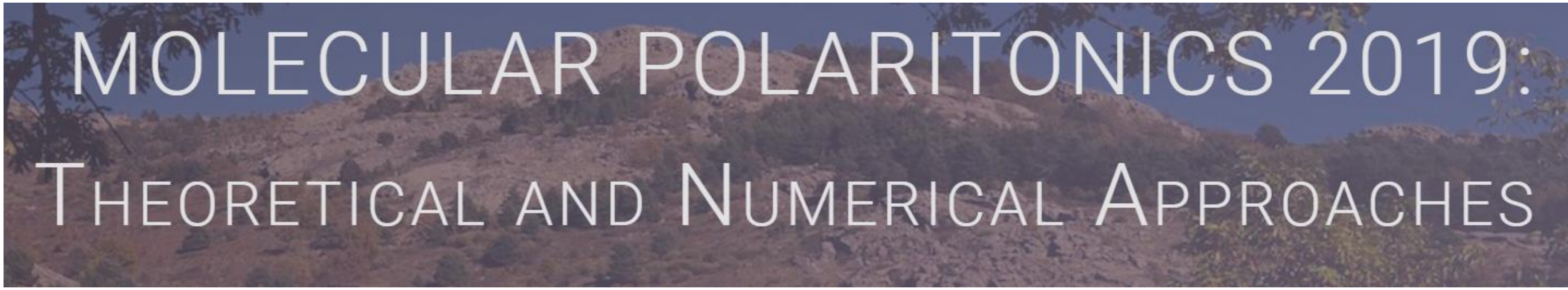


Suppression of photo-oxidation of organic dyes under strong plasmon-exciton coupling

Timur Shegai

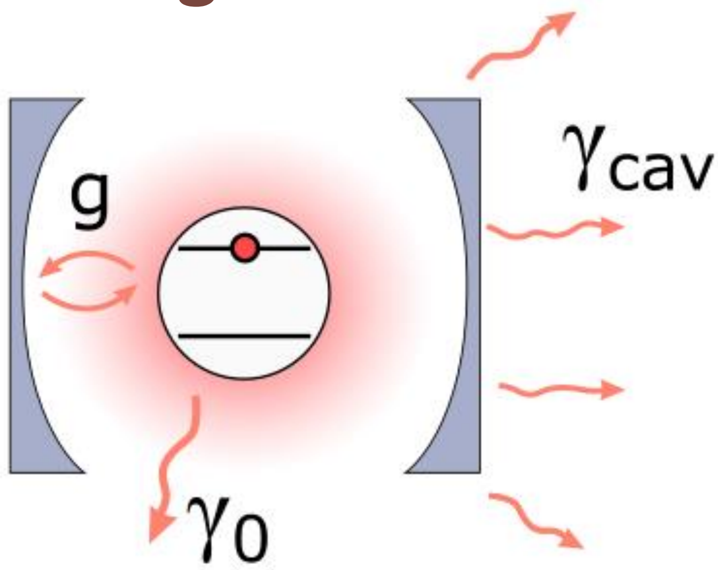
Chalmers University of Technology, Göteborg, SWEDEN

- Tel: (+46) 31 772 3123, e-mail: timurs@chalmers.se

More information is on our website and Google scholar:

- https://scholar.google.se/citations?user=btt8op4AAAAJ&hl=en
- http://www.chalmers.se/en/departments/physics/research/bionanophotonics/Pages/ShegaiGroup.aspx

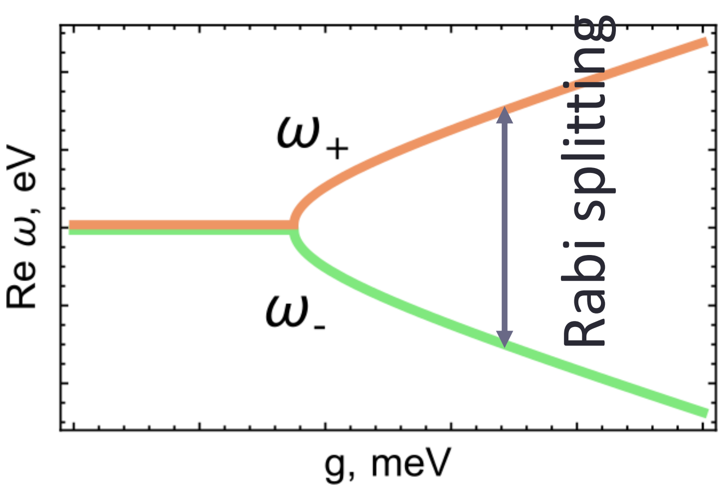
Light-matter interaction: Hamiltonian picture

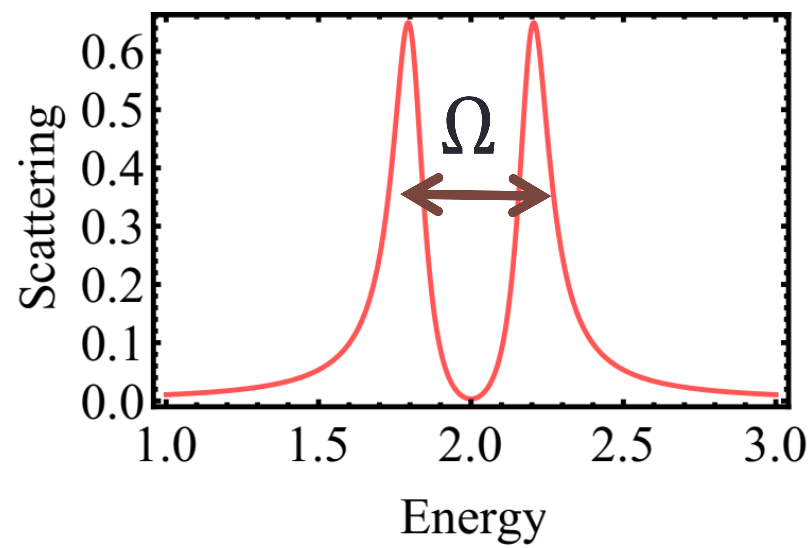


- Response of the driven system

$$\hat{\mathcal{H}} = \hbar \begin{pmatrix} \omega_{cav} - i\gamma_{cav}/2 & g \\ g & \omega_0 - i\gamma_0/2 \end{pmatrix},$$

$$\hbar g = \mathbf{E}_{vac}\mathbf{d}_{eg}$$



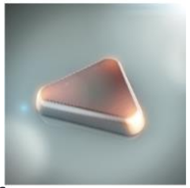


$$\Omega = 2\sqrt{g^2 - (\gamma_{cav} - \gamma_0)^2/16}$$

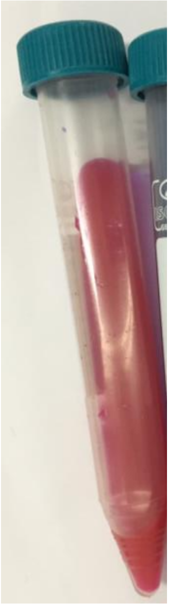
Ingredients = plasmons + molecules or 2D semiconductors

$$g \sim \sqrt{N} \mu_e / \sqrt{V}$$

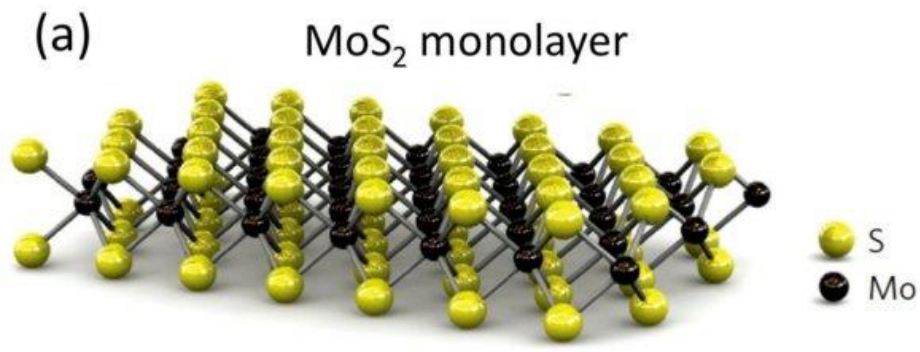
Plasmonics



Ultracompact effective mode volume

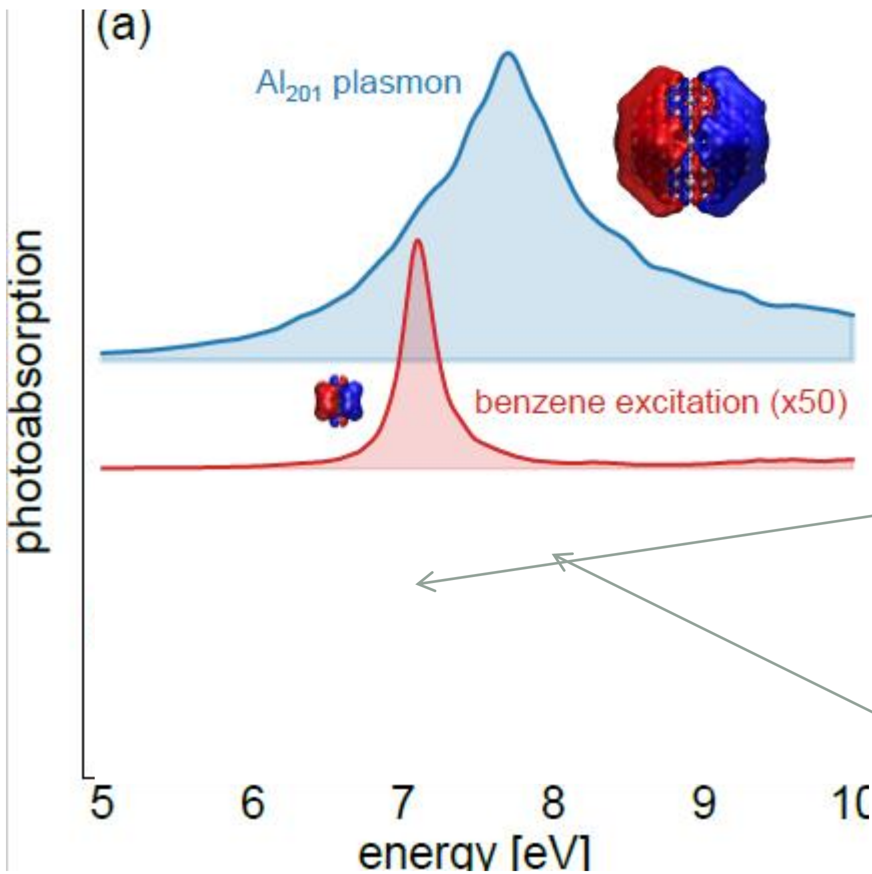


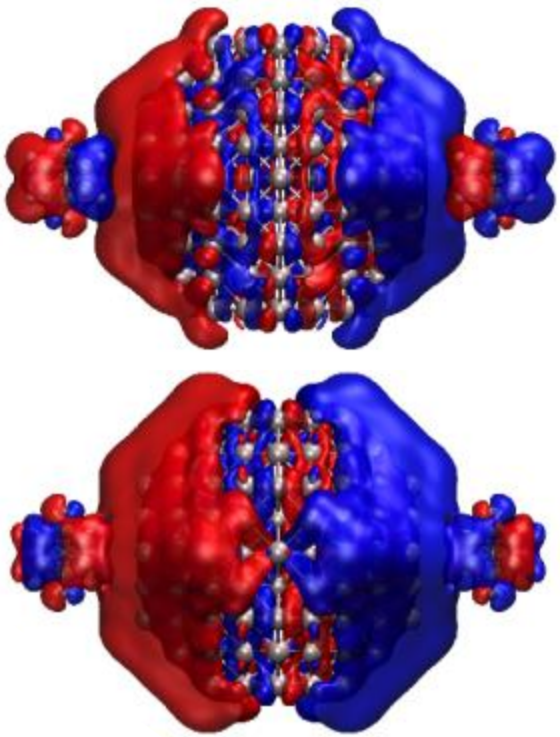
Dye Molecules



Intense absorption bands and exciton transitions

Polaritons from first principles using TDDFT:

