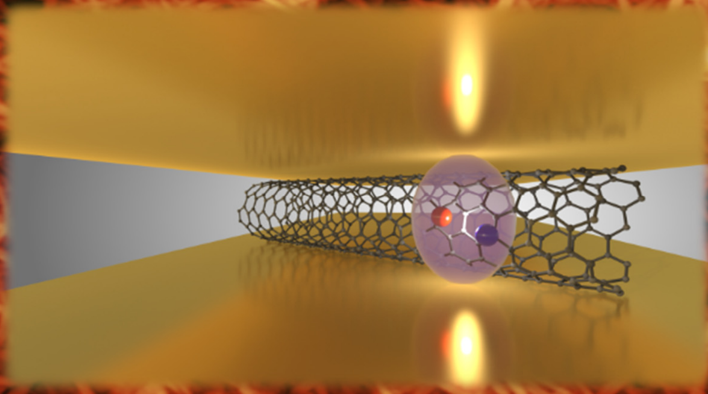
Exciton-Polariton Relaxation in Single-Walled Carbon Nanotube Networks



Jana Zaumseil
Heidelberg University
Applied Physical Chemistry

Open PhD Position

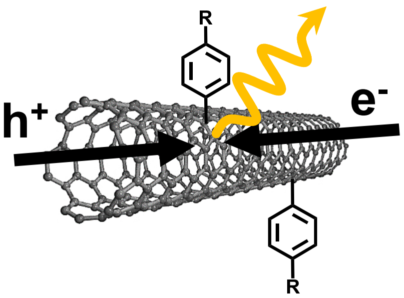
ERC Consolidator Grant Project **TRIFECTs**

“Trions and sp^3-Defects in Single-walled Carbon Nanotubes for Optoelectronics”

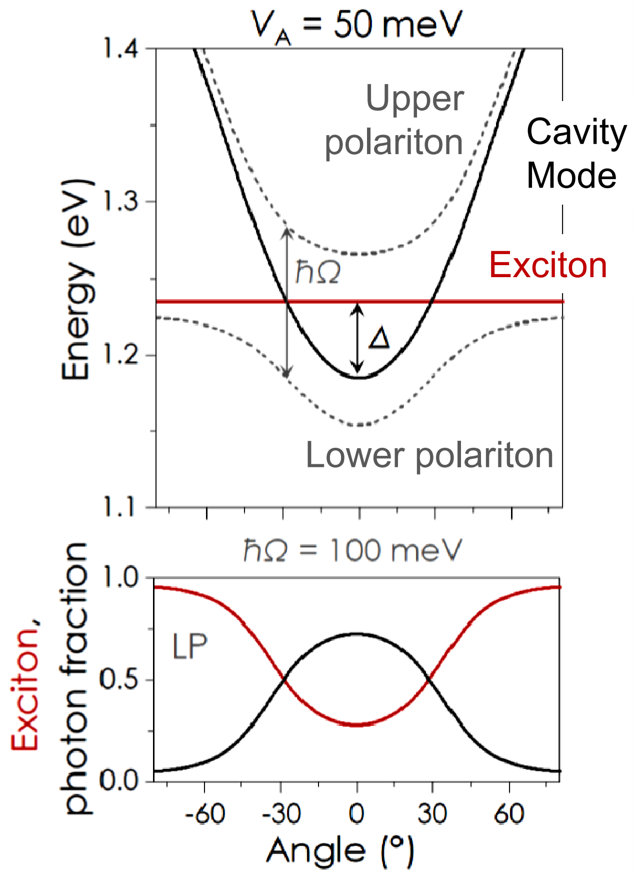
Topic: SWNT-based polariton devices/trion-polariton transport

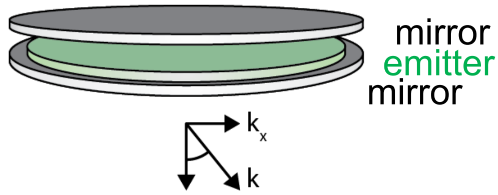
Requirements: Master in Physics (good at optics etc.)

Contact: zaumseil@uni-heidelberg.de
http://apc.pci.uni-heidelberg.de/



Strong-Coupling & Exciton Polaritons





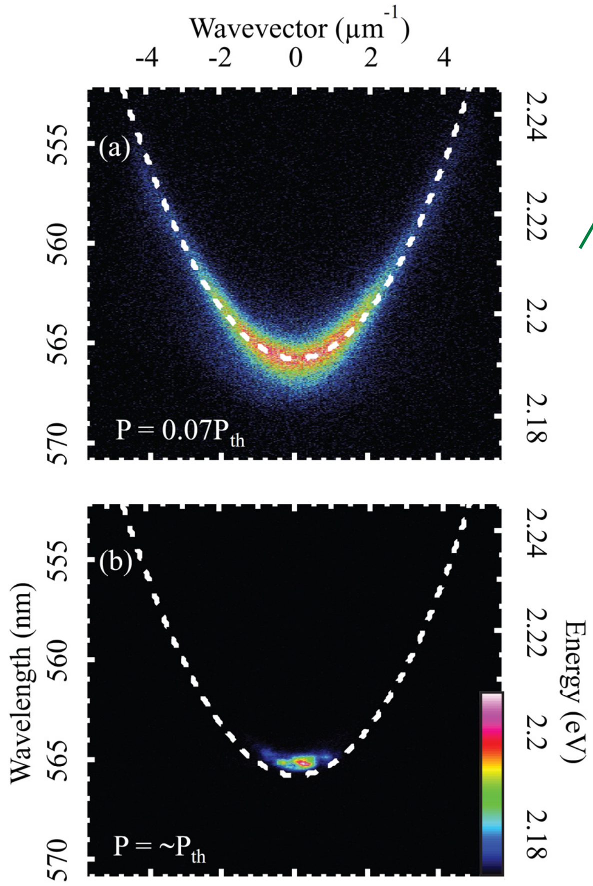
Coupling faster than decay

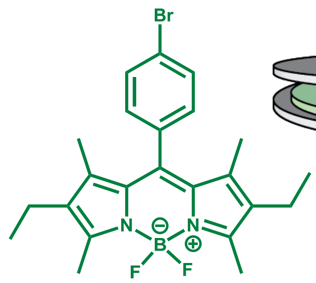
$$\Omega > \frac{\tau_X{}^{-1} + \tau_C{}^{-1}}{2}$$

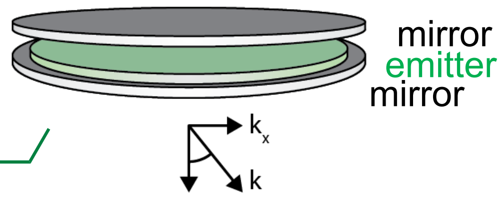
$$\Omega \sim \sqrt{\frac{N\,f}{V_m}} \qquad \tau_C \sim \frac{1}{\ln(\frac{1}{R})}$$

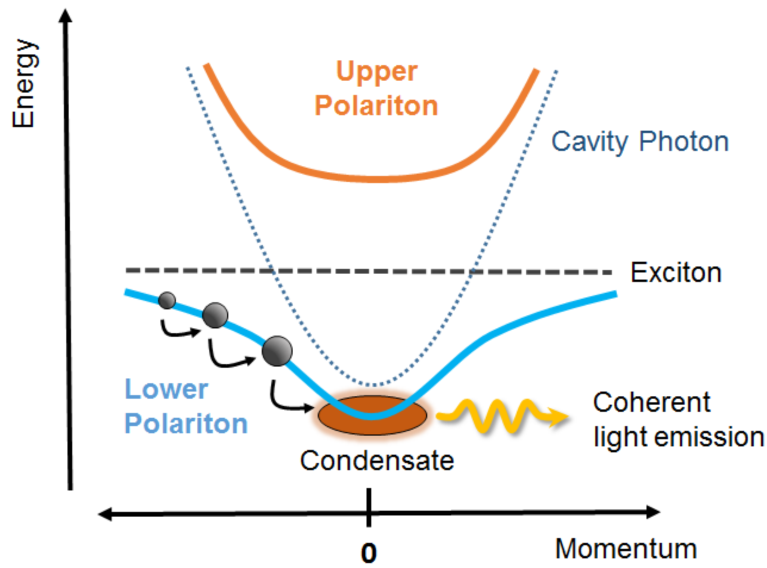
$$\begin{bmatrix} E_X - i\hbar\Gamma_X/2 & V_A \\ V_A & E_C(\theta) - i\hbar\Gamma_C/2 \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = E \begin{bmatrix} \alpha \\ \beta \end{bmatrix}$$

Strong-Coupling & Exciton Polaritons



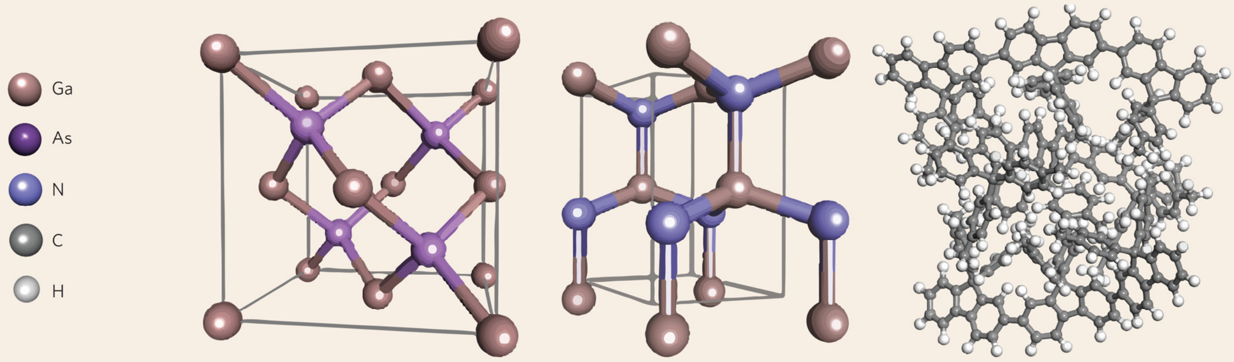






From Cookson et al. *Adv. Opt. Mater.* **2017**, 30, 1700203.

Polaritons in Semiconductor Materials



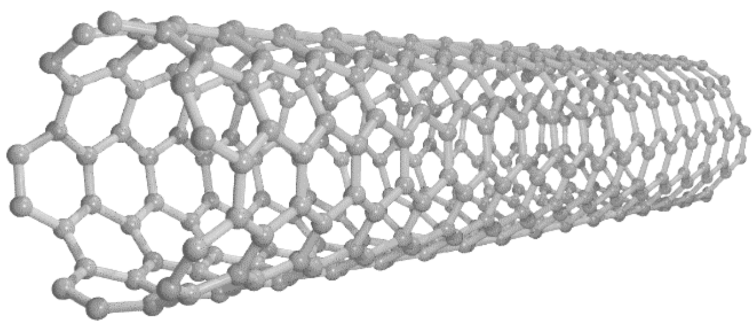
	Inorganic (large ε)	Inorganic (small ε)	Organic
Material	For example, GaAs, CdTe	For example, GaN, ZnO	For example, anthracene, MeLPPP, TDAF, cyanine dyes
Packing	Crystal (typically zincblende)	Crystal (typically wurtzite)	Amorphous, polycrystalline, single crystal (anthracene)
Exciton	Wannier-Mott	Wannier-Mott	Frenkel
Binding energy	5-25 meV	25-60 meV	0.5-1 eV
Linewidth	0.1-1 meV	5-10 meV	25-200 meV
Rabi splitting	3-25 meV	30-150 meV	0.1-1 eV
Dominant relaxation pathways	Acoustic phonons and exciton-exciton scattering	Acoustic, LO phonons and exciton-exciton scattering	Molecular vibrations and radiative
Source of exciton-exciton nonlinearity	Coulomb, saturation	Coulomb, saturation	Saturation

from D. Sanvitto, S. Kena-Cohen, *Nat. Mater.* **2016**, 15, 1061.

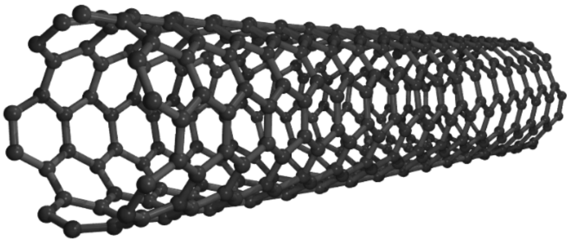
New materials: Hybrid Perovskites, Monolayered Transition Metal Dichalcogenides (TMDCs) & Single-walled Carbon Nanotubes

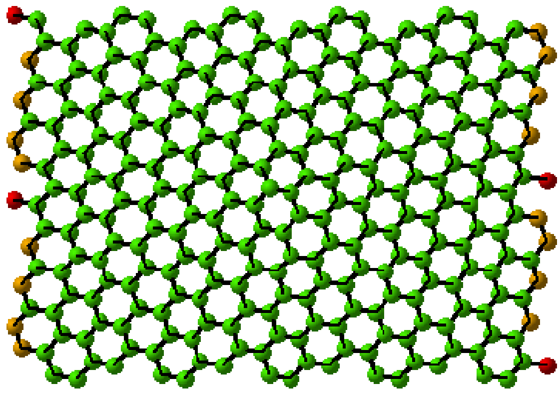
Outline

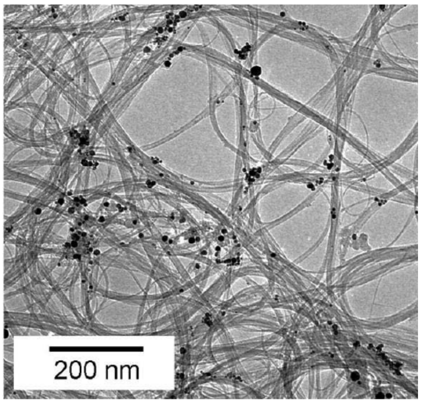
- ❑ **Photophysics of Single-walled carbon nanotubes (SWNTs)**
- ❑ **Exciton-Polaritons in SWNTs**
- ❑ **Trion-Polaritons in SWNTs**
- ❑ **Relaxation Pathways**

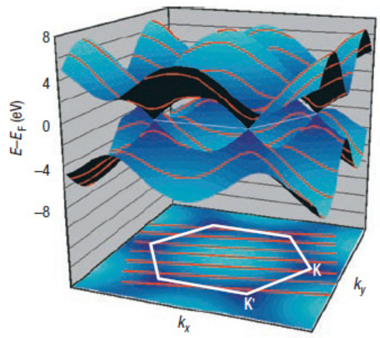


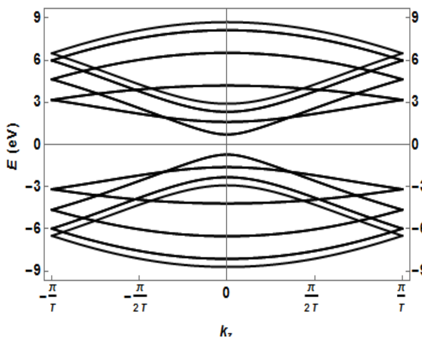
Single-walled Carbon Nanotubes (SWNTs)



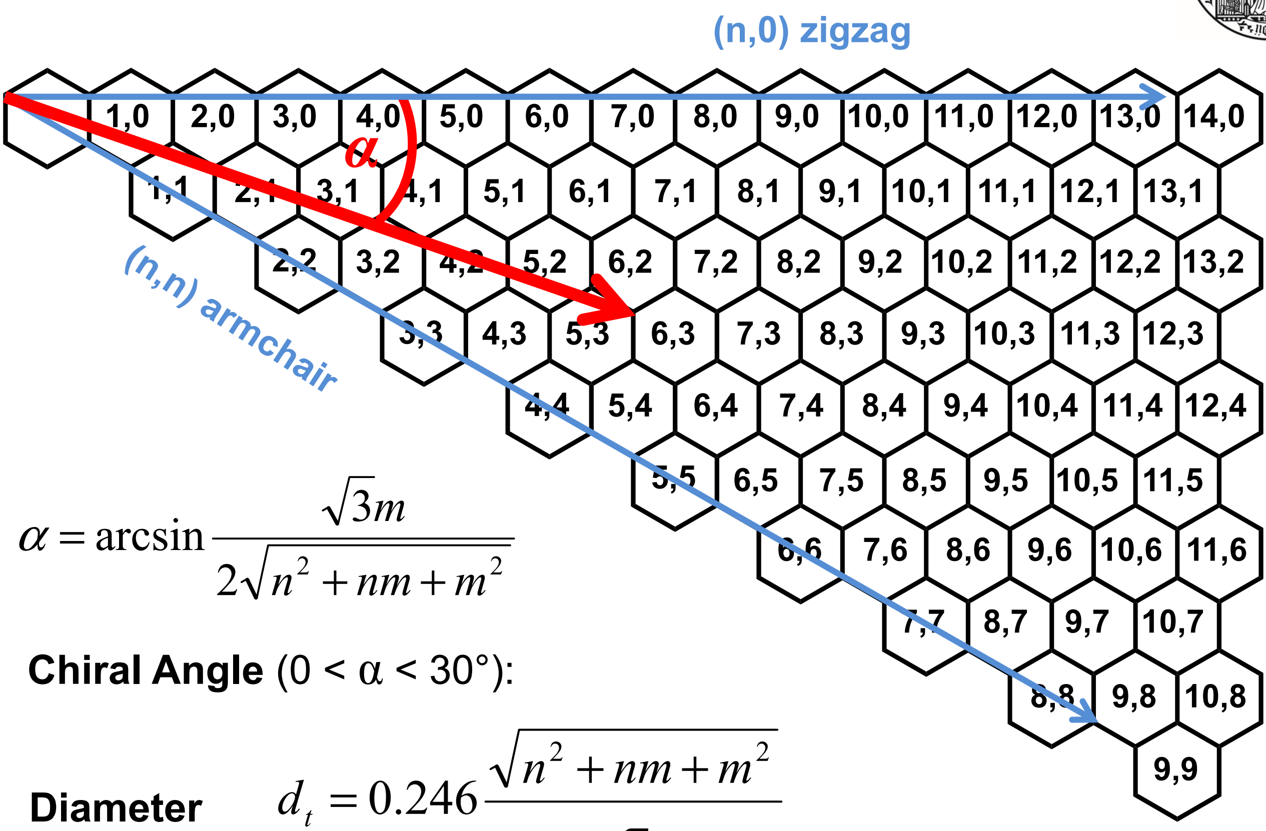








Basics: Vector Notation (n,m)



$$\alpha = \arcsin \frac{\sqrt{3}m}{2\sqrt{n^2 + nm + m^2}}$$

Chiral Angle (0 < α < 30°):

