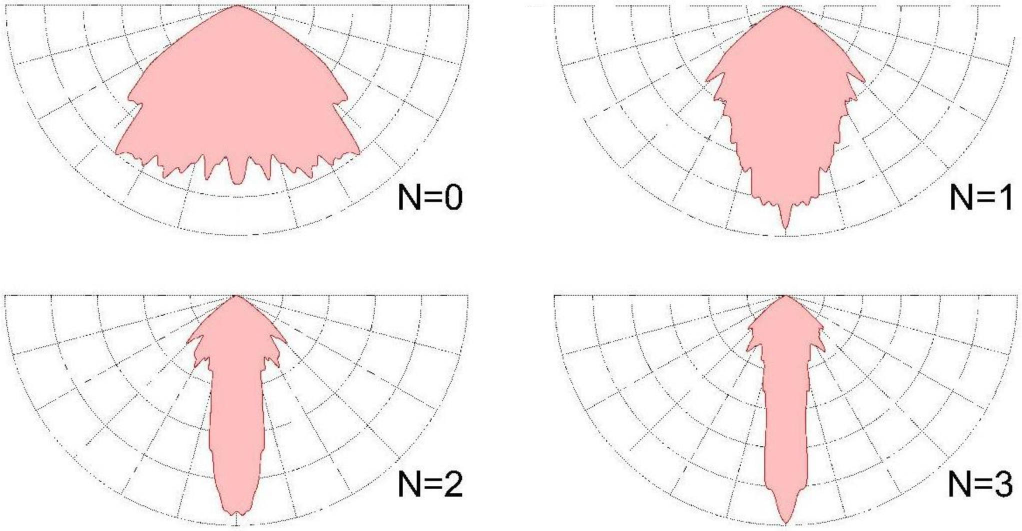


Collection numerical aperture / efficiency

Enhancement always proportional to collection efficiency

Boost enhancement: depends on antenna radiation pattern

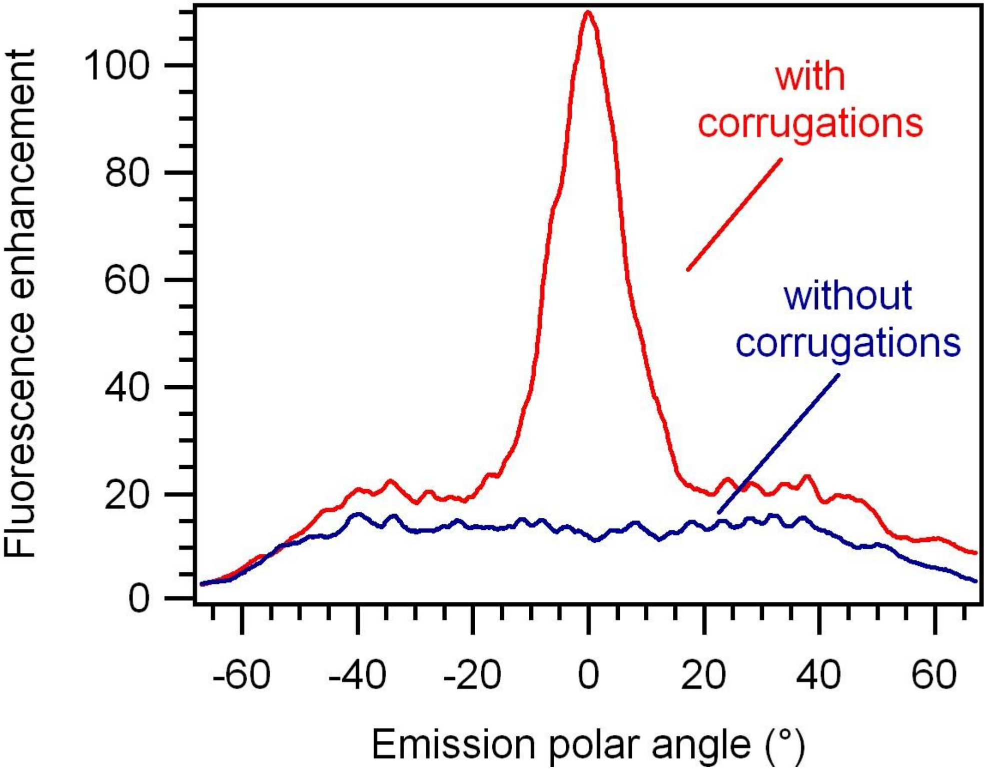




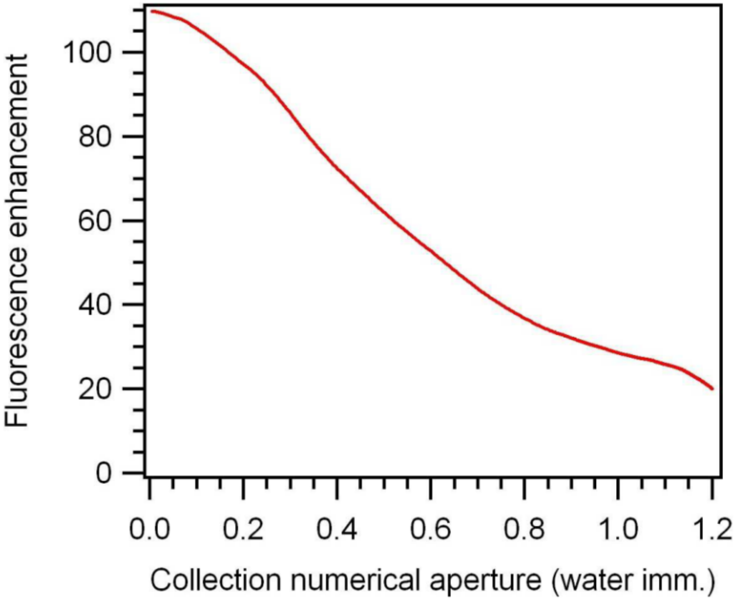
Aouani *et al*, Nano Lett **11**, 2400 (2011)