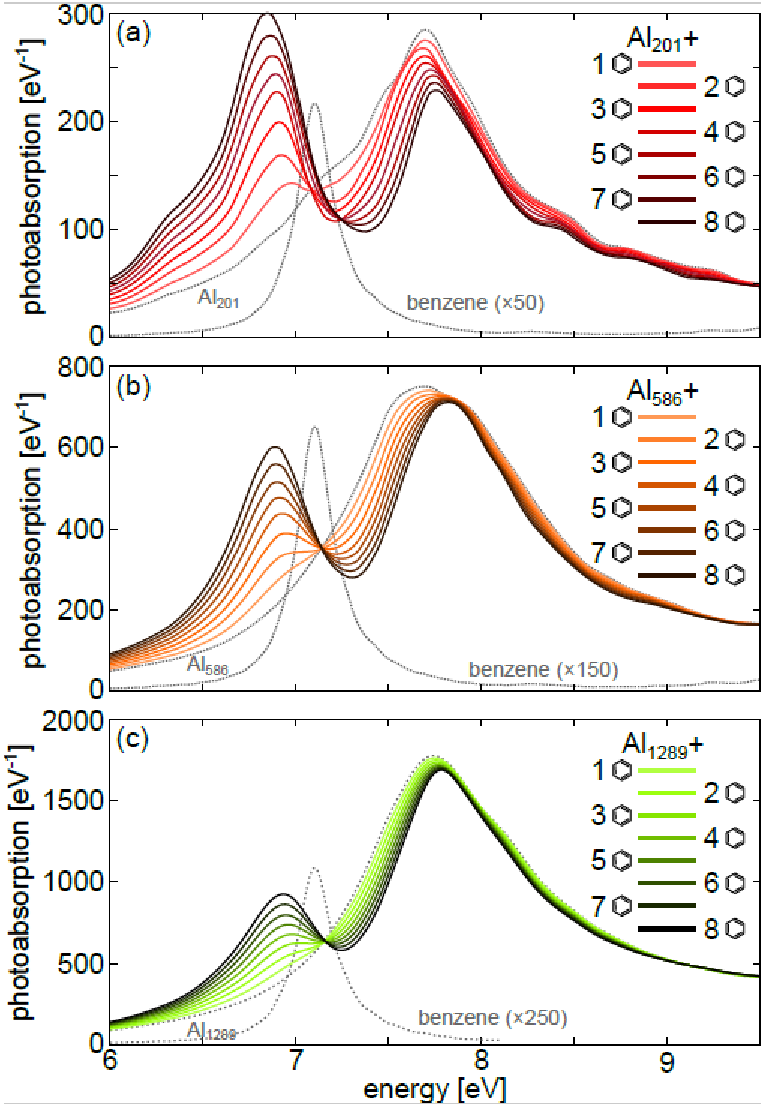




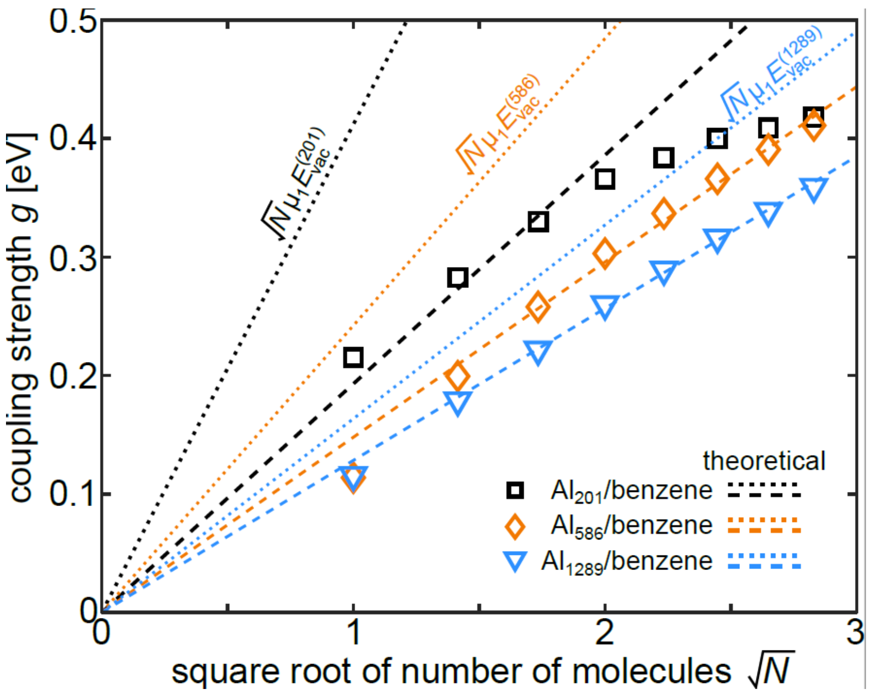
- Usial TDDFT approximations (polariton orbitals)
- Provides much more details about the system.
- Can give insights to ”chemistry modification” in strong coupling regime

Rossi et al, arXiv:1904.02097
To appear in Nature Comm.

Strong coupling in TDDFT:



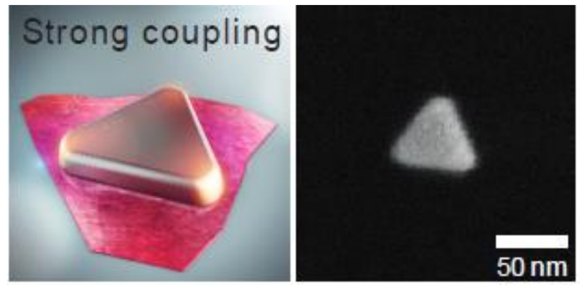
$$g \propto \sqrt{N}$$



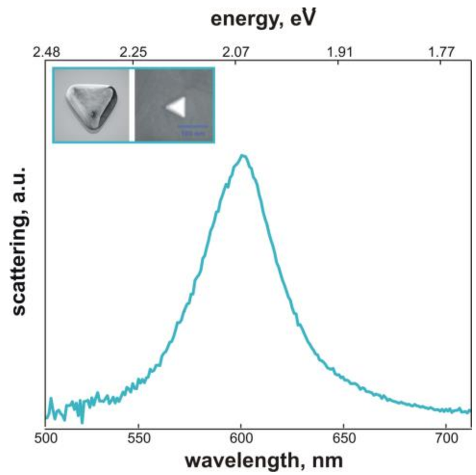
Rossi et al, arXiv:1904.02097

Summary of activities on molecule-plasmon interactions:

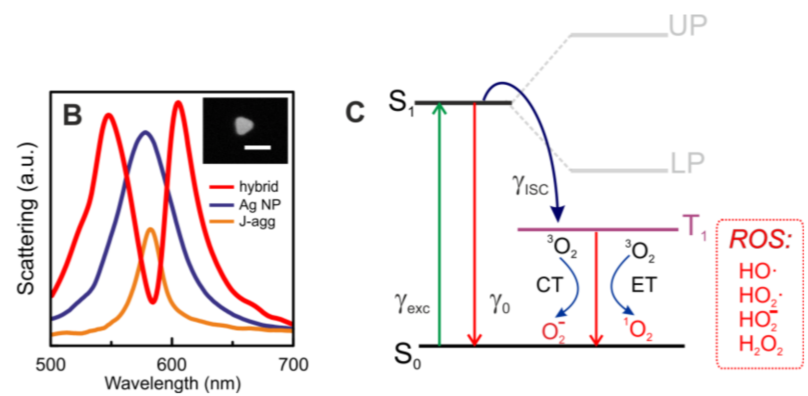
Room T strong coupling with J-aggregates:
Zengin et al., PRL, 2015



Very strong coupling up to 500 meV:
Wersäll et al., Nano Lett. (2017), *18*, 1777–1785

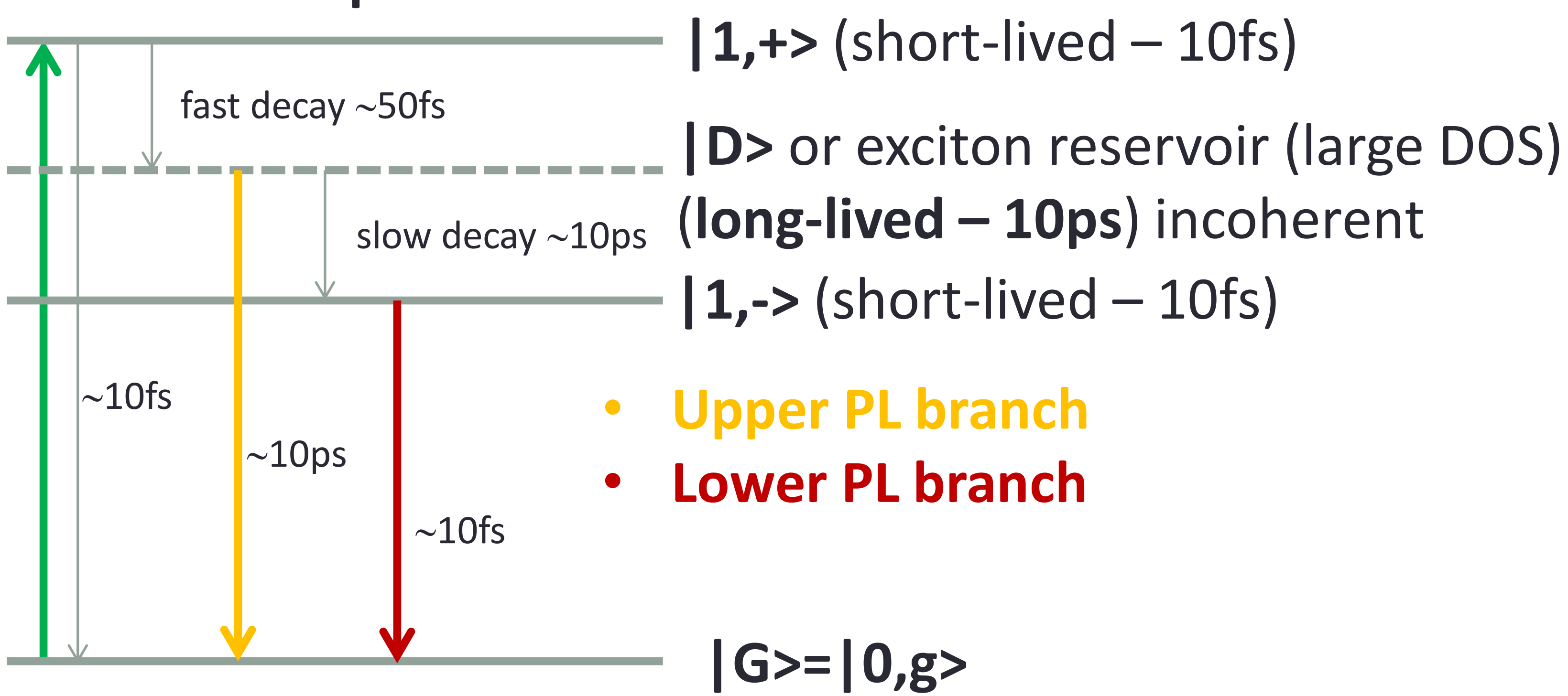


100× slow down of photo-oxidation:
Munkhbat et al., Science Adv. (2018)



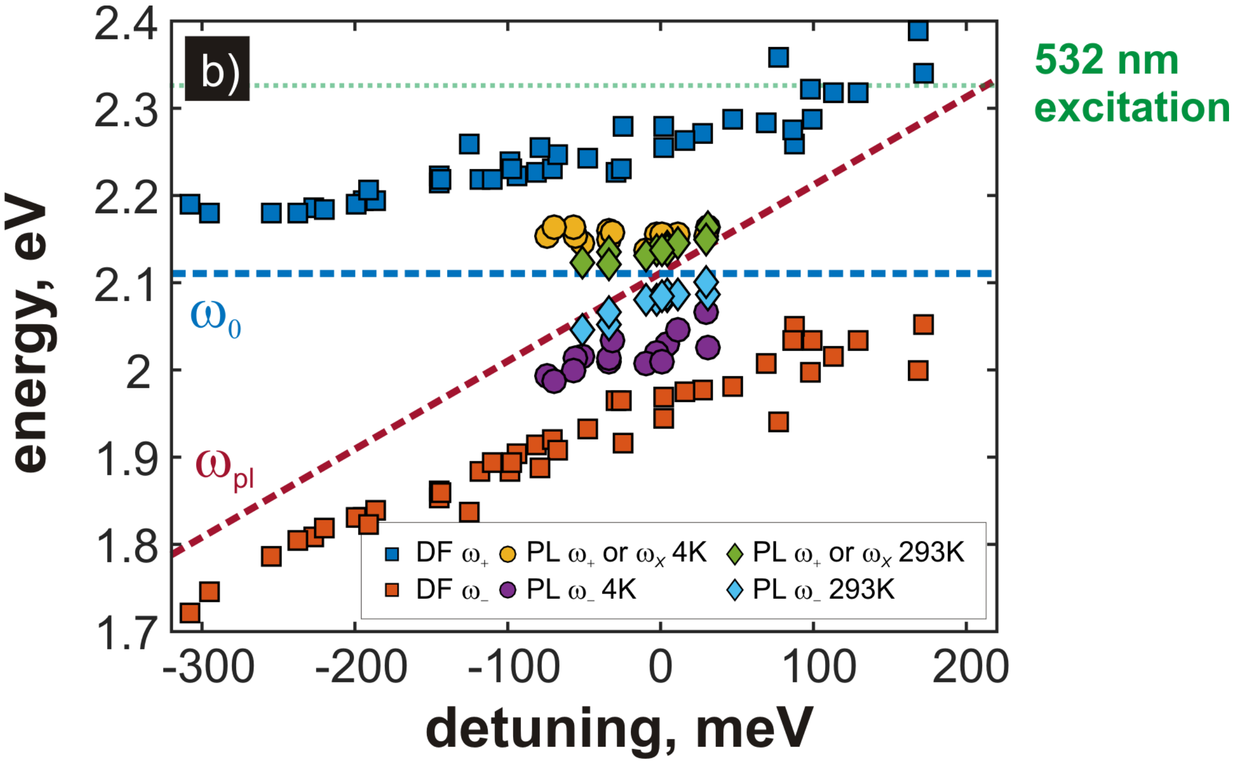
Polariton emission requires a change in the excited state dynamics:

- **Long-lived intermediate states are necessary!**
- **Lifetime is tens of ps.**



Theory: • Agranovich *et al*, **PRB**, (2003), 67, 085311
• Litinskaya *et al*, **J. Lumin.** (2004), 110, 364–372
• La Rocca *et al*, Feist *et al*, Herrera *et al*.