Diameter $$d_t = 0.246 \frac{\sqrt{n^2 + nm + m^2}}{\pi}$$

Basics: (n,m) "Chiralities"

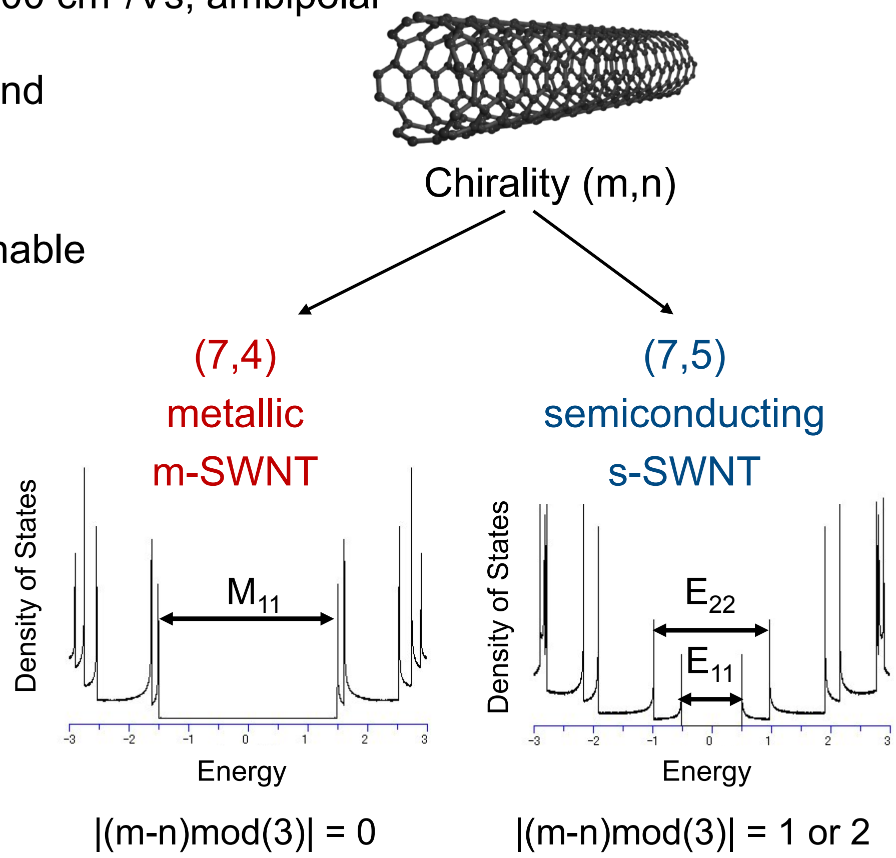
Different Single-Walled Carbon Nanotubes: chiral and achiral

(6,5) (9,4) (8,0) (7,7)

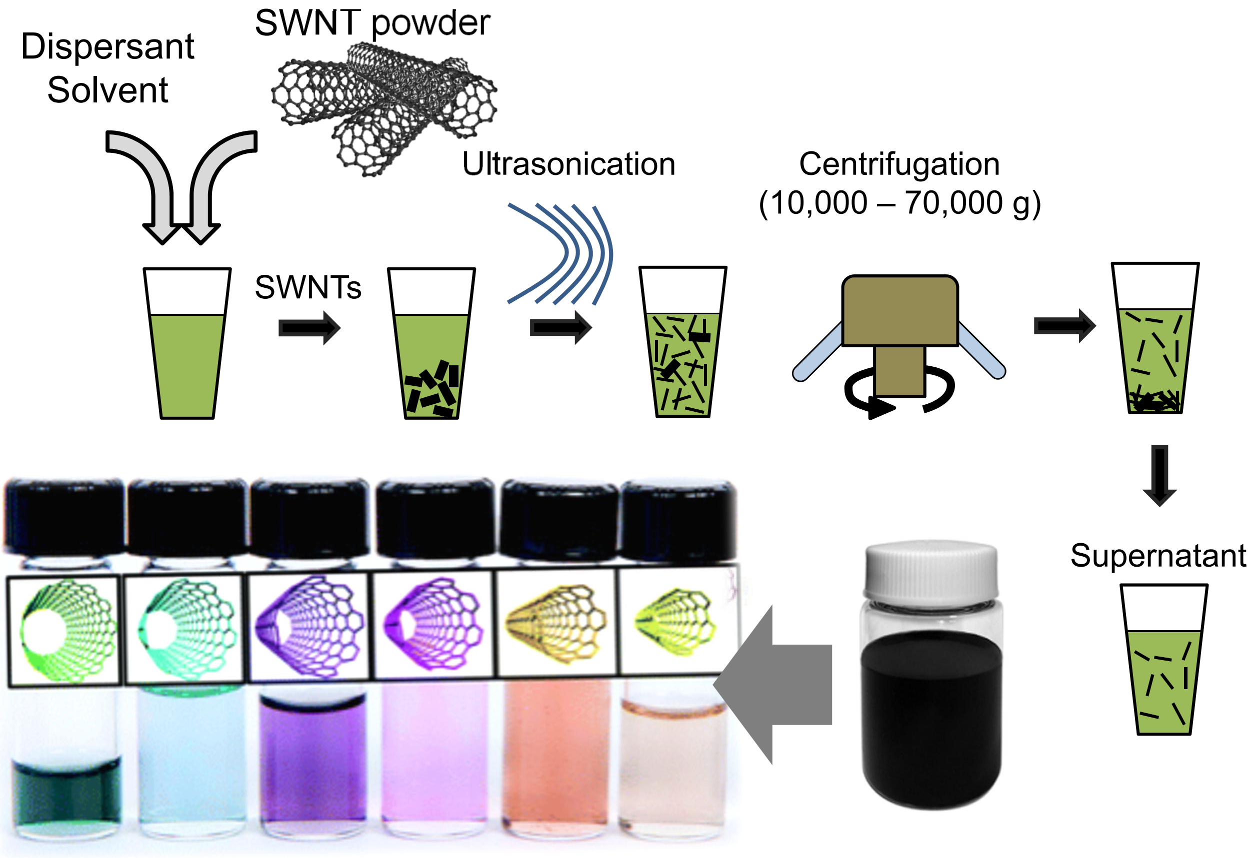
Single-walled Carbon Nanotubes

- **High Mobilities**: >10,000 cm²/Vs, ambipolar
- Solution-processable and printable
- Highly flexible & stretchable
- Raw material: **mix of metallic and semiconducting SWNTs !**

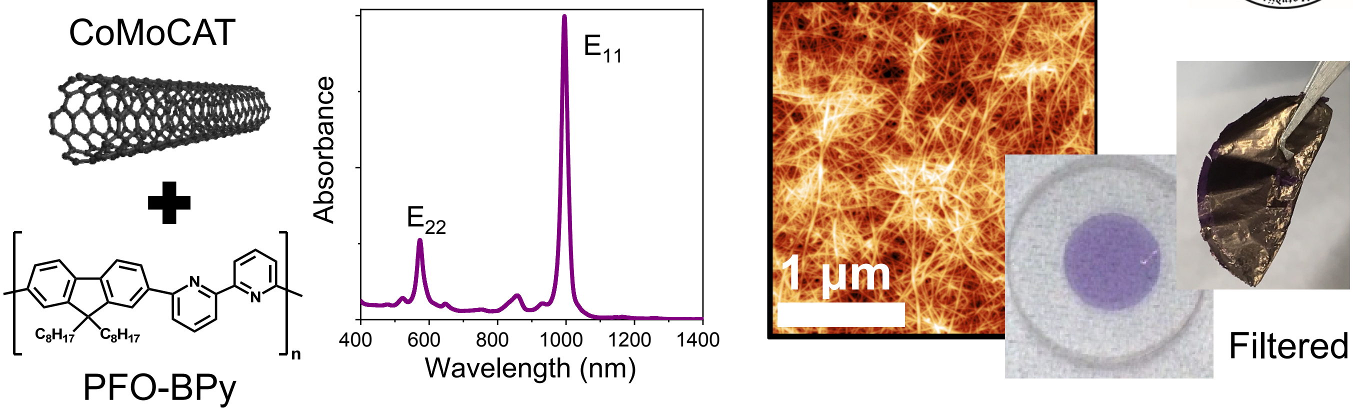
→ **Separation by selective polymer wrapping or DGU or chromatography**



Dispersion and Centrifugation



Purified, Polymer-wrapped (6,5) SWNTs

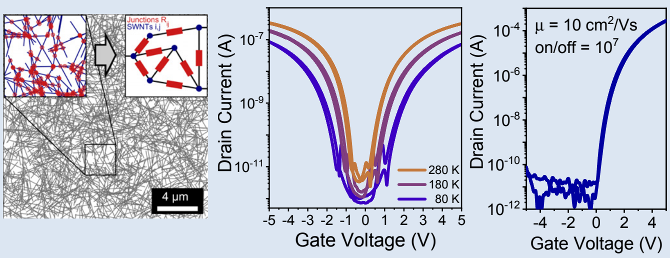


→ **(6,5) SWNTs as a pure bulk material**

Graf et al. *Carbon* **2016,** *105*, 593-599.

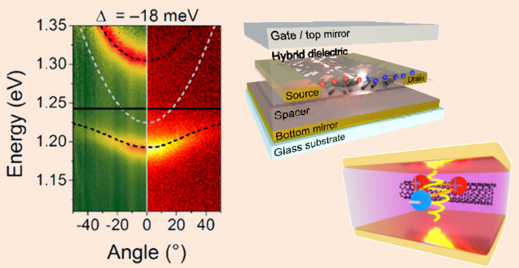
Applications of Purified (6,5) SWNTs

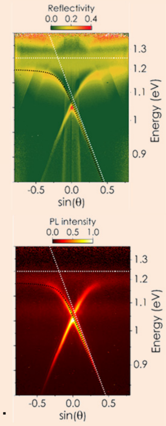
Charge Transport in Network FETs



Brohmann et al. ***ACS Nano*** 2019, 13, 7323.
Schneider et al. ***ACS Nano*** 2018, 12, 5895.
Brohmann et al. ***J. Phys. Chem. C*** 2018, 122, 19886.
Schießl et al. ***Phys. Rev. Mater.*** 2017, 1, 046003.

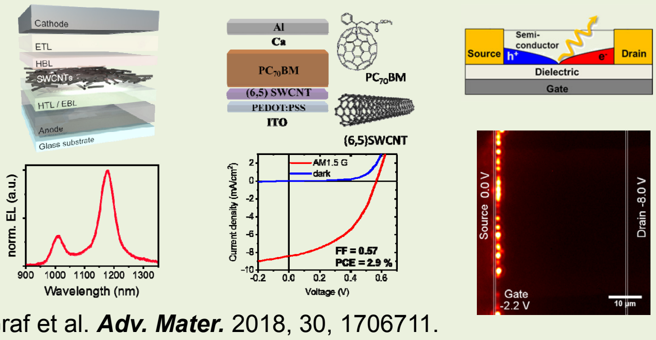
Strong Light-Matter Coupling





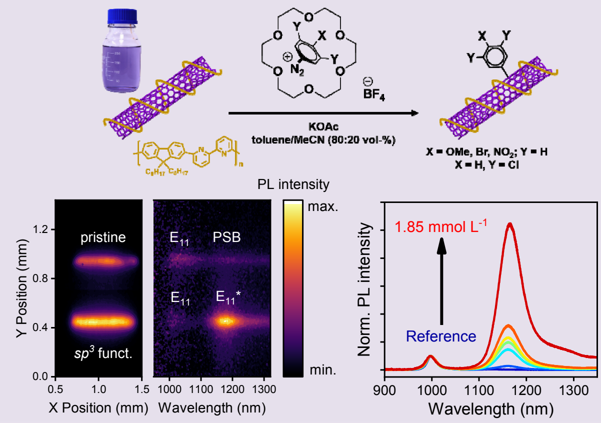
Möhl et al. ***ACS Photonics*** 2018, 5, 2074.
Zakharko *et al.* ***Nano Lett.*** 2018, *18*, 4927.
Graf et al., ***Nature Commun.***, 2016, 7, 13078.
Graf & Held et al. ***Nature Mater.***, 2017, 16, 911.

Optoelectronic Devices



Graf et al. ***Adv. Mater.*** 2018, 30, 1706711.
Classen et al. ***Adv. Energy Mater.*** 2019, *9*, 1801913.
Berger et al. ***ACS Appl. Mater. Interfaces*** 2018, *10*, 11135.
Rother et al. ***ACS Appl. Mater. Interfaces*** 2016, *8*, 5571

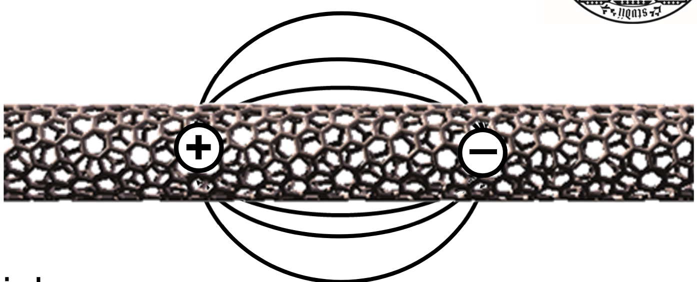
Luminescent sp³-Defects



Near-Infrared Emission from SWNTs

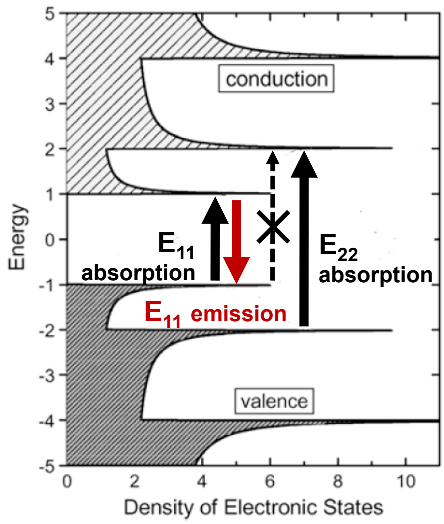
Excitonic Emission:

- Very **narrow linewidths** (FWHM < 50 nm)
- Values for PL quantum yield vary widely → Overall not very high (<10%)