Collection numerical aperture / efficiency

As function of emission angle



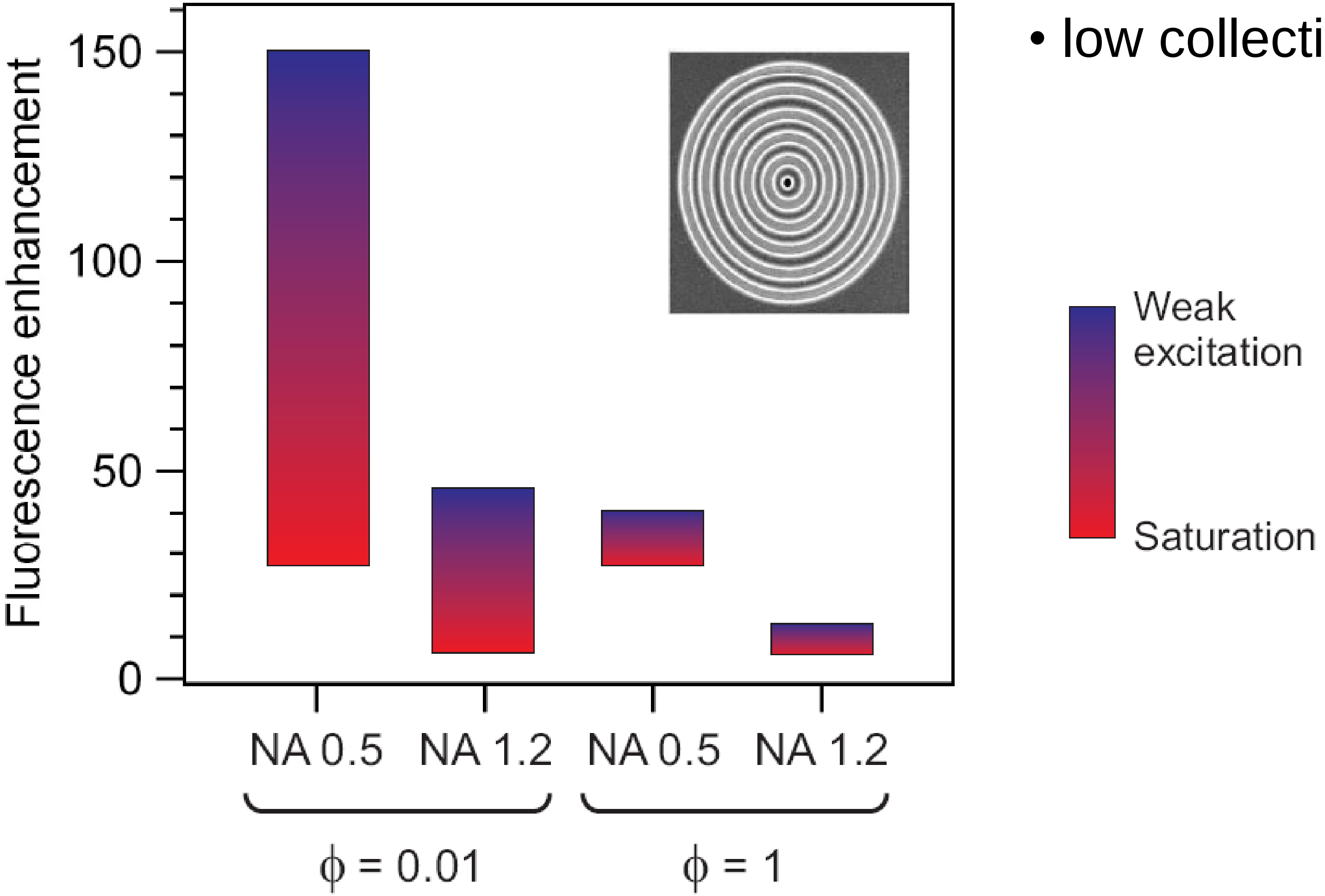
Integrated over collection NA