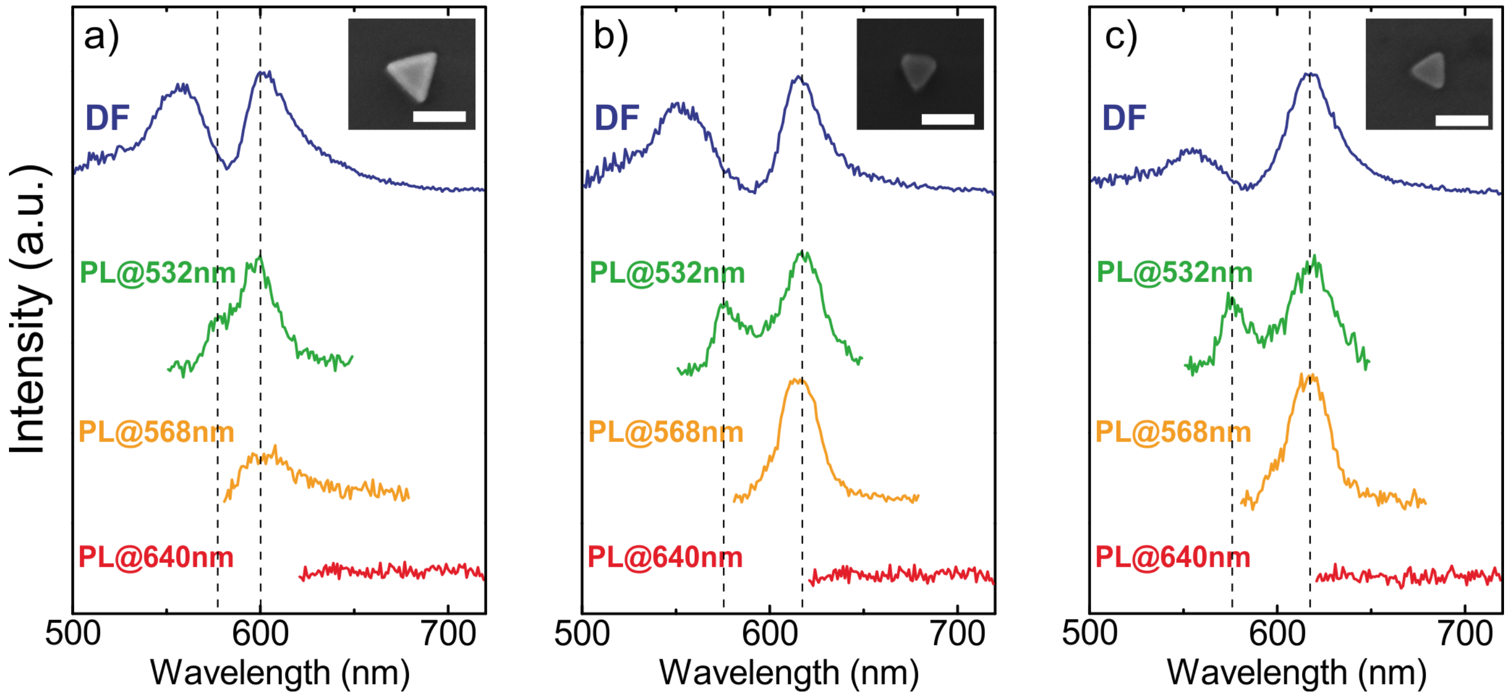
Anti-crossing in scattering vs PL:



- **Photoluminescence requires detailed understanding of the excited state dynamics, which in these disordered systems is complex!**

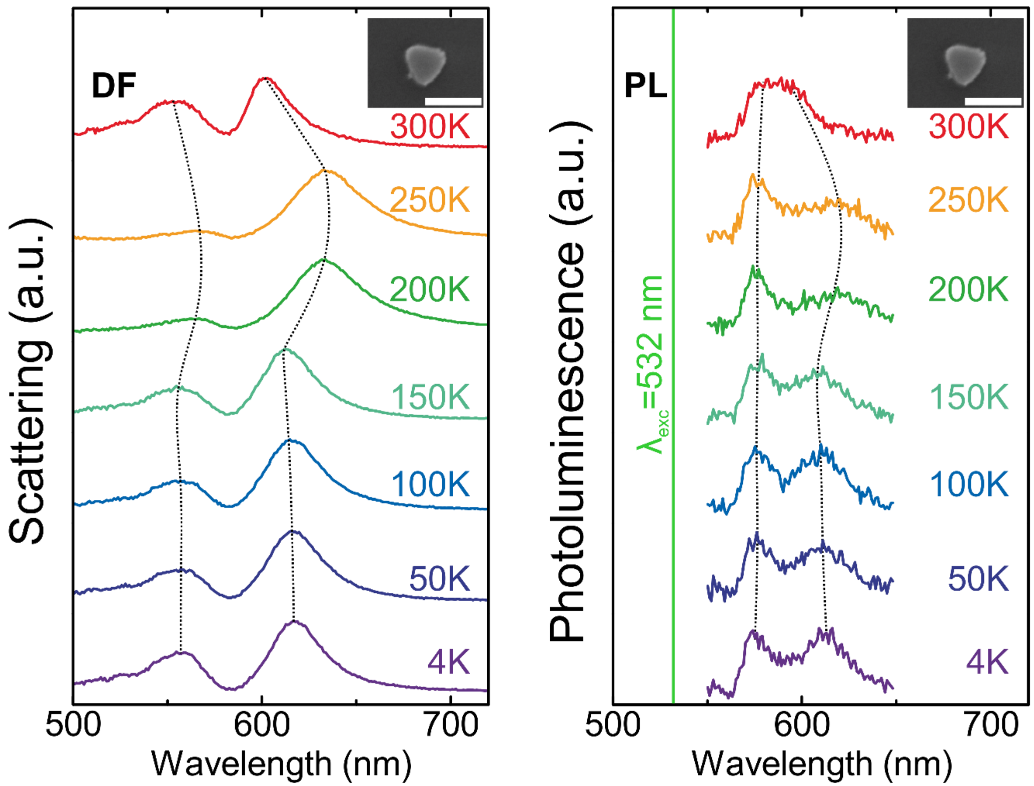
Wersäll *et al.*, Nano Lett., **2017**, 17, 551-558

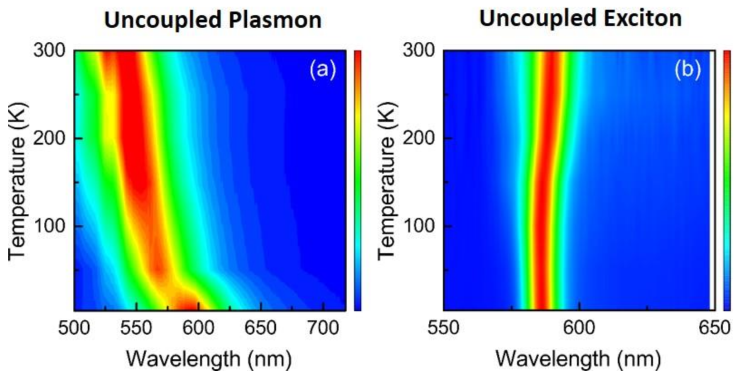
(I) Excitation Wavelength dependence:



- Individual nanoprisms investigated in both DF scattering and PL inside cryostat T=77K here
- PL shows two peaks, one peak, or nothing depending on excitation wavelength
- Lower energy peak coincides with LP independently of excitation
- Upper energy peak is below UP

(II) Temperature dependence:

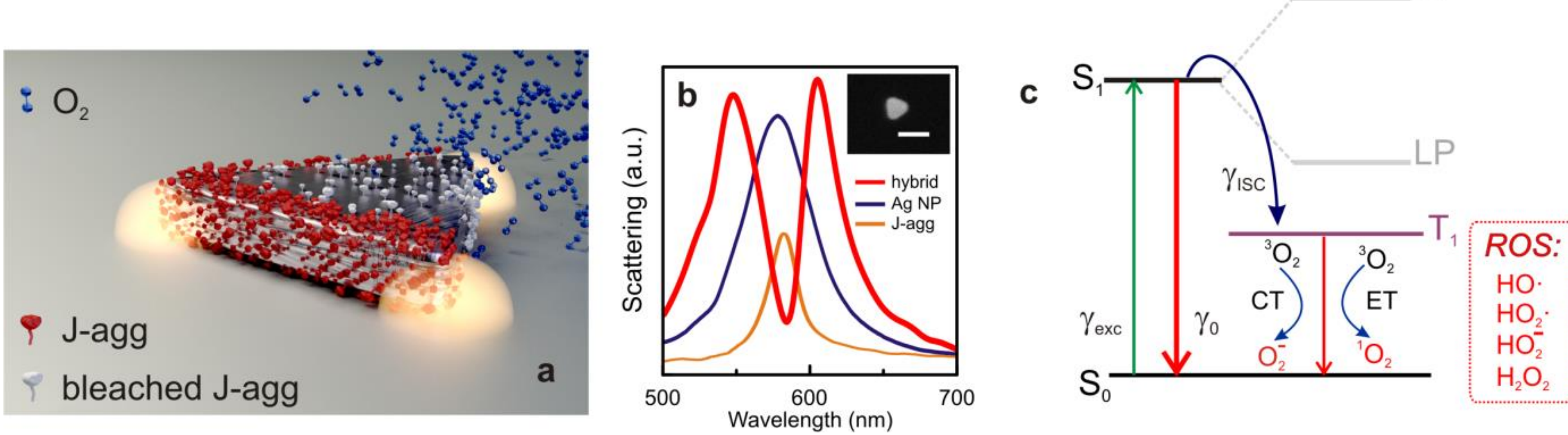




- **Higher energy peak is due to exciton reservoir**
- **Lower energy peak follows LP exactly**
- **Peculiar behavior around Debye temperature for Ag (requires further understanding)**

Wersäll *et al.*, in preparation with F. Herrera

- **J-aggregates are unstable...**
- **But in strong coupling regime, we see 100-fold supression of photo-oxidation rate. ”Collective protection”.**



Coupled systems: splitting ~200-300meV

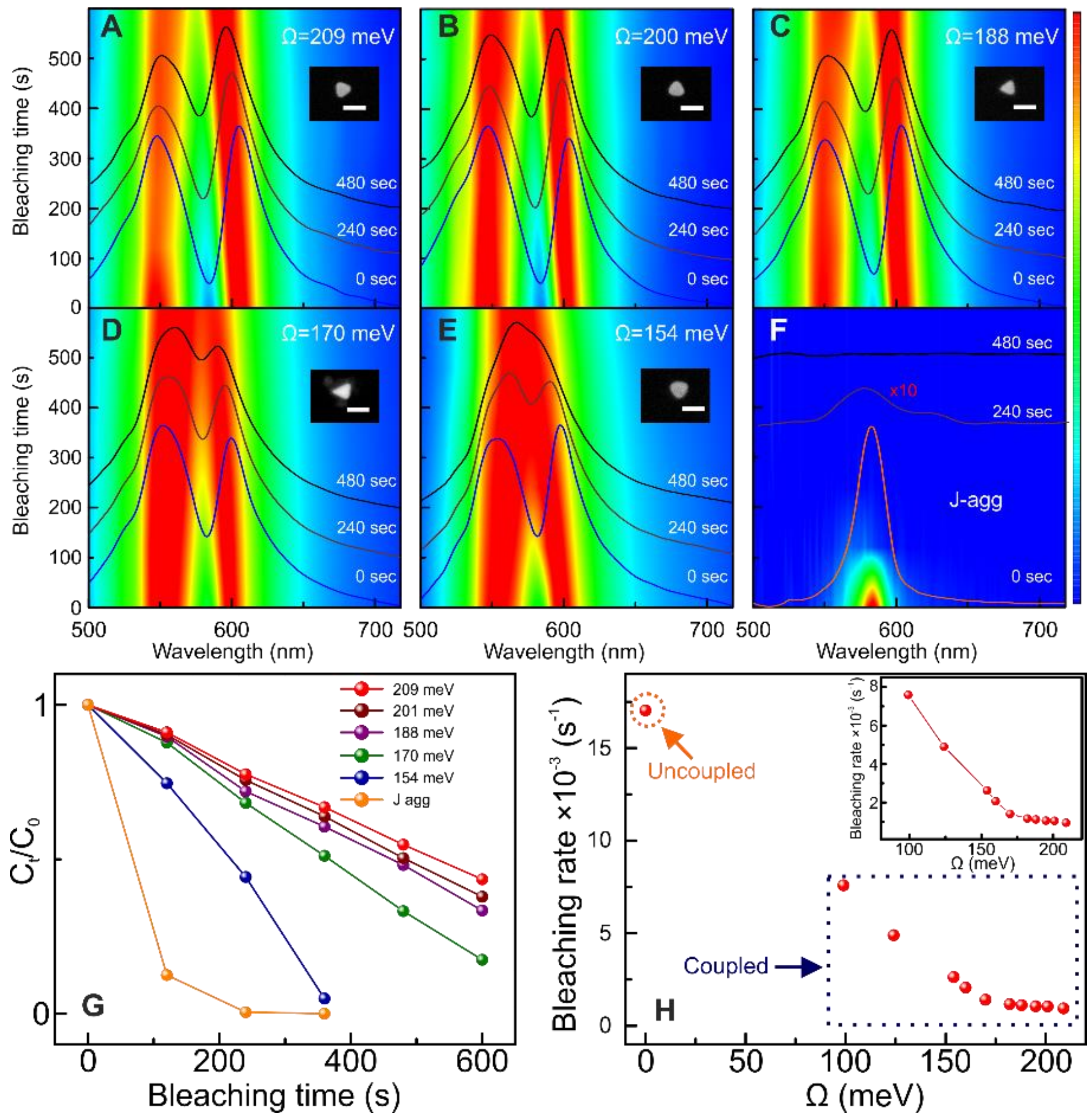
Related theory:

1) Galego et al. Nature Comm, (2016), 7, 13841
2) Herrera et al., PRL, (2016), 116, 238301
3) Matrtinez et al., ACS Photonics, (2018), 5, 167-176

Munkhbat *et al.*, Science Adv. 2018, 4, eaas9552

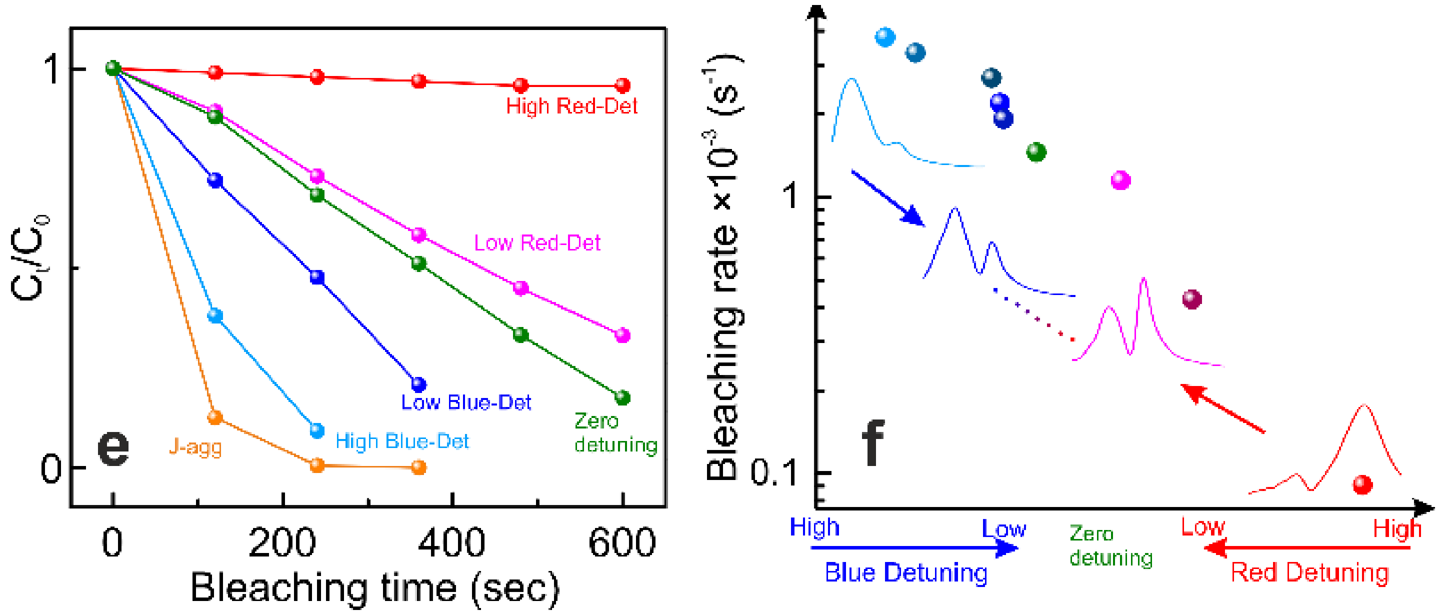
Role of Rabi splitting: much slower bleaching for larger Rabi!

- All experimental conditions are exactly same
- Particles are about the same size
- Bleaching rates are extracted from the kinetics
- Broadband excitation (400-700nm)



Munkhbat *et al.*, Science Adv. 2018, 4, eaas9552

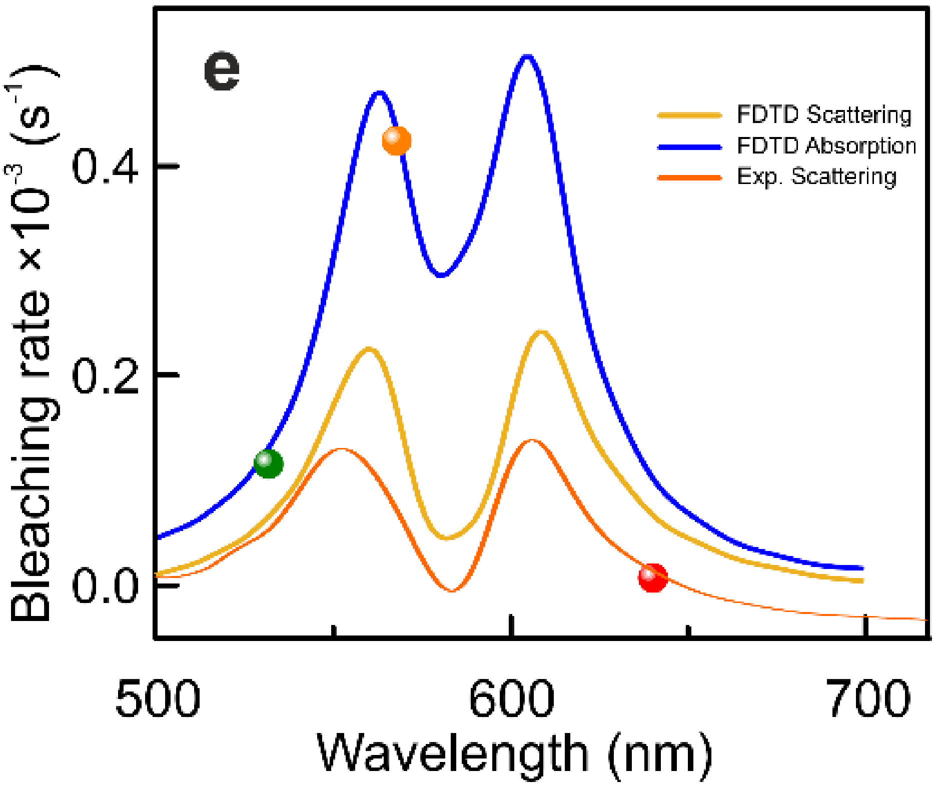
Role of plasmon-exciton detuning: Detuning is extremely important!



- Red-detuned hybrids are **much (100-fold) more stable** than blue-detuned ones!
- This implies δ-dependent internal dynamics.
- Broadband excitation (400-700nm)

Munkhbat *et al.*, Science Adv. 2018, 4, eaas9552

Dependence on excitation wavelength:



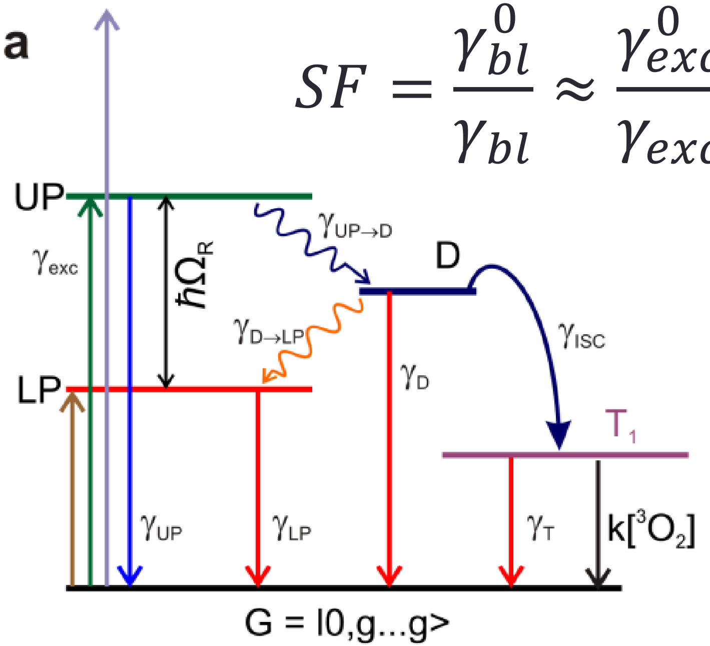
- Resonant UP excitation is the most harmful!
- Absorption at exciton resonance is not negligible

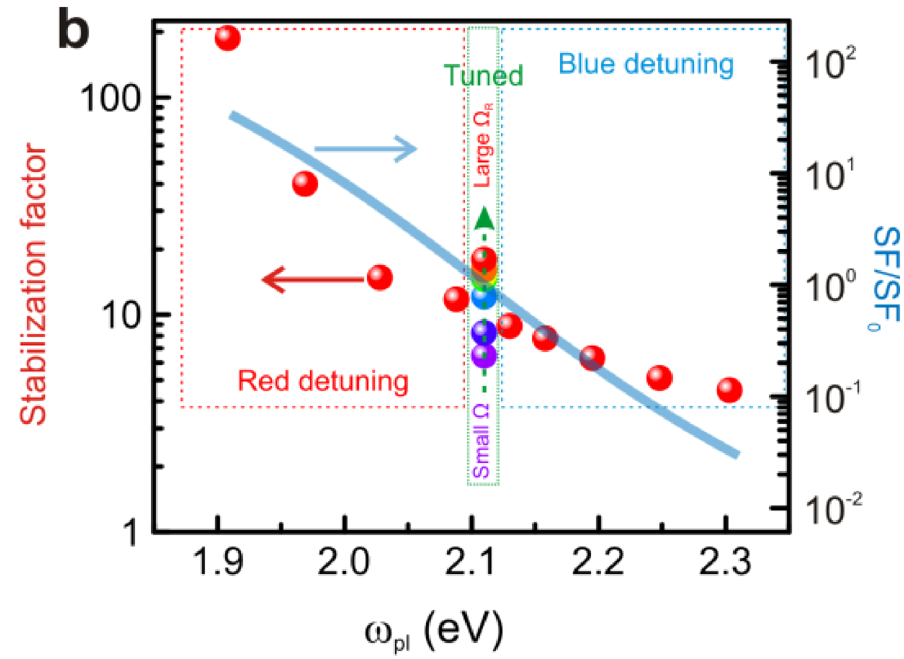
Munkhbat *et al.*, Science Adv. 2018, 4, eaas9552

Stabilization factor:

>100-fold stabilization!

$$SF = \frac{\gamma_{bl}^{0}}{\gamma_{bl}} \approx \frac{\gamma_{exc}^{0}}{\gamma_{exc}} \frac{\phi_{bl}^{0}}{\phi_{bl}}$$



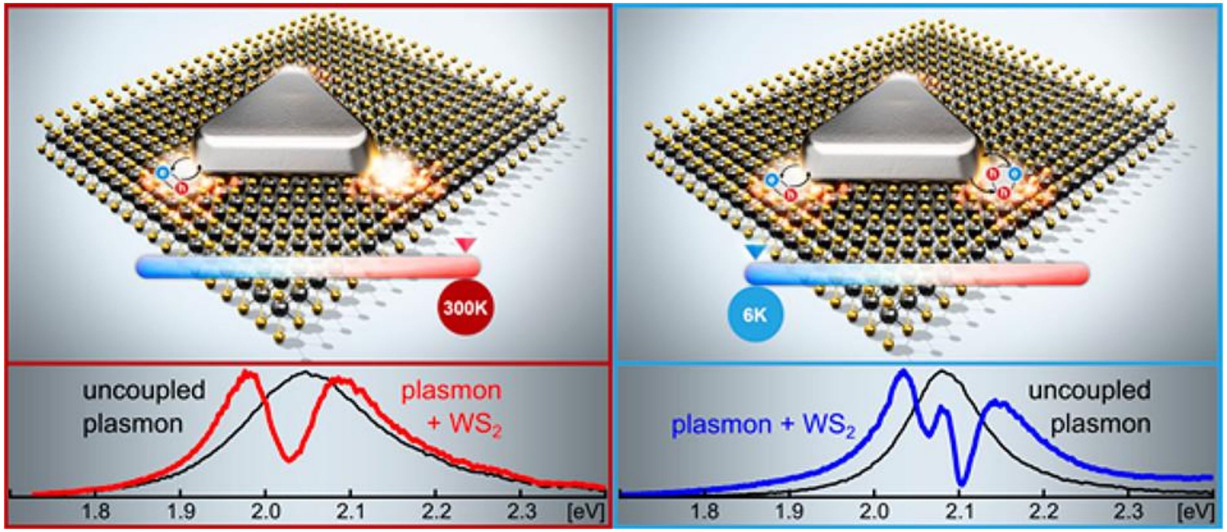


- Photobleaching QY drops down very significantly (due to collective protection and short polariton lifetime)
- Dynamics can be derived assuming a set of rate equations