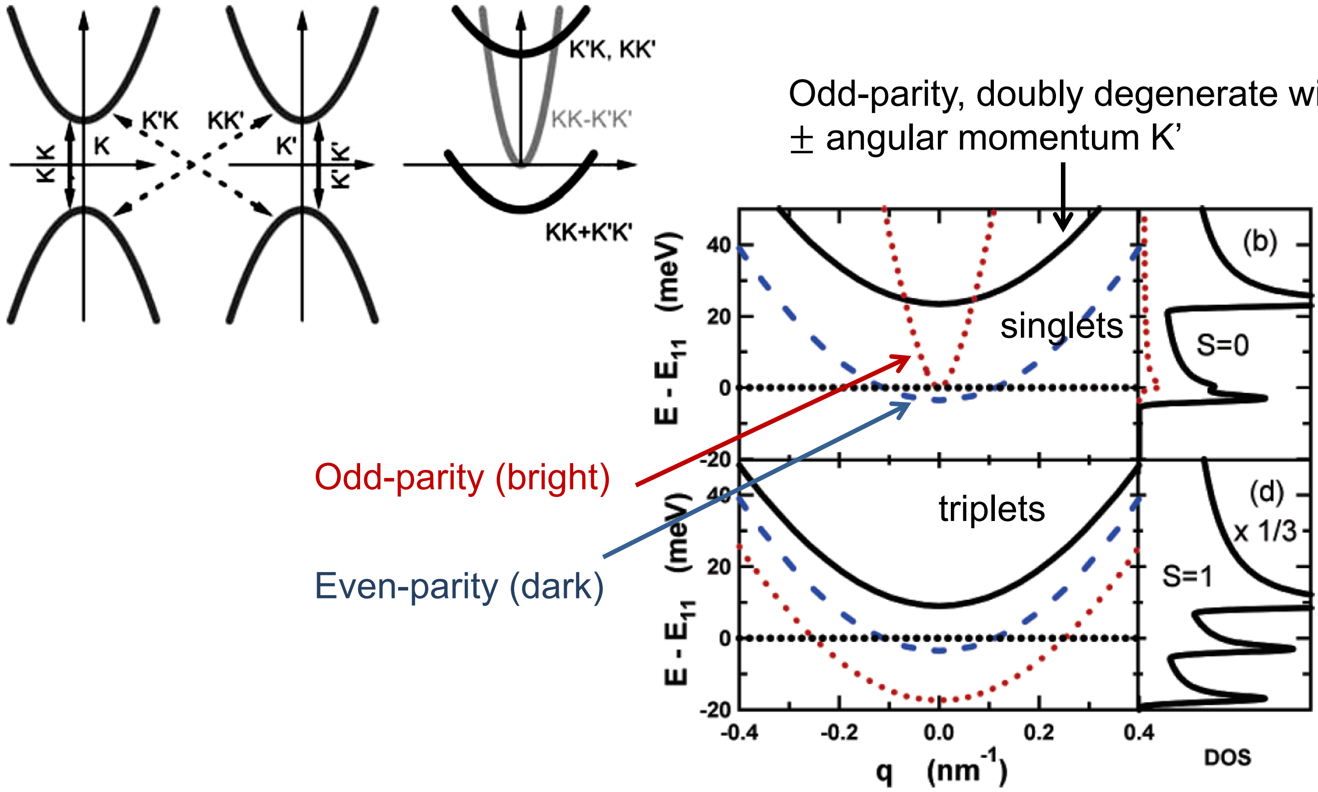


Excitons:

- Size: ~10-15 nm
- Binding energy: 200-300 meV
- Diffusion coefficient: ~ 11 cm²/s
- Fast exciton diffusion (50 – 100 nm) to defect sites
- 16 excitons, only one bright exciton

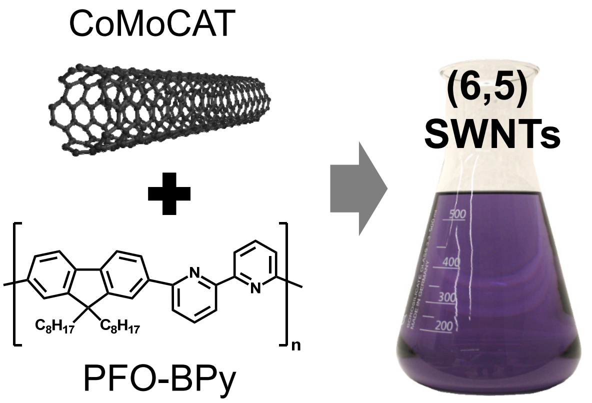


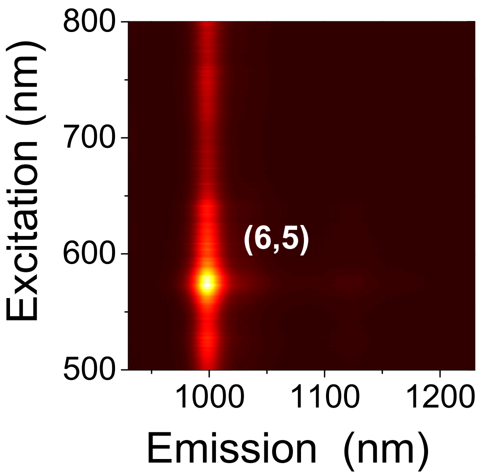
Bright & Dark Excitons

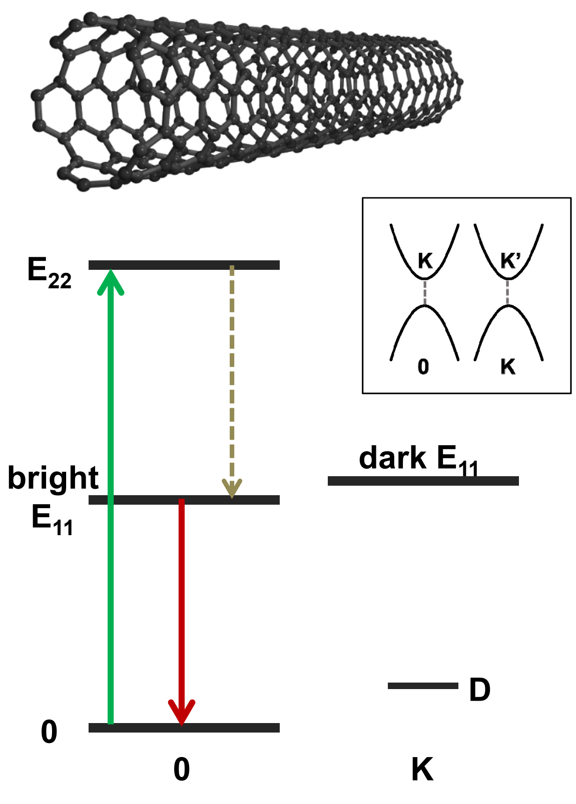


V. Perebeinos, J. Tersoff, P. Avouris, *Nano Lett.* **2005**, 5, 2495.

Near-infrared light emission of SWNTs







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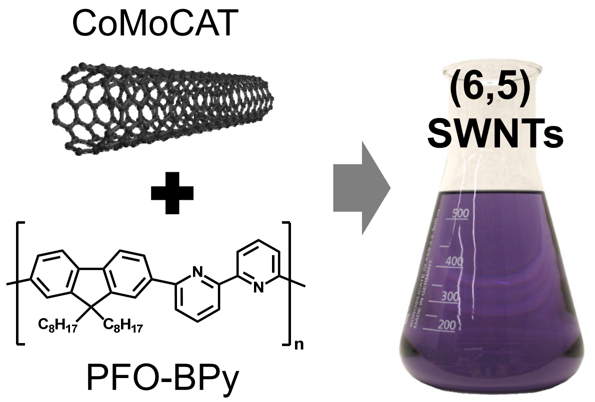
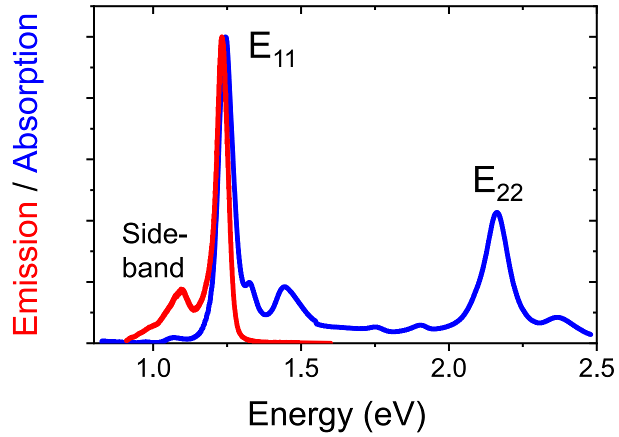
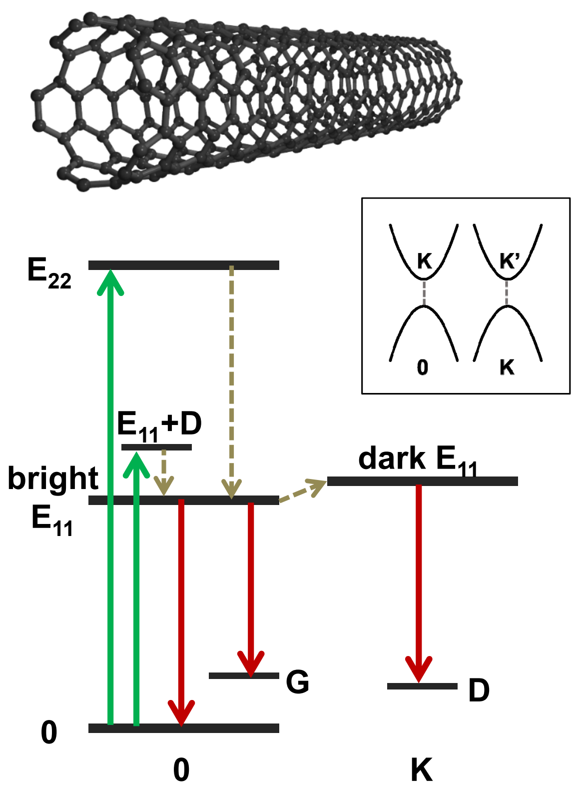
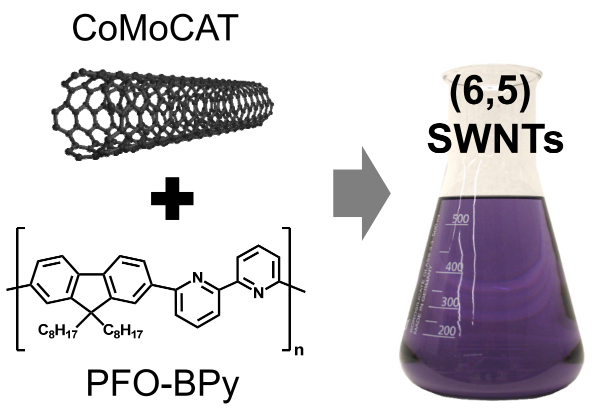
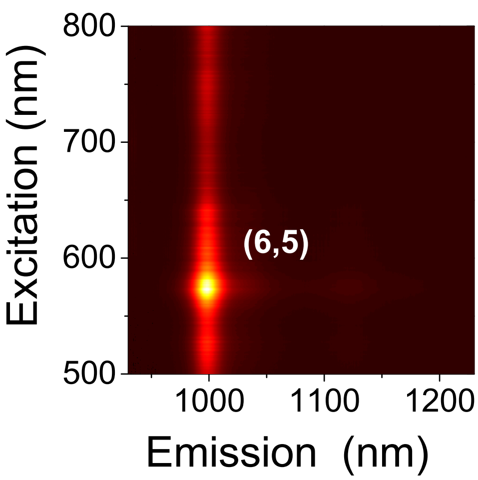


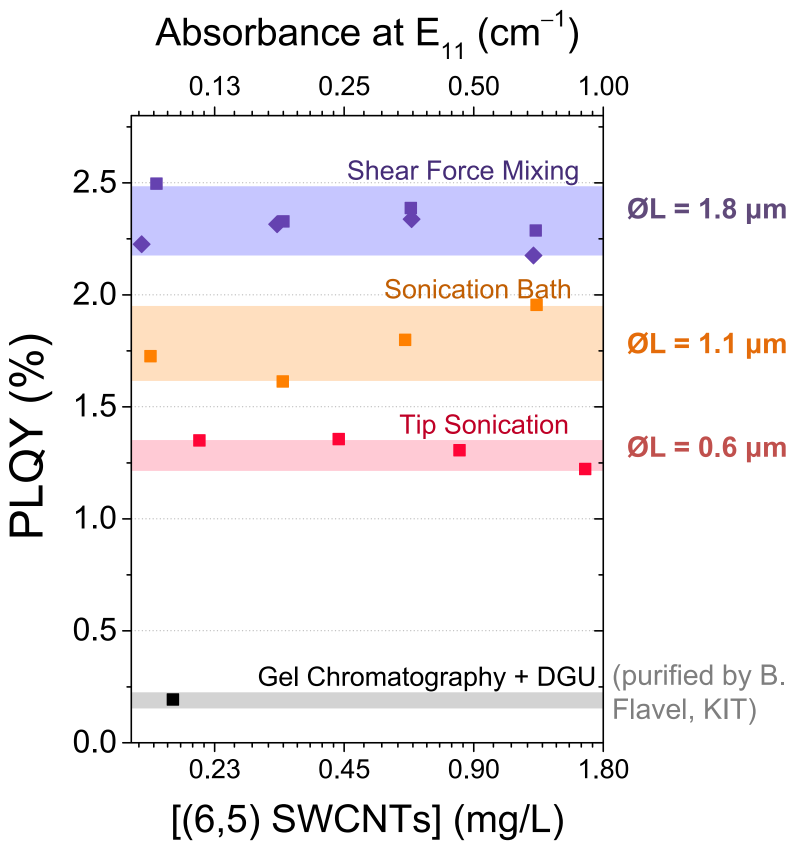




(6,5) SWNT as near-IR emitters







Graf et al. ***Carbon*** (2016), 105, 593-599.

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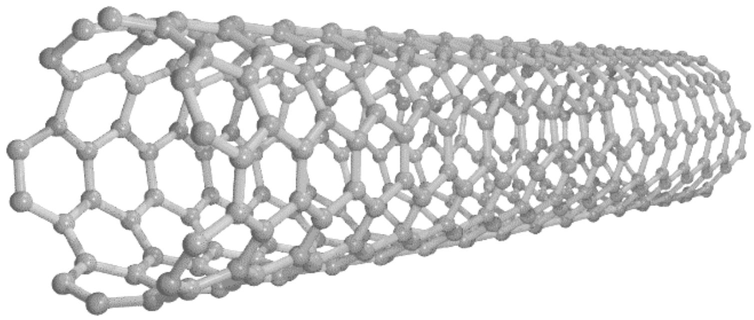
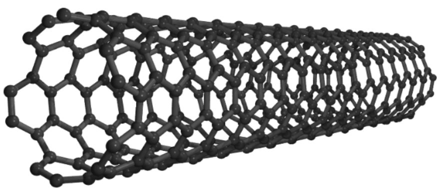
- ❑ Relaxation Pathways

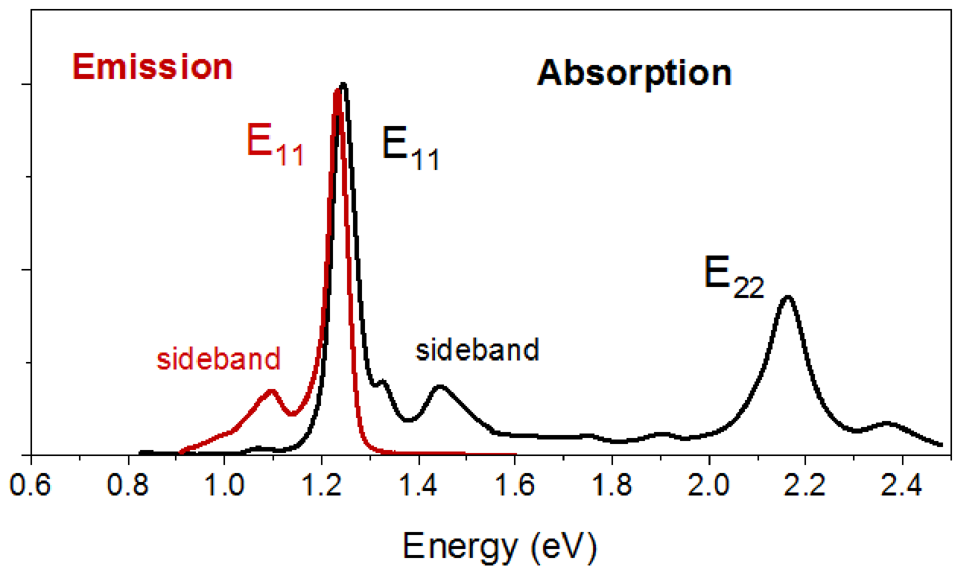


SWNT for Strong Light-Matter Coupling

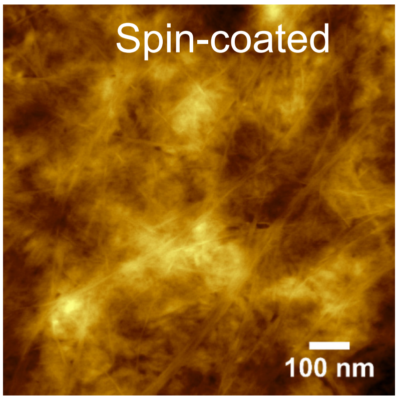


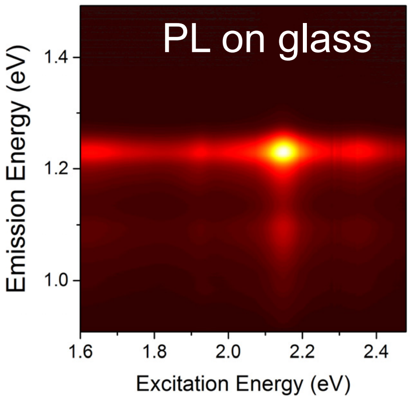
(6,5) SWNT

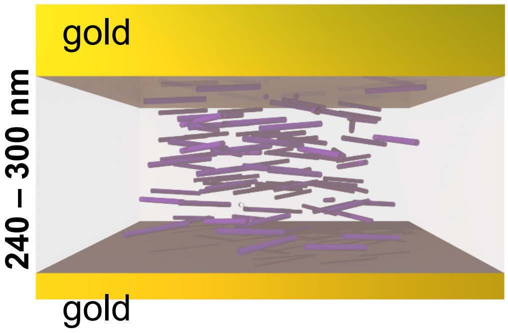
- High Oscillator strength
- Large exciton binding energy
- Narrow linewidth
- Small Stokes-shift