A recipe to enlarge the enhancement factor

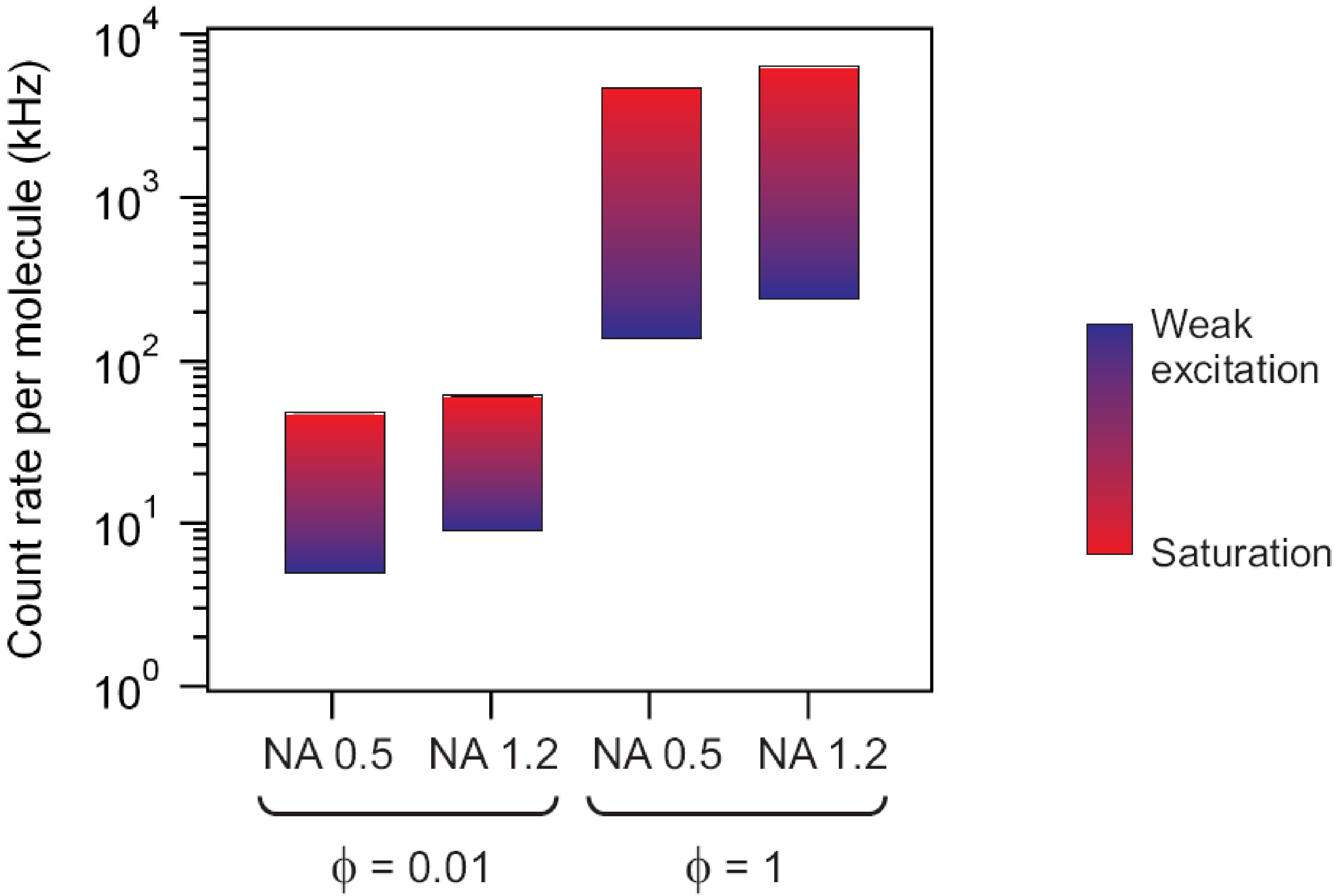
Maximize η_F ➔ take a low reference signal :