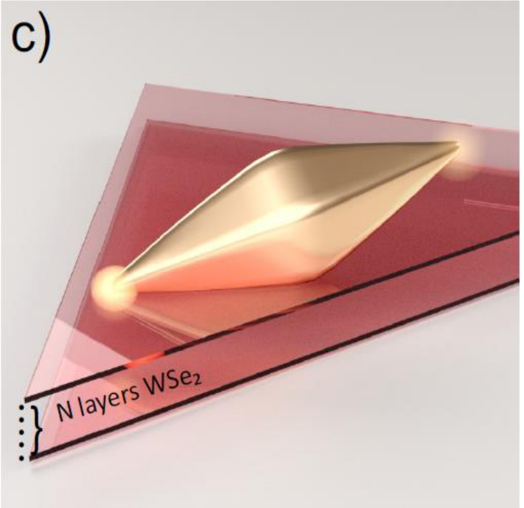
Munkhbat *et al.*, Science Adv. 2018, 4, eaas9552

Summary of activities on TMDC-plasmon interactions:

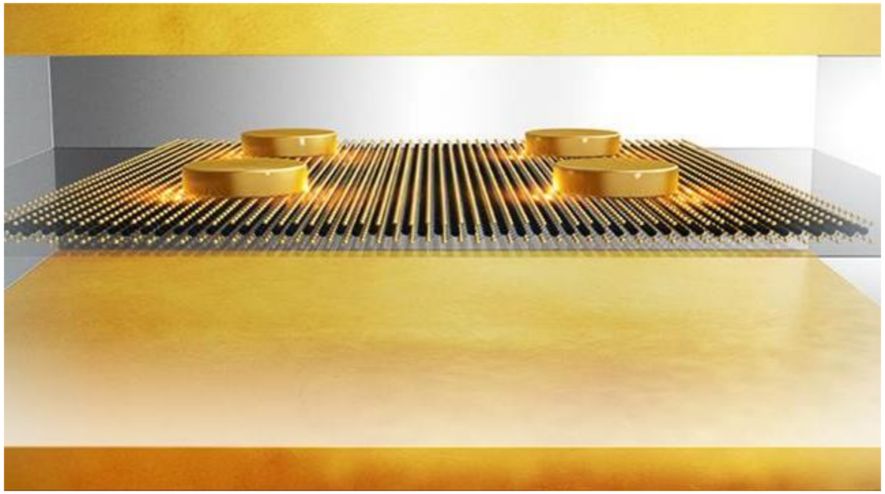
Trions: Nano Lett. (2018), **18**, 1777–1785



Confinement: *Nano Lett.*, **18**, 5938–5945, (2018)

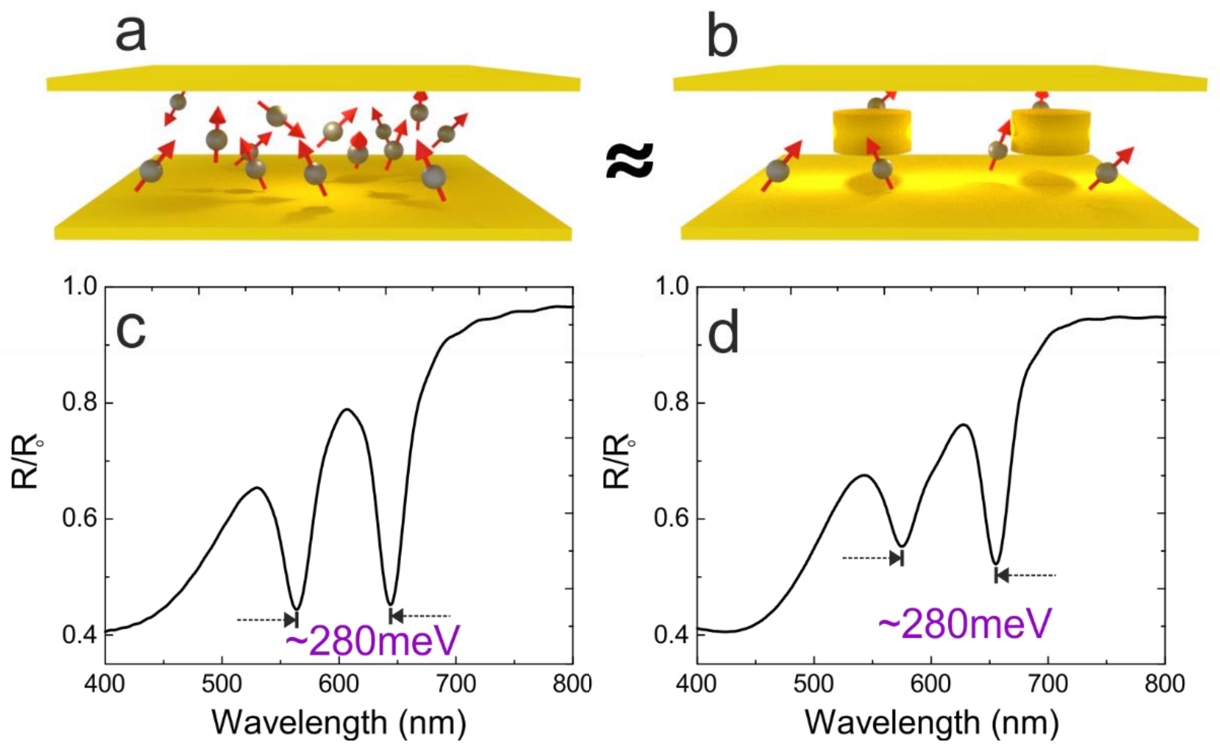


Hierarchical microcavitites:
Nano Lett. **19**, 189-196, (2019).



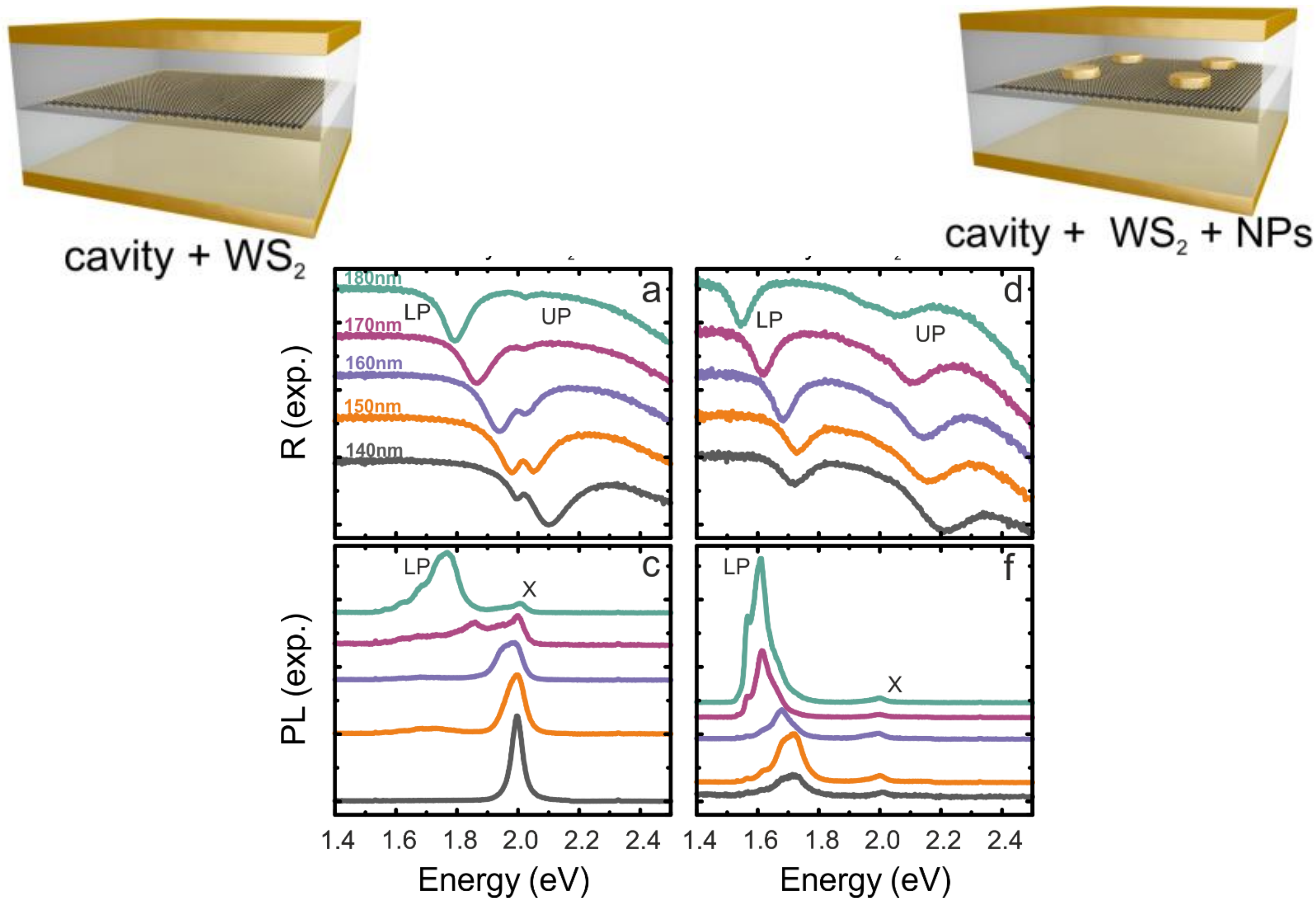
Hierarchical microcavitites:

Collective effect



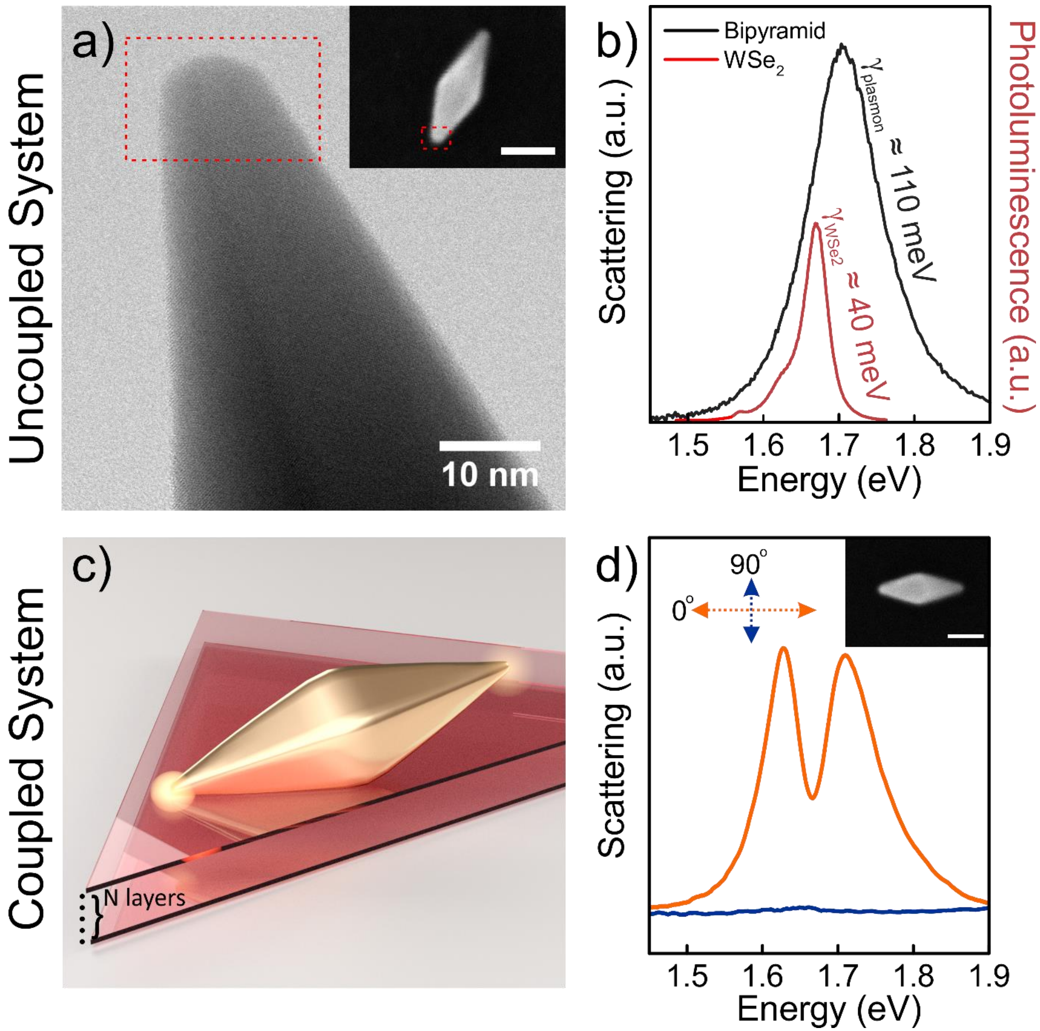
- Similar to intermixed Frenkel – Wanier-Mott polaritons **(Agranovich)**
- **Bisht et al., Nano Lett., 19, 189-196, (2019)**

Plasmon-exciton-microcavity mixtures:



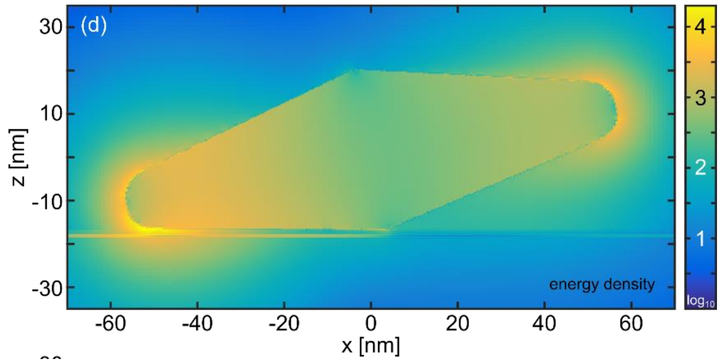
- **Bisht et al.** *Nano Lett.*, **2019**, 189–196

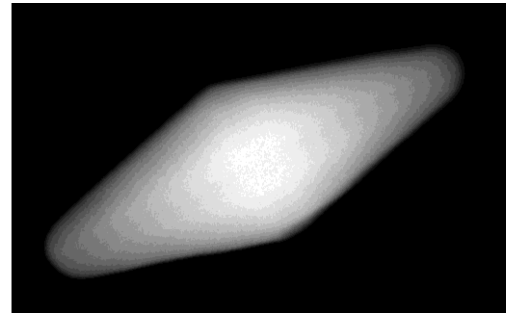
Multilayers of WSe_2 coupled to individual bipyramides:

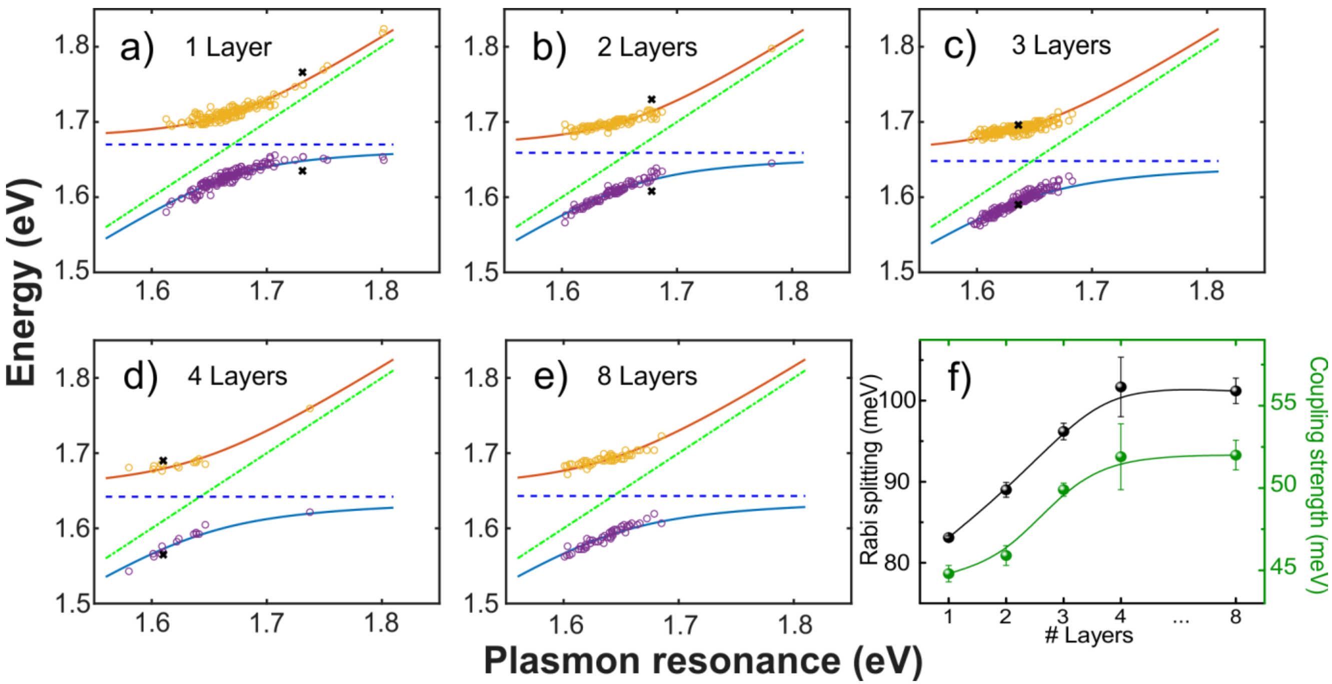


Stührenberg et al., Nano Lett. (2018), 5938–5945

- Coupling to in a very localized region
- Extremely reproducible (hundreds of individual nanoparticles)!

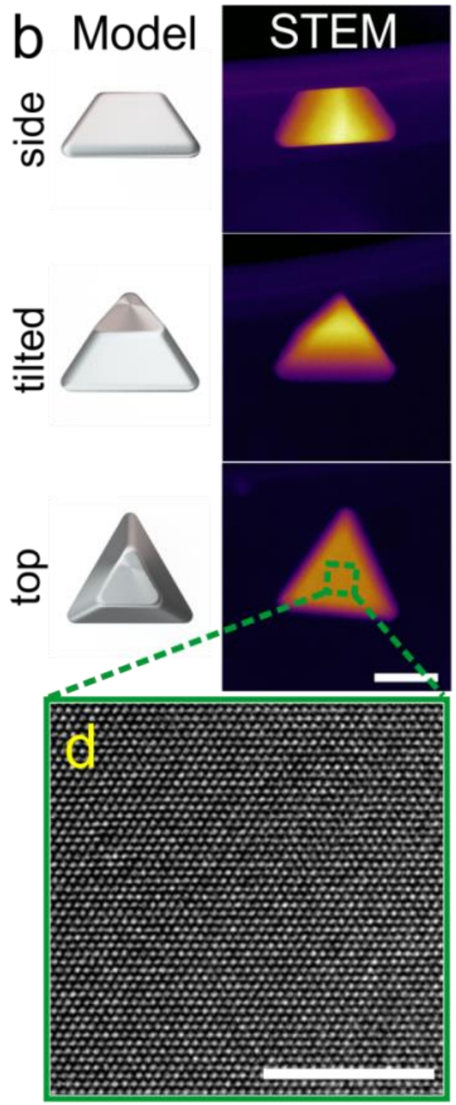


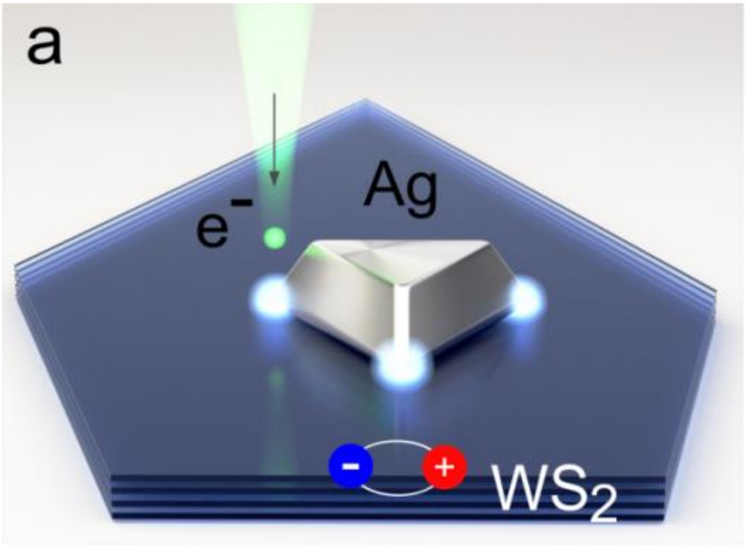




Stührenberg et al., Nano Lett. (2018), *18*, 5938–5945

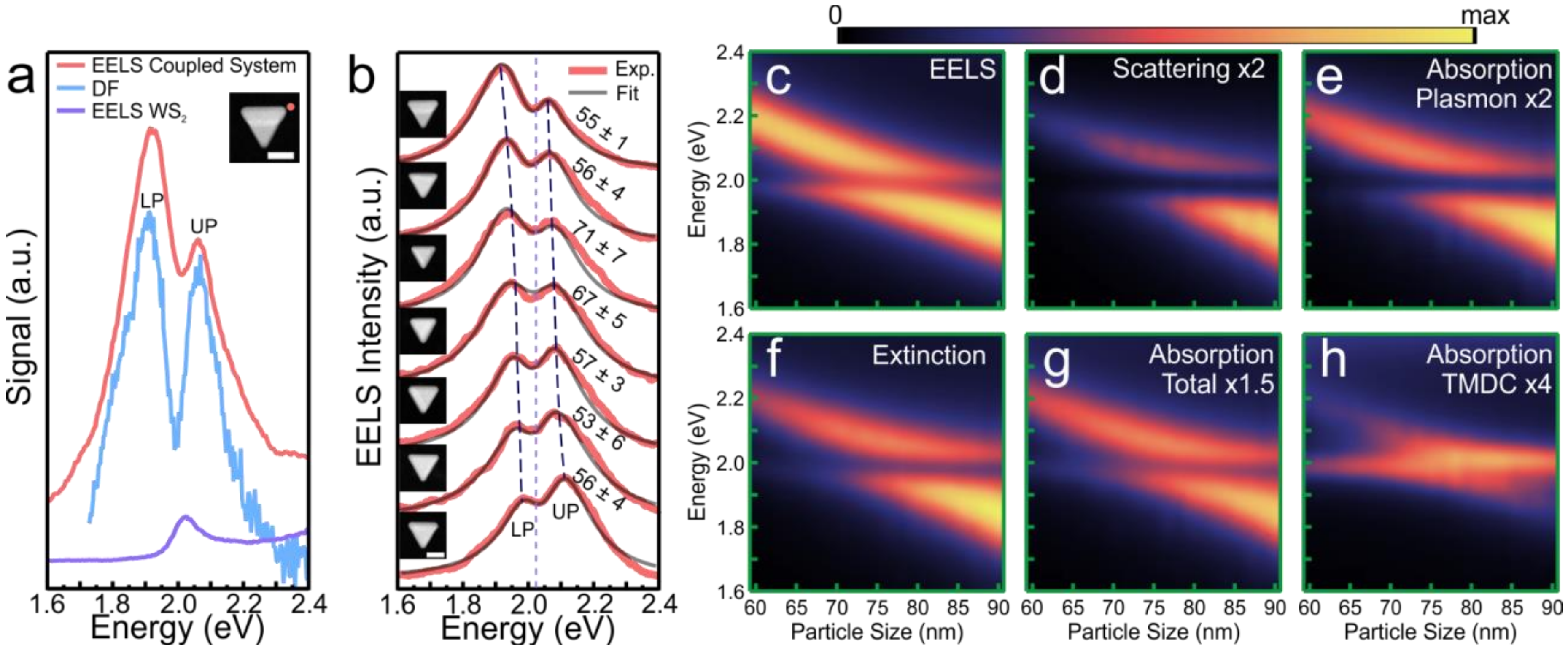
Is it possible to visualize polaritons on nanoscale?
Electron energy loss spectroscopy (EELS)





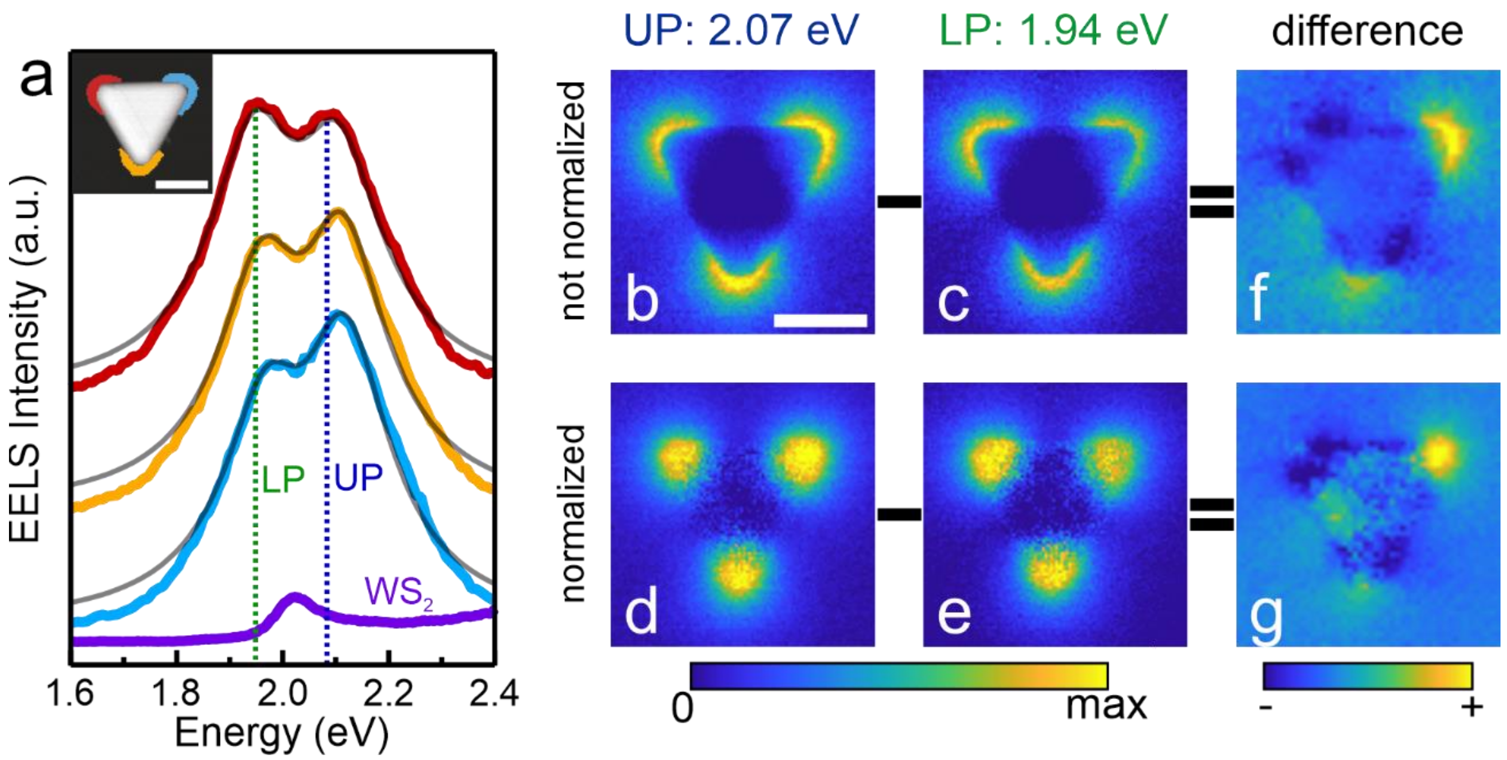
Yankovich et al, arXiv:1905.04067

Observation of anti-crossing in EELS signal:



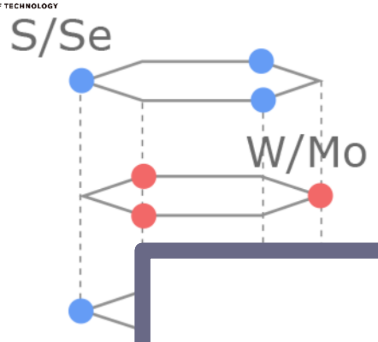
Yankovich et al, arXiv:1905.04067

Observation of plexcitons in EELS with nanometer resolution:

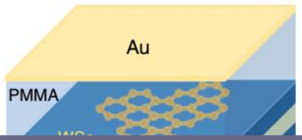


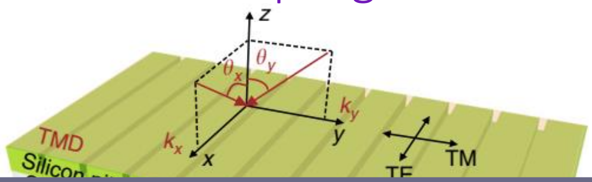
Yankovich et al, arXiv:1905.04067

Monolayer vs multilayer TMDC



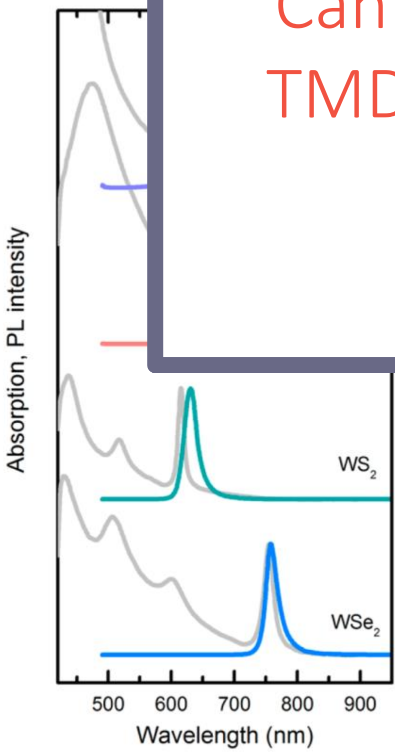
- Coupling with **monolayer** TMDCs



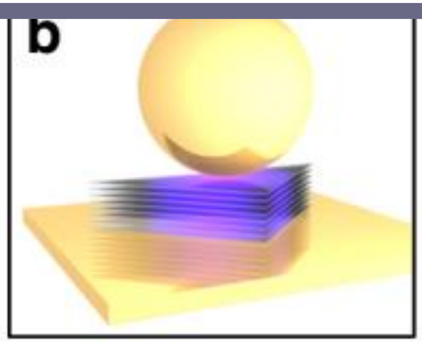


; Shegai

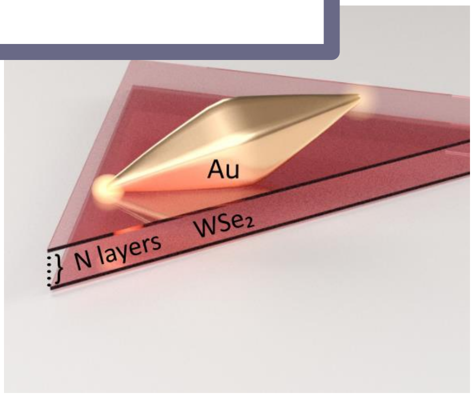
Can we go further and couple a multilayer TMDC flake *to itself* without any additional cavity?



Eda & Maier, ACS Nano 2017

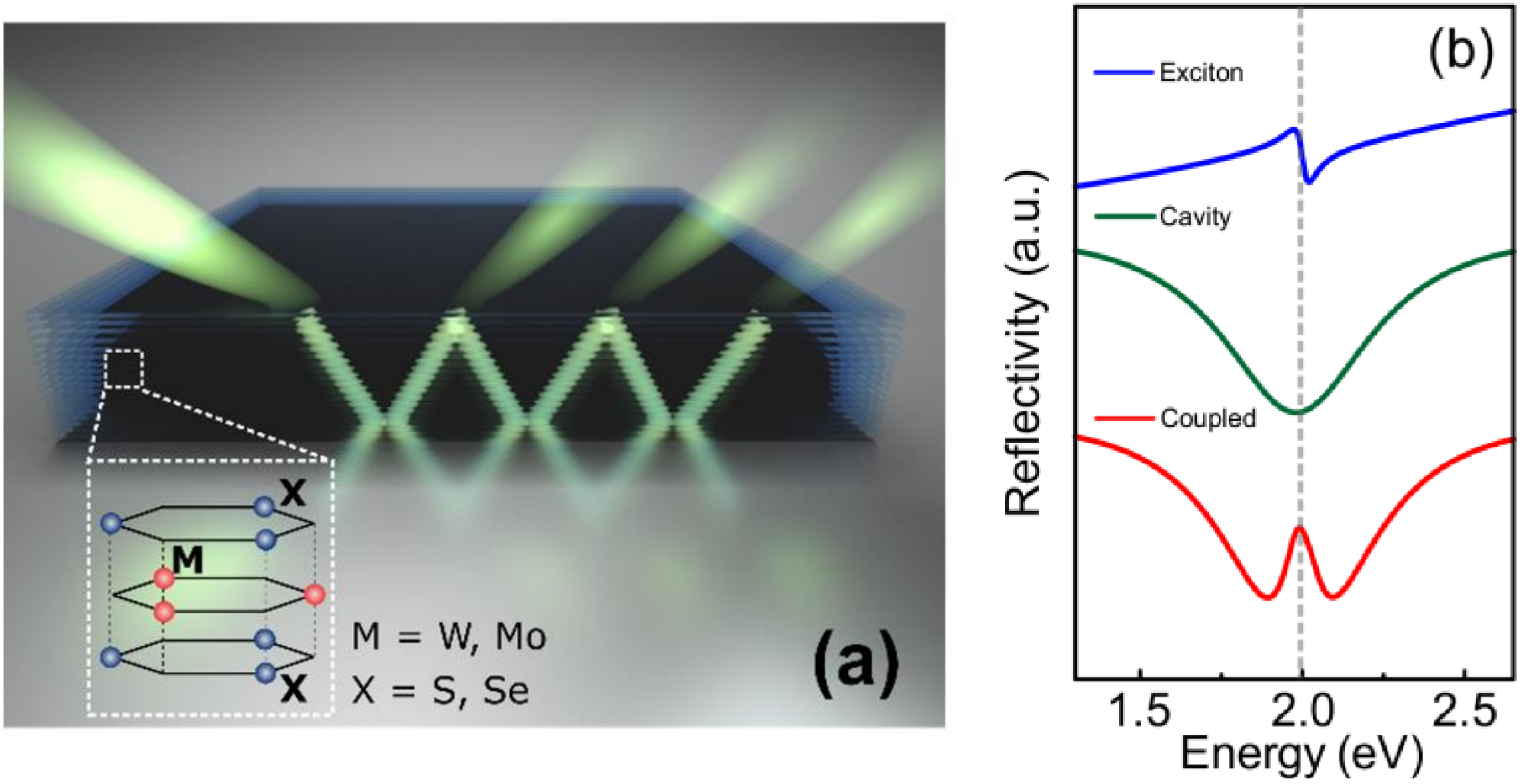


Baumberg (2017)



Shegai (2018)

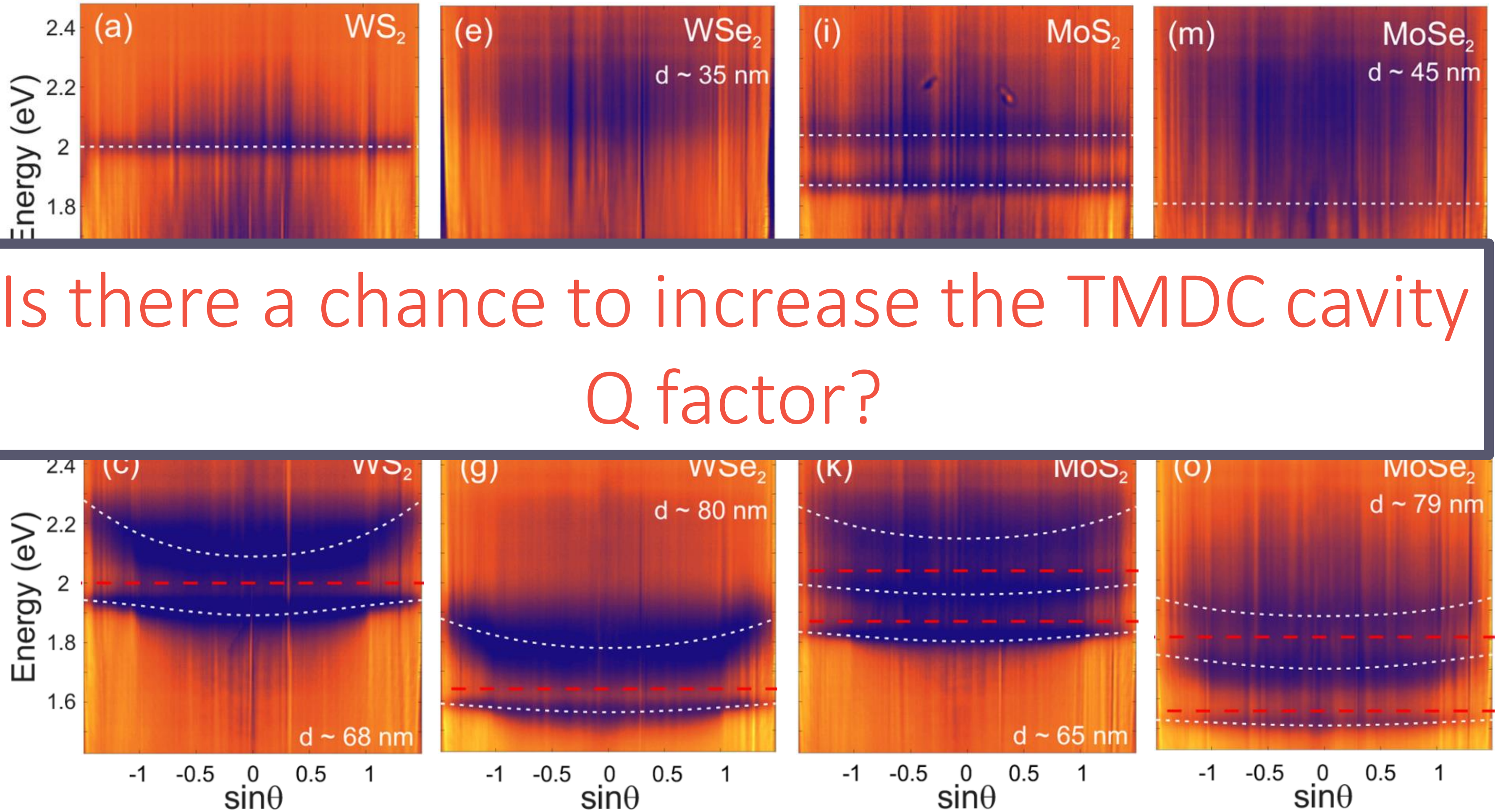
Self-hybridization in TMDC flakes



ACS Photonics, 6, 139-147, (2018)

Self-hybridization in TMDC flakes

- Reflection from **thin** flakes



Is there a chance to increase the TMDC cavity Q factor?