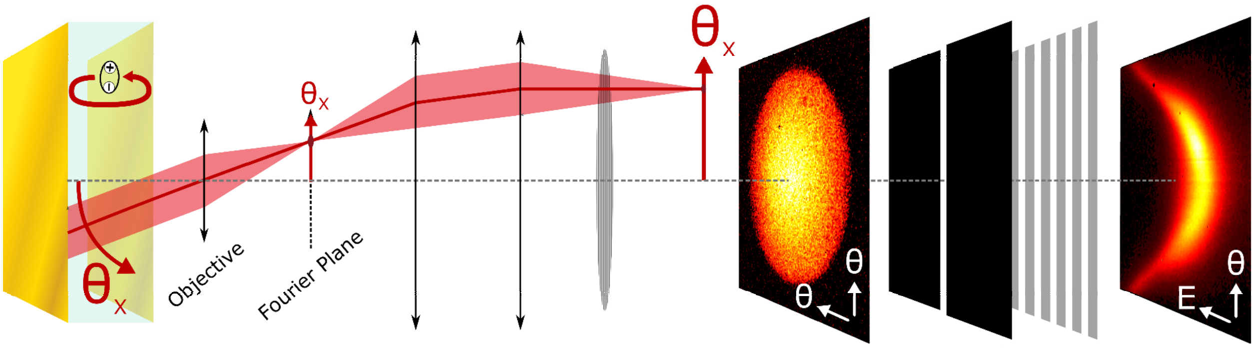
Creating a Cavity with (6,5) SWNTs







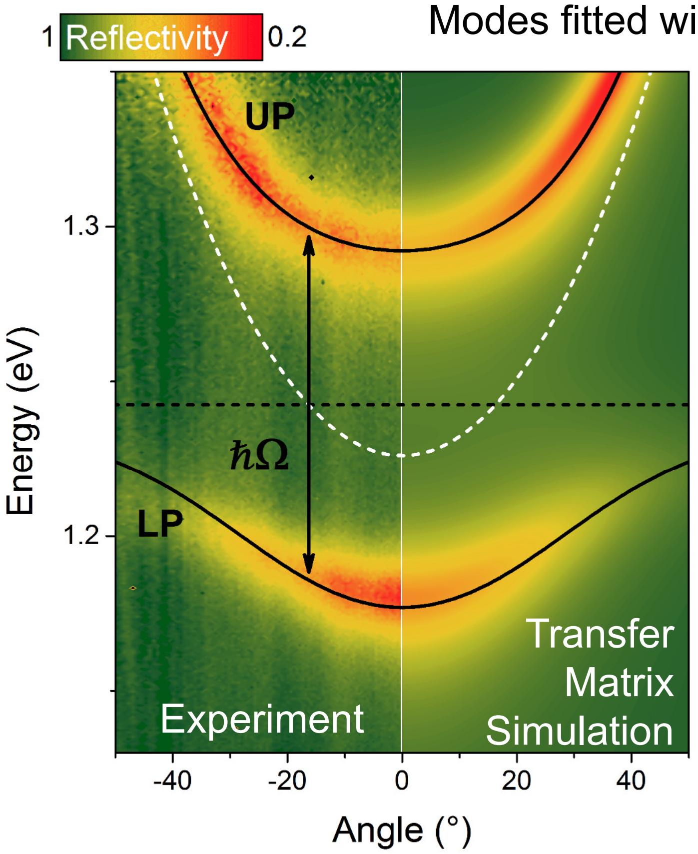
Dense SWNT networks



Angle-resolved spectroscopy (Fourier Imaging)

Strong Coupling with (6,5) SWNTs

Modes fitted with coupled oscillator model



$$H = \begin{pmatrix} E_X + i\hbar\Gamma_X & V_A \\ V_A & E_C + i\hbar\Gamma_C \end{pmatrix}$$

E_X - energy of first excitonic transition

Γ_X - HWHM of exciton

E_C - energy of photon

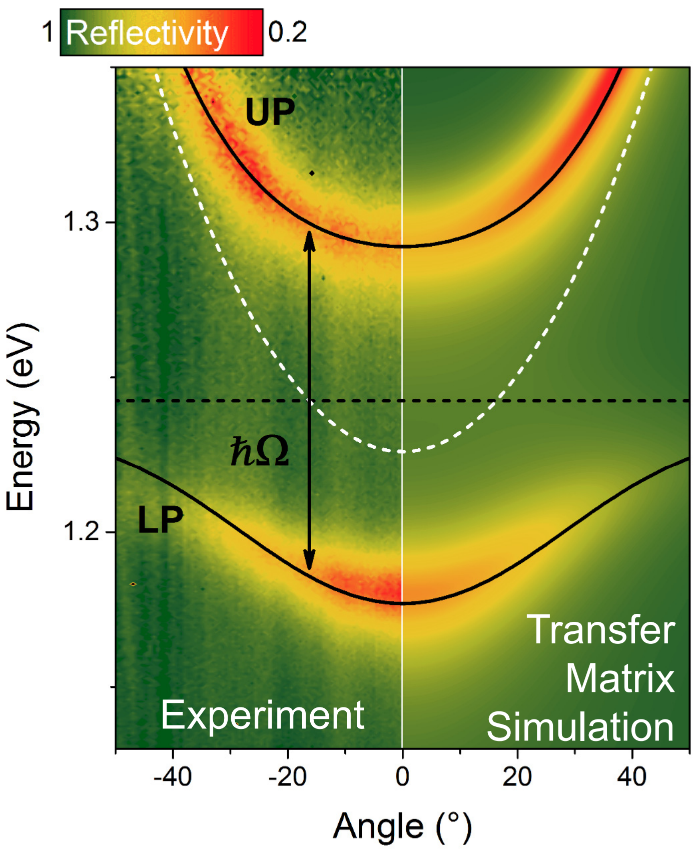
Γ_C - HWHM of photon

V_A - coupling strength

$$V_A = 0.5 \cdot \sqrt{\hbar\Omega^2 + (\hbar\Gamma_X - \hbar\Gamma_C)^2}$$

Graf, A. *et al.*, ***Nature Comm.*** *(2016)*, 7, 13078

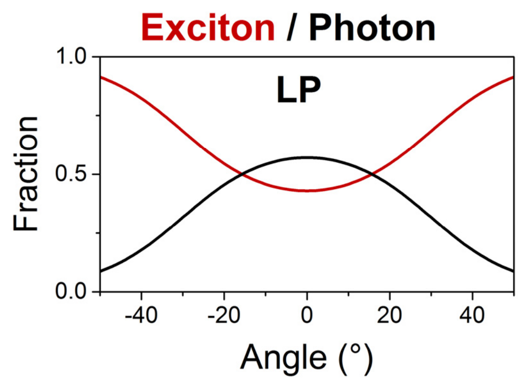
Strong Coupling with (6,5) SWNTs



Rabi Splitting ħΩ = 114 meV

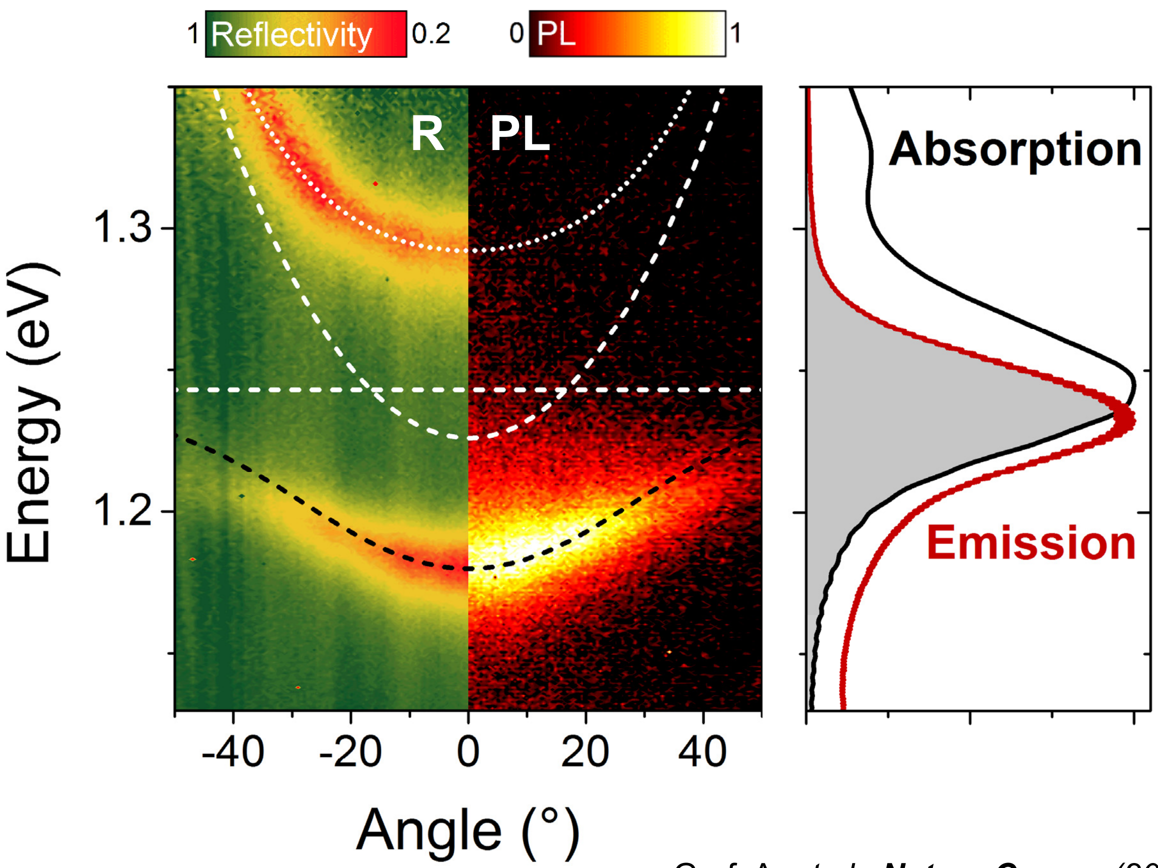
$\hbar\Omega > \hbar\Gamma_X + \hbar\Gamma_C = 50\ \text{meV}$

→ **Strong coupling regime**



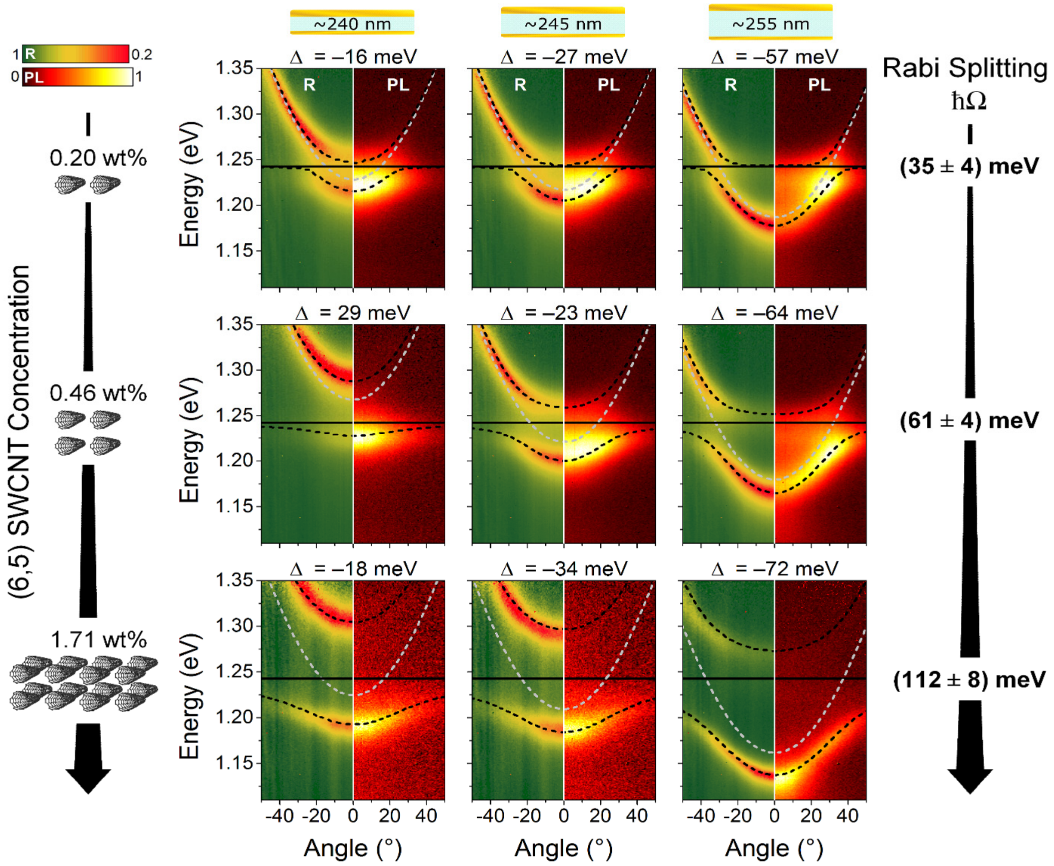
Graf, A. *et al.*, ***Nature Comm.*** *(2016)*, 7, 13078

Reflectivity vs. Photoluminescence



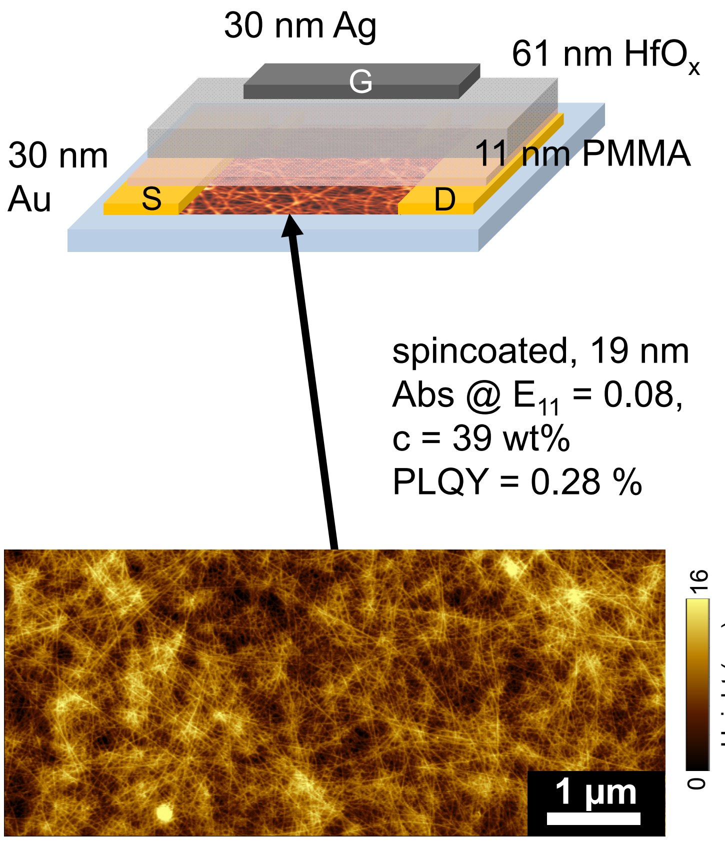
Graf, A. *et al.*, ***Nature Comm.*** *(2016)*, 7, 13078