- weak excitation regime
- low quantum yield
- low collection NA

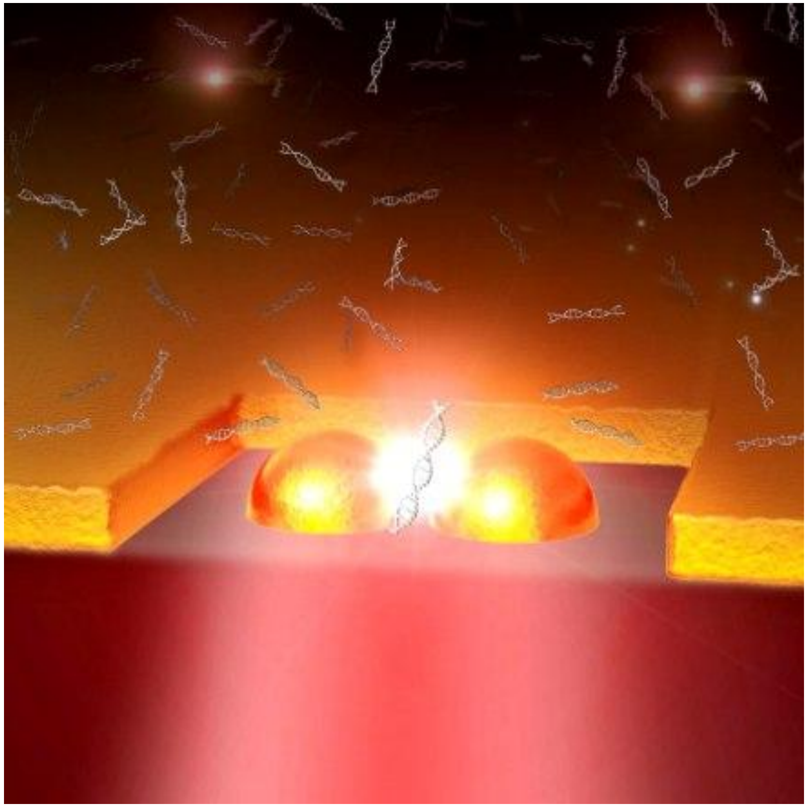


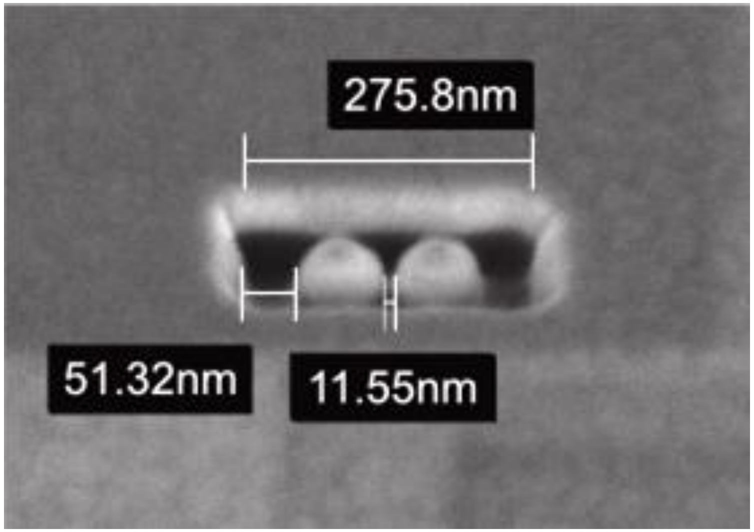
Does this recipe really make sense ?

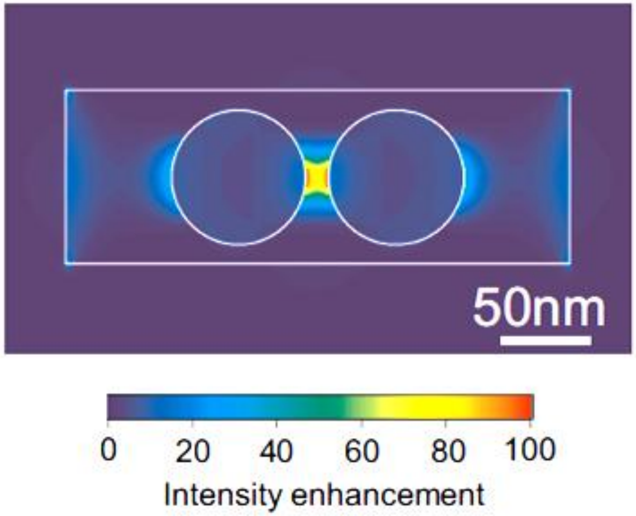
High enhancement factor does NOT mean bright source !