$\gamma_{cav} \approx 600$ meV $\gamma_X \approx 50$ meV "Splitting" $\cong 200$ meV

ACS Photonics, **6**, **139-147**, (2018)

CHALMERS
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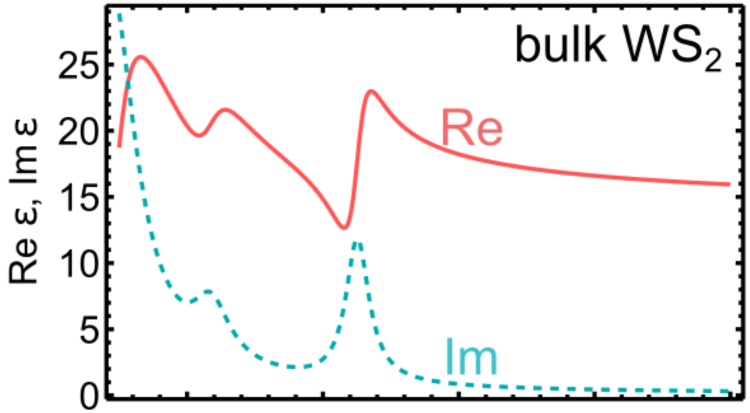
High-index TMDC nanodisks as nanoantennas

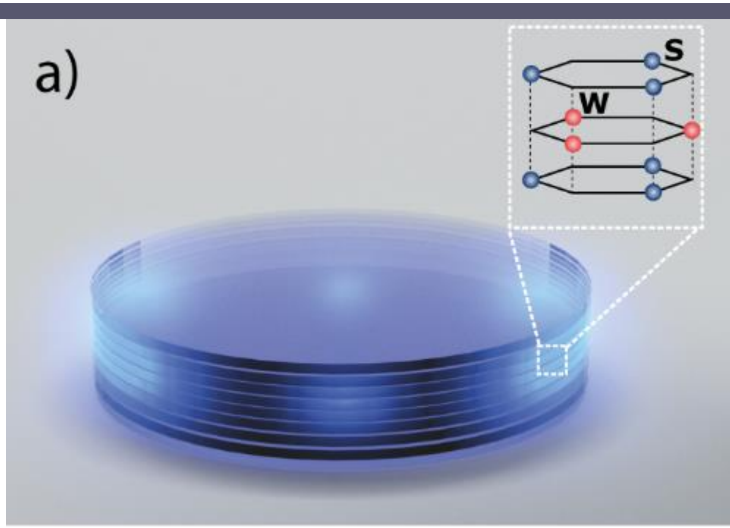


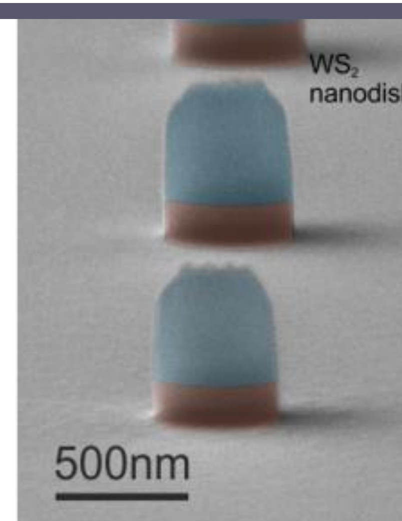
Optically resonant dielectric nanostructures

Arseniy I. Kuznetsov,[1] Andrey E. Miroshnichenko,[2] Mark L. Brongersma,[3*] Yuri S. Kivshar,[2*] Boris Luk'yanchuk[1,4*]

- Si, Ge, GaAs, other conventional semiconductors

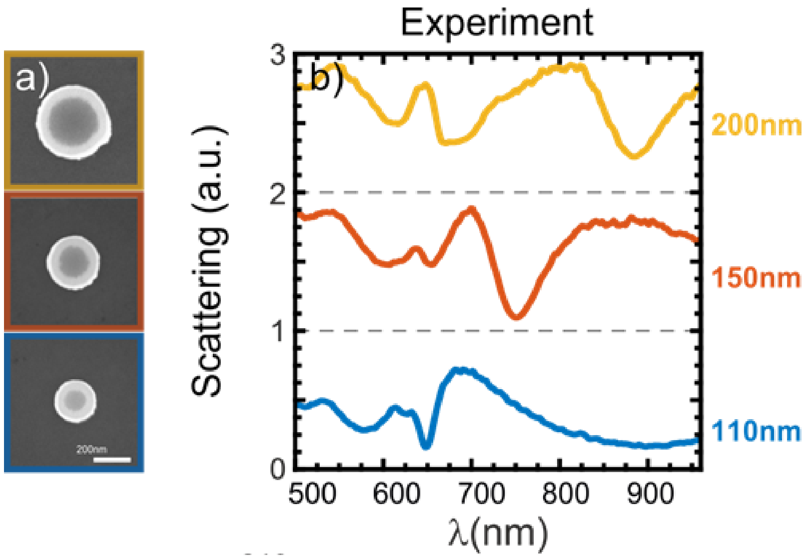
Can we make use of WS_2 high refractive index and make a **nanoantenna** out of it?



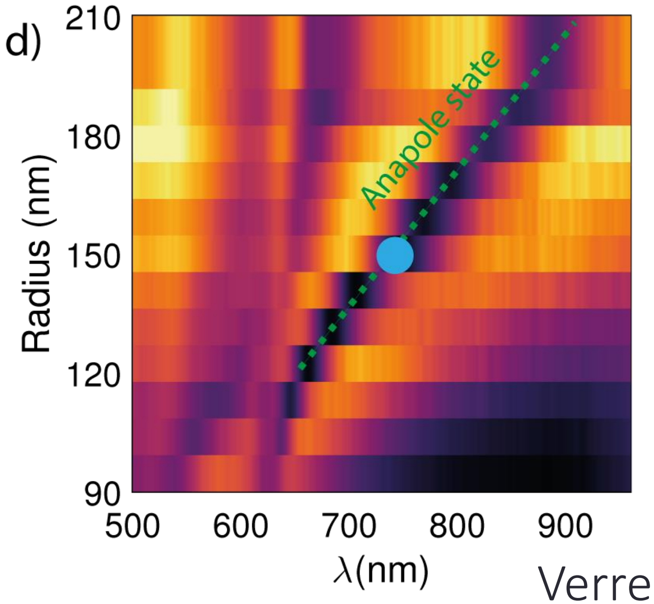


Verre, Baranov, et al. Nat Nano (2019)

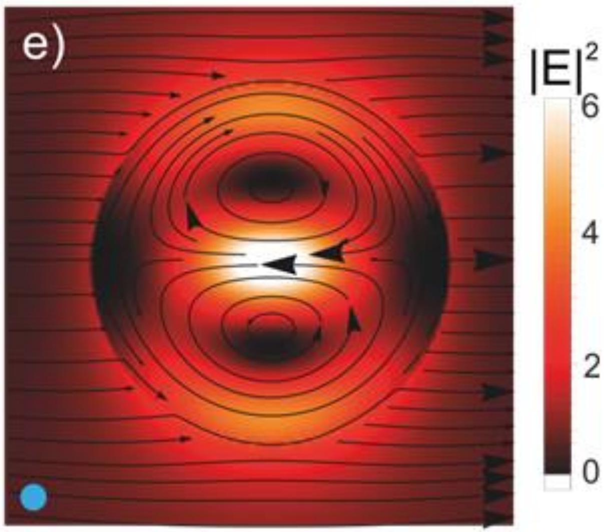
WS_2 nanodisks as Mie resonators



DF spectra *vs* nanodisk radius

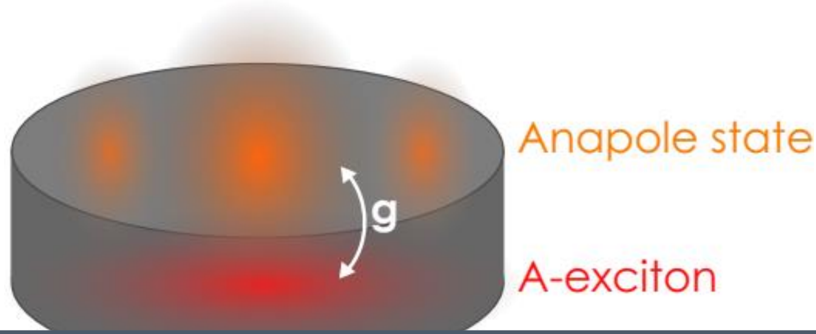


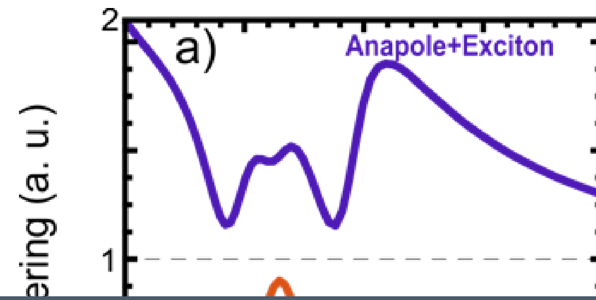
- Scattering dip is the **anapole** state:



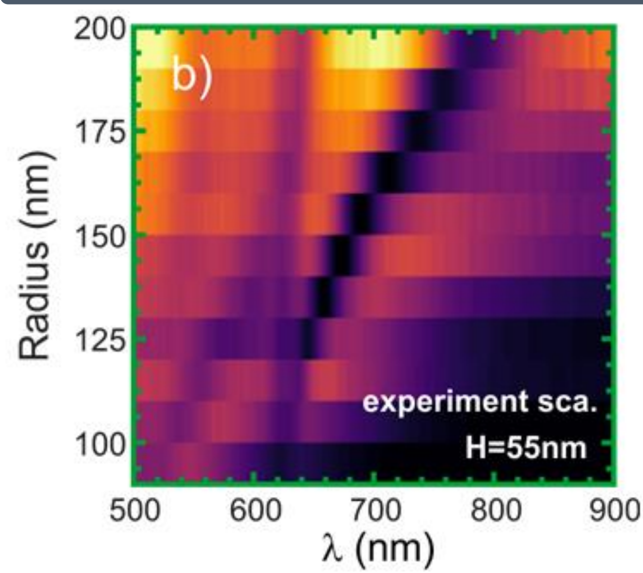
Verre, Baranov, et al. Nat Nano (2019)

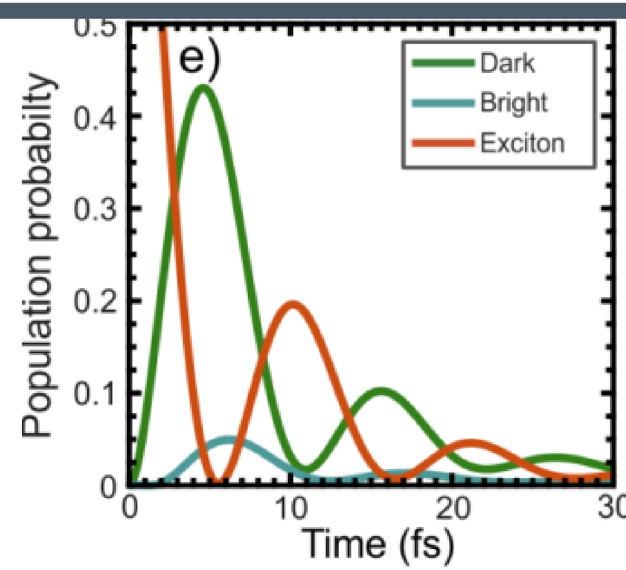
Exciton-anapole coupling in a WS_2 nanodisk





- Rabi oscillations between the exciton and the narrow optical mode in a nanoobject made of a single material





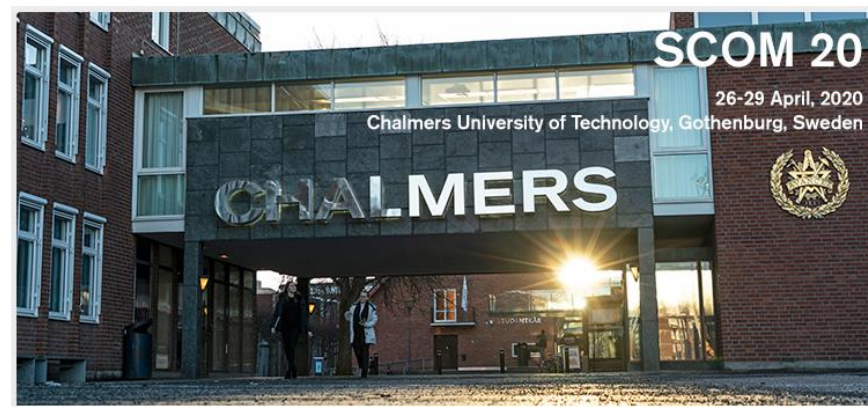
Verre, Baranov, et al. Nat Nano (2019)

Conclusions:

- (1) TDDFT can be used to observe plexcitons in Al-cluster – benzene molecules system
- (2) We observe PL from polaritons, and supress photo-oxidation almost 100-fold for certain configurations
- (3) Multilayers of TMDC can increase Rabi splitting
- (4) EELS can be employed to observe plexcitons with nm resolution
- (5) Multilayer TMDC are quite interesting: (a) self-hybridization, (b) anapole-exciton hybridization.
- Is this going to modify photochemistry and exciton transport?

Strong Coupling with Organic Molecules (SCOM):

Bill Barnes, Jaime Gomez Rivas, Francisco Garcia Vidal, Javier Aizpurua



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[Webpage available: search for SCOM2020](https://www.chalmers.se/en/conference/scom2020/Pages/default.aspx)

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