Strong-Coupling with SWNTs

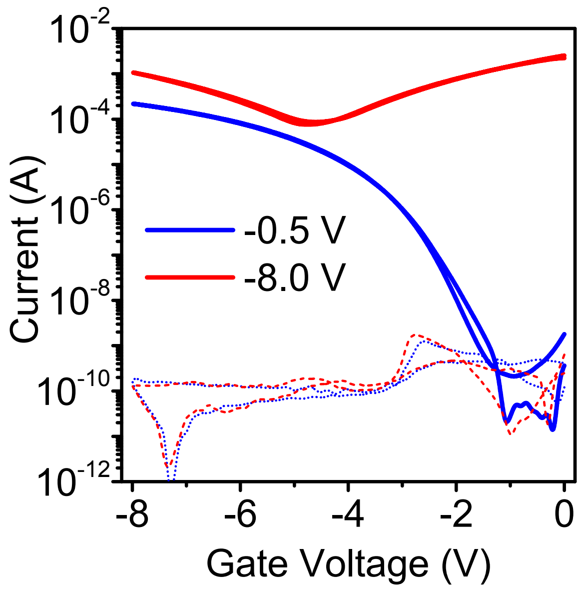


Graf, A. *et al.*, ***Nature Comm.*** *(2016)*, 7, 13078

(6,5) SWNT Field-effect Transistor



spincoated, 19 nm
Abs @ E_{11} = 0.08,
c = 39 wt%
PLQY = 0.28 %

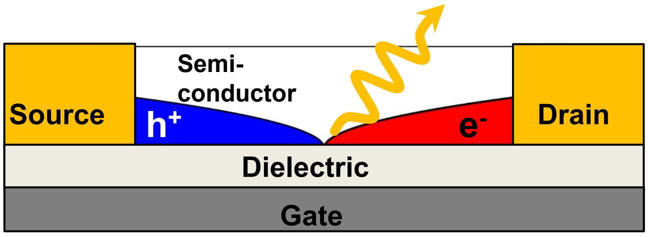


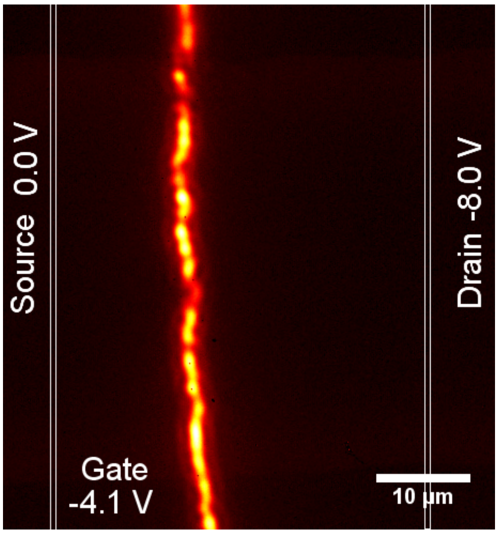
Electron mobility: 3.8 cm^2 V^{-1} s^{-1}

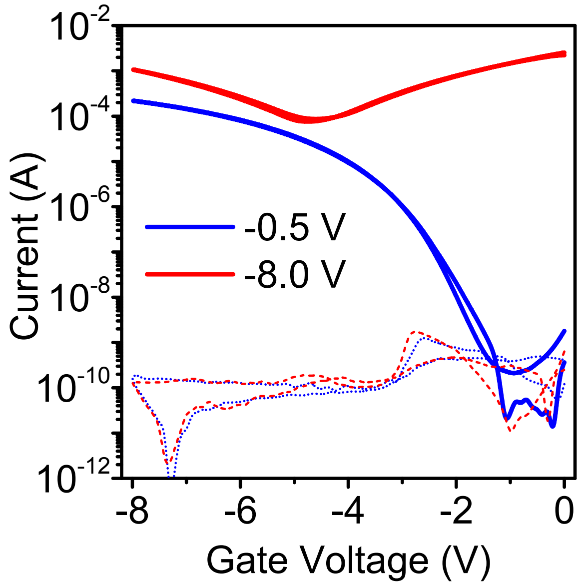
Hole mobility: 5.2 cm^2 V^{-1} s^{-1}

On/off ratio: 10^6

SWNT Light-emitting Transistor (LEFET)







Electron mobility: 3.8 cm^2 V^{-1} s^{-1}

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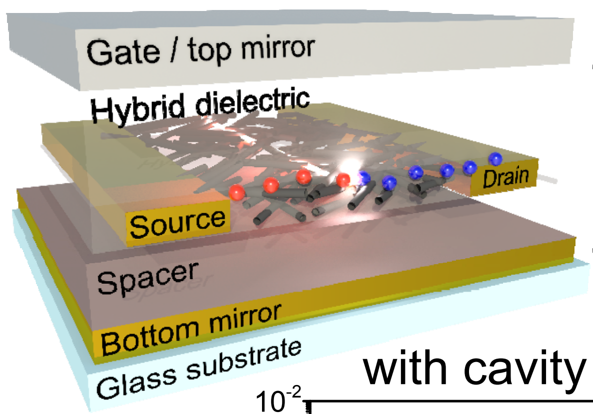
Graf & Held *et al.*, ***Nature Mater.*** 16, 911–917 (2017)

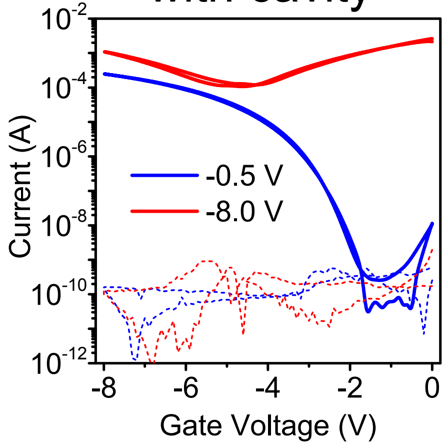
Strong Coupling in SWNT- LEFETs



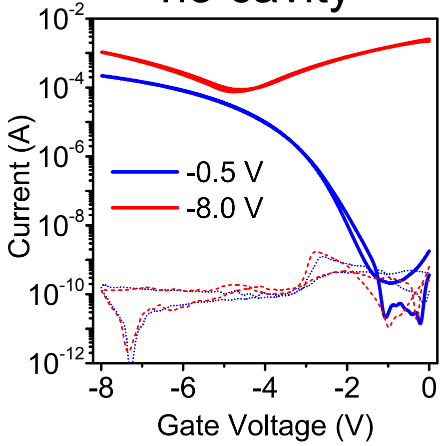
cavity

Ag	60 nm
HfOx	60 nm
PMMA	11 nm
(6,5) SWNTs	32 nm
AlOx	155 nm
Au	30 nm
Glass	1 mm

with cavity

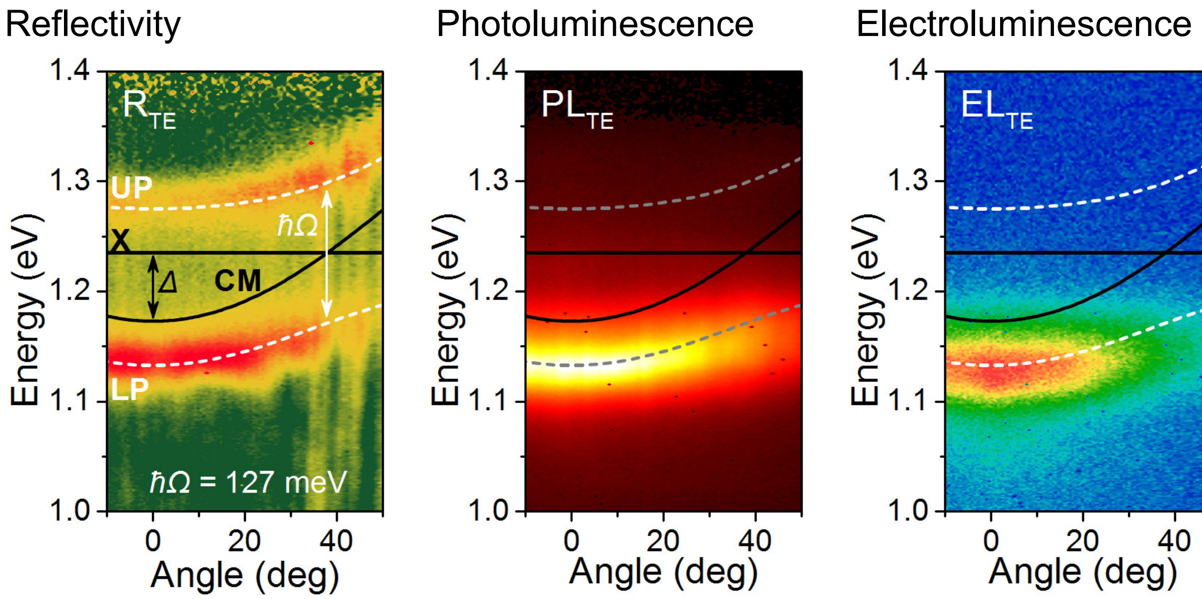


no cavity



Graf & Held *et al.*, ***Nature Mater.*** 16, 911–917 (2017)

Polariton-Electroluminescence

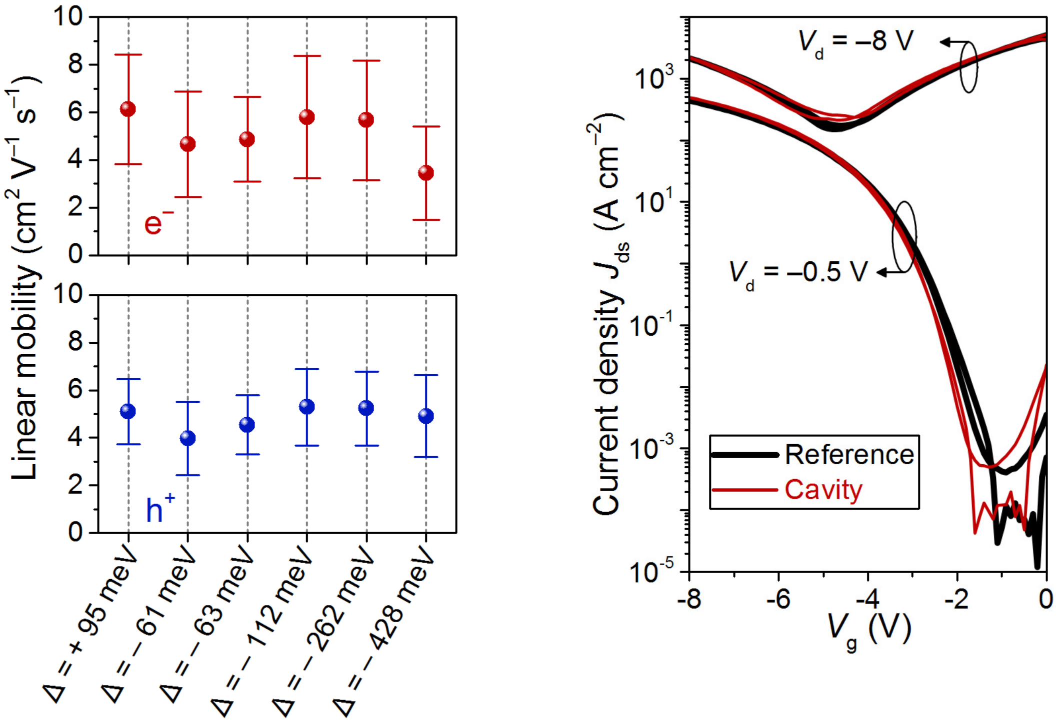


→ Electrically pumped exciton-polaritons at high current densities (18 kA/cm^2)

→ Apparently better thermalization of polaritons

Graf & Held *et al.*, ***Nature Mater.*** 16, 911–917 (2017)

Cavity LEFETs and Mobility



Graf & Held *et al.*, ***Nature Mater.*** 16, 911–917 (2017)

A Side Note on Transport in Polymers

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zaumseil@uni-heidelberg.de

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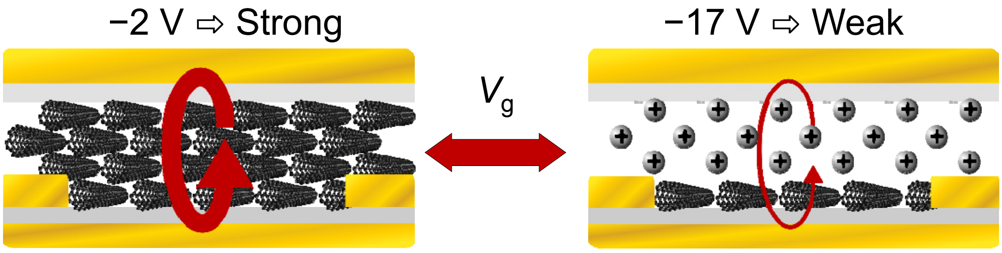
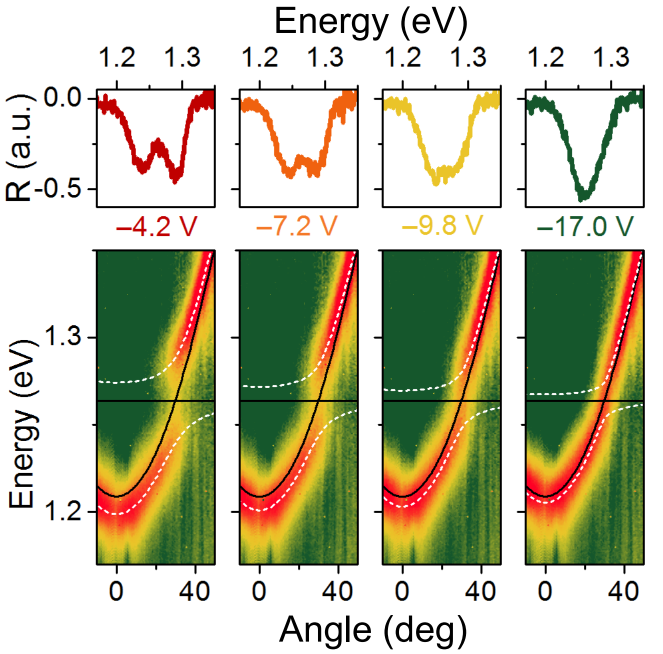
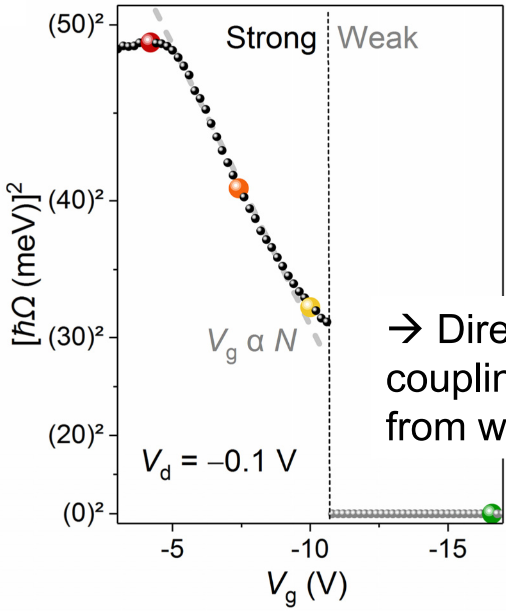
Tuning Coupling with Gate Voltage



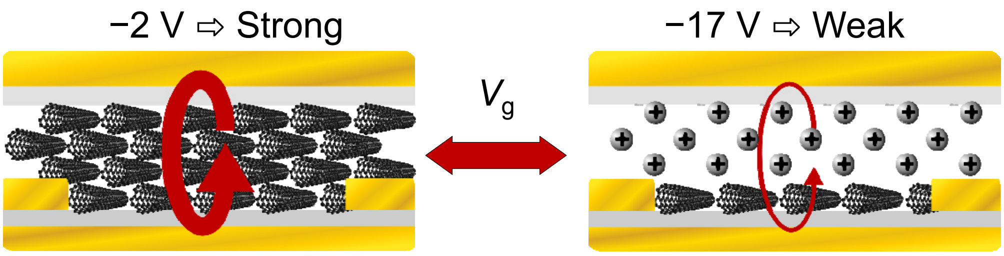
E_{11} – Bleaching
→ fewer oscillators
→ weaker coupling



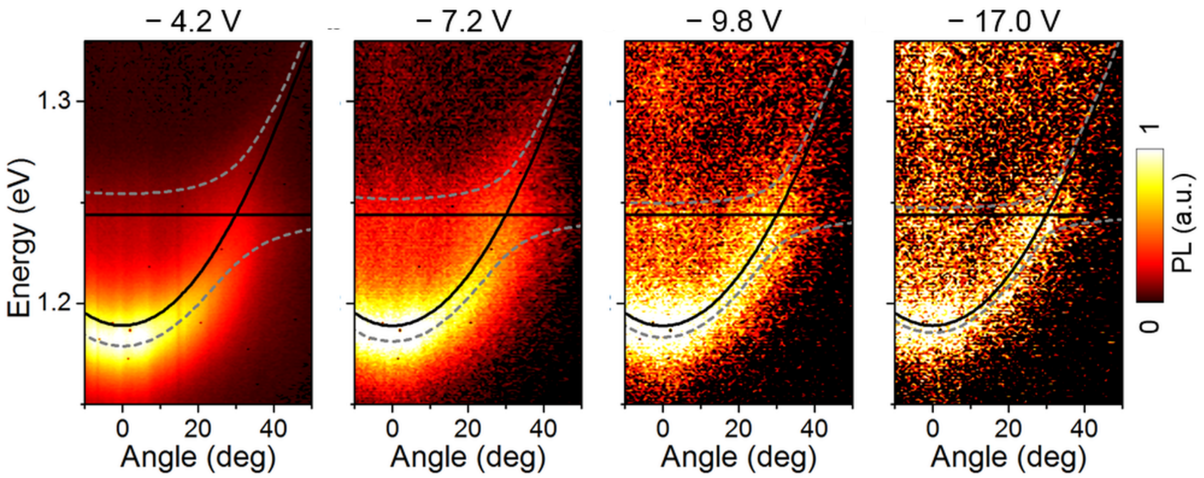


→ Direct tuning of coupling strength from weak to strong

Tuning Coupling with Gate Voltage



$V_d = -0.1$ V

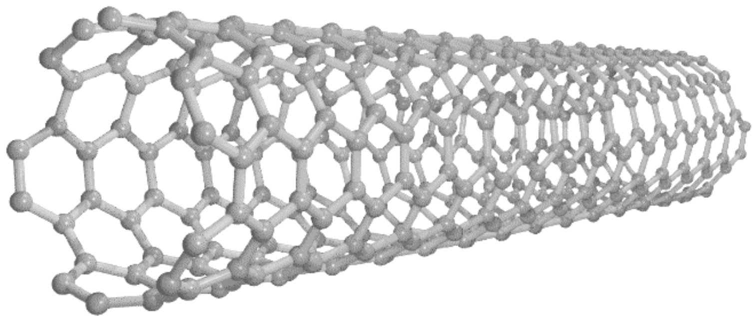


→ Less efficient relaxation for doped SWNT film

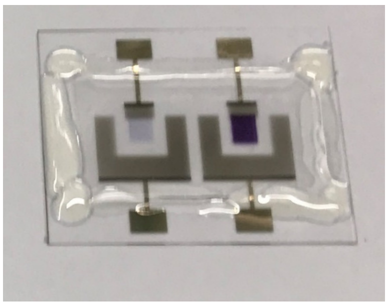
Graf & Held *et al.*, ***Nature Mater.*** 16, 911–917 (2017)

Outline

- ❑ Photophysics of Single-walled carbon nanotubes (SWNTs)
- ❑ Exciton-Polaritons in SWNTs
- ❑ **Trion-Polaritons in SWNTs**
- ❑ Relaxation Pathways



Trions in (6,5) SWNTs

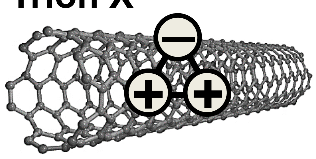


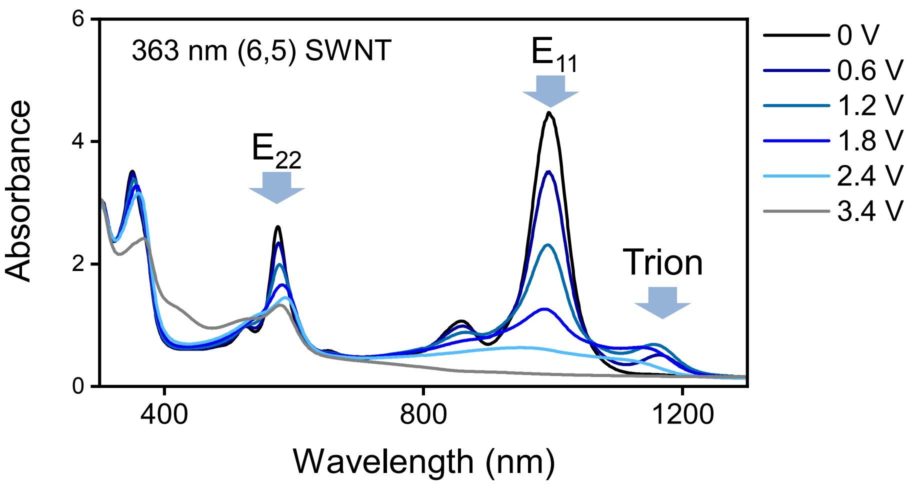
Electrochemical charging of thick films of (6,5) SWNT (electrochromic cell)

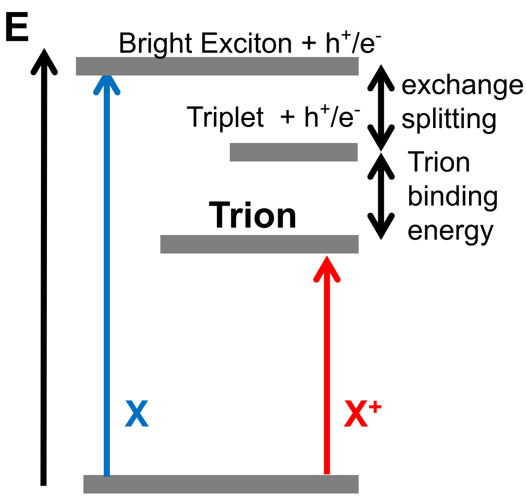
→ Bleaching of E_{11} and E_{22} transition

→ Red-shifted **trion** absorption and emission
(Trion = 2 holes + 1 electron)

Trion X^+

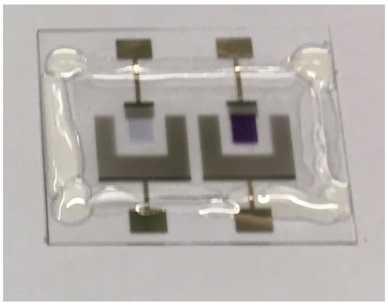






Berger *et al., ACS Appl. Mater. Interfaces* **2018,** *10*, 11135–11142.

Trions in (6,5) SWNTs



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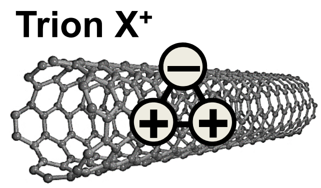
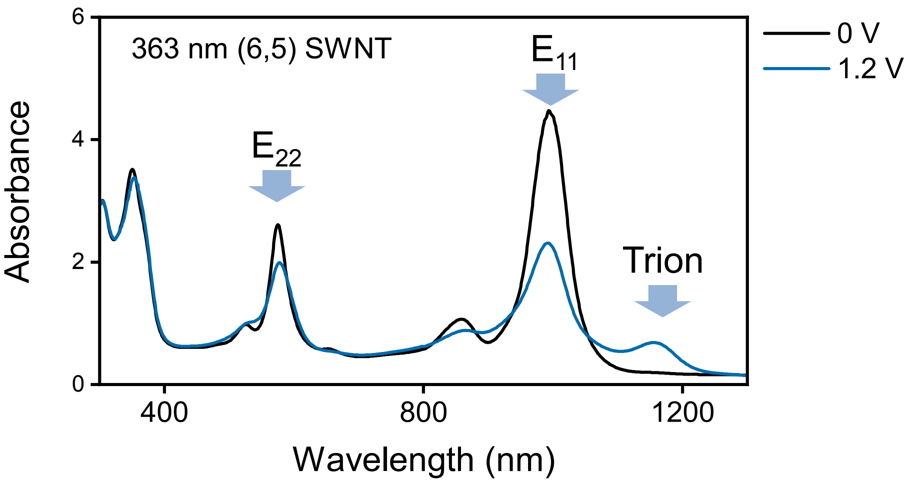
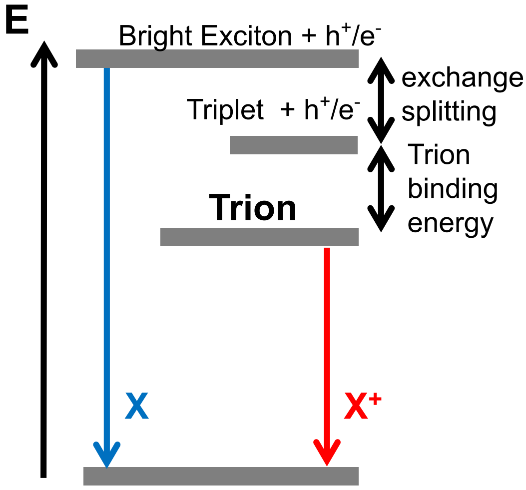


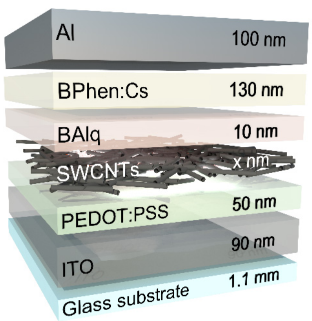


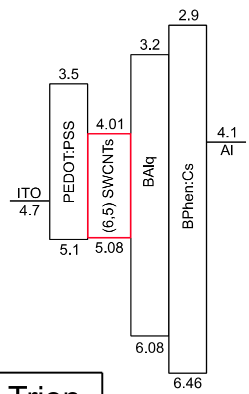


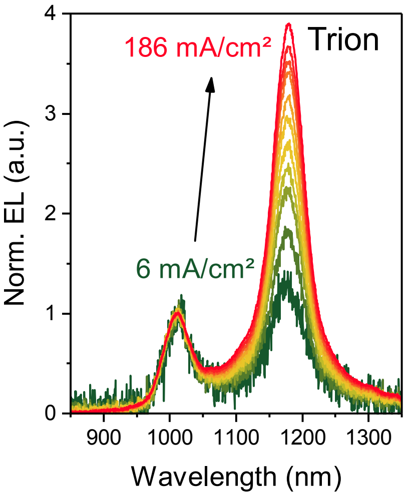
Berger *et al., ACS Appl. Mater. Interfaces* **2018,** *10*, 11135–11142.

Trion Electroluminescence

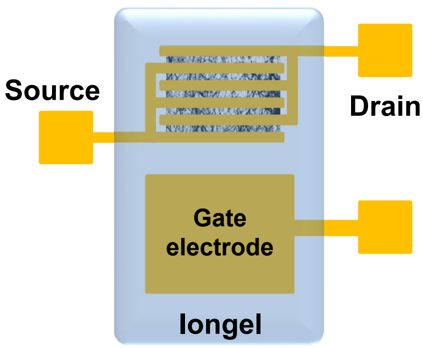
SWNT-OLED

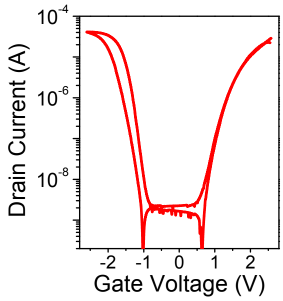


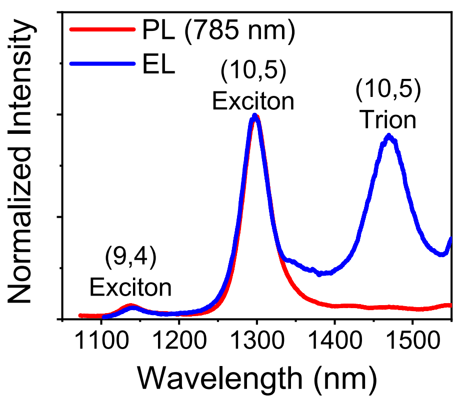




Electrolyte-gated LEFET



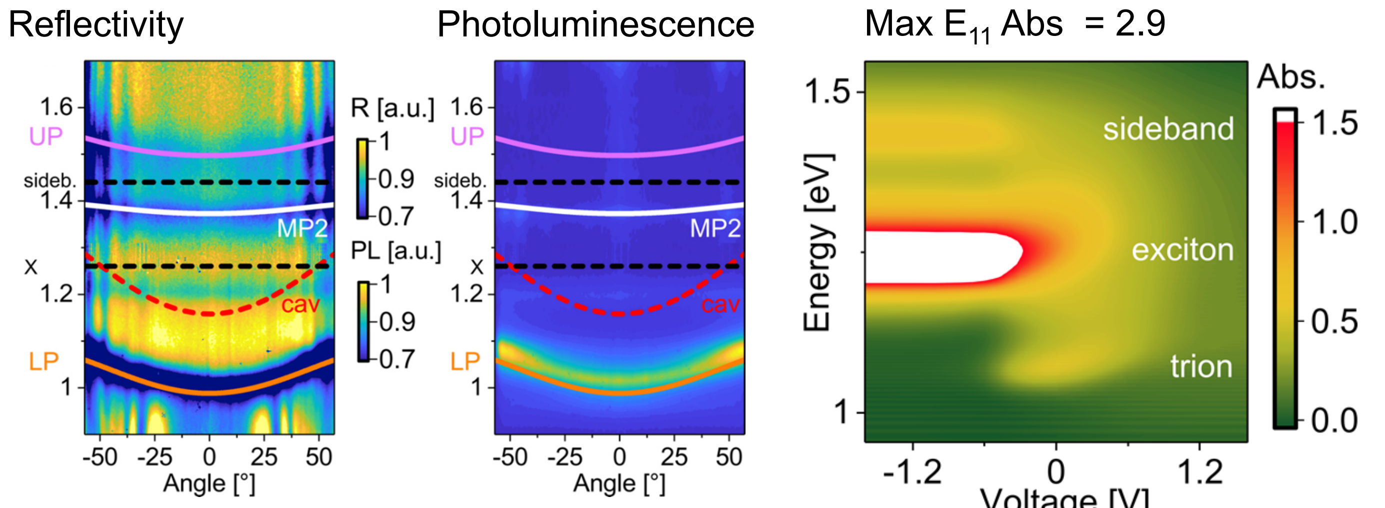




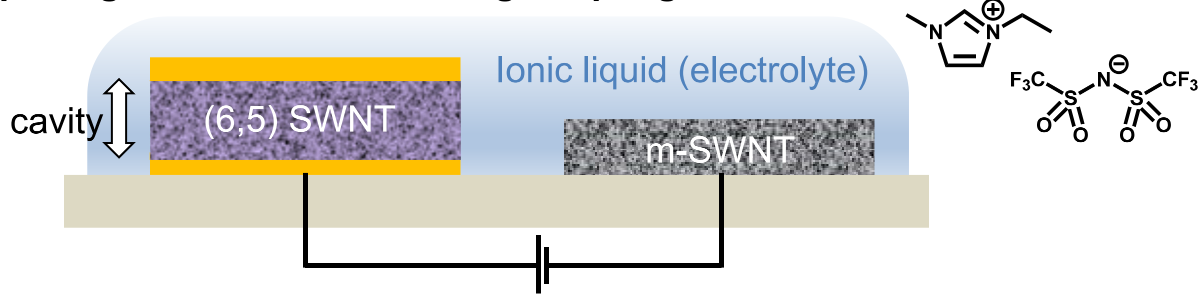
Graf et al. *Adv. Mater.* ***2018****, 30 (12), 1706711.*

Jakubka et al. *ACS Nano* **2014,** *8* (8), 8477-8486.

Excitons & Trions in Microcavities

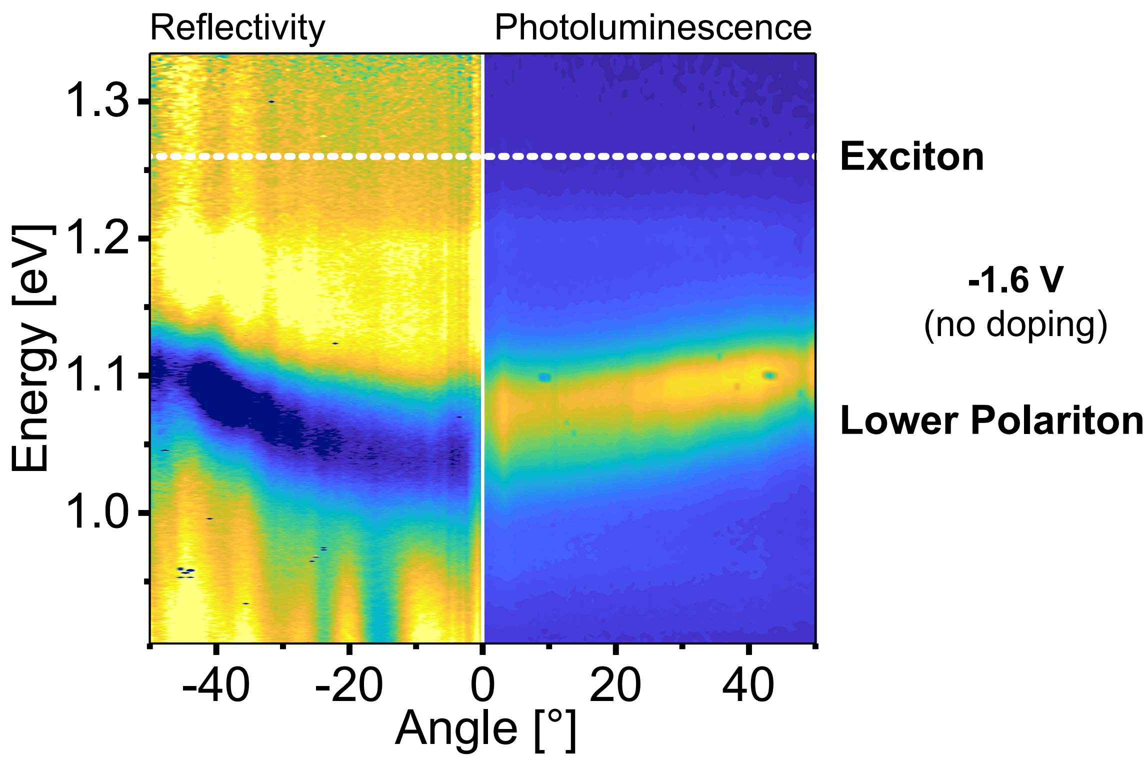


energy splitting = 0.5 eV → ultrastrong coupling



Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

Voltage sweep: Reflectivity and PL



Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

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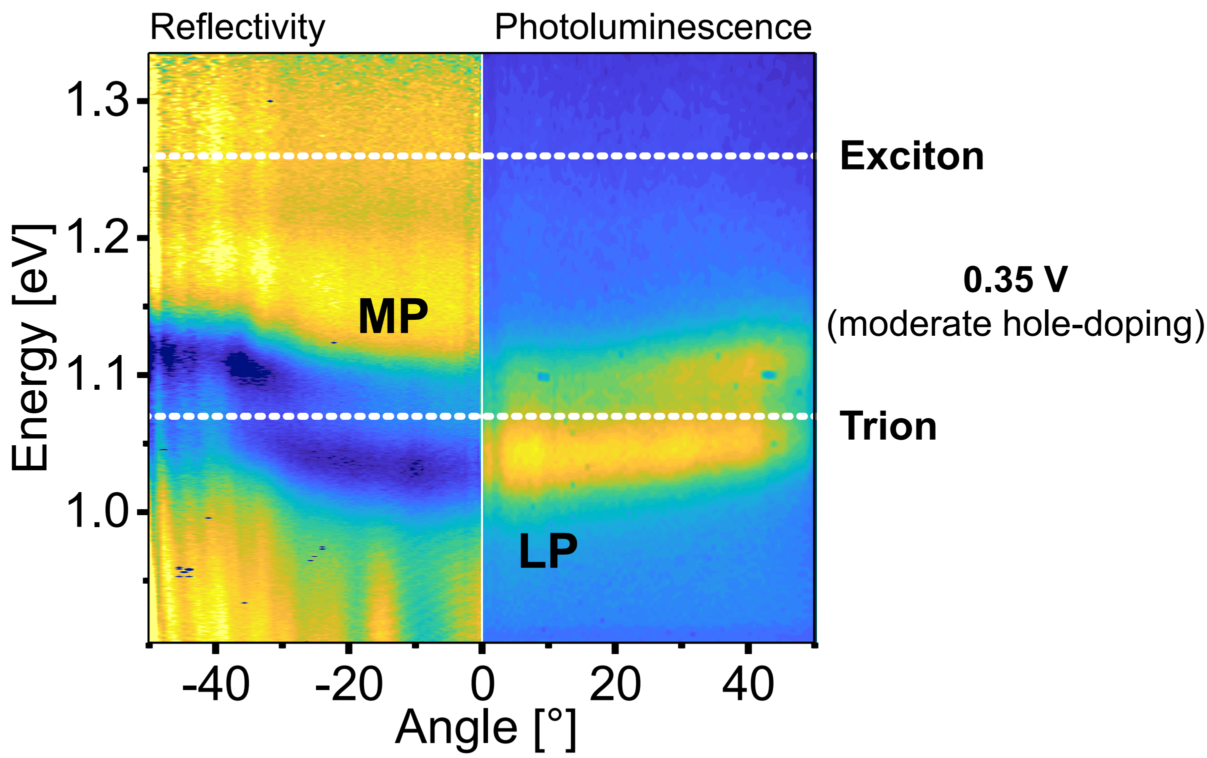

Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

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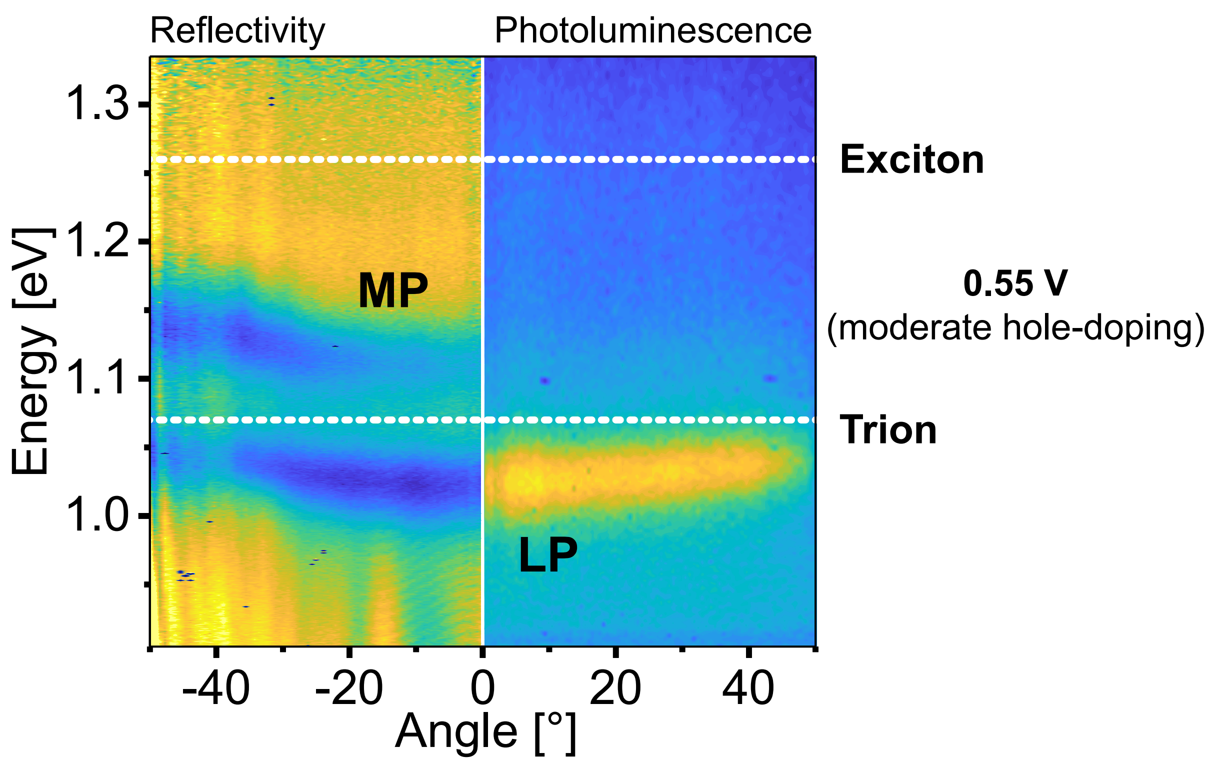

Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

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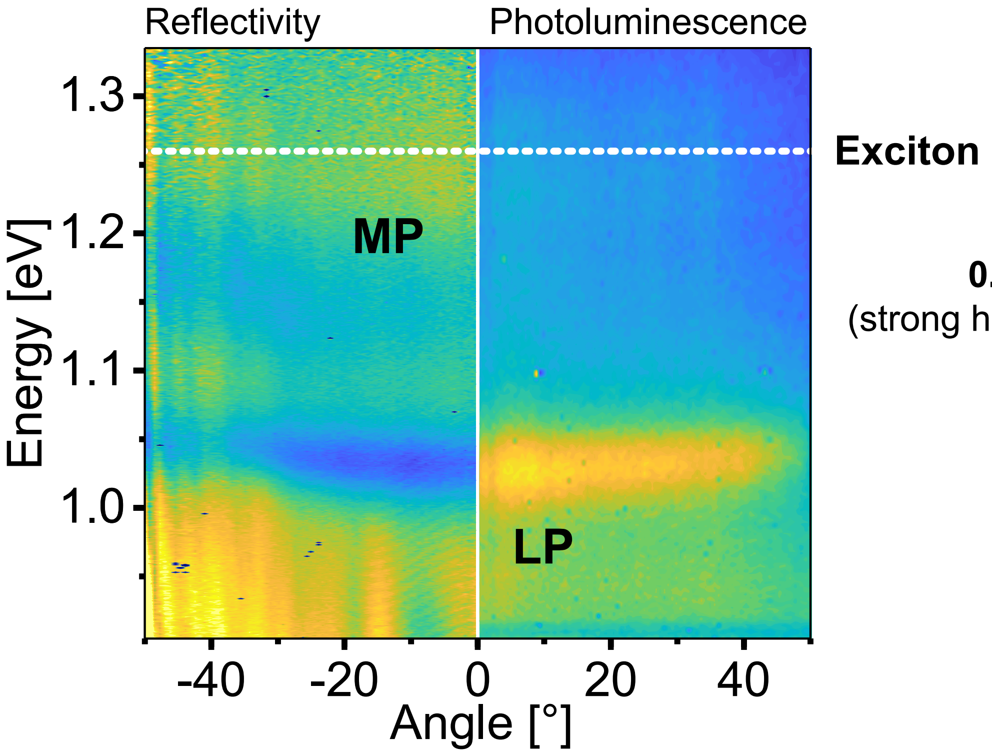
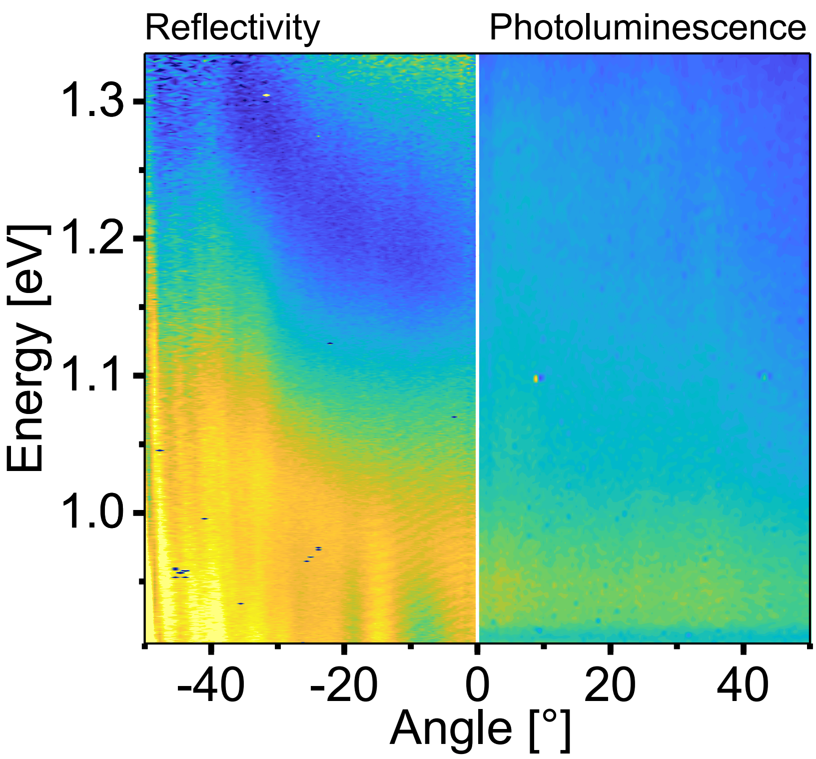


0.8 V
(strong hole-doping)

Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

Voltage sweep: Reflectivity and PL



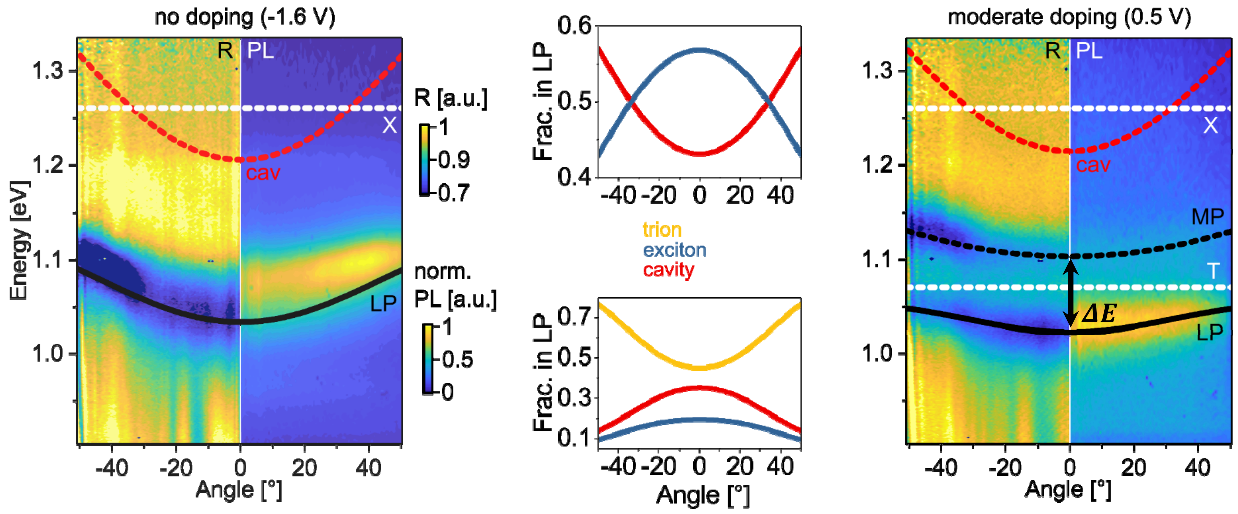
1.4 V
(strong hole-doping)

Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

Exciton Polariton *vs.* Trion Polariton

Exciton-Polariton

Trion-Exciton-Polariton



$$H(\theta) = \begin{pmatrix} X & V_X \\ V_X^* & C(\theta) \end{pmatrix}$$

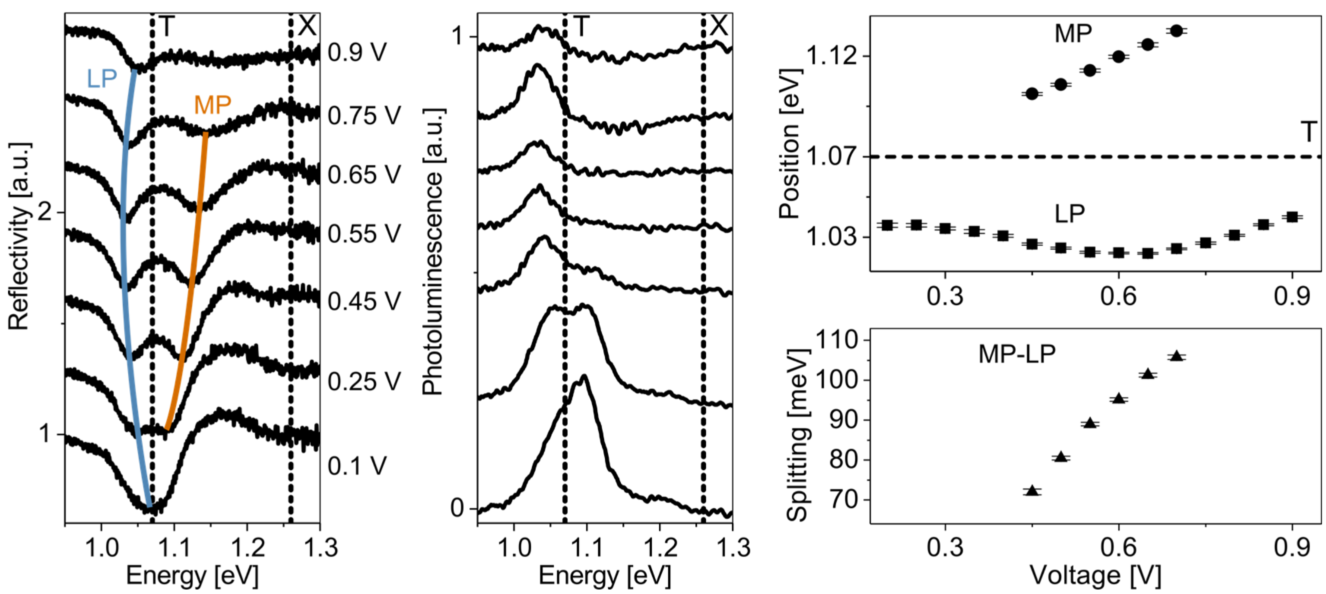
$$H(\theta) = \begin{pmatrix} X & 0 & V_X \\ 0 & T & V_T \\ V_X^* & V_T^* & C(\theta) \end{pmatrix}$$

Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

Exciton Polariton *vs.* Trion Polariton

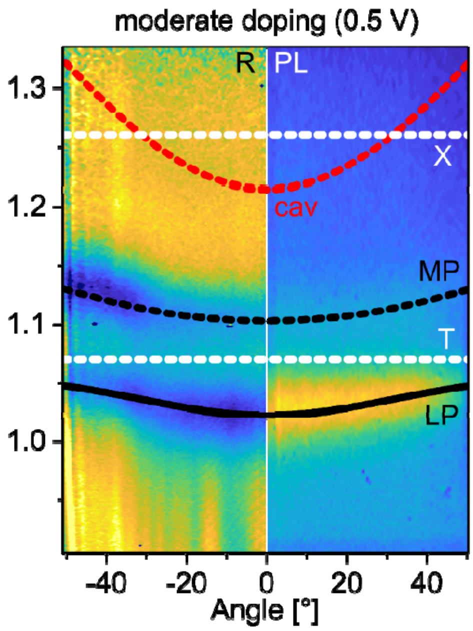
Reflectivity

Photoluminescence



Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

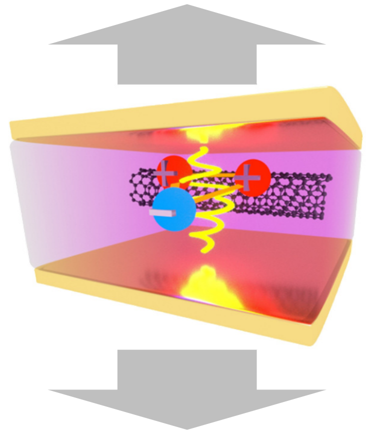
Potential Application of Trion-Polaritons



Trion-Polariton
Charged Light-Matter Hybrid

Charge/effective mass ratio $\approx 4000\ e_0/m_e$

Manipulate **light with electric field** (e.g. polariton propagation direction)

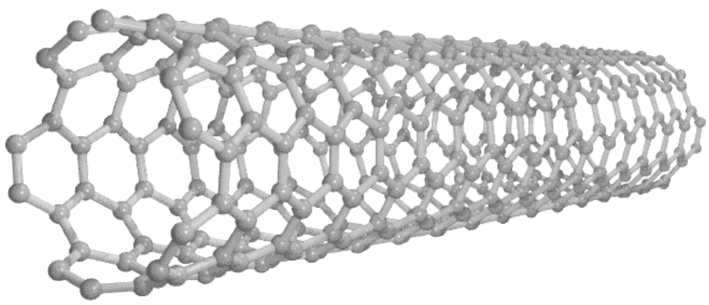


Manipulate **charge transport** (e.g. photocurrent, carrier mobility)

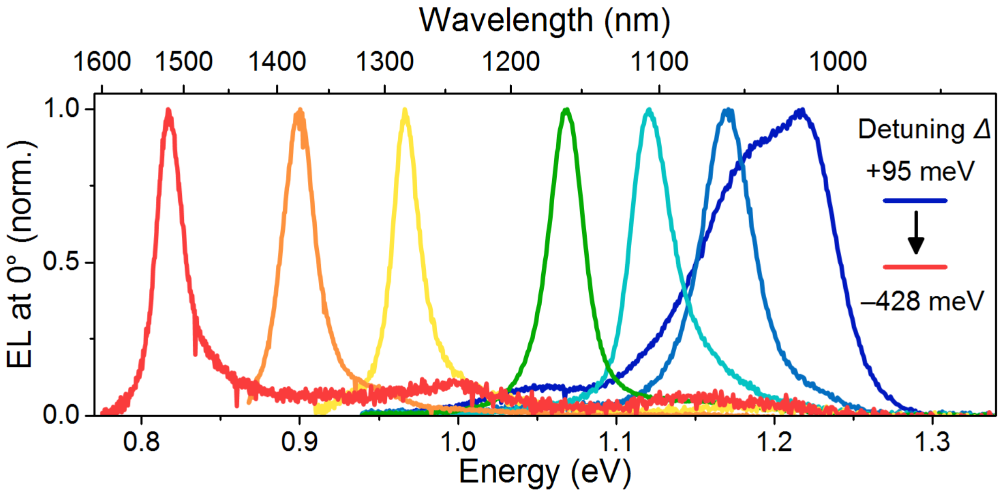
Möhl *et al.*, *ACS Photonics* **2018,** *5* (6), 2074-2080.

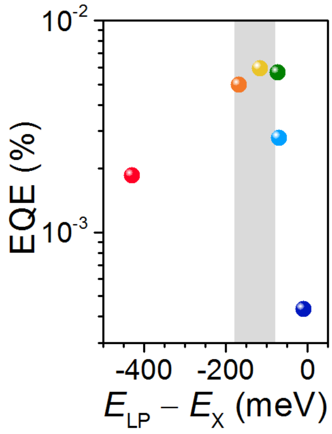
Outline

- ❑ Photophysics of Single-walled carbon nanotubes (SWNTs)
- ❑ Exciton- & Trion-Polaritons in SWNTs
- ❑ **Relaxation Pathways**
- ❑ Strong coupling in semiconducting polymers



Tuning Polariton-Electroluminescence





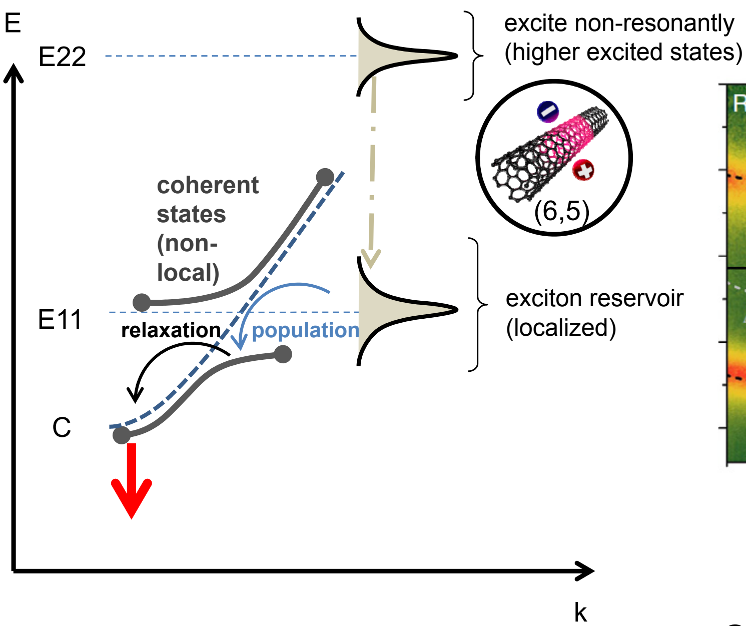
Apparent dependence of EQE on detuning, max at phonon sideband

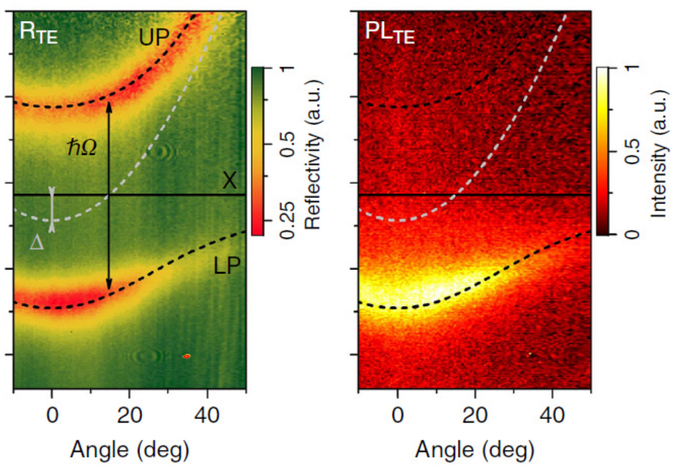
→ **Phonon-assisted relaxation ?**

→ **Brightening of dark excitons ?**

Graf & Held *et al.*, ***Nature Mater.*** 16, 911–917 (2017)

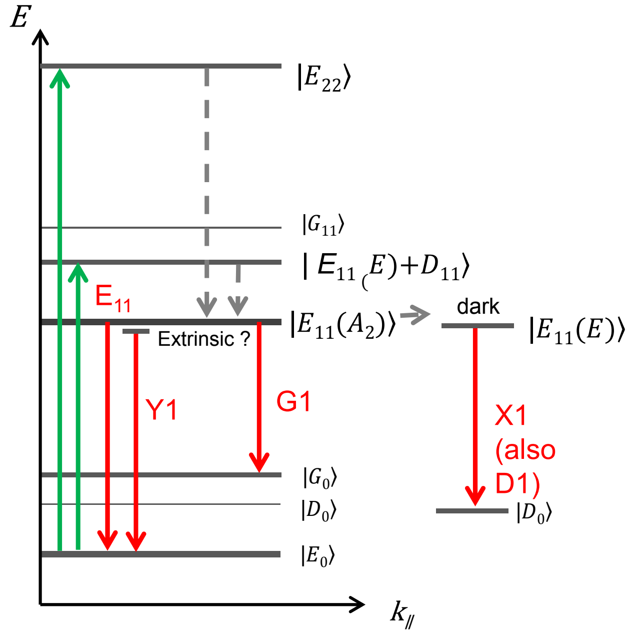
Polariton photoluminescence

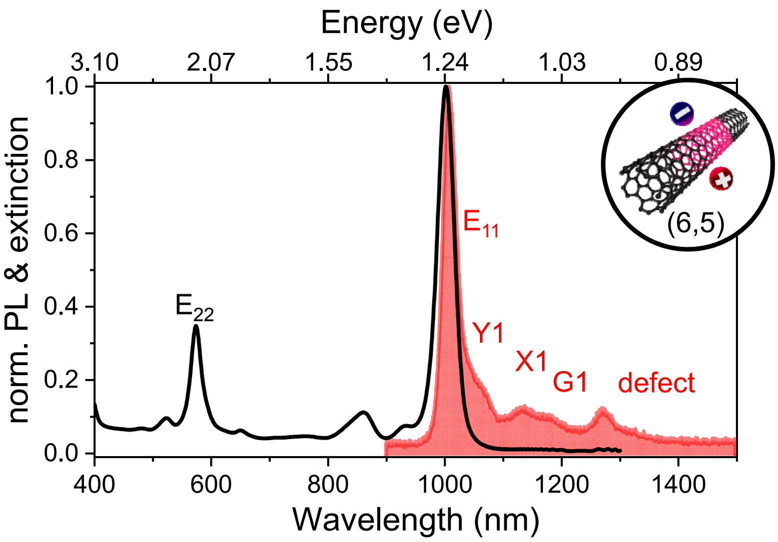




Graf, A. *et al.*, Nat. Comm. 7, 13078 (2016)

Origin of PL sidebands





Strong variation of PL with sample position

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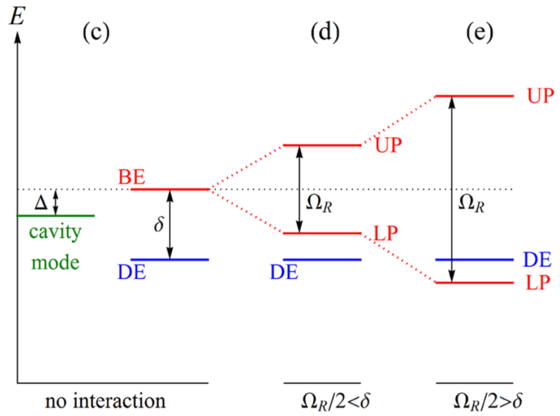
zaumseil@uni-heidelberg.de

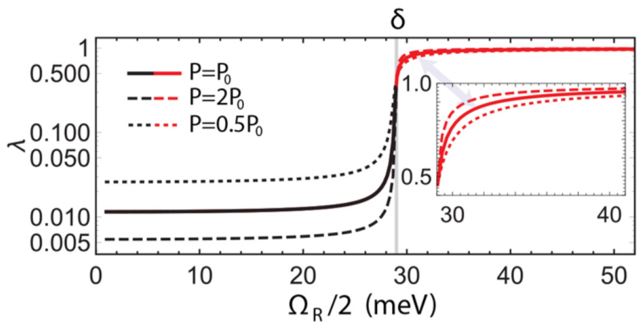
Brightening Dark Excitons?

Strong Light−Matter Coupling in Carbon Nanotubes as a Route to Exciton Brightening

Vanik A. Shahnazaryan,[†] Vasil A. Saroka,[‡,§,⊥] Ivan A. Shelykh,[†,∥] William L. Barnes,[‡] and Mikhail E. Portnoi[*,†,‡]

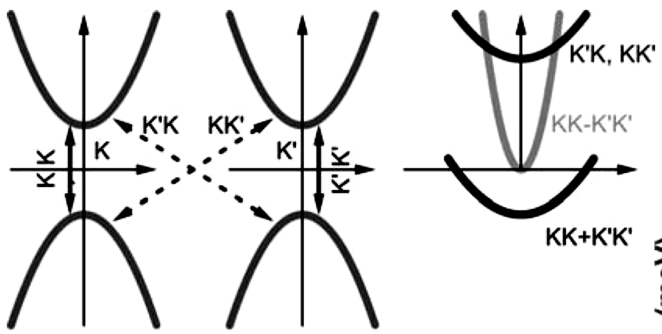
ACS Photonics **2019**, 6, 904.



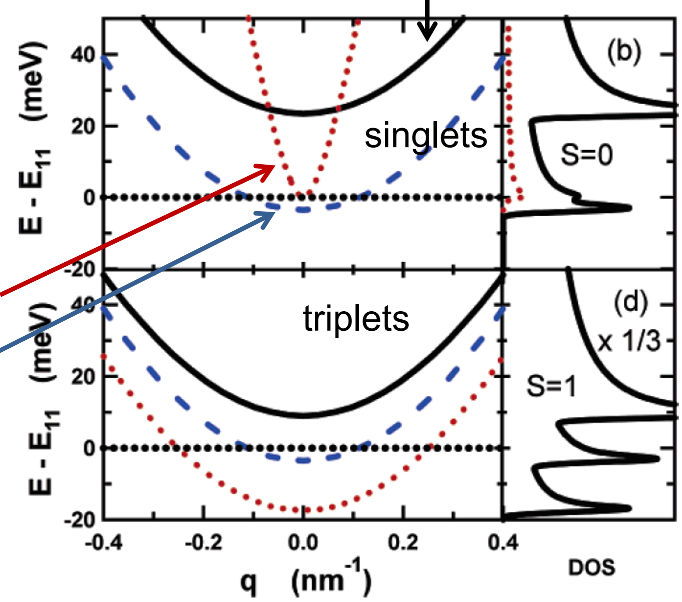


"… for realistic parameters of the system the value of the Rabi splitting can be greater than the splitting between bright and dark energy states. As a result, the lower polariton mode can have an energy lower than that of the dark exciton. It is this reordering of the energy of the bright and dark states that leads to a dramatic improvement of the emissive properties of nanotube-based systems."

Bright & Dark Excitons



Odd-parity, doubly degenerate with ± angular momentum K'



Odd-parity (bright)

Even-parity (dark)

V. Perebeinos, J. Tersoff, P. Avouris, *Nano Lett.* **2005**, 5, 2495.

Brightening Dark Excitons?

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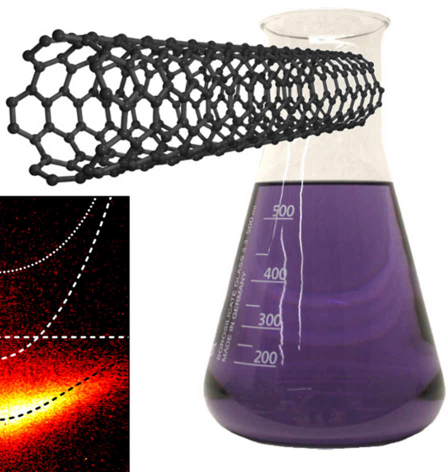
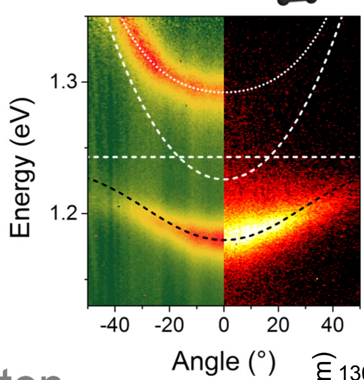
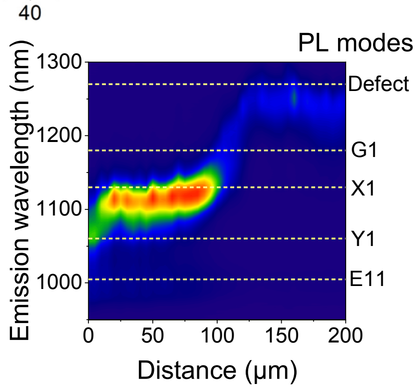
Summary

- Strong light-matter coupling with (6,5) SWNT in microcavities
- Electrically pumped and tuned exciton-polaritons in cavity-integrated LEFETs
- Trion-Polaritons possible for intermediate doping
- Strong dependence of polariton emission on detuning
- Indication for radiative pumping of exciton-polaritons by SWNT PL sidebands







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MSc. Nicolas Zorn

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MSc. Stefan Schießl
MSc. Arko Graf
BSc. Charles Möhl
MSc. Matthias Sinnwell

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(St Andrews Univ., UK)

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Alfried Krupp von Bohlen und Halbach - Stiftung

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DFG Deutsche Forschungsgemeinschaft