Antenna-in-box





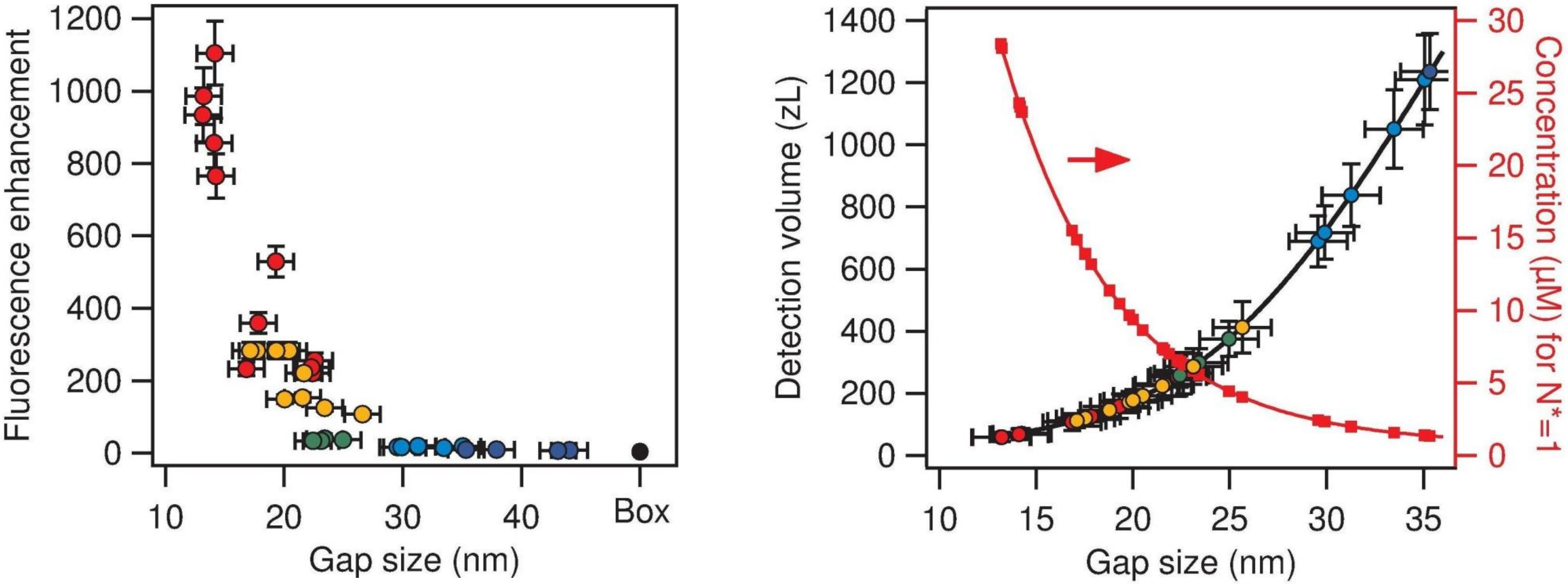


Gap-antenna → Fluo. enhancement

Aperture-box → Background screening

Punj et al, Nat. Nanotech. **8**, 512 (2013)

Gap size dependence

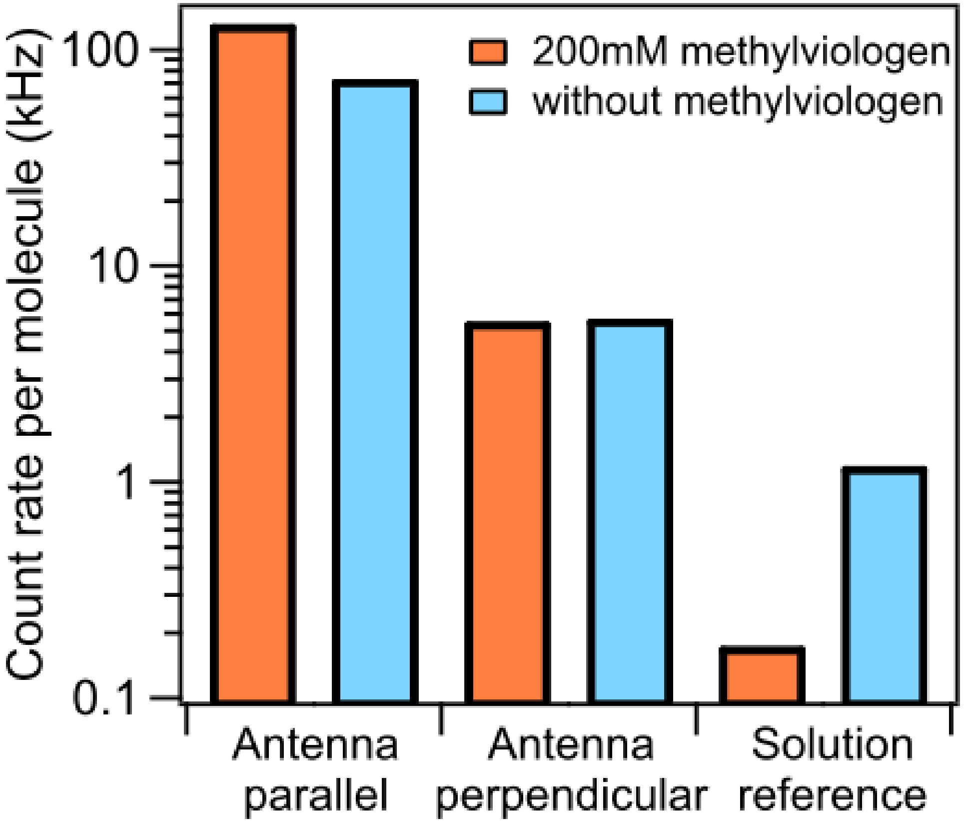


At best, gap 12nm:

- Fluorescence Enhancement → **1100x**
- Detection volume reduction → **8500x**

Punj et al, Nat. Nanotech. **8**, 512 (2013)

Low Quantum Yield… still high count rates



Conclusions

- The fluorescence enhancement factor is not an absolute figure of merit for a given antenna design.
- Comparison between enhancement factors / experiments must be made with caution.
- Lifetime reduction (‘Purcell factor’) must not be confused with fluorescence enhancement.
- High enhancement factors do not necessarily indicate bright photon sources.

J. Wenger, Int. J. Optics **2012**, 828121 (2